

Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO₂ Capture

primary project goal

Gas Technology Institute (GTI) is developing a transformational graphene oxide (GO)-based membrane process that can be installed in a new or retrofitted into an existing pulverized coal or natural gas power plant for carbon dioxide (CO₂) capture ready for demonstration by 2030. The expected product from this project will be a compact, GO-based membrane prototype system capable of achieving at least 70% CO₂ removal with a single-stage process and 90% CO₂ removal with a two-stage process. The system will be tested over an extended duration on actual flue gas at GTI and the National Carbon Capture Center (NCCC).

technical goals

- Scale-up the GO-based membranes to 50 to 100 cm² area and demonstrate that the scaled membranes show CO₂/nitrogen (N₂) selectivity ≥ 200 and CO₂ permeance $\geq 1,000$ gas permeation units (GPU) for the high-selectivity membranes (designated as GO-1 membranes), and CO₂/N₂ selectivity ≥ 20 and CO₂ permeance $\geq 2,500$ GPU for the high-flux membranes (designated as GO-2 membranes).
- Perform 100 hours of stability testing to demonstrate the CO₂ permeance and CO₂/N₂ selectivity decrease by less than 10% in the presence of flue gas contaminants (oxygen [O₂], sulfur oxide [SO_x], nitrogen oxide [NO_x]).
- Scale-up the GO-based membranes to 500 to 1,000 cm² area and demonstrate that the scaled membranes show CO₂/N₂ selectivity ≥ 200 and CO₂ permeance $\geq 1,000$ GPU for the GO-1, and CO₂/N₂ selectivity ≥ 20 and CO₂ permeance $\geq 2,500$ GPU for the GO-2.
- Achieve 95% CO₂ purity by integrating the GO-1 and GO-2 membranes in a skid (designated as GO²) for both natural gas and coal-derived flue gases.
- Perform a techno-economic analysis (TEA) to validate that the cost of electricity (COE) is 30% less than the U.S. Department of Energy (DOE) baseline CO₂ capture approach.

technical content

GTI is developing GO-based membranes for CO₂ capture from flue gases. The high-selectivity membranes (GO-1) show CO₂ permeances as high as 1,020 GPU with a CO₂/N₂ selectivity of 680, which is much higher than state-of-the-art membranes. In addition, GTI is also developing high-flux membranes (GO-2) with CO₂ permeance as high as 2,500 GPU using GO quantum dots (GOQD) as a membrane building block. The transformational GO-based membrane process integrates the GO-1 and GO-2 membranes (GO²), offering a new opportunity to explore further reductions in the cost of CO₂ capture.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Membrane

project focus:

Graphene Oxide Membranes for Coal-Derived Flue Gases

participant:

Gas Technology Institute

project number:

FE0031598

predecessor project:

FE0026383

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start date:

06.01.2018

percent complete:

75%

Graphene-based materials, such as graphene and GO (Figure 1), have been considered as next-generation membrane materials. They are only sub-nanometer thick and thus may form ultrathin separation membranes to minimize transport resistance and maximize flux. The feasibility of using a vacuum filtration process to fabricate ultrathin GO membranes (thickness of ~1.8 nm) has been demonstrated. It was observed that the molecular-sized pores of structural defects on GO flakes could serve as a transport pathway for selective gas separations.

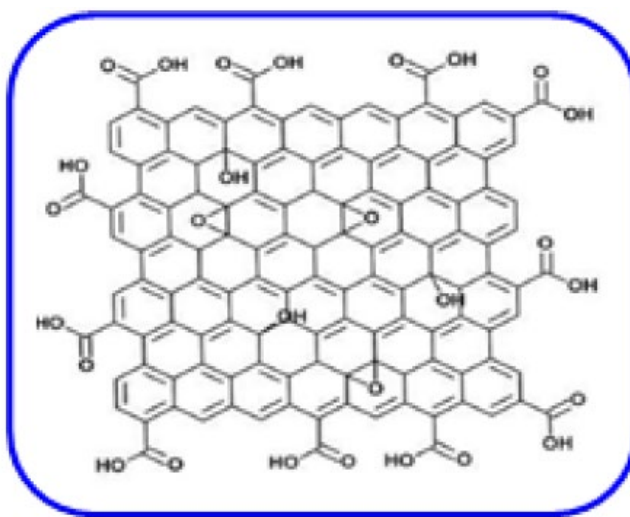


Figure 1: Chemical structural model of GO.

Because of the different morphologies of GO and GOQDs, ultrathin membranes (less than 20 nm) composed of these two different building blocks are expected to have different nanostructures. Figure 2 shows different membrane nanostructures of GO-1 and GO-2 membranes and the proposed transport pathways.

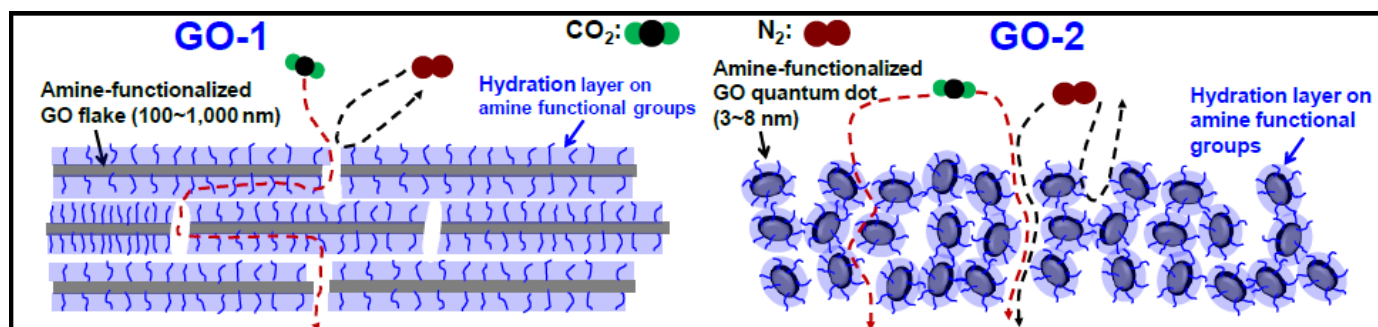


Figure 2: Membrane nanostructures of GO-1 and GO-2 membranes and proposed CO₂ separation mechanisms.

Large GO flakes (greater than 100 nm) with high aspect ratio of lateral size to the flake thickness typically led to regular and uniform lamellar structure (GO-1, left in Figure 2) with a negligible quantity of defects after hydration of surface functional amine groups with water in the flue gas. As a result, CO₂ molecules can quickly transport through the membrane by a facilitated transport mechanism via reaction with amine ($\text{CO}_2 + \text{R-NH}_2 \leftrightarrow \text{R-NH}_3^+ + \text{HCO}_3^-$) and block the permeation of N₂ molecules. Therefore, GO-1 membranes have moderate CO₂ permeance but high CO₂/N₂ selectivity. In contrast, in GO-2 membranes, the small GOQDs may form a randomly packed nanostructure (right in Figure 2) containing defects that cannot be effectively sealed by the hydration layer. These defects greatly increase the CO₂ permeance, but also decrease the selectivity. Therefore, GO-2 membranes are expected to have high CO₂ permeance but lower CO₂/N₂ selectivity compared to the GO-1 membranes.

In addition to the hollow fiber GO-based membranes, the project team demonstrated for the first time an easy, fast, and scalable printing method with advanced computational controls to deposit ultrathin, high-quality GO-based membranes on a polymeric support for gas separation. A commercial ink cartridge was used to hold an appropriate GO dispersion for printing (Figure 3a). Using only GO “ink,” ultrathin GO membranes for highly effective water nanofiltration have been printed. To promote membrane separation performance for a CO₂/N₂ mixture, an extra cartridge was added that holds various amine solutions, such as ethylene diamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA),

tetraethylenepentamine (TEPA), and pentaethylenehexamine (PEHA), to increase both CO₂ permeance and CO₂/N₂ selectivity (Figure 3b). Uniform GO coatings with well-controlled thickness and a membrane area as large as 225 cm² have been printed (Figure 3c). Figure 3d shows a typical cross-sectional scanning electron microscopy (SEM) of the printed membrane. Figure 3e indicates the thicknesses of the printed membranes are between 6 and 60 nm and can be well-controlled by the GO concentration.

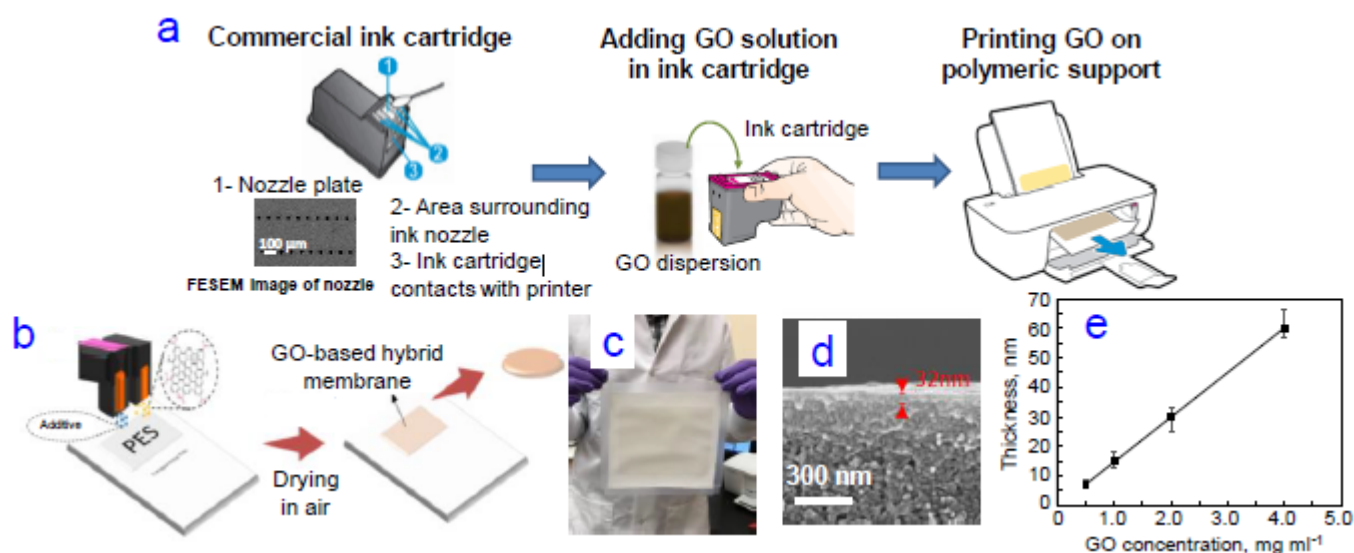


Figure 3: (a) Schematics of GO membrane fabrication by inkjet printing; (b) GO-based membrane preparation by printing from two cartridges containing GO ink and additives; (c) a picture of a printed GO membrane (15 cm × 15 cm); (d) cross-sectional SEM of the membrane; (e) dependence of membrane thickness on GO ink concentration.

The project team prepared GO-based flat-sheet membranes on a polyether sulfone (PES) substrate by printing. The resulting membrane was sealed in a plate-and-frame module for characterization and CO₂/N₂ separation testing. The process parameters for the membranes developed are given in Table 1.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Graphene Oxide	
Materials of Fabrication for Support Layer	—	Polyether sulfone	
Nominal Thickness of Selective Layer	μm	0.002-0.05 for GO-1 0.005-0.1 for GO-2	0.002-0.02 for GO-1 0.005-0.05 for GO-2
Membrane Geometry	—	Hollow fiber and flat sheet	Hollow fiber and flat sheet
Max Trans-Membrane Pressure	bar	<5	1
Hours Tested without Significant Degradation	—	20	>200 (actual flue gas)
Manufacturing Cost for Membrane Material	\$/m ²	TBD	TBD
Membrane Performance			
Temperature	°C	80 for GO-1 70 for GO-2	65
CO ₂ Pressure Normalized Flux	GPU	1,020 for GO-1 2,500 for GO-2	1,000 for GO-1 2,500 for GO-2
CO ₂ /H ₂ O Selectivity	—	1/10 for GO-1 N/A for GO-2	<1/10 for GO-1 <1/10 for GO-2
CO ₂ /N ₂ Selectivity	—	680 for GO-1 >30 for GO-2	>200 for GO-1 >20 for GO-2

CO ₂ /SO ₂ Selectivity	—	N/A for GO-1 N/A for GO-2	<1/10 for GO-1 <1/10 for GO-2
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		<i>(for equipment developers)</i>	
Flow Arrangement	—	Crossflow	
Packing Density	m ² /m ³	1,000	
Shell-Side Fluid	—	CO ₂ -rich permeate	
Flue Gas Flowrate	kg/hr	TBD	
CO ₂ Recovery, Purity, and Pressure	%/%/bar	70-90%, >95%, TBD	
Pressure Drops Shell/Tube Side	psi/m	Feed and permeate: <1.5	

The project team coated GO-based membranes on 50- to 100-cm² PES porous hollow-fiber modules by a vacuum filtration process. The sub-recipient systematically synthesized and optimized single-layered GO flakes via different GO synthesis methods. A variety of equipment was used to characterize the membrane morphology, thickness, composition, and structural defects density. The CO₂/N₂ separation properties were measured using an existing laboratory-scale testing system and simulated flue gas.

For coal-fired flue gas, the proposed GO² technology is designed to capture 90% CO₂ with greater than 95% CO₂ purity. The system will be installed downstream of flue gas desulfurization (FGD), as shown in Figure 4. It is a compact, stand-alone, membrane-based process, enabling easy integration into the power plant. For the TEA, the data for the current research and development (R&D) values is shown in Table 2.

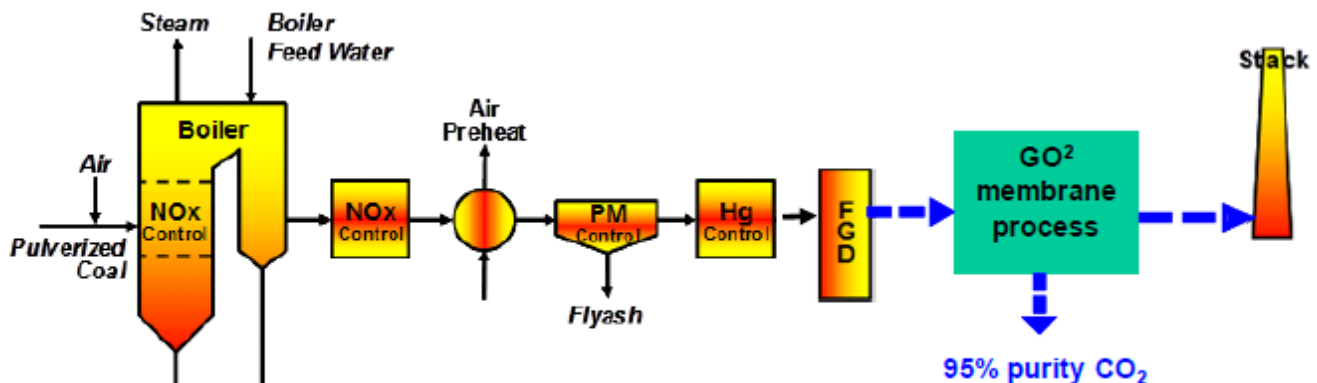


Figure 4: Process flow diagram for the proposed GO² process for CO₂ capture.

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	NA	30
Cost of Carbon Avoided	\$/tonne CO ₂	NA	NA
Capital Expenditures	\$/MWhr	NA	NA
Operating Expenditures	\$/MWhr	NA	NA
Cost of Electricity	\$/MWhr	NA	93.24

* Current values are not available (NA). Techno-economic analysis will be performed at the end of the project under Task 10

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO₂ captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO₂ avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

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)/ $\text{cm}^2/\text{s}/\text{cm}$ 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: $1 \text{ GPU} = 3.3464 \times 10^{-6} \text{ kg mol}/\text{m}^2\text{-s-kPa}$ (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 – A vacuum pump is used on the permeate side to provide a vacuum of 2.9 pounds per square inch absolute (psia; 0.2 bar). Because the GO-based membranes are highly water-permeable, the water vapor in the flue gas permeates through the membrane and lowers the partial pressure of CO_2 in the permeate side. Thus, the applied vacuum provides enough driving force for CO_2 permeation. The CO_2 -depleted residue leaving the GO-1 unit is sent to a second membrane unit, GO-2, which also uses a vacuum on the permeate side to create the driving force for separation.

Contaminant Resistance – GO is typically prepared under strong acid and oxidation conditions in an aqueous solution, so it is expected to be very stable under these harsh conditions. Additionally, GO is hydrothermally stable at 150°C and has good chemical stability and mechanical strength. Therefore, GO is expected to be stable under flue gas conditions and with flue gas contaminants, such as nitrogen dioxide (NO_2), SO_x , etc.

Flue Gas Pretreatment Requirements – The proposed GO^2 system will be installed downstream of FGD.

Membrane Replacement Requirements – To be determined.

Waste Streams Generated – No waste streams are generated. The GO-based membranes are selective for water (H_2O) over CO_2 , and the proposed GO^2 technology can recover the water vapor from the permeate streams. The recovered, mineral-free, high-purity water can be reused by the power plant.

technology advantages

- The technology achieves high CO_2 capture rates ($\geq 70\%$) with 95% CO_2 purity.
- The water-permeable feature of the GO membrane overcomes the process pressure limitation issue, enhancing mass transfer.
- GO membranes have high thermal/chemical stability and mechanical strength.
- Graphene-based materials such as GO have been considered next-generation membrane materials. They are only sub-nanometer thick and thus may form ultrathin separation membranes to minimize transport resistance and maximize flux.
- GTI's printing method for GO membrane formation has several advantages, including:
 - Low-cost, fast, and scalable deposition of ultrathin GO-based membranes.
 - Capability of controlling coating properties by controlling printing parameters.
 - High utilization efficiency of GO material without waste.

- Flexibility of forming GO-hybrid coatings by introducing desired additives.

R&D challenges

- When scaling-up GO-based membranes, the CO₂ permeance and/or CO₂/N₂ selectivity may not scale with size.
- There is risk that membrane sealing issues will be encountered in the development process.
- The commercial PES substrate quality is not currently sufficiently high for scale-up of GO-based membranes.

status

Budget Period 2 tasks are currently underway. GO membranes are being scaled to 1,000 cm². After scaling, they will be subjected to stability tests for 100 hours. Concurrently, a GO² system will be constructed for the purposes of testing the membranes at bench-scale at NCCC.

available reports/technical papers/presentations

Li, S., 2021, "Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO₂ Capture." Presented at the 2021 NETL Carbon Management and Natural Gas & Oil Research Project Review Meeting. Pittsburgh, PA. https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Li_1.pdf.

Li, Shiguang, et al., 2018, "Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO₂ Capture," presented at the 2018 NETL CO₂ Capture Technology Project Review Meeting, Pittsburgh, PA. <https://netl.doe.gov/sites/default/files/netl-file/S-Li1-GTI-Graphene-Oxide-based-Membrane.pdf>.

Li, S.; Xu, W.; Meyer, H.; Yu, M.; Zhang, S.; Zhou, F.; Ding, Y.; Sexton, A.; Sachde, D.; Biggott, B., 2020, "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion Carbon Dioxide Capture." Final Scientific/Technical Report. Report No. GTI 21881. DOE Award No. DE-FE0026383. <https://www.osti.gov/servlets/purl/1750959>.

Li, Shiguang, et al. "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion Carbon Dioxide Capture," presented at the 2018 NETL CO₂ Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. <https://netl.doe.gov/sites/default/files/netl-file/S-Li-GTI-Energy-Efficient-GO-PEEK-Hybrid-Membrane-Process.pdf>.

Li, Shiguang, et al. "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion Carbon Dioxide Capture," presented at the 2017 NETL CO₂ Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. <https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/2-Tuesday/S-Li-GTI-Hybrid-Membrane-Process.pdf>.

Li, Shiguang, et al. "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion CO₂ Capture," presented at the BP1 Review Meeting, Pittsburgh, PA, March 2017.

Li, Shiguang, et al. "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion CO₂ Capture," presented at the presented at the 2016 NETL CO₂ Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. <https://netl.doe.gov/sites/default/files/event-proceedings/2016/c02%20cap%20review/4-Thursday/S-Li-GTI-Go-Peek-Hybrid-Membrane-Process.pdf>.

Li, Shiguang, et al. "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion CO₂ Capture," presented at the project kickoff meeting, Pittsburgh, PA, December 2015.