Bench-scale Development of a Transformational Graphene Oxide-based Membrane Process for Post-combustion CO$_2$ Capture

DOE Contract No. DE-FE0031598

Shiguang Li, Gas Technology Institute (GTI)
Miao Yu, Rensselaer Polytechnic Institute (RPI)
Project overview

- **Performance period**: June 1, 2018 – Sep. 30, 2021
- **Funding**: $2,914,074 from DOE; $728,738 cost share
- **Objective**: Develop a transformational graphene oxide (GO)-based membrane process (GO²) for CO₂ capture with 95% CO₂ purity and a cost of electricity (COE) at least 30% lower than DOE amine reference baseline SC PC plant case

- **Team:**

<table>
<thead>
<tr>
<th>Member</th>
<th>Roles</th>
</tr>
</thead>
</table>
| ![gti](image) | • Project management and planning  
• Quality control  
• CO₂ capture performance tests |
| ![Rensselaer](image) | • GO membrane development and scale-up |
| ![Ohio State University](image) | • Scale-up of flat sheet GO membrane modules  
• Process design and optimization |
| ![Trimeric Corporation](image) | • Technical & economic study |
GO membrane technology based on our work published in *Science* and *Nature Communications*

**Science**

*Ultrathin, Molecular-Sieving Graphene Oxide Membranes for Selective Hydrogen Separation*
Hang Li *et al.*
*Science* **342**, 95 (2013);
DOI: 10.1126/science.1236686

**Nature Communications**

**ARTICLE**

*Ultrathin graphene oxide-based hollow fiber membranes with brush-like CO$_2$-philic agent for highly efficient CO$_2$ capture*
Fanglei Zhou$^1$, Huynh Ngoc Tien$^2$, Weiwei L. Xu$^2$, Jung-Tsai Chen$^2$, Qiuli Liu$^2$, Ethan Hicks$^2$, Mahdi Fathizadeh$^2$, Shiguang Li$^3$ & Miao Yu$^1$
**GO² process description**

GO² process integrates a high-selectivity GO-1 membrane and a high-flux GO-2 membrane for optimal performance.
GO-1 and GO-2 membranes developed under laboratory-scale program (DE-FE0026383)

GO-1
(High selectivity)

Amine-functionalized GO flake (100~1,000 nm)

GO-2
(High flux)

Amine-functionalized GO quantum dot (3~8 nm)
Procedure developed for coating GO membranes on hollow fibers under lab-scale program (DE-FE0026383)

Polyethersulfone fiber

Coated fiber (GO-PZ) cross section

PES Hollow Fiber

16 nm

50 nm
1,000 GPU CO\textsubscript{2} permeance achieved in both sweep gas and vacuum permeation modes with selectivity >200

**Sweep gas mode**
- GO-PZ membrane
- Feed gas: 15% CO\textsubscript{2}/85% N\textsubscript{2} with saturated water vapor

**Vacuum mode**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Improved GO-PZ membrane</th>
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<tbody>
<tr>
<td>Temperature</td>
<td>75°C</td>
</tr>
<tr>
<td>Humidity</td>
<td>85%</td>
</tr>
<tr>
<td>Feed gas</td>
<td>15% CO\textsubscript{2}/85% N\textsubscript{2}</td>
</tr>
<tr>
<td>CO\textsubscript{2} permeance, GPU</td>
<td>1080 ± 55</td>
</tr>
<tr>
<td>CO\textsubscript{2}/N\textsubscript{2} selectivity</td>
<td>650 ± 31</td>
</tr>
</tbody>
</table>
In addition to hollow fiber membranes, flat sheet membranes were successfully prepared by printing.
Overview/roadmap

Task 1: Project management and planning (throughout the project) → We are here

Membrane Development

BP1

- Task 2 – Development of GO membrane with area of 50-100 cm²
- Task 3 – Improvement of 50-100 cm² membranes towards higher selectivities
- Task 4 – Stability testing of membranes at near realistic flue gas conditions
- Task 5 – Scale-up of GO membrane modules to effective areas of 1000 cm²
- Task 6 – 100-h stability tests for GO membranes developed under Task 5

Process Development

BP2

- Task 7 – Design and construction of a GO² system

- Task 8 – Testing of the GO² system using NG flue gas
- Task 9 – Testing of the GO² system using coal flue gas
- Task 10 – TEA
# Success criteria and key milestones

## Success criteria:

<table>
<thead>
<tr>
<th>Decision Point</th>
<th>Date</th>
<th>Success Criteria</th>
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</table>
| Go/no-go decision points | 3/31/20 | 1) Production of 50-100 cm² area membranes with CO₂/N₂ selectivity ≥200 and CO₂ permeance ≥1,000 GPU for the GO-1, and with CO₂/N₂ selectivity ≥20 and CO₂ permeance ≥2,500 GPU for the GO-2  
2) Stability testing shows the CO₂ permeances and CO₂/N₂ selectivities decreased by less than 10% in the presence of flue gas contaminants |
| Completion of the project | 9/30/21 | 1) Production of 1,000 cm² area membranes with CO₂/N₂ selectivity ≥200 and CO₂ permeance ≥1,000 GPU for the GO-1, and with CO₂/N₂ selectivity ≥20 and CO₂ permeance ≥2,500 GPU for the GO-2  
2) Testing with flue gas complete, 95% CO₂ purity validated  
3) Final TEA report issued; final report submitted |

## Key milestones set to effectively measure progress

- Each task has at least one milestone
Preliminary risk assessment: technical challenges and mitigation strategies

Challenges/Risks

1) Scaled membrane CO$_2$/N$_2$ separation performance not sufficiently high

   **Mitigation:**
   - 1a: Improve PES substrate quality
   - 1b: Identify new approaches to improve separation performance

2) 95% CO$_2$ purity not achieved

   **Mitigation:**
   - 2a: Improve process design

3) Cost of the process not in line with expected outcome

   **Mitigation:**
   - 3a: Increase CO$_2$ permeance for the membranes
   - 3b: Improve manufacturing process to lower membrane costs
Summary

- In a laboratory-scale program (DE-FE0026383), we have developed high-selectivity (GO-1) and high-flux (GO-2) graphene oxide-based membranes.

- In the current program, we will scale up the membranes for bench-scale development.

- The GO$^2$ process integrates the GO-1 and GO-2 membranes offering a new opportunity to explore further reductions in the cost of CO$_2$ capture.

- The GO$^2$ process will be tested at the NCCC with actual flue gas for CO$_2$ capture with 95% CO$_2$ purity.
Acknowledgements

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Andrew Sexton, Trimeric Corporation (Trimeric)

CO₂ Capture Project - Phase 4
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