DOE Contract DE-FE0026383

# Energy Efficient GO-PEEK Hybrid Membrane Process for Post-combustion $CO_2$ Capture


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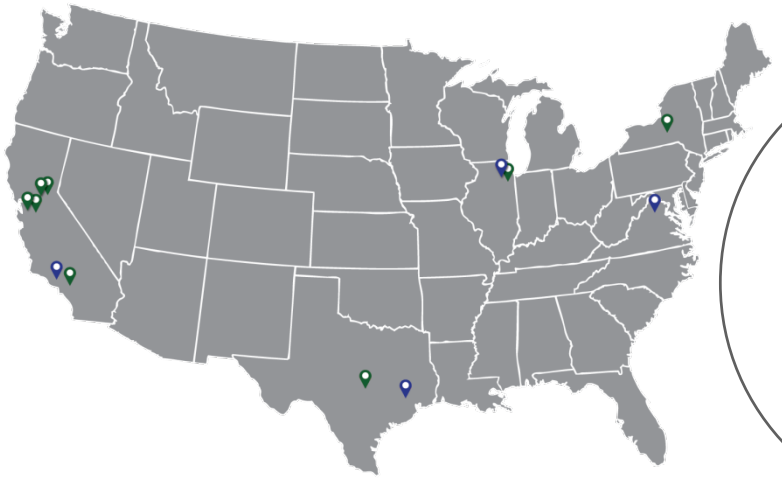
**2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting**

**August 26 - 30, 2019, Pittsburgh, PA**

# Introduction to GTI

- Research organization, providing energy and environmental solutions to the government and industry since 1941
- Facilities: 18 acre campus near Chicago

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- Idea
- Market Analysis
- Technology Analysis
- Product Development
- Lab and Field Testing
- Demonstration
- Commercialization

# GO-PEEK project overview

- **Performance period**: Oct. 1, 2015 – Sep. 30, 2019
- **Funding**: $1,999,995 from DOE; $500,000 cost share

  U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY DE-FE0026383
- **Objectives**: Develop a hybrid membrane process combining a graphene oxide (GO) gas separation membrane unit and a PEEK hollow fiber membrane contactor (HFMC) unit to capture ≥90% of the $CO_2$ from flue gases with 95% $CO_2$ purity at a cost of electricity 30% less than the baseline $CO_2$ capture approach
- **Team:**

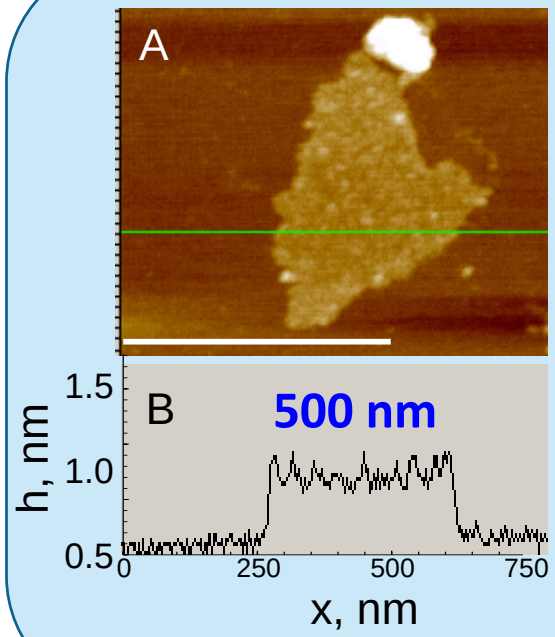
| Member | Roles |
|---|---|
| gti | ▪ Project management and planning<br>▪ Quality control and $CO_2$ capture performance tests |
| University of South Carolina; Rensselaer Polytechnic Institute | ▪ GO membrane development |
| Air Liquide Advanced Business & Technologies; ALaS | ▪ PEEK membrane development |
| Trimeric Corporation | ▪ High-level technical & economic feasibility study |

GO = graphene oxide; PEEK = polyether ether ketone; HFMC = hollow fiber membrane contactor

# GO membrane technology based on our work published in *Science, Nature Communications, and Journal of Membrane Science*

Science
AAAS

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




- **Contribution**:
  - Single-layered GO flake prepared as thin as 1 nm
  - Structural defects on GO flakes can be controlled as transport pathway for selective gas separations

nature COMMUNICATIONS

ARTICLE

DOI: 10.1038/s41467-017-02318-1 OPEN

Ultrathin graphene oxide-based hollow fiber membranes with brush-like $CO_2$-philic agent for highly efficient $CO_2$ capture

ELSEVIER

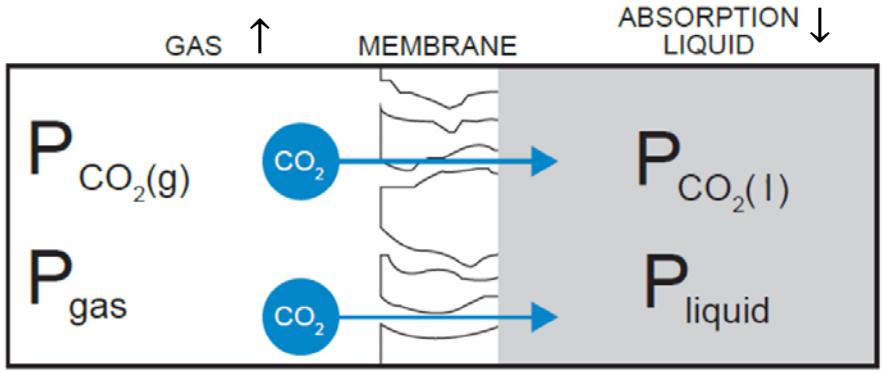
Journal of Membrane Science
Volume 573, 1 March 2019, Pages 184-191

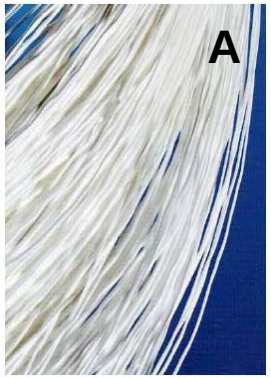
Ultrathin, ethylenediamine-functionalized graphene oxide membranes on hollow fibers for $CO_2$ capture

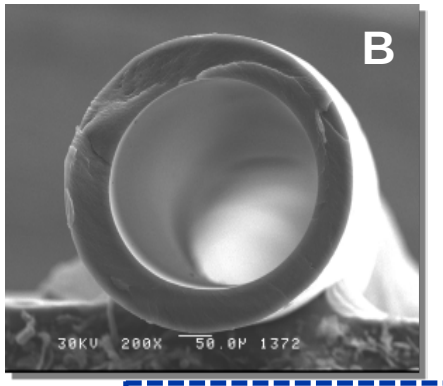
gti

# Singular PEEK HFMC technology currently at pilot scale development stage (DE-FE0012829)

**Membrane contactor: high surface area device that facilitates mass transfer**

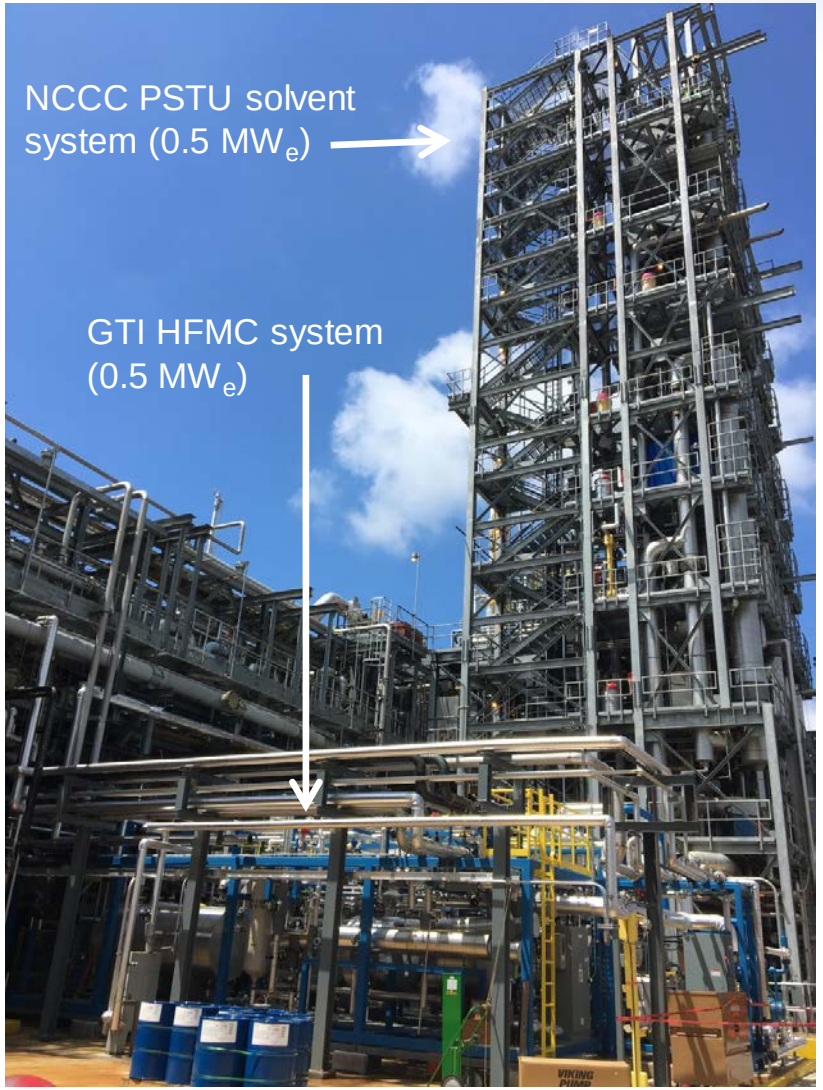



**PEEK spun into high-packing density, hollow fibers**

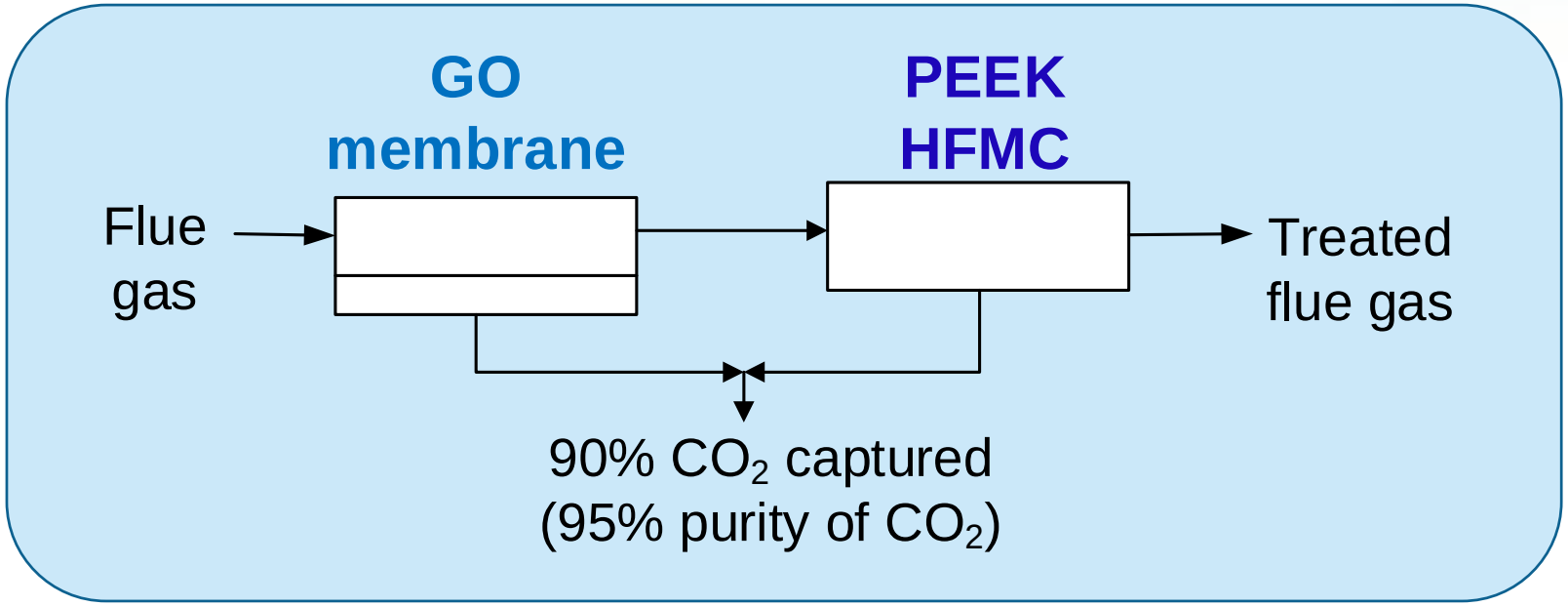
**8-inch-diameter commercial modules with ~2,000 GPU intrinsic $CO_2$ permeance used in pilot scale testing**




**Pilot plant being tested at NCCC**

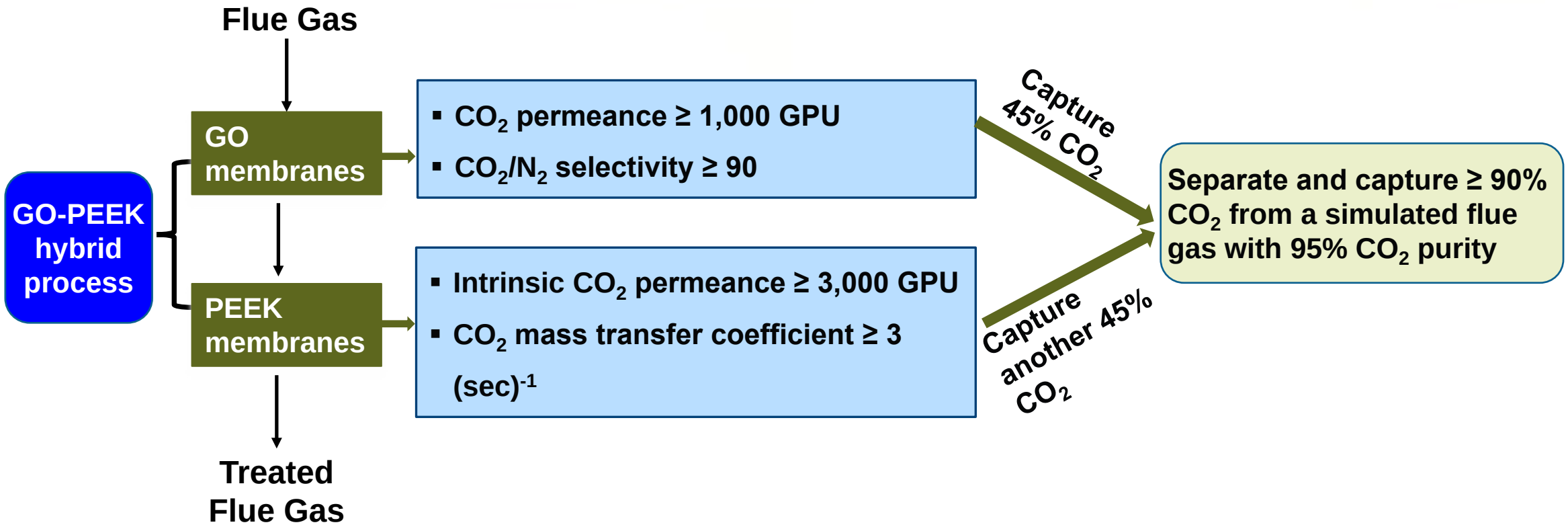
**PEEK = Polyether Ether Ketone; HFMC = Hollow fiber membrane contactor**

# GO-PEEK process description



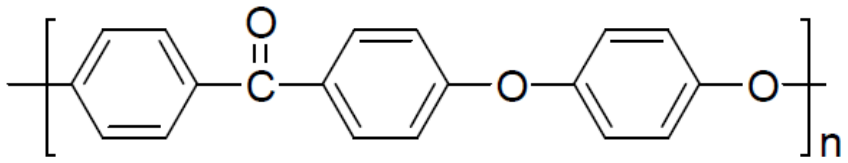

- GO-PEEK uses a conventional gas separation membrane unit to capture bulk of the $CO_2$ from flue gas followed by a PEEK HFMC unit to further capture $CO_2$ to achieve DOE's technical target
- Takes advantages of the "Pros" of two processes while overcoming their "Cons", offering opportunity to explore further reductions in $CO_2$ capture cost

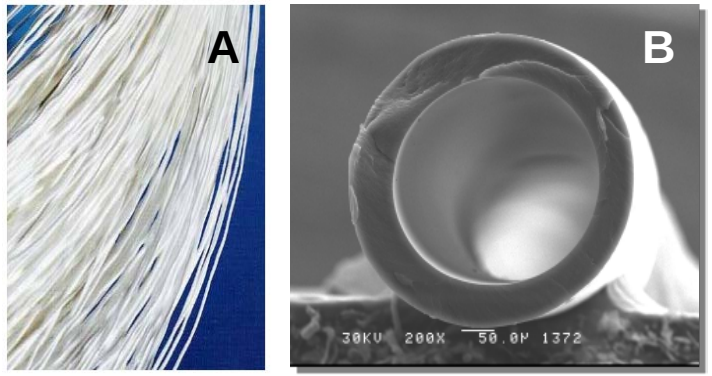
# GO-PEEK technical goals



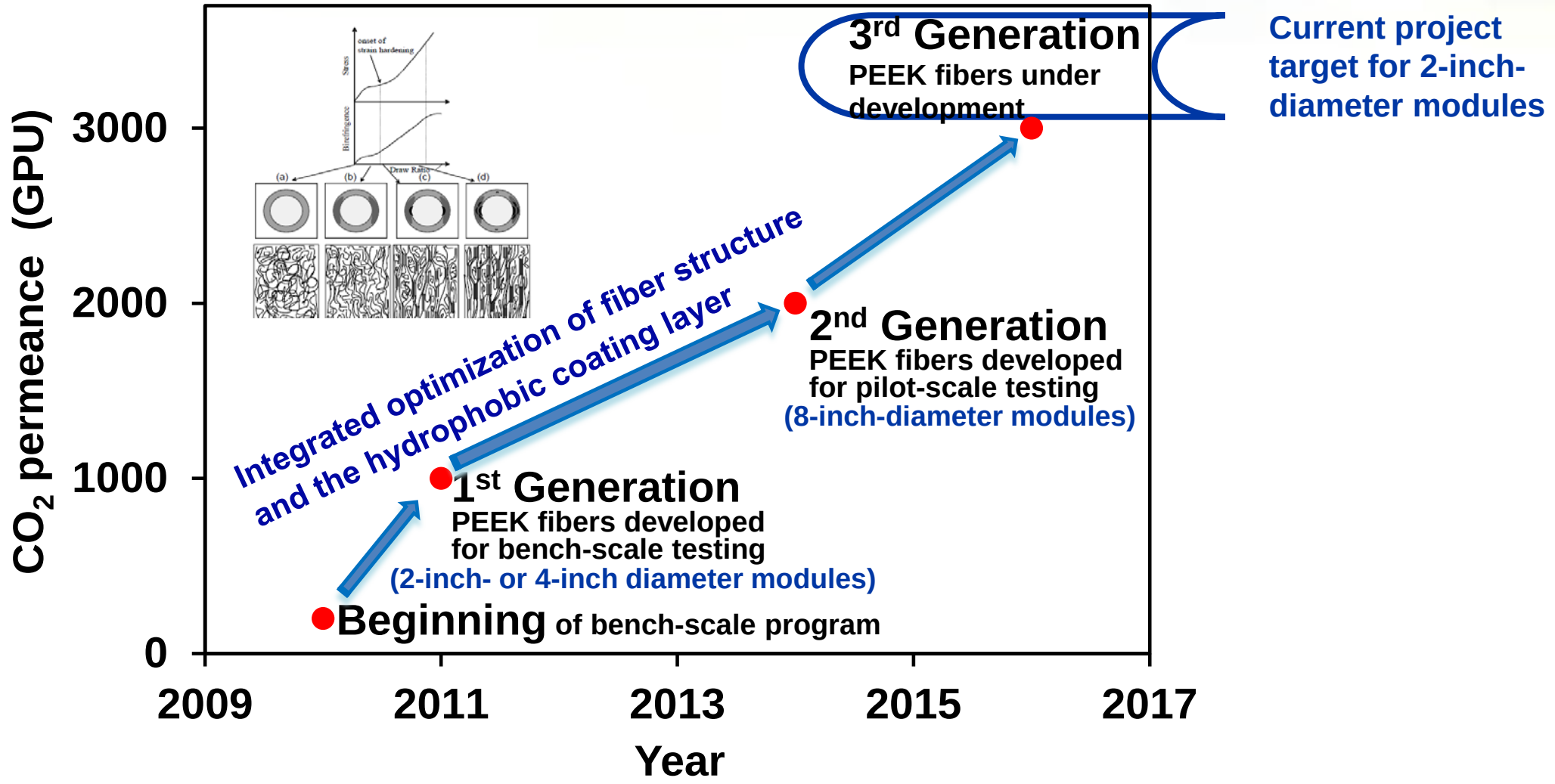

**GPU**= **G**as **P**ermeation **U**nit

# PEEK membrane development



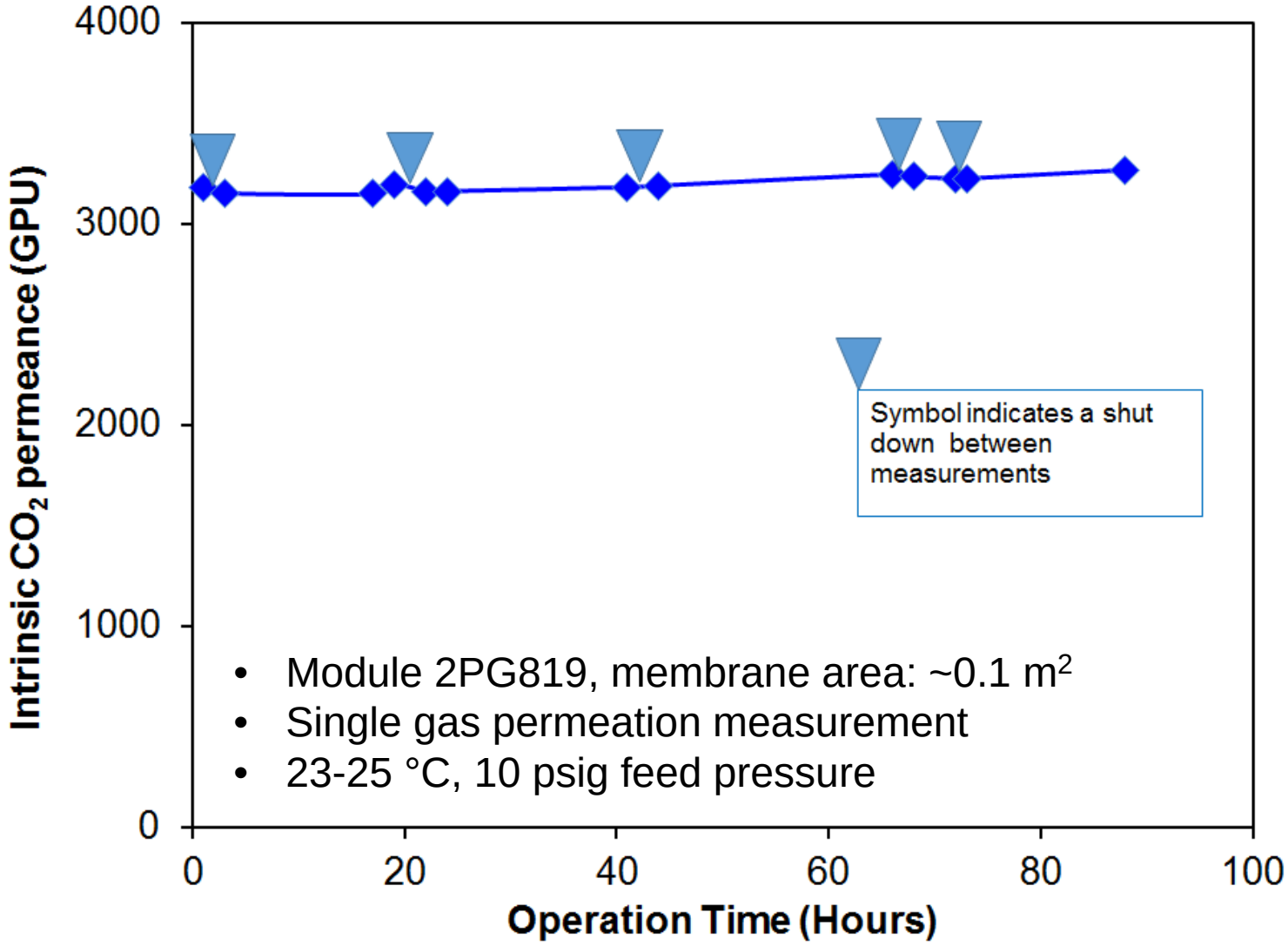



# Under the current program, we have been developing PEEK fibers with intrinsic $CO_2$ permeance of 3,000 GPU

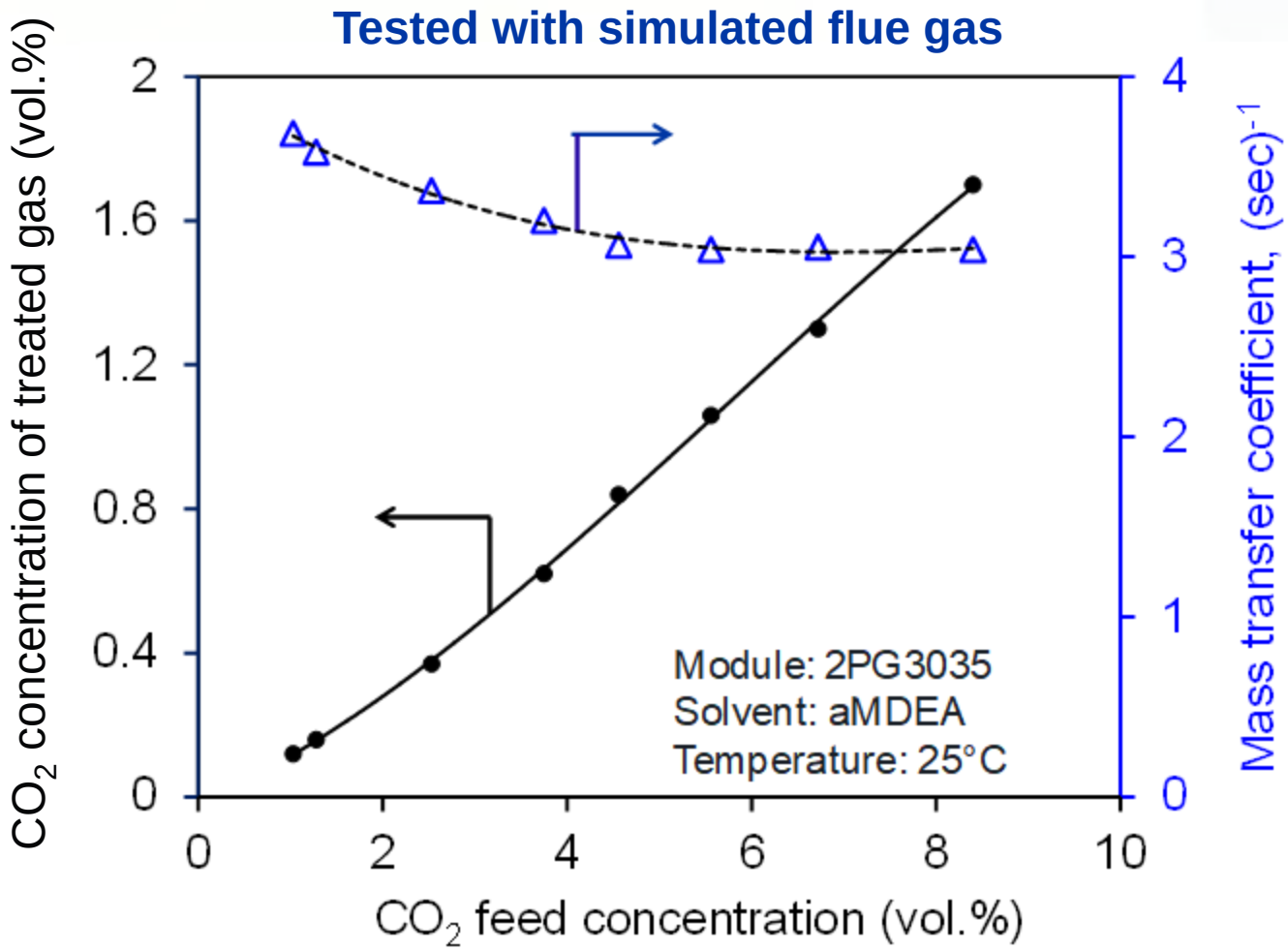



1 GPU = 3.348 x $10^{-10}$ mol/$m^2$/s/Pa

# 3rd Gen fibers developed; 2-inch-diameter module using the fibers showed $CO_2$ permeance >3,000 GPU

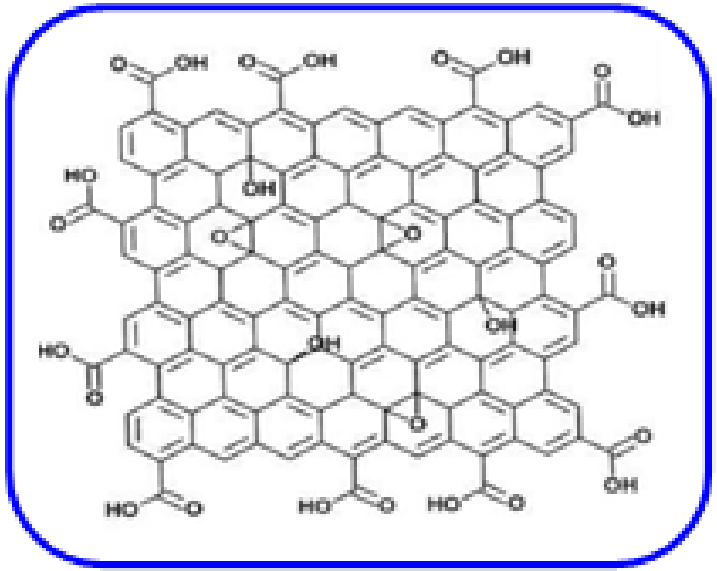


# PEEK membrane module effective in capturing $CO_2$ from low $CO_2$-concentration feeds in membrane contactor



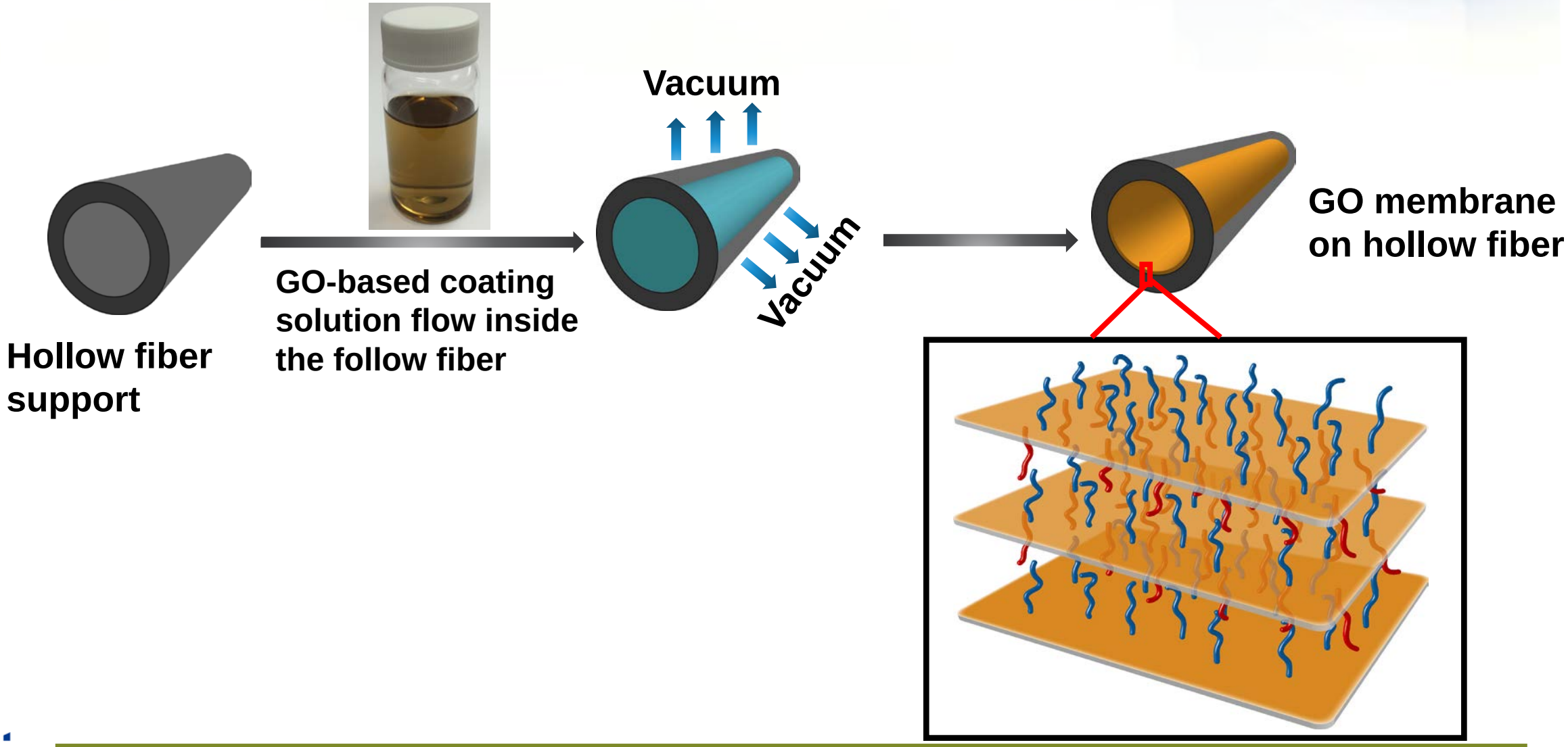

Goal of mass transfer coefficient > 3 $(sec)^{-1}$ achieved

# GO membrane development



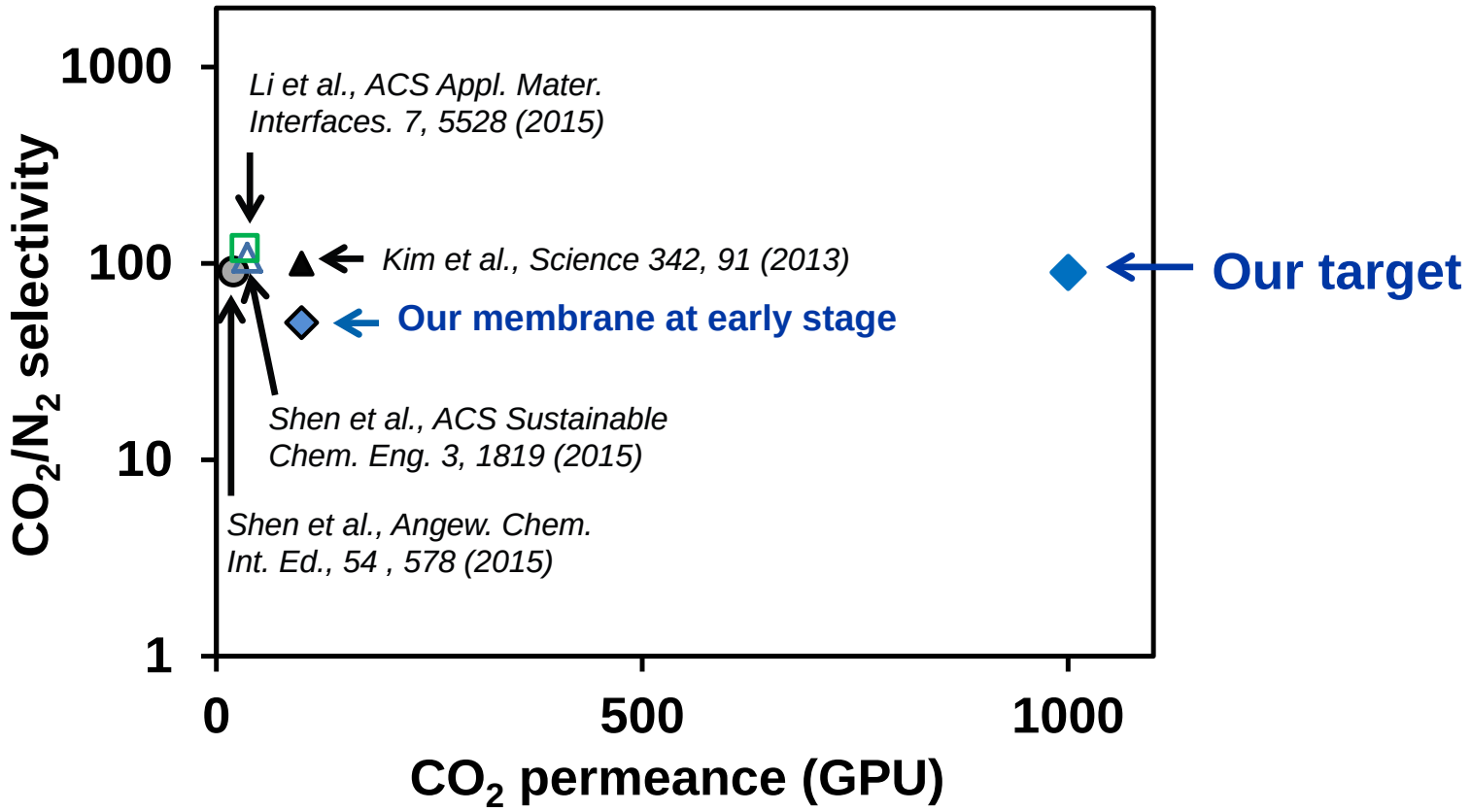
**GO**: single-atomic layered, oxidized graphene

# An scalable procedure developed for fabrication of GO membranes on hollow fibers



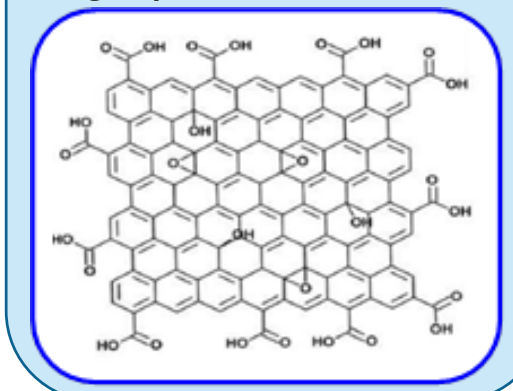
# Challenge: initial GO membrane performance needed significant improvement

- Initial GO membrane performance under simulated flue gas condition (humidified 15%/85% $CO_2/N_2$ mixture):
  - $CO_2$ permeance: 100 GPU; selectivity: 49

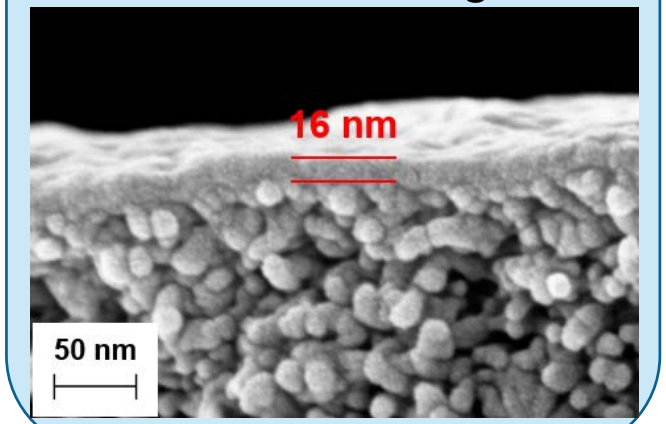


# Unique GO properties + $CO_2$-philic agent → High performance $CO_2$ capture membrane

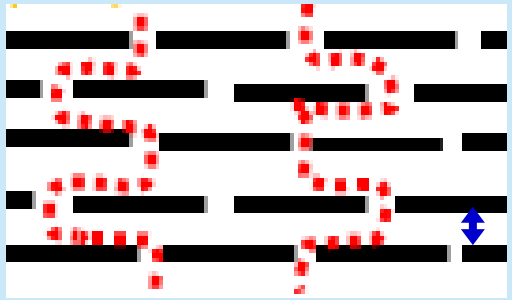
- GO: single-atomic layered, oxidized graphene



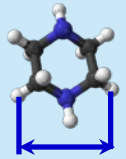
- Can be made ultra-thin, and thus high flux



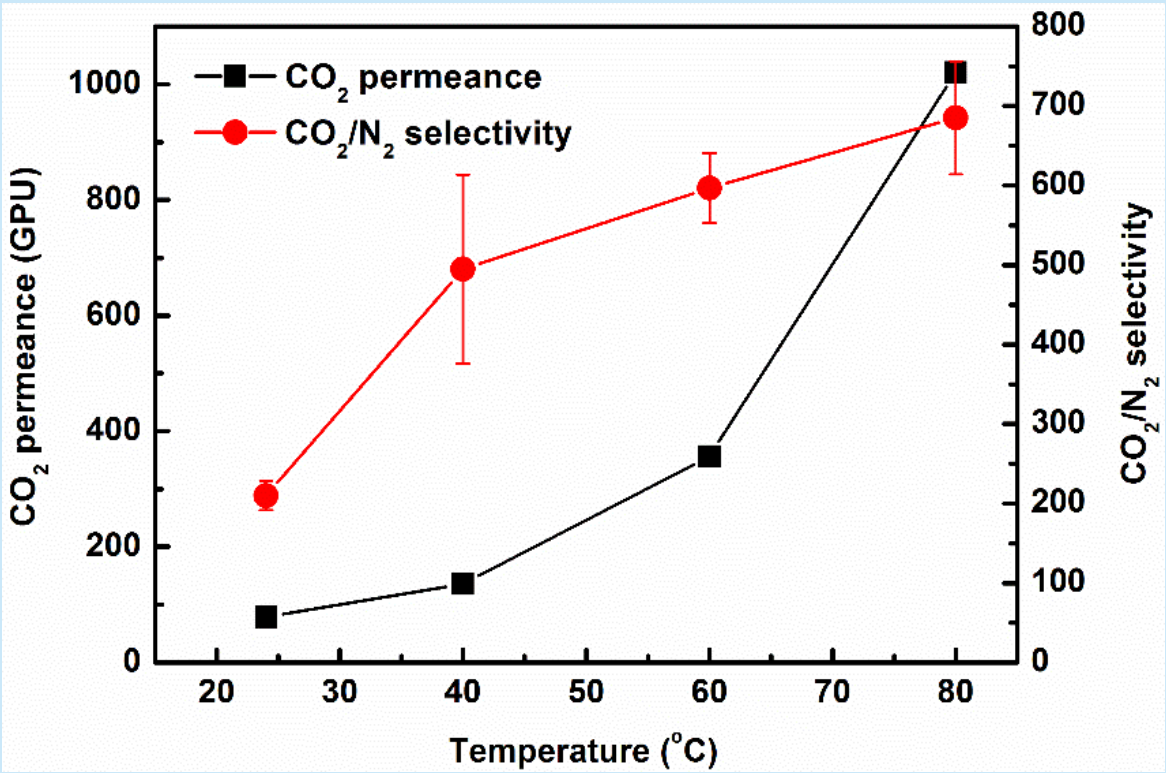

- Space in between GO layers filled with $CO_2$-philic agent, and thus high selectivity




$CO_2$-philic agent example: piperazine (PZ)

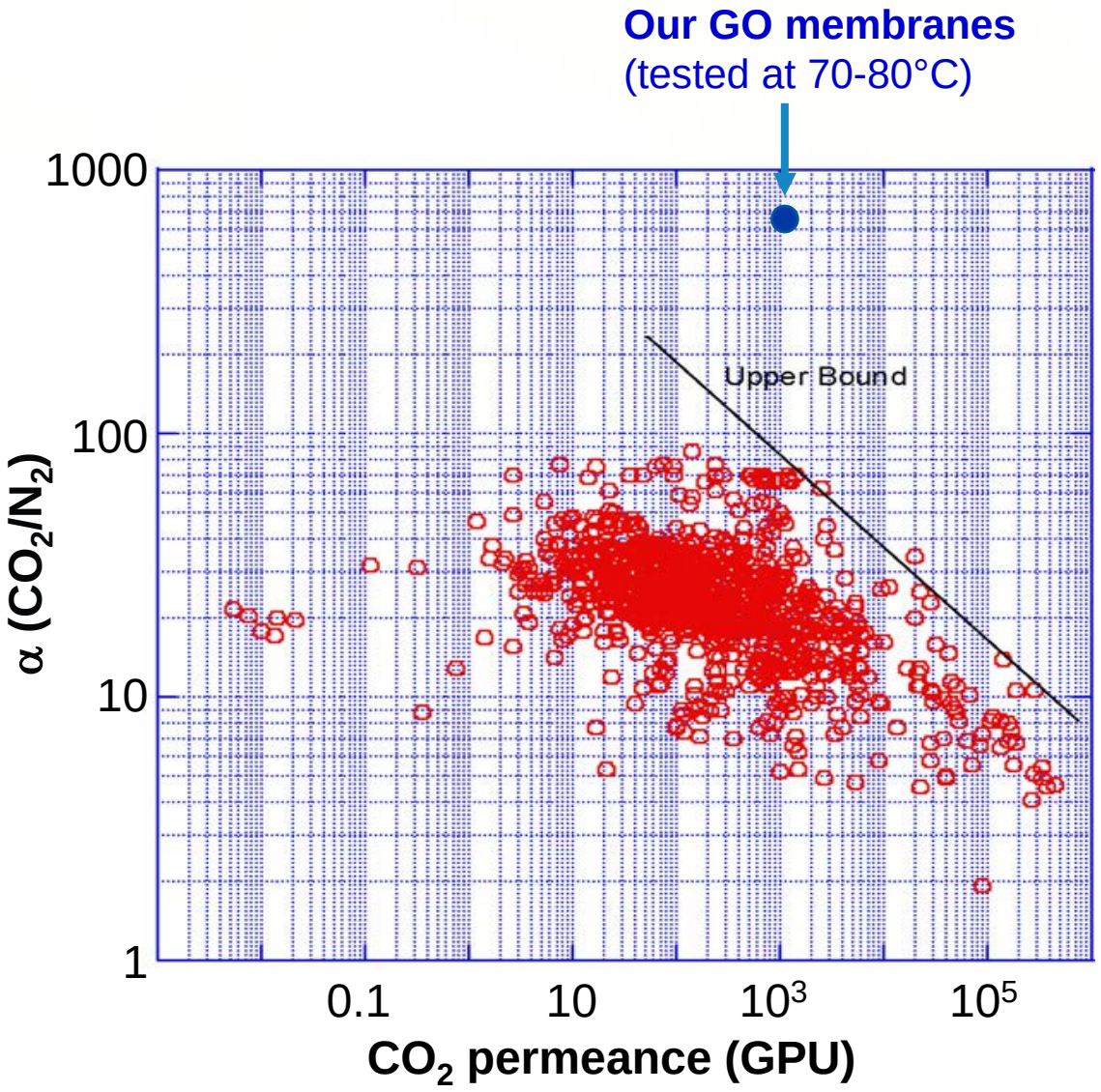


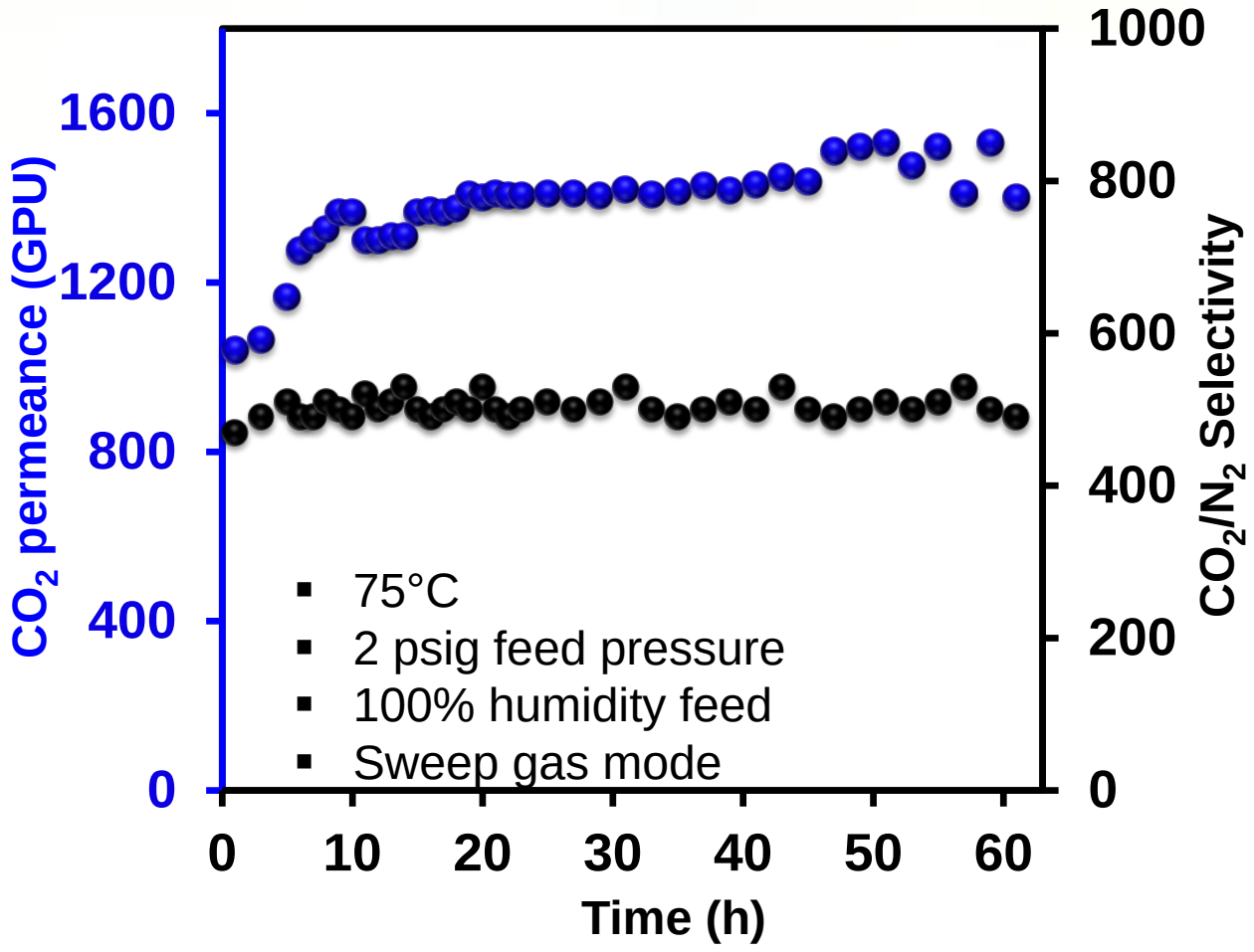

- High performance GO-PZ membrane




**Feed:** 15% $CO_2$/85%$N_2$ with saturated water vapor
**Permeate:** with sweep gas

# Superior performance to polymeric membranes and stable



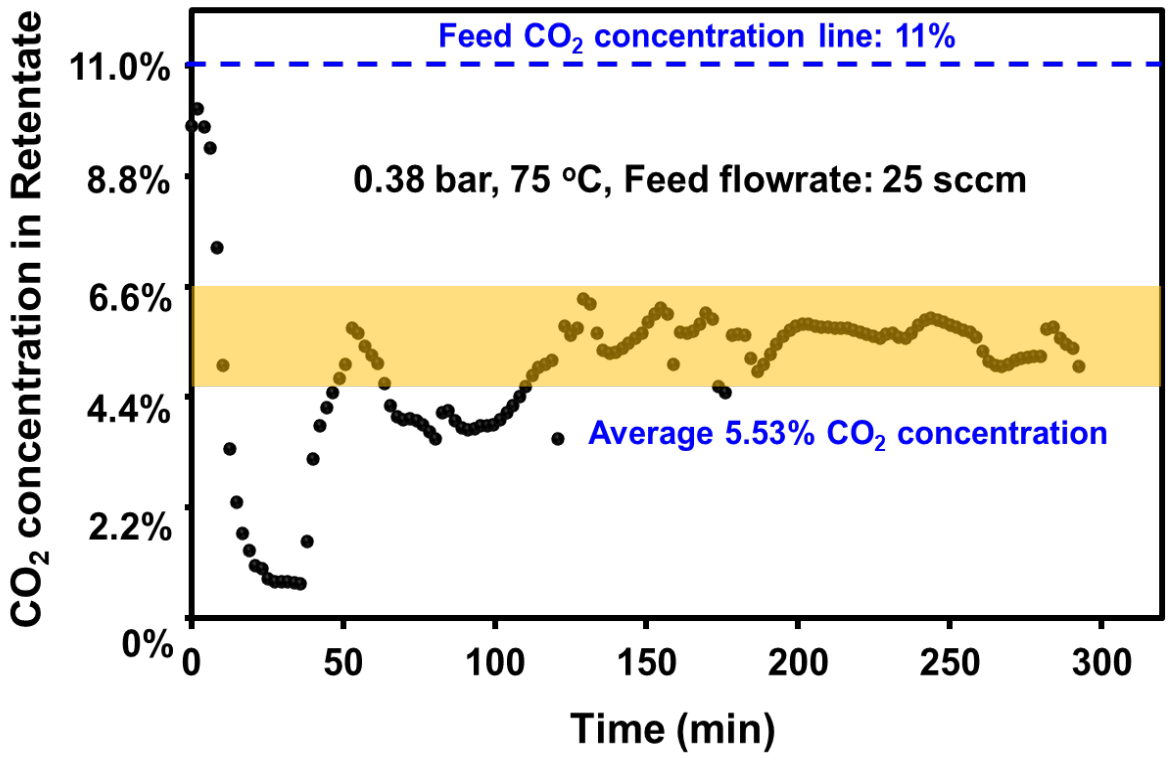

*Robeson, J. Membrane Sci.* ***2008****, Vol. 320, p390*

Note: Polymer data points (red): 100 nm membrane thickness assumed

# Integrated testing ongoing, results indicated >90% $CO_2$ removal and >95% $CO_2$ purity

**GO unit**: Feed $CO_2$ concentration: 11 vol.%

- Retentate $CO_2$ concentration: 5.53 vol.%




**PEEK unit**: Feed $CO_2$ concentration: 5.53 vol.%

- Retentate $CO_2$ concentration: 0.21 vol.%
- $CO_2$ purity from regeneration: 96.9 vol.%

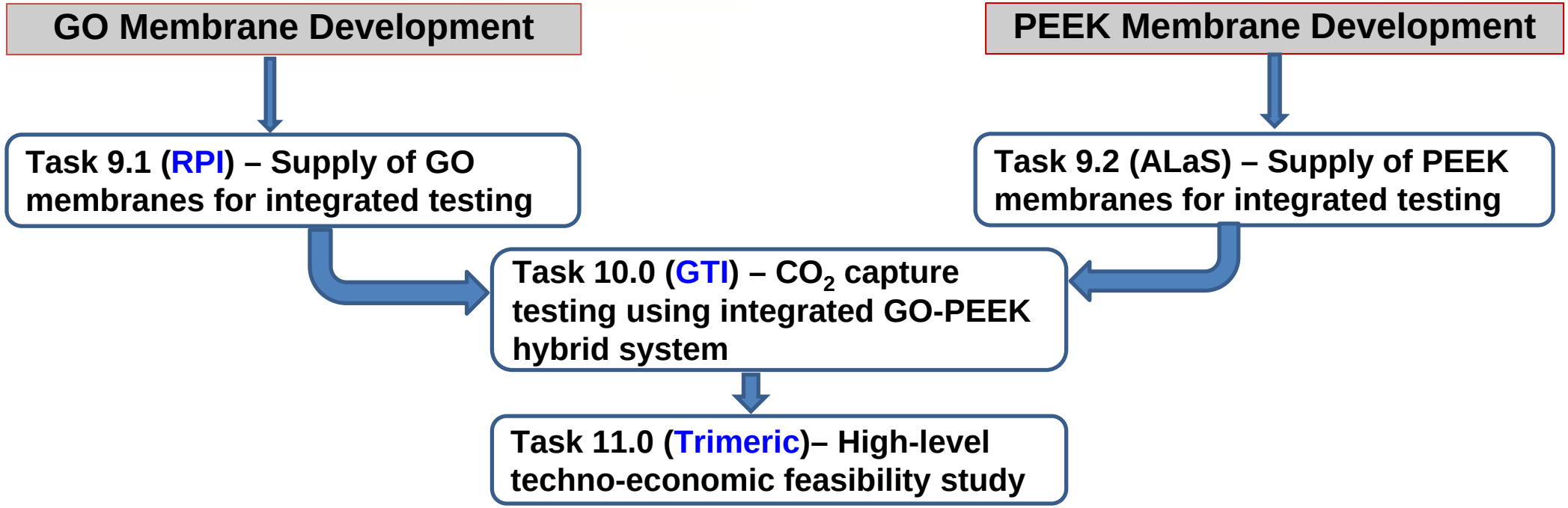
| Component | Mol % | Det. Limit | Weight % |
|---|---|---|---|
| Helium | | 0.1% | |
| Hydrogen | | 0.1% | |
| Carbon Dioxide | 96.9% | 0.03% | 97.9% |
| Oxygen/Argon | 0.50% | 0.03% | 0.37% |
| Nitrogen | 2.62% | 0.03% | 1.68% |
| Carbon Monoxide | | 0.03% | |
| Methane | | 0.002% | |
| Ethane | | 0.002% | |
| Ethene | | 0.002% | |
| Ethyne | | 0.002% | |
| Propane | | 0.002% | |
| Propene | | 0.002% | |
| Cyclopropane | | 0.002% | |
| Propadiene | | 0.002% | |
| Propyne | | 0.002% | |
| i-Butane | | 0.002% | |
| n-Butane | | 0.002% | |
| 1-Butene | | 0.002% | |
| i-Butene | | 0.002% | |
| trans-2-Butene | | 0.002% | |
| cis-2-Butene | | 0.002% | |
| 1,3-Butadiene | | 0.002% | |
| neo-Pentane | | 0.002% | |
| i-Pentane | | 0.002% | |
| n-Pentane | | 0.002% | |
| Pentenes | | 0.002% | |
| Hexane Plus | | 0.002% | |
| Hydrogen Sulfide | | 0.10% | |
| Total | 100.0% | | 100.0% |

# High-level TEA study commenced

- Completed activities
  - Process design basis
  - Process simulation (Aspen HYSYS) with heat and material balance
  - Process flowsheet with all major equipment identified
- GTI is currently completing testing to verify assumptions for
  - $CO_2$ flux
  - Water, $NO_2$ and $SO_2$ permeance
  - Operating temperatures
- Next steps
  - Equipment sizing and costing
  - CAPEX, OPEX, cost of $CO_2$ capture
  - Sensitivity studies

# Future work overview/roadmap

- **In this project**




- **After this project**
  - **Bench-scale development for GO-based membranes (DE-FE0031598)**

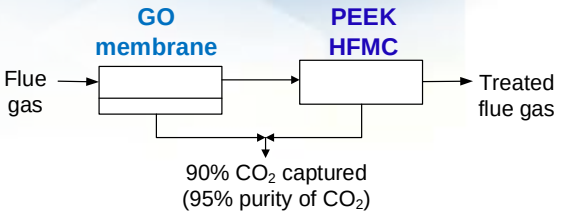
# Summary

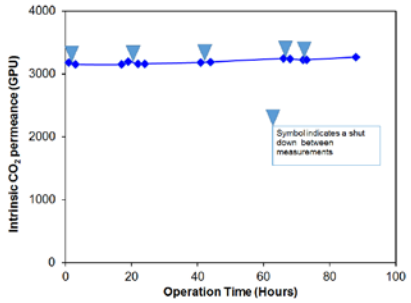
- We are developing a transformational **hybrid process** for $CO_2$ capture combining a conventional gas membrane unit and a HFMC unit to explore further reductions in the cost of $CO_2$ capture

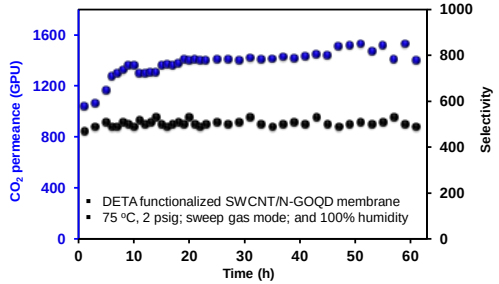
- **The 3rd Generation PEEK fibers** developed to date
  - Showed intrinsic $CO_2$ permeance >3,000 GPU at 25°C
  - Effective in capturing $CO_2$ from low $CO_2$-concentration feeds with aMDEA solvent

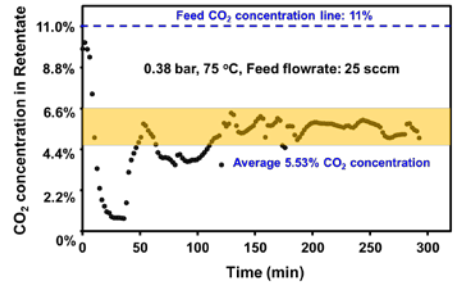
- **GO-based membranes** developed to date
  - Showed $CO_2$ permeance > 1,000 GPU and $\alpha_{CO_2/N_2}$ > 600
  - Good stability

- **Integrated GO-PEEK** testing ongoing, results indicated >90% $CO_2$ removal and >95% $CO_2$ purity. High-level TEA study commenced.



# Acknowledgements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- **DOE NETL Andrew O'Palko, Steven Mascaro. José Figueroa and Lynn Brickett**
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- **Dr. Ding Group at Air Liquide Advanced Separations**

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