DOE Contract DE-FE0026383

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

Shiguang Li, Travis Pyrzynski, Weiwei Xu, Howard Meyer, ***GTI***
Miao Yu, Shenxiang Zhang, Fanglei Zhou, ***Rensselaer Polytechnic Institute (RPI)***
Yong Ding, ***Air Liquide Advanced Separations (ALaS)***
Andrew Sexton, Darshan Sachde, Brad Piggott, ***Trimeric Corporation (Trimeric)***

NATIONAL ENERGY TECHNOLOGY LABORATORY

2020 Carbon Capture Project Review Meeting

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GO-PEEK project overview

- **Performance period**: Oct. 1, 2015 – Sep. 30, 2020
- **Funding**: $1,999,995 from DOE; $500,000 cost share

  U.S. DEPARTMENT OF ENERGY   NATIONAL ENERGY TECHNOLOGY LABORATORY   DE-FE0026383

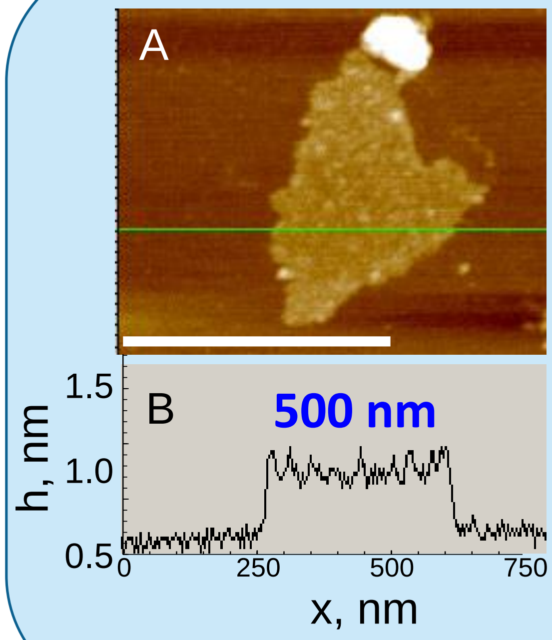
- **Objectives**: Develop a hybrid membrane process combining a graphene oxide (GO) gas separation membrane unit and a PEEK hollow fiber membrane contactor (HFMC) unit to capture ≥90% of the CO_2 from coal flue gases with 95% CO_2 purity at a cost of electricity 30% less than the baseline CO_2 capture approach
- **Team:**

Member	Roles
gti	▪ Project management and planning ▪ 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*

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

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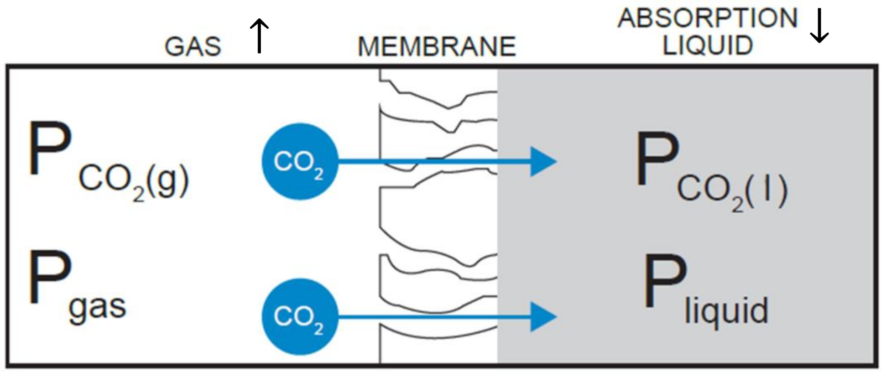
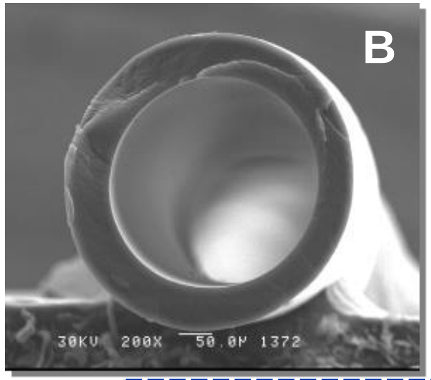
Singular PEEK HFMC technology currently at pilot scale development stage (DE-FE0012829)

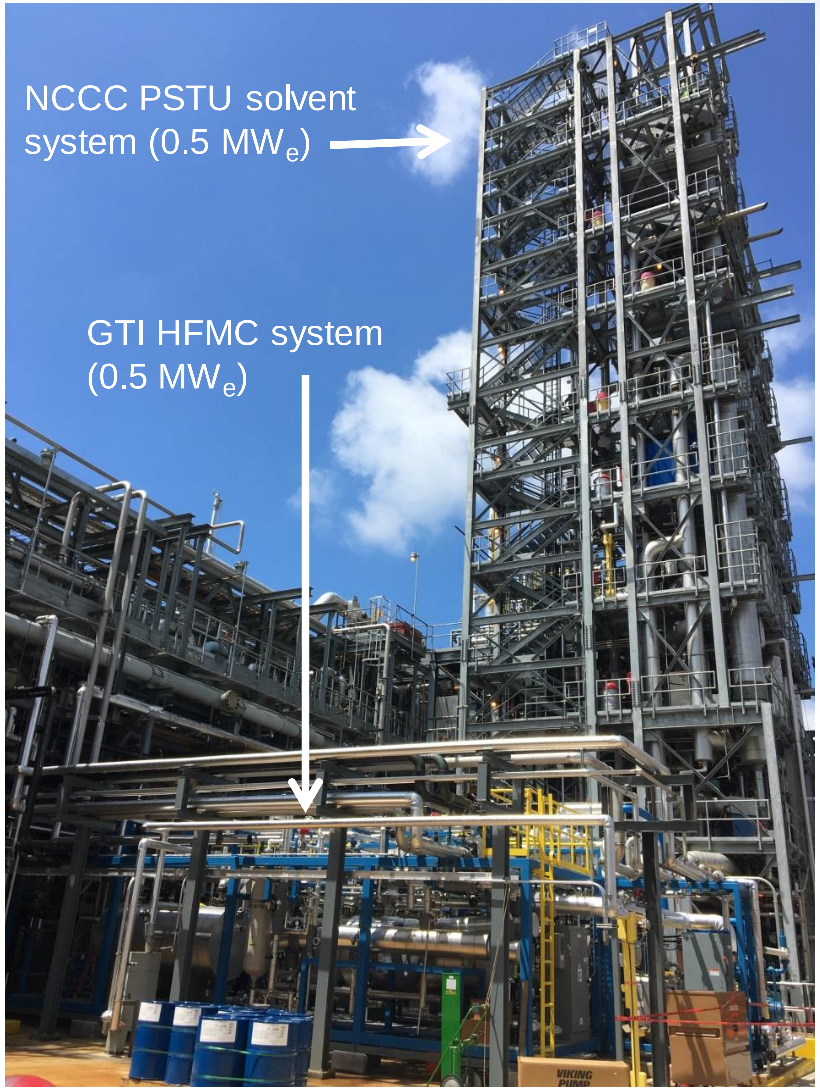
Membrane contactor: high surface area device that facilitates mass transfer





PEEK spun into high-packing density, hollow fibers

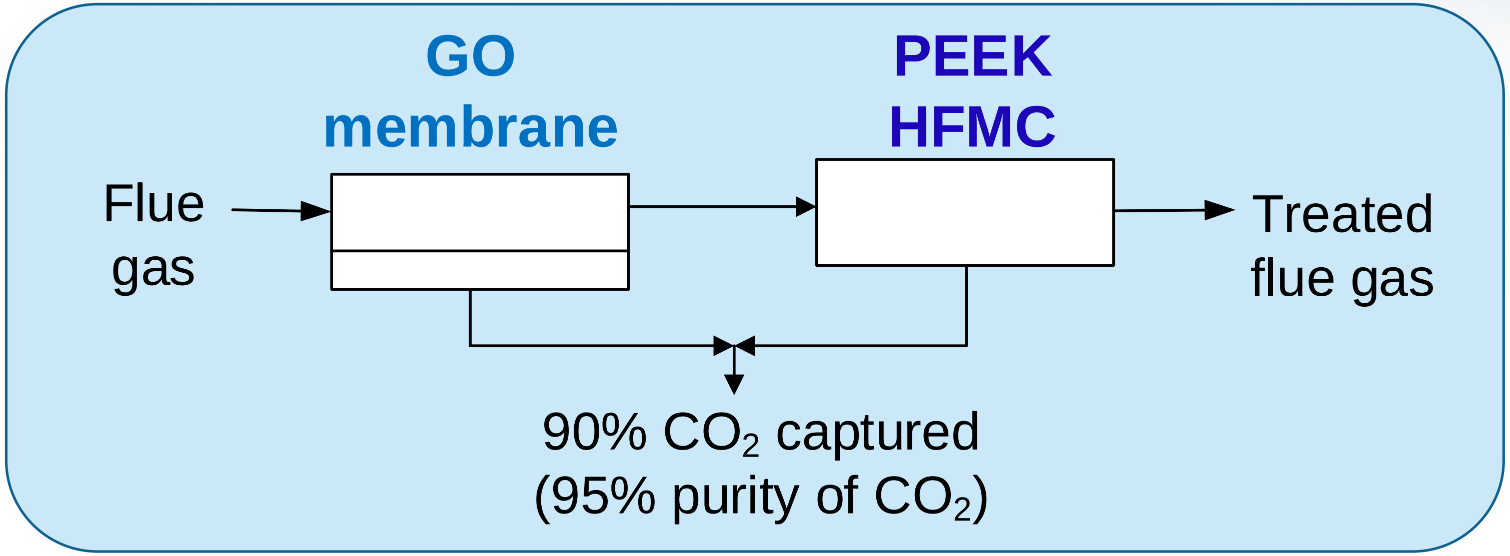
8-inch-diameter commercial modules with ~2,000 GPU intrinsic CO_2 permeance used in pilot scale testing



Pilot plant being tested at NCCC

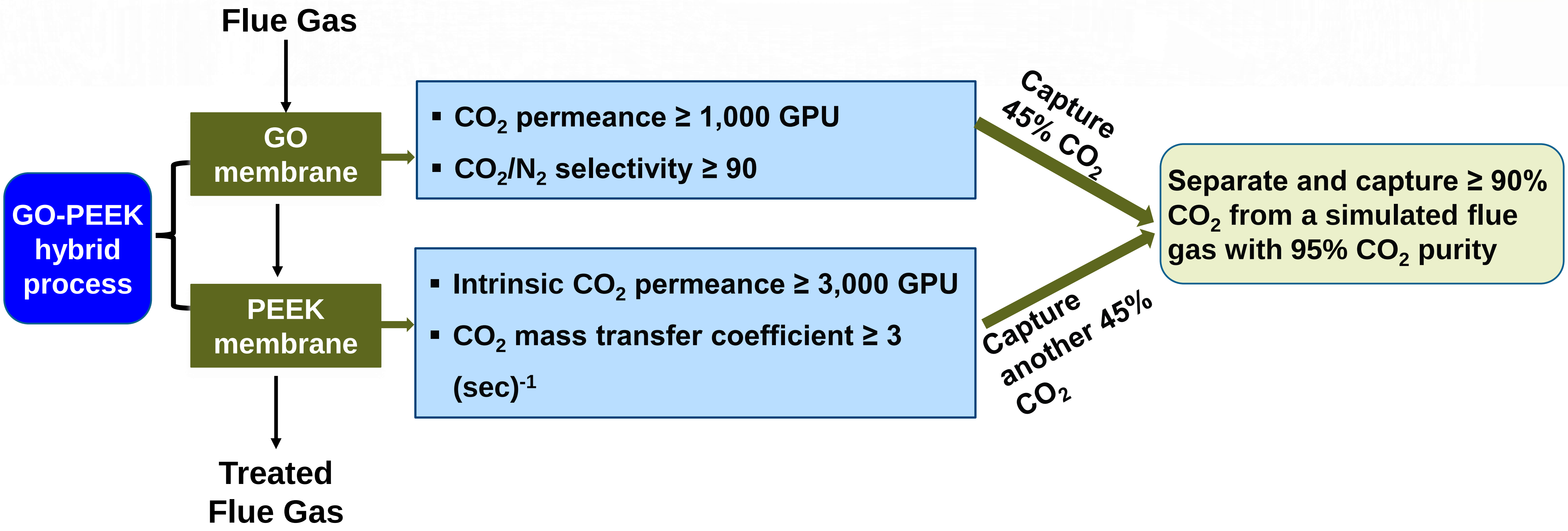
PEEK = **P**oly**e**ther **E**ther **K**etone; HFMC = **H**ollow **f**iber **m**embrane **c**ontactor

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
  - Conventional gas membrane process: simply equipped, and efficient at partial CO_2 capture (40-60%)
  - PEEK HFMC process: effective in capturing CO_2 from low CO_2-concentration feeds (< 5 vol.%)
  - Hybrid process: having less moles of CO_2 captured by the solvent in the PEEK HFMC, and thus less overall energy is required for regeneration

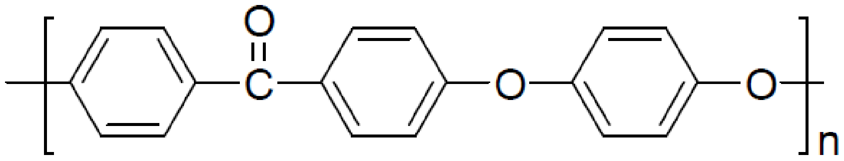
GO-PEEK technical goals

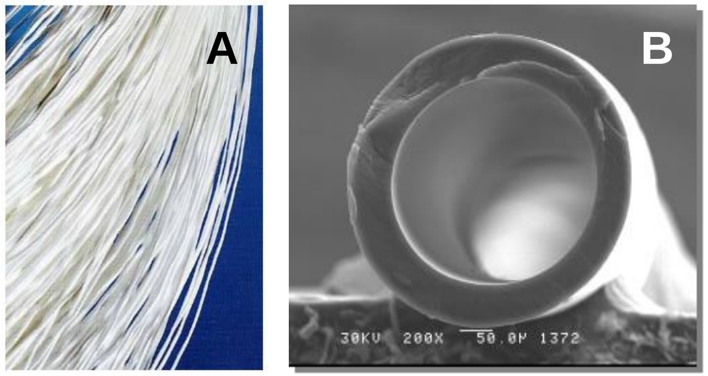


GPU= **G**as **P**ermeation **U**nit

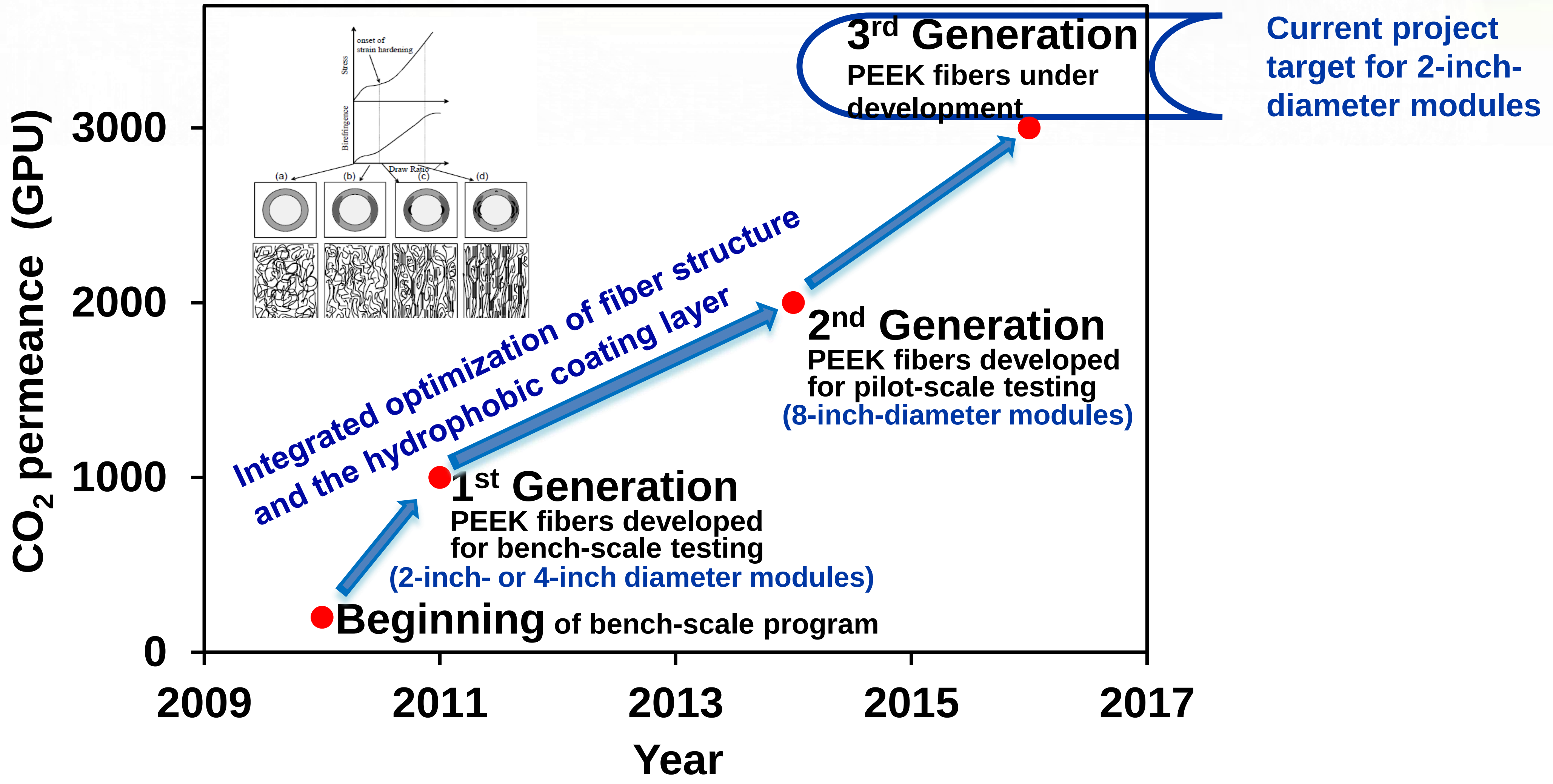
1 GPU = 3.348 x 10^{-10} mol/m^2/s/Pa

PEEK membrane development



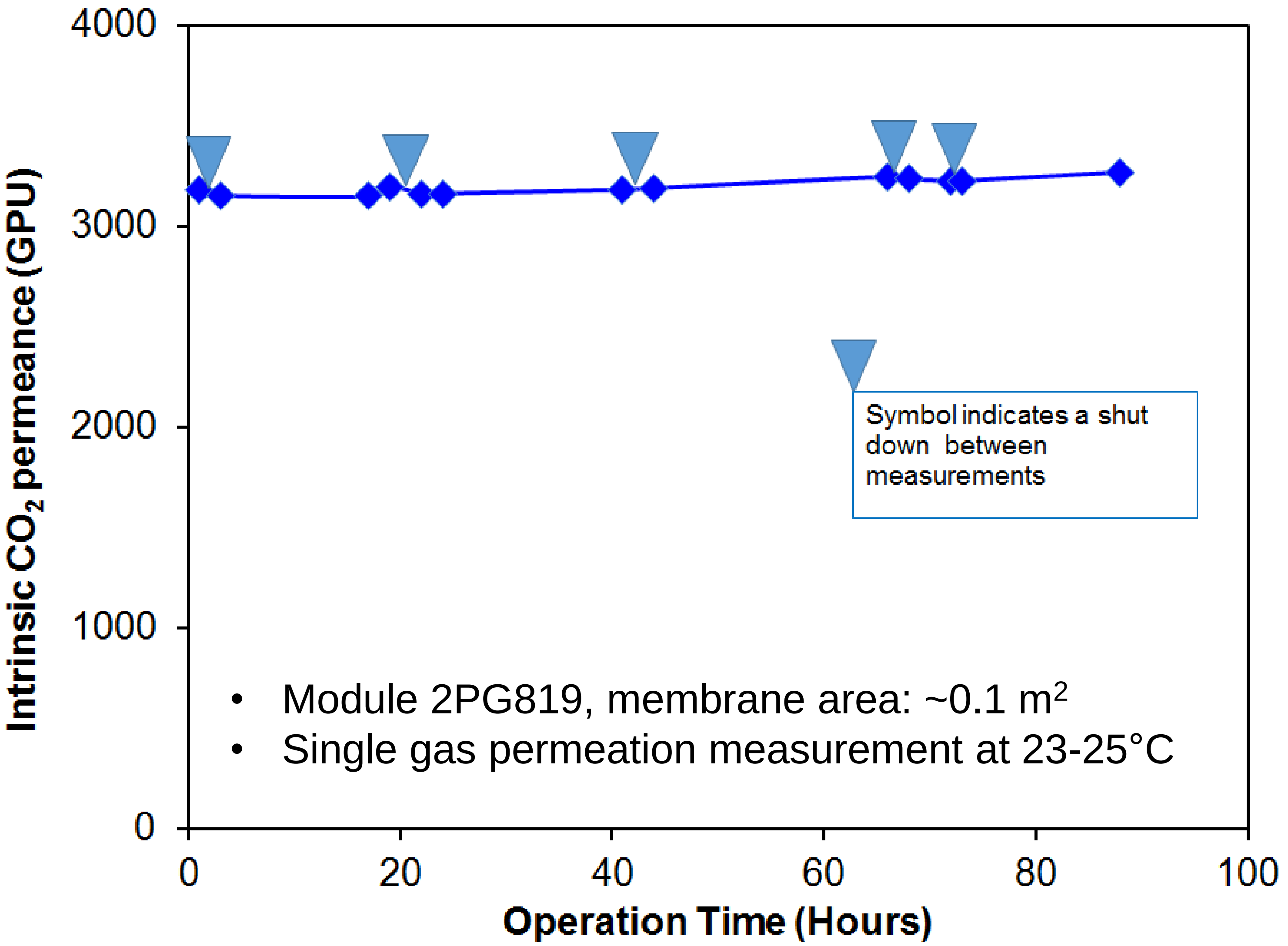


Under the current program, we have been developing PEEK fibers with intrinsic CO_2 permeance of 3,000 GPU



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

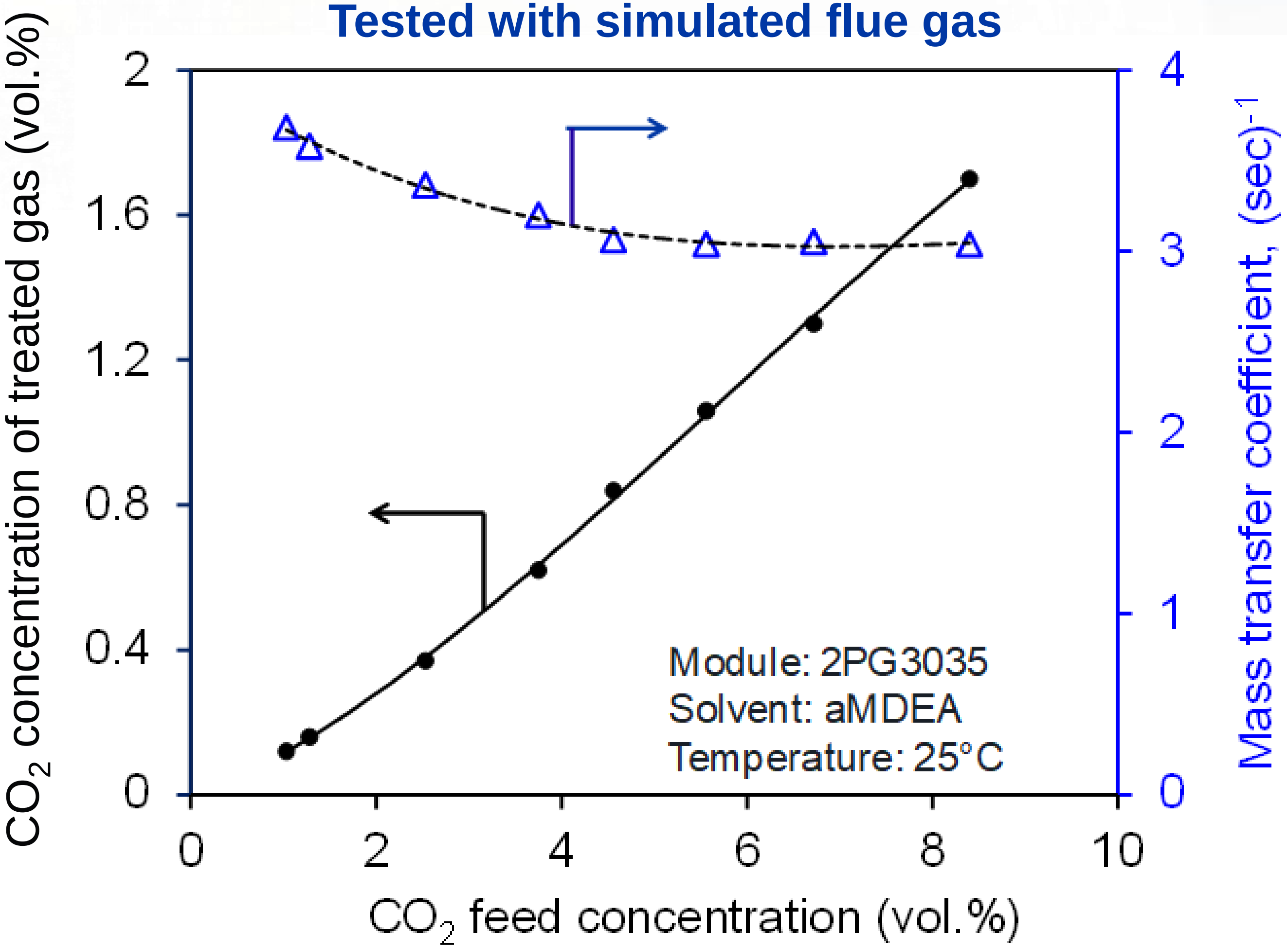
3rd Gen fibers developed; 2-inch-diameter module using the fibers showed CO_2 permeance >3,000 GPU



- Module 2PG819, membrane area: ~0.1 m^2
- Single gas permeation measurement at 23-25°C

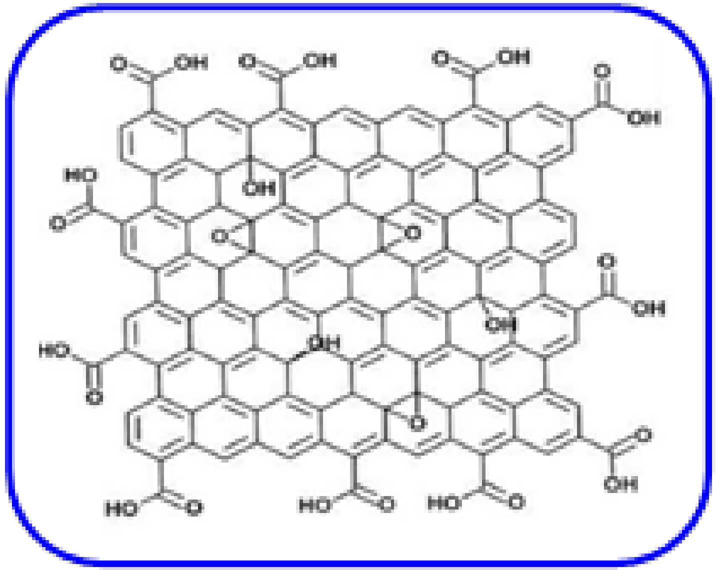
PEEK membrane module effective in capturing CO_2 from low CO_2-concentration feeds in membrane contactor

Tested with simulated flue gas



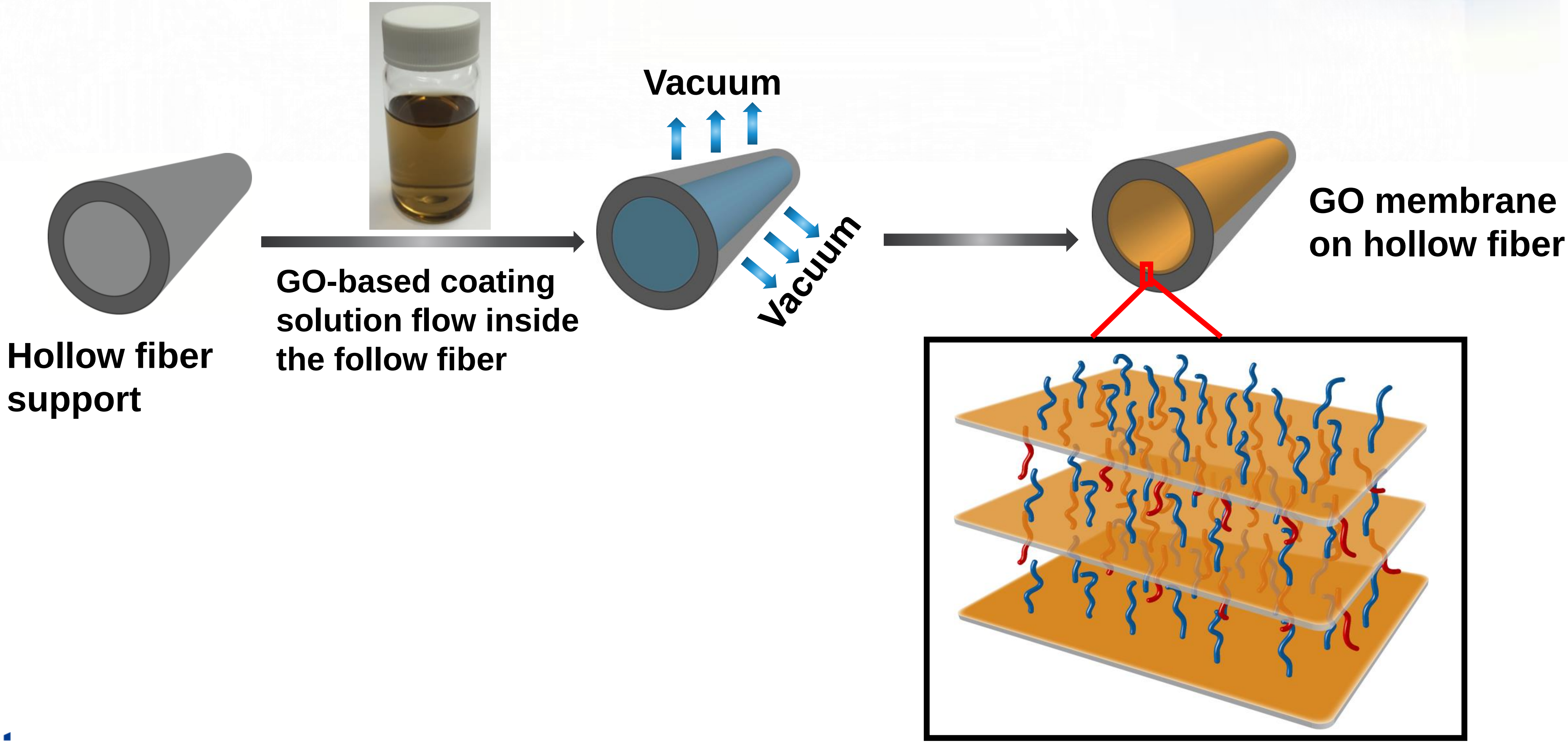
Goal of mass transfer coefficient > 3 $(sec)^{-1}$ achieved

GO membrane development



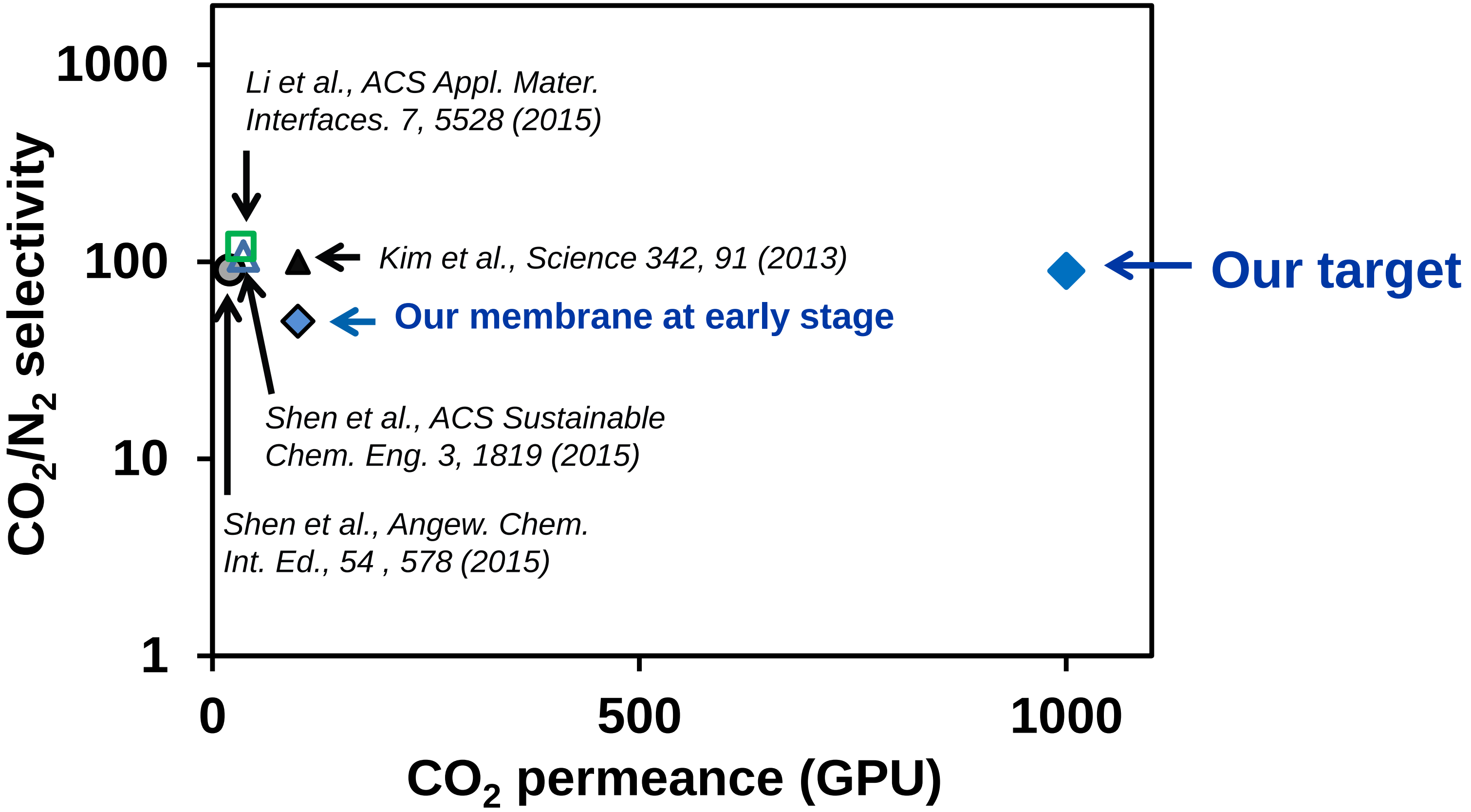
<u>GO</u>: single-atomic layered, oxidized graphene

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



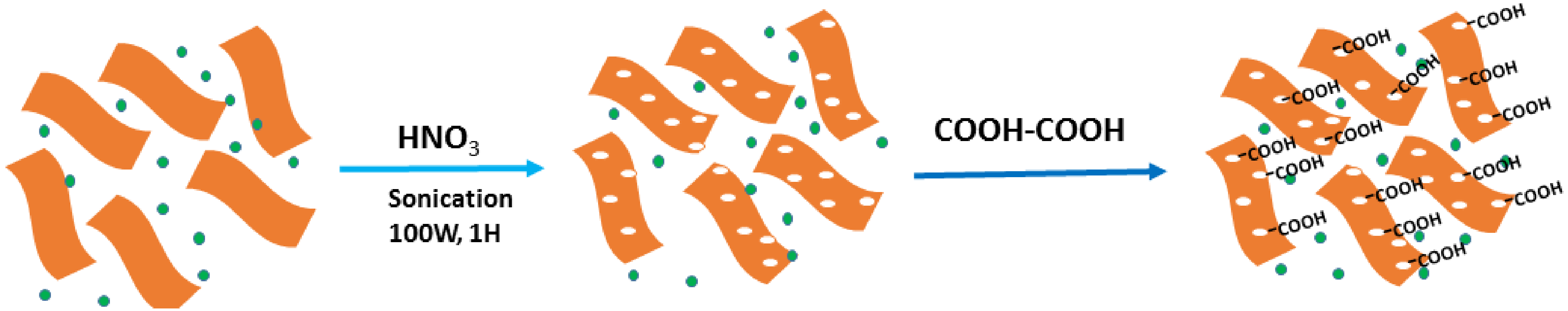
Challenge: initial GO membrane performance needed significant improvement

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



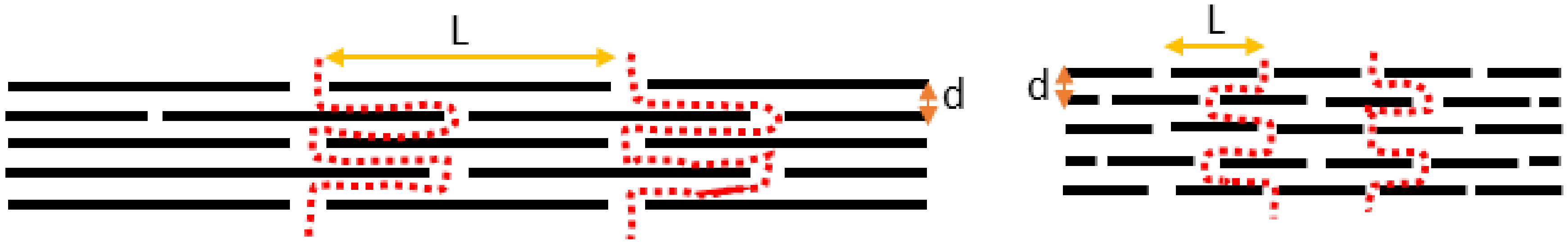
Approaches to improve CO_2 permeance

- Create more structural defects on GO flake by HNO_3 etching



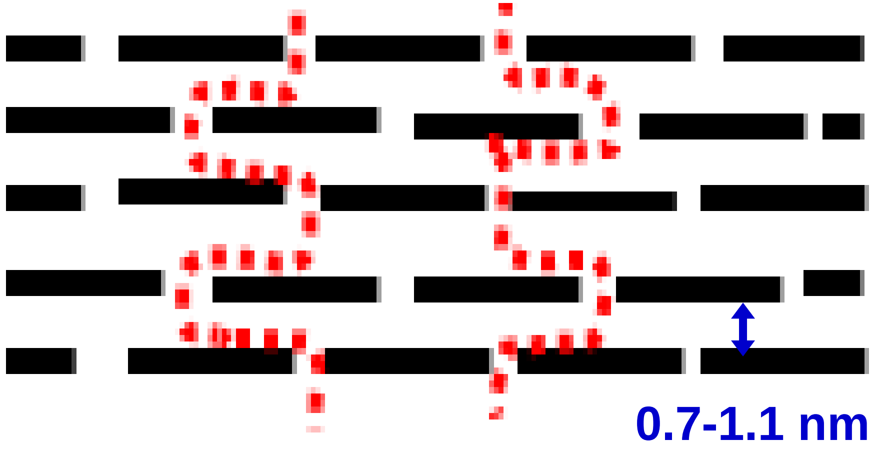
- Reduce GO flake lateral size by ultra-sonication

W/O ultra-sonication **W/ ultra-sonication**

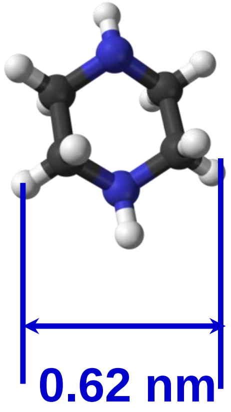


Approach to improve CO_2/N_2 selectivity: fill the space between GO layers with CO_2-philic agent

- CO_2-philic agent enables facilitated transport mechanism to separate CO_2 from N_2

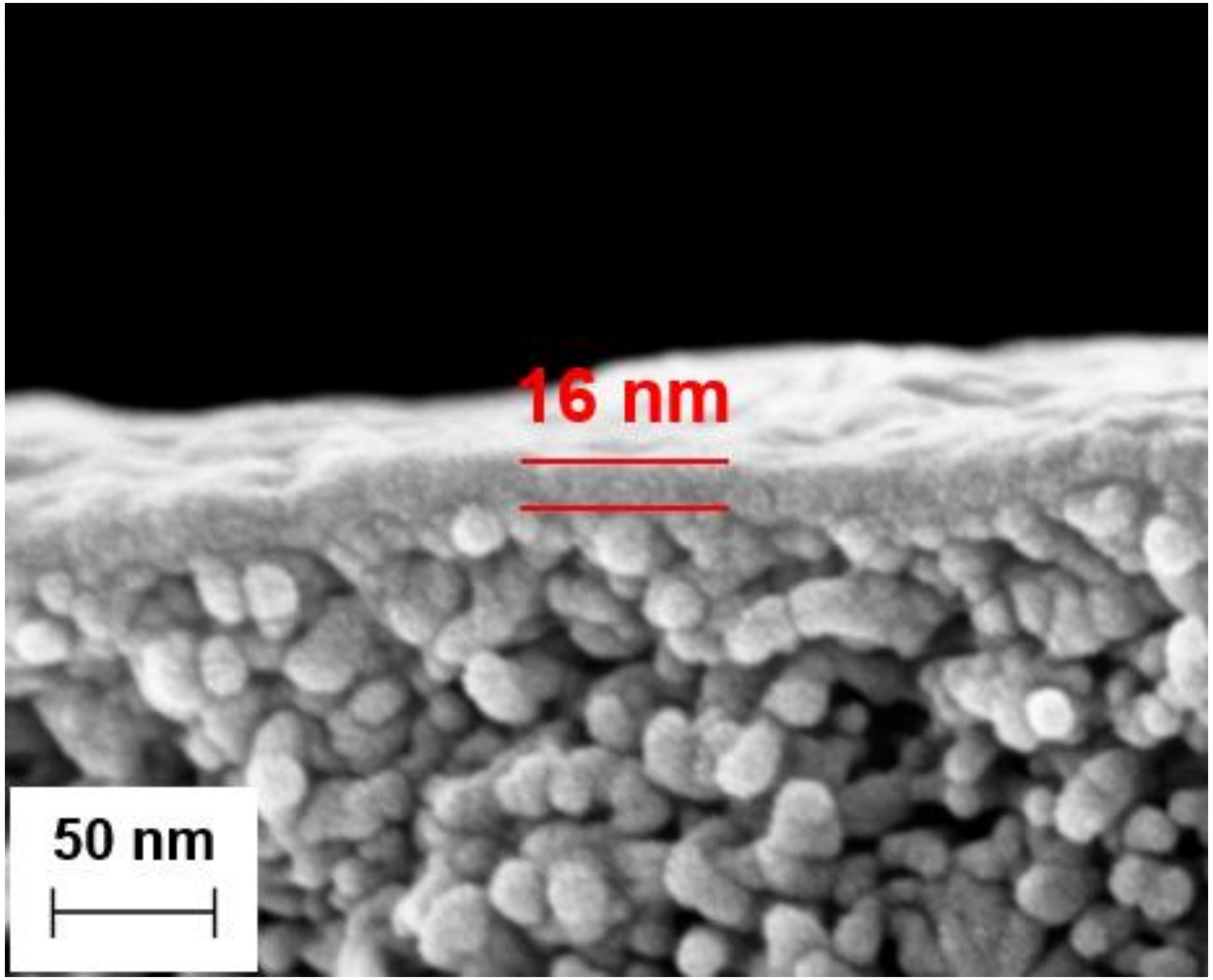


CO_2-philic agent example: piperazine (PZ)



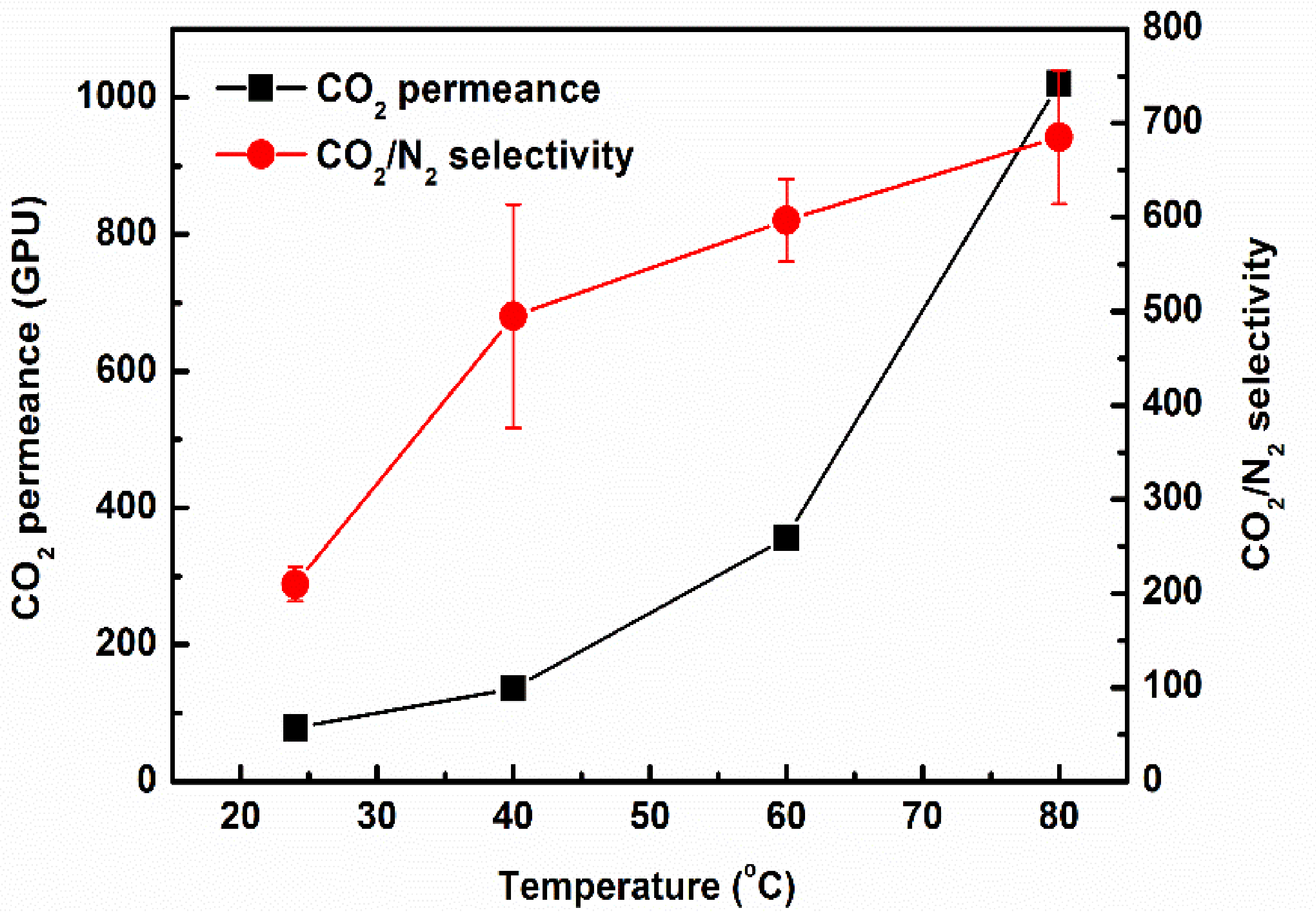
- XPS and FTIR analysis confirmed the crosslinking of PZ with GO sheets

Cross-sectional SEM of the PZ filled GO membrane

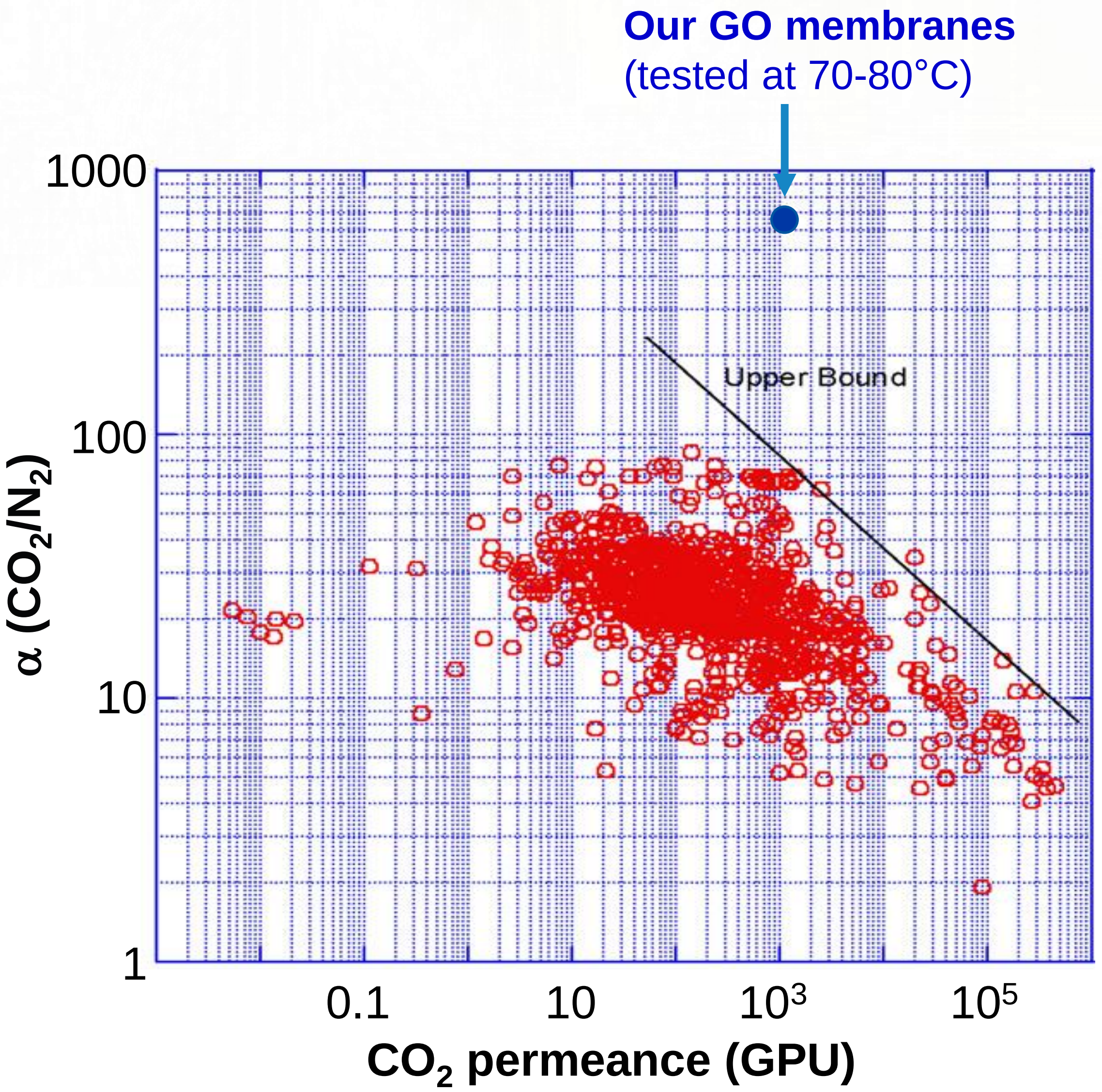


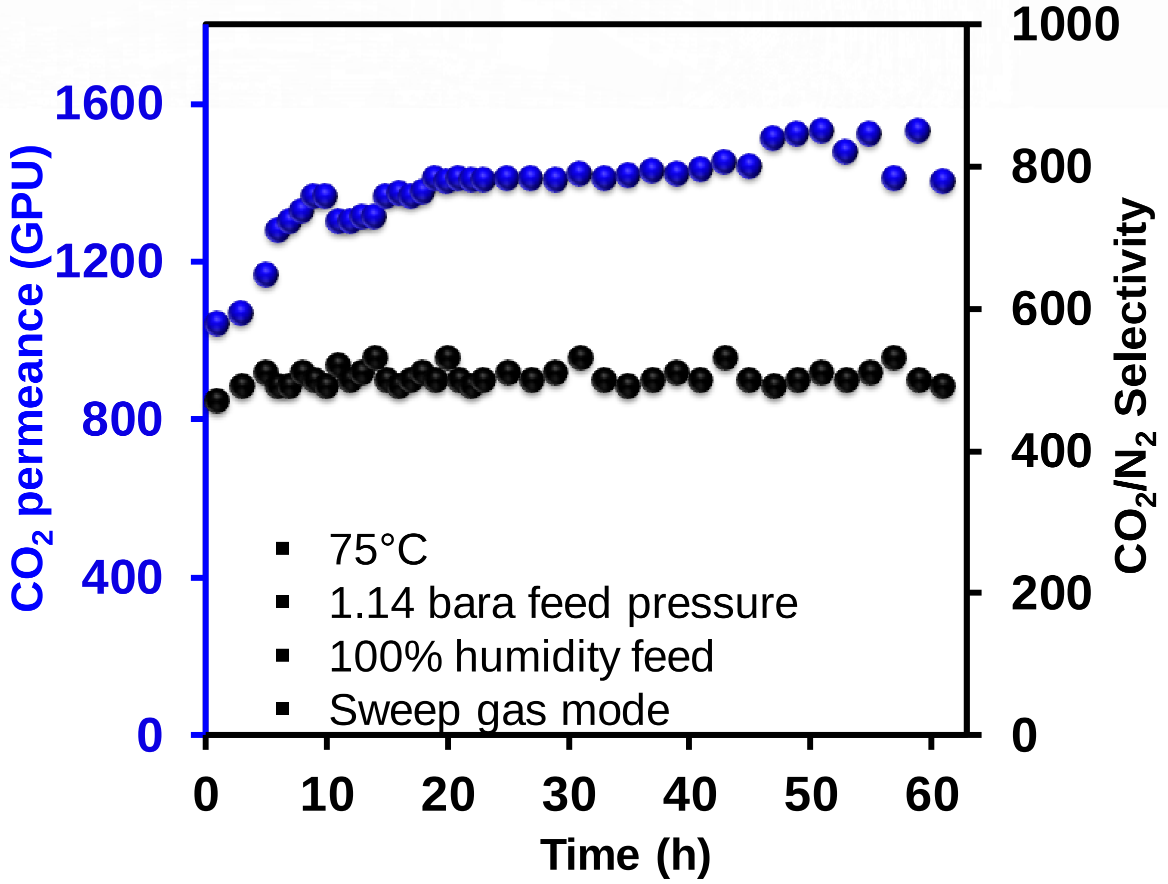
GO-PZ membrane separation performance

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



Superior performance to polymeric membranes and stable

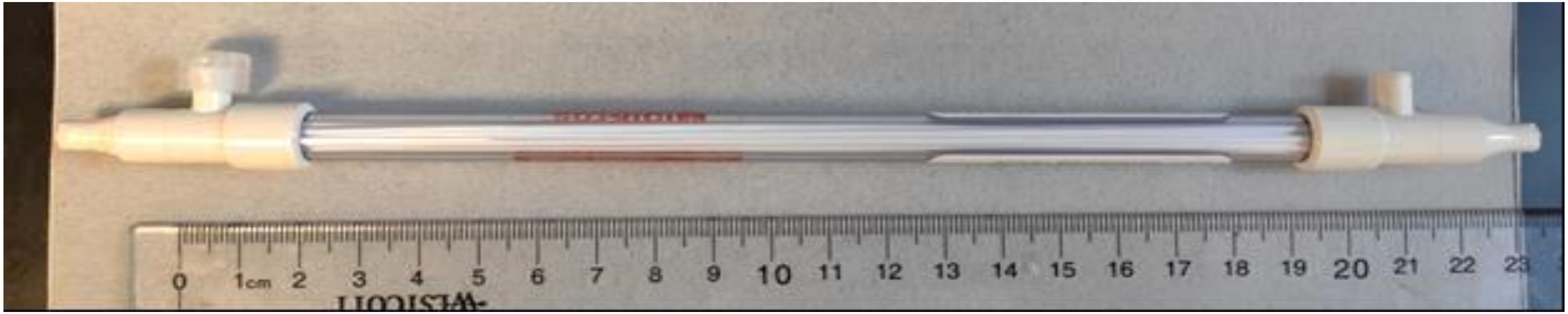




Robeson, J. Membrane Sci. ***2008****, Vol. 320, p390*

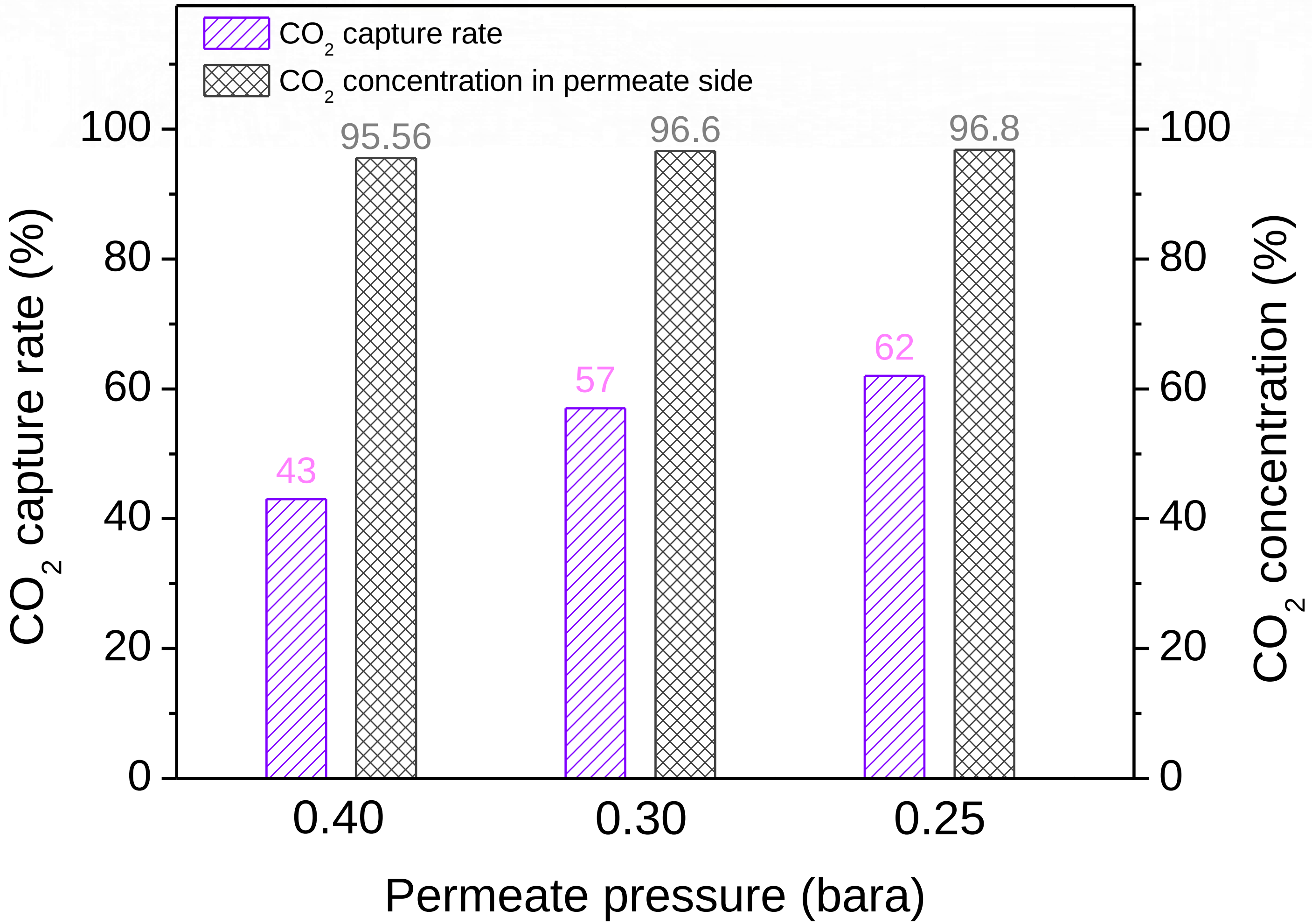
Note: Polymer data points (red): 100 nm membrane thickness assumed

Membrane successfully fabricated on commercial substrates



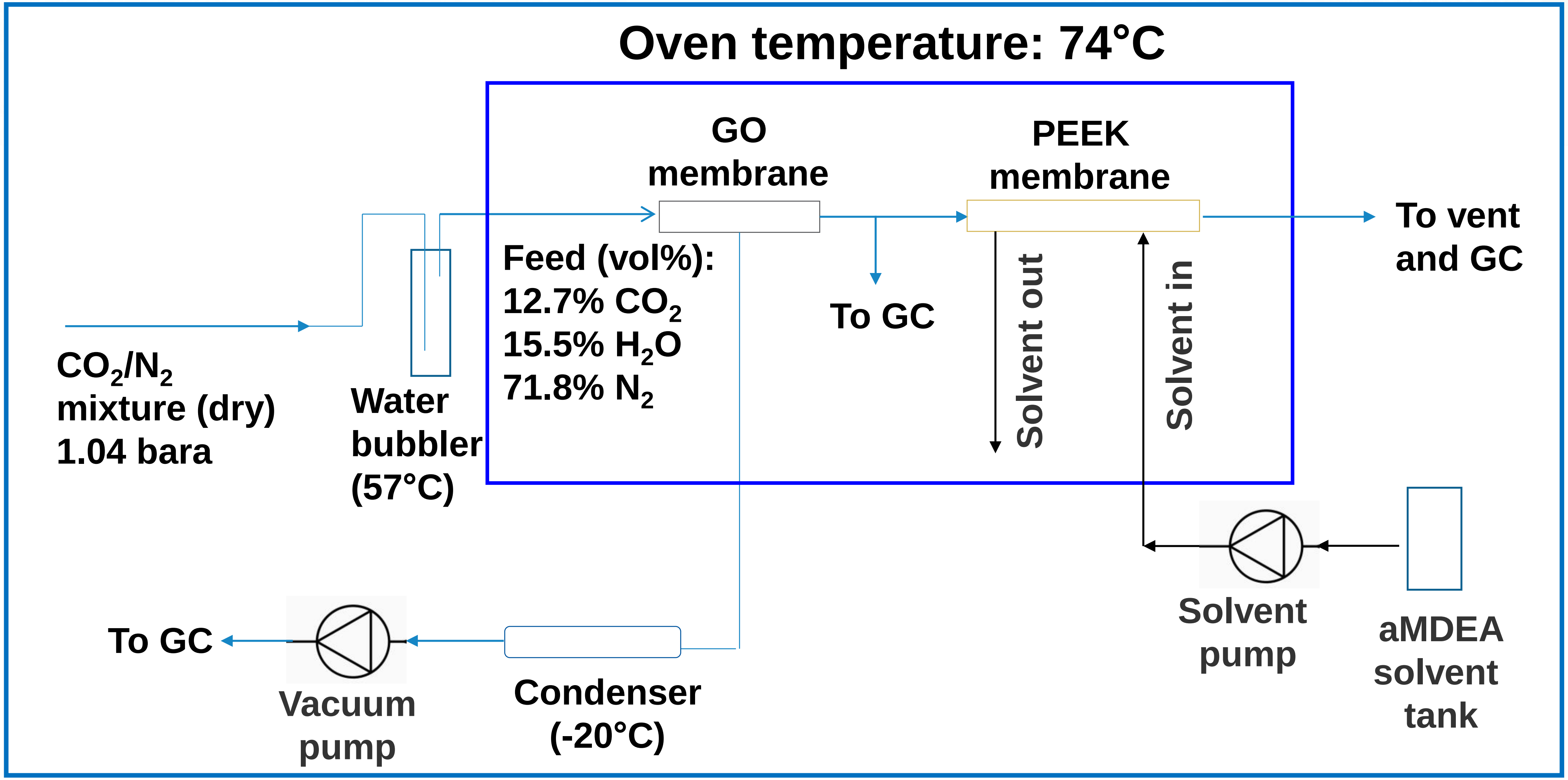
Substrate material: polyether sulfone (PES)
Membrane fabrication method: vacuum filtration
Membrane area: 75 cm^2

GO membrane achieved partial CO_2 capture (43-62%) from a simulated flue gas (13.3 vol%) with >95% CO_2 purity



- 80°C
- 1.04 bara feed pressure

Integrated GO-PEEK testing showed >90% CO_2 removal and >95% CO_2 purity



High-level technoeconomic analysis (TEA) overview

- Process flow and heat & material balance (H&MB)
  - Includes CO_2 purification and compression
- Energy performance
  - Use H&MB to estimate energy requirements
  - Re-scale to 550 MW_e (net) electrical output
- CAPEX
  - Bottom-up costs from equipment sizing
- OPEX
  - Bottom-up from H&MB data

TEA suggests 26% reduction electrical parasitic losses

Energy Performance Summary		GO-PEEK	NETL Rev 2a Baseline, Case 12
Gross Generating Capacity + Electrical Value of Process Steam	**MWe**	**745**	**812**
Total Steam Derate (elec. equiv. of steam)	**MWe**	**79**	**149**
Reboiler/Regeneration Duty	*MWth*	286	542
Direct Electrical Derate	**MWe**	**90**	**75**
CO_2 Compression and Processing	*MWe*	77	45
CO_2 Capture (Pumps, Fans, CW system)	*MWe*	13	30
Steam Turbine Energy Recovery/Penalty	**MWe**	**-8**	**0**
Total Derate for CO_2 Capture	**MWe**	**160**	**224**
Power Plant Auxiliary Req. for Capture	**MWe**	**35**	**38**
Total parasitic demands for entire plant	**MWe**	**195**	**262**
Net Electricity Produced	**MWe**	**550**	**550**

- 28% reduction in total CO_2 capture power derating
- 26% reduction in electrical parasitic losses
- CAPEX and OPEX calculations ongoing

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Summary

- A **hybrid process** developed 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
  - 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
  - Showed CO_2 permeance > 1,000 GPU and α_{CO_2/N_2} > 600
  - Good stability
- **Integrated GO-PEEK** testing showed >90% CO_2 removal and >95% CO_2 purity
- **High-level TEA** suggests 26% reduction electrical parasitic losses as compared to DOE baseline Case 12 (NETL Rev 2a); CAPEX and OPEX calculations ongoing
- **Future work** after this project: bench-scale development for GO-based membranes (DE-FE0031598)

Acknowledgements

- Financial and technical support

DE-FE0026383

- 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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