the Energy to Lead

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

DOE Contract No. DE-FE0026383

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NATIONAL ENERGY TECHNOLOGY LABORATORY

CO_2 Capture Technology Project Review Meeting

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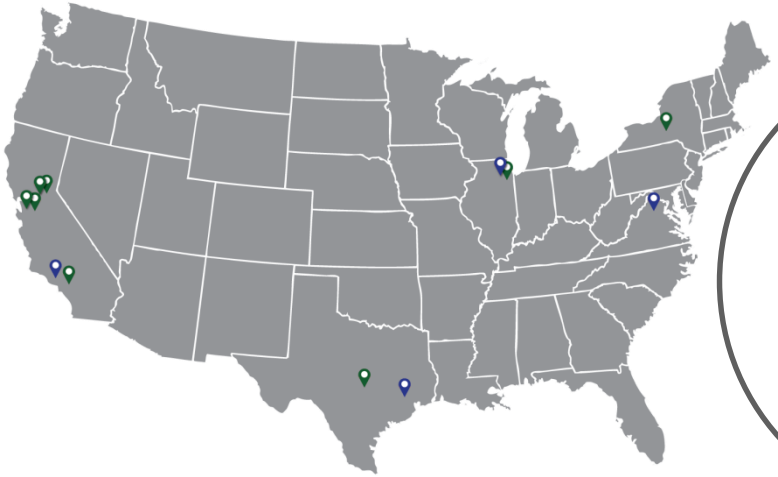
Introduction to GTI

- 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

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GO-PEEK project overview

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

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

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

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]

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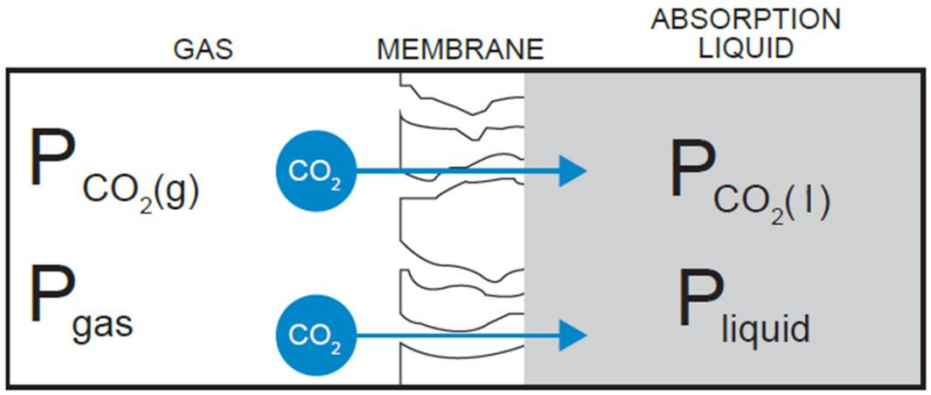
Singular PEEK HFMC technology currently at pilot scale development stage (DE-FE0012829)

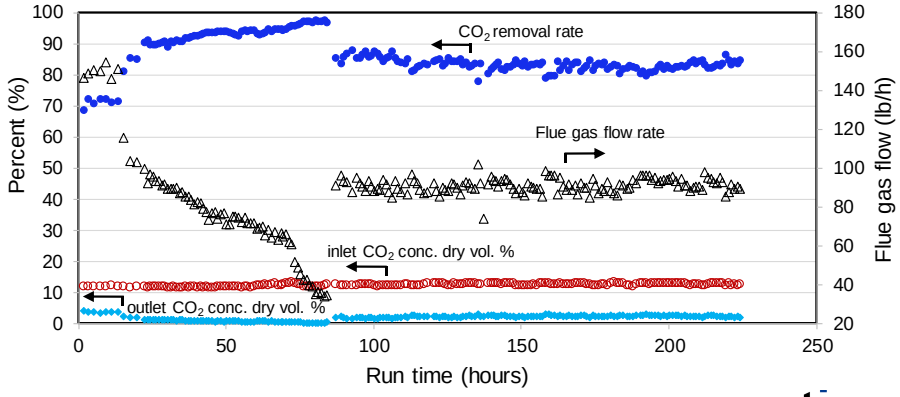


Membrane contactor: high surface area device that facilitates mass transfer

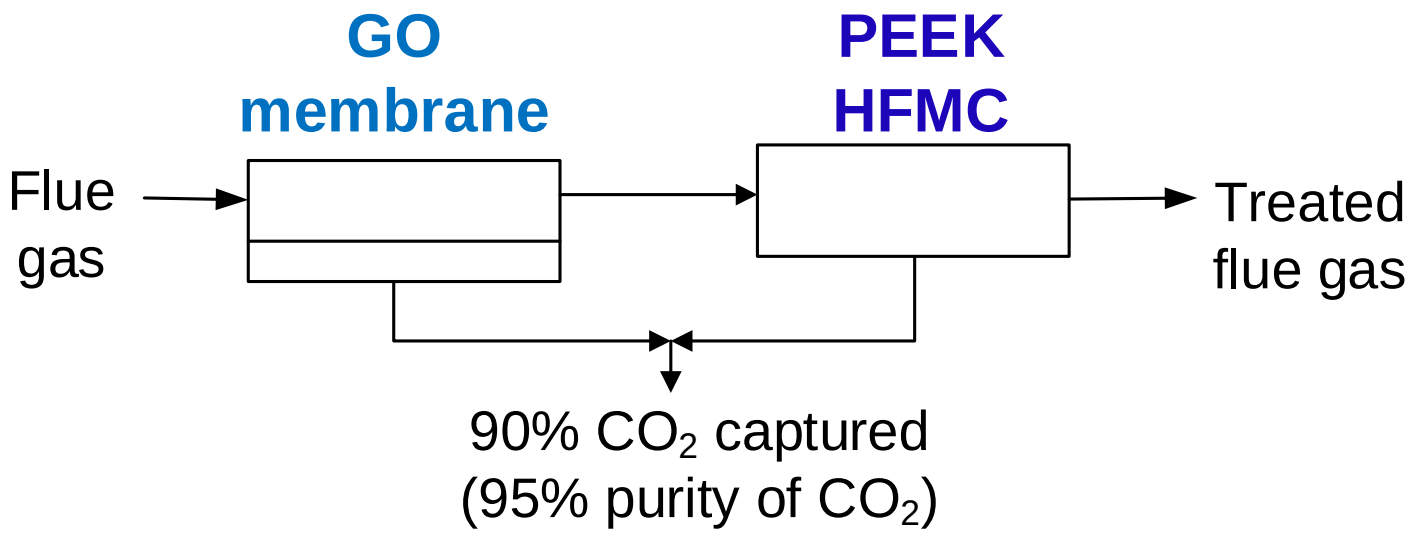
Commercial-sized (8-inch-diameter) modules with intrinsic CO_2 permeance of ~2,000 GPU used in pilot scale testing

Plant constructed and installed at NCCC

Achieved steady state performance during 224-h continuous testing with a single 8-inch-diameter module at NCCC with actual flue gas

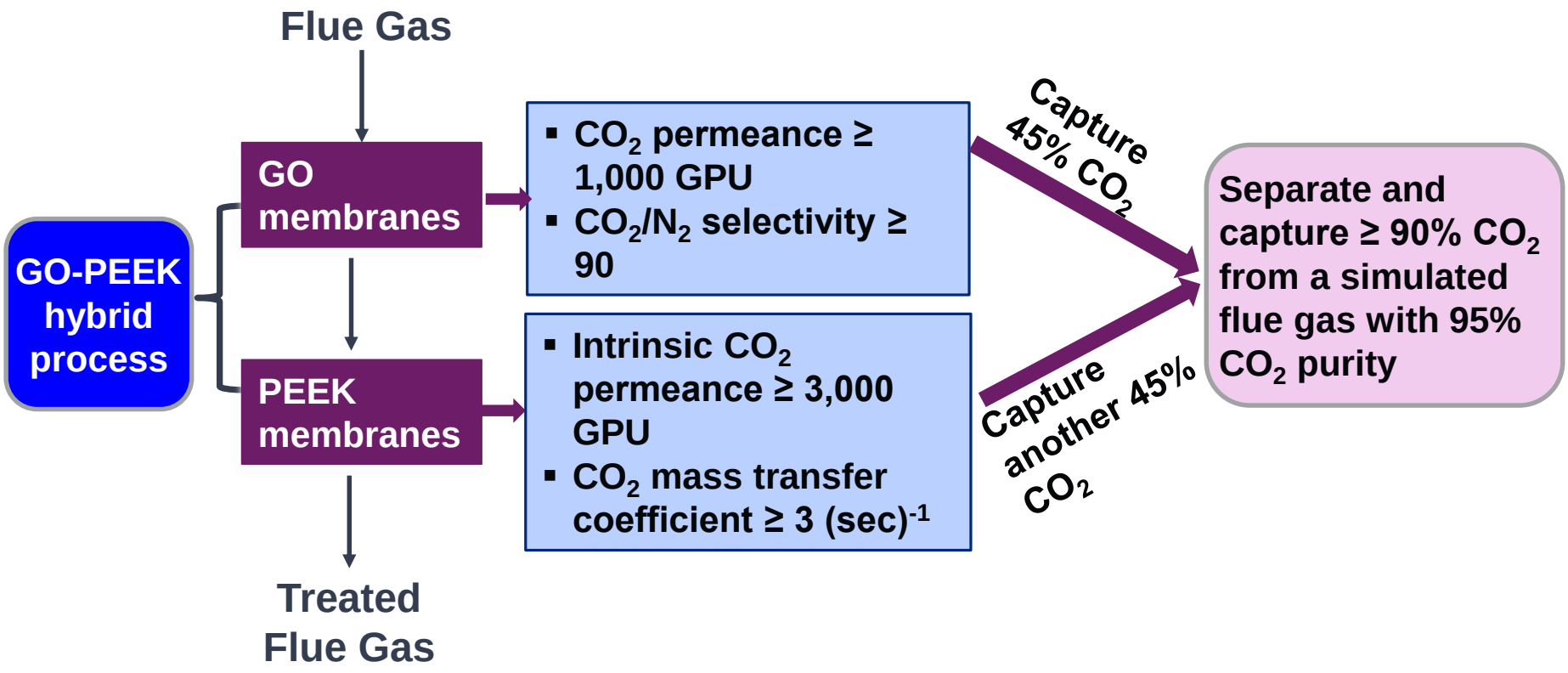


Process description



- GO-PEEK uses a conventional gas separation membrane unit to capture bulk of the CO_2 from coal-fired 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

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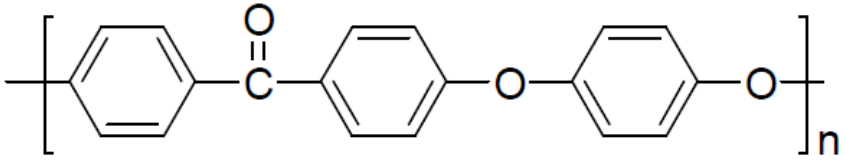
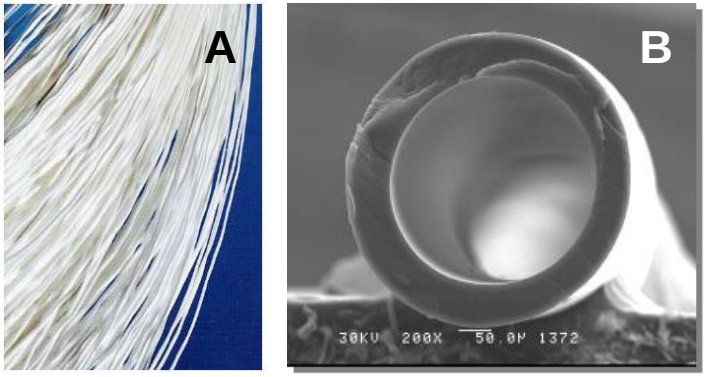
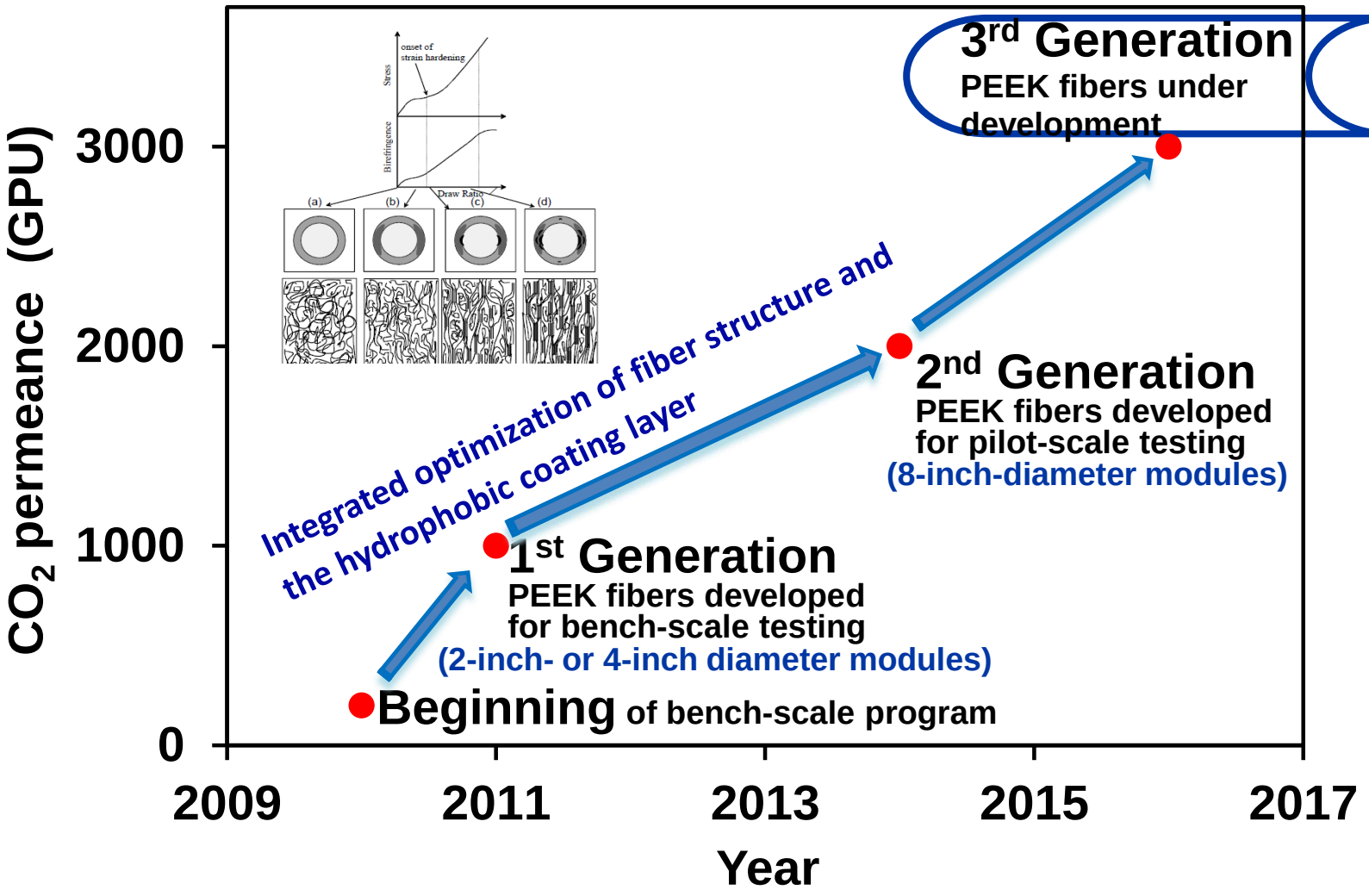
Progress on PEEK Membranes





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



1 GPU = 3.348×10^{-10} mol/m²/s/Pa

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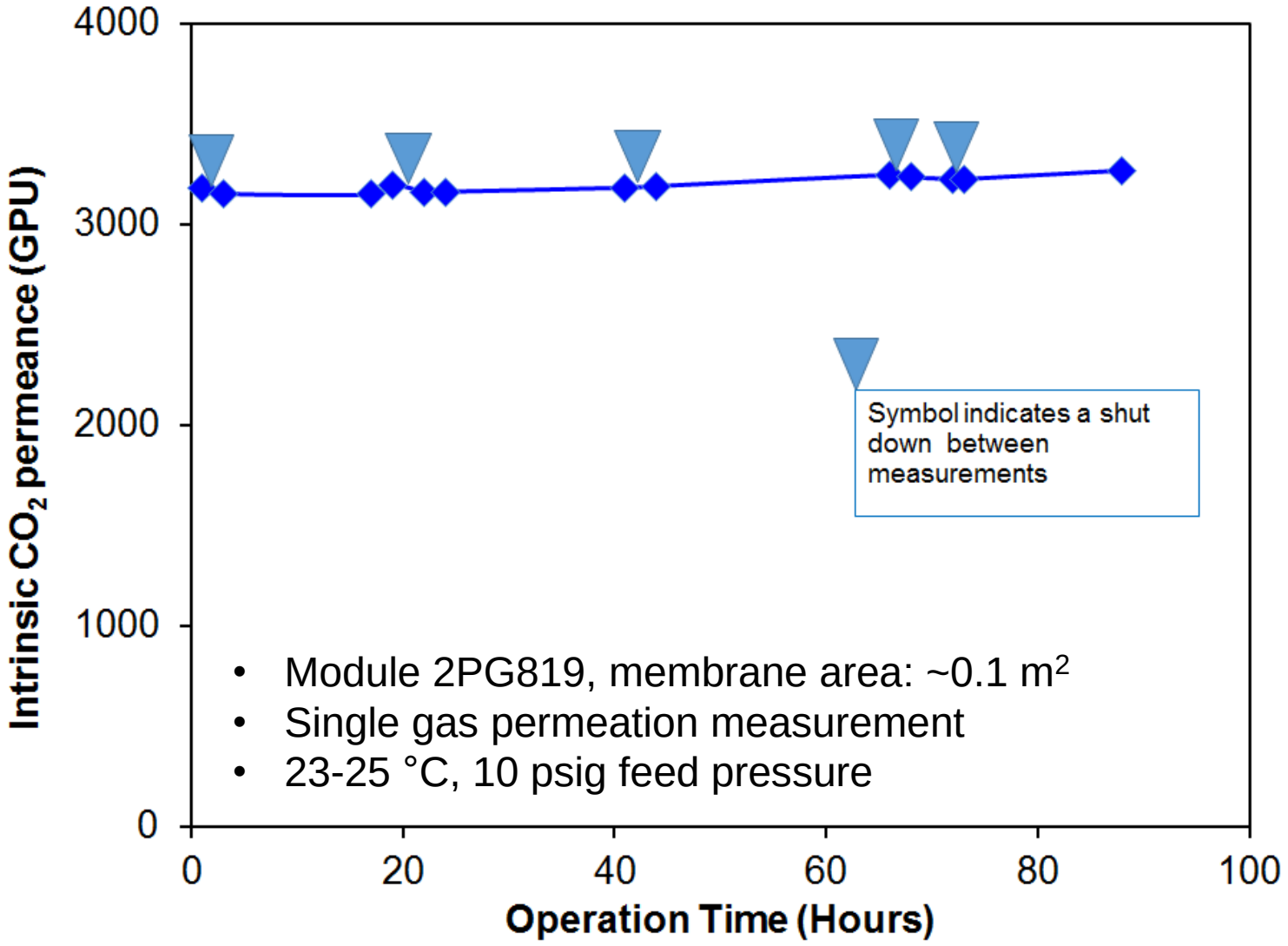
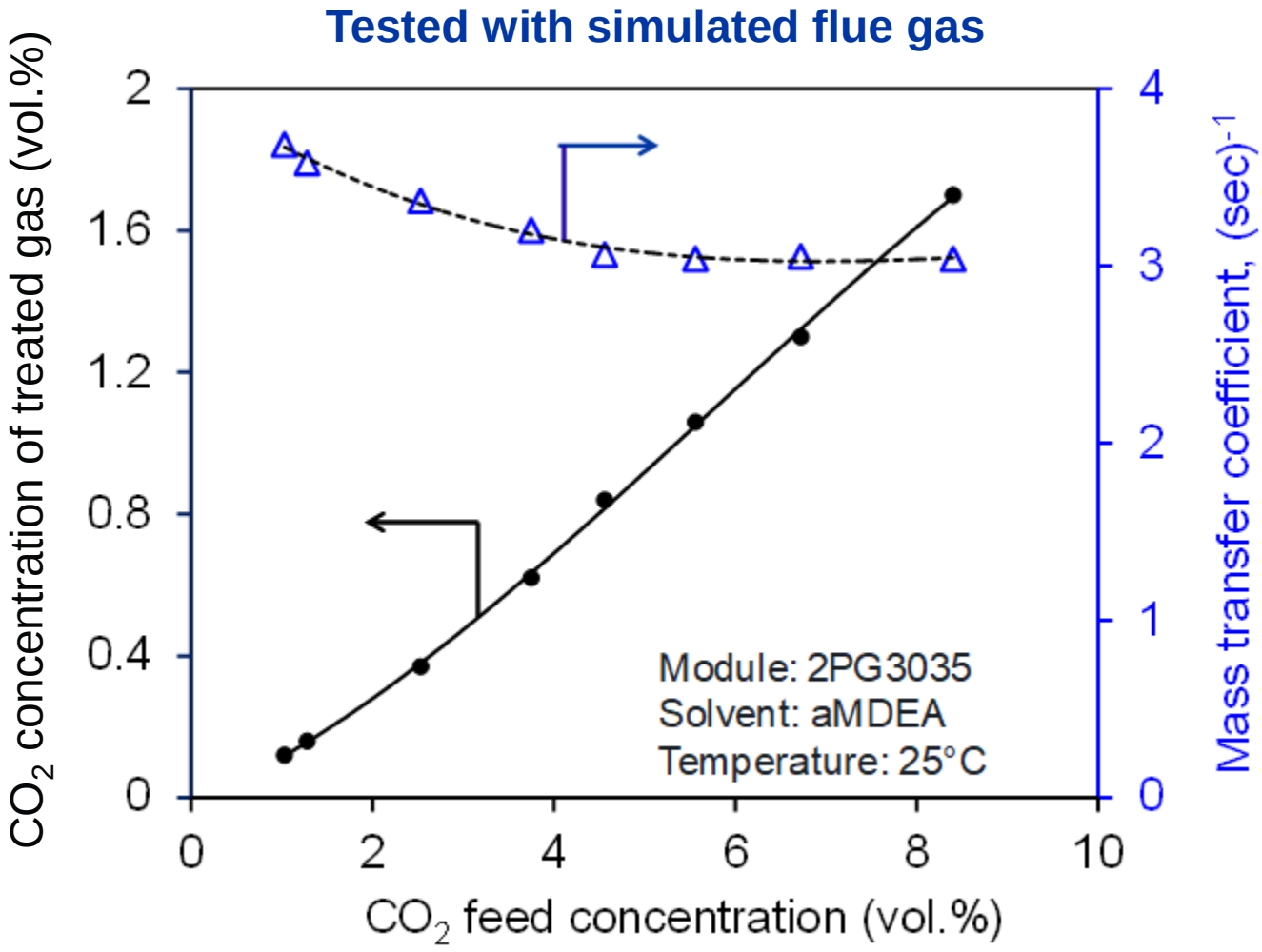
3rd Gen fibers developed; 2-inch-diameter module using the fibers showed CO_2 permeance >3,000 GPU



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

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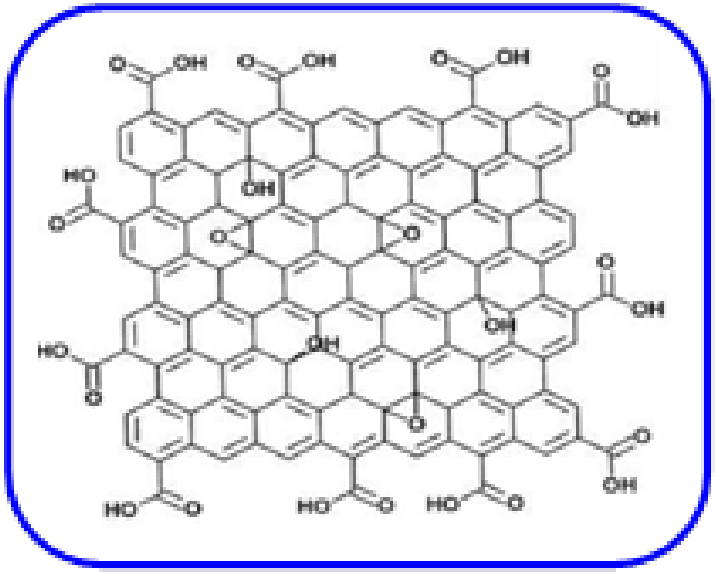
Progress on GO Membranes



GO: single-atomic layered, oxidized graphene

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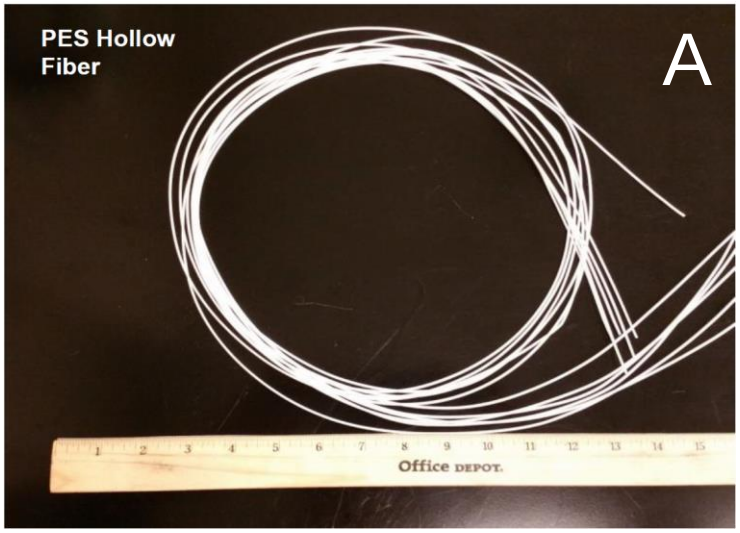
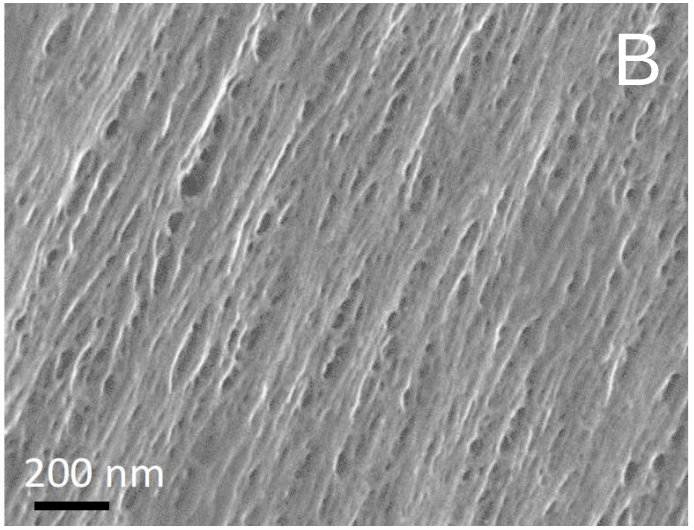
Procedure developed for coating GO membrane on the inside surface of the hollow fiber (HF) support

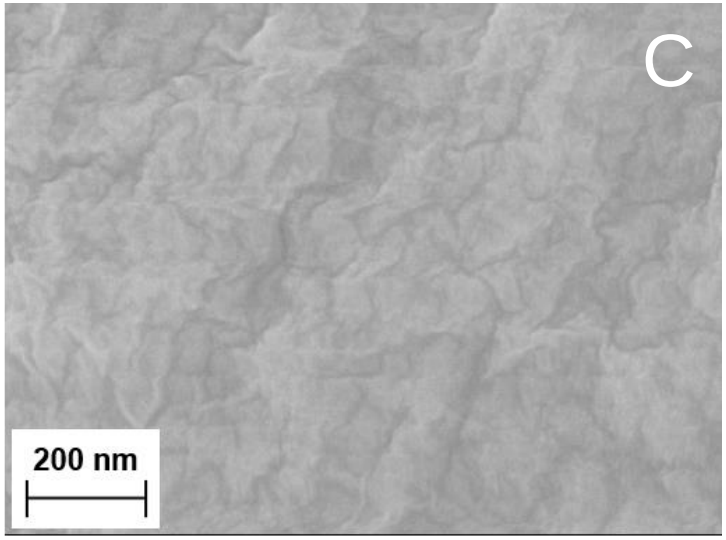
PES fiber

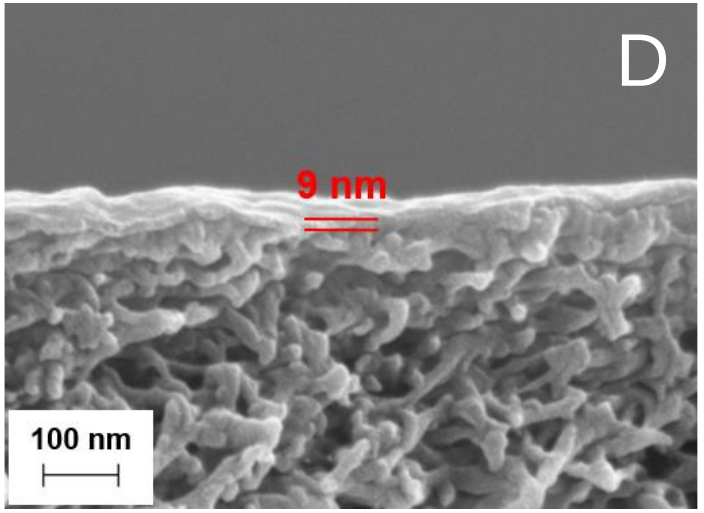




Uncoated fiber surface

Coated fiber surface





Coated fiber cross section

PES = polyethersulfone

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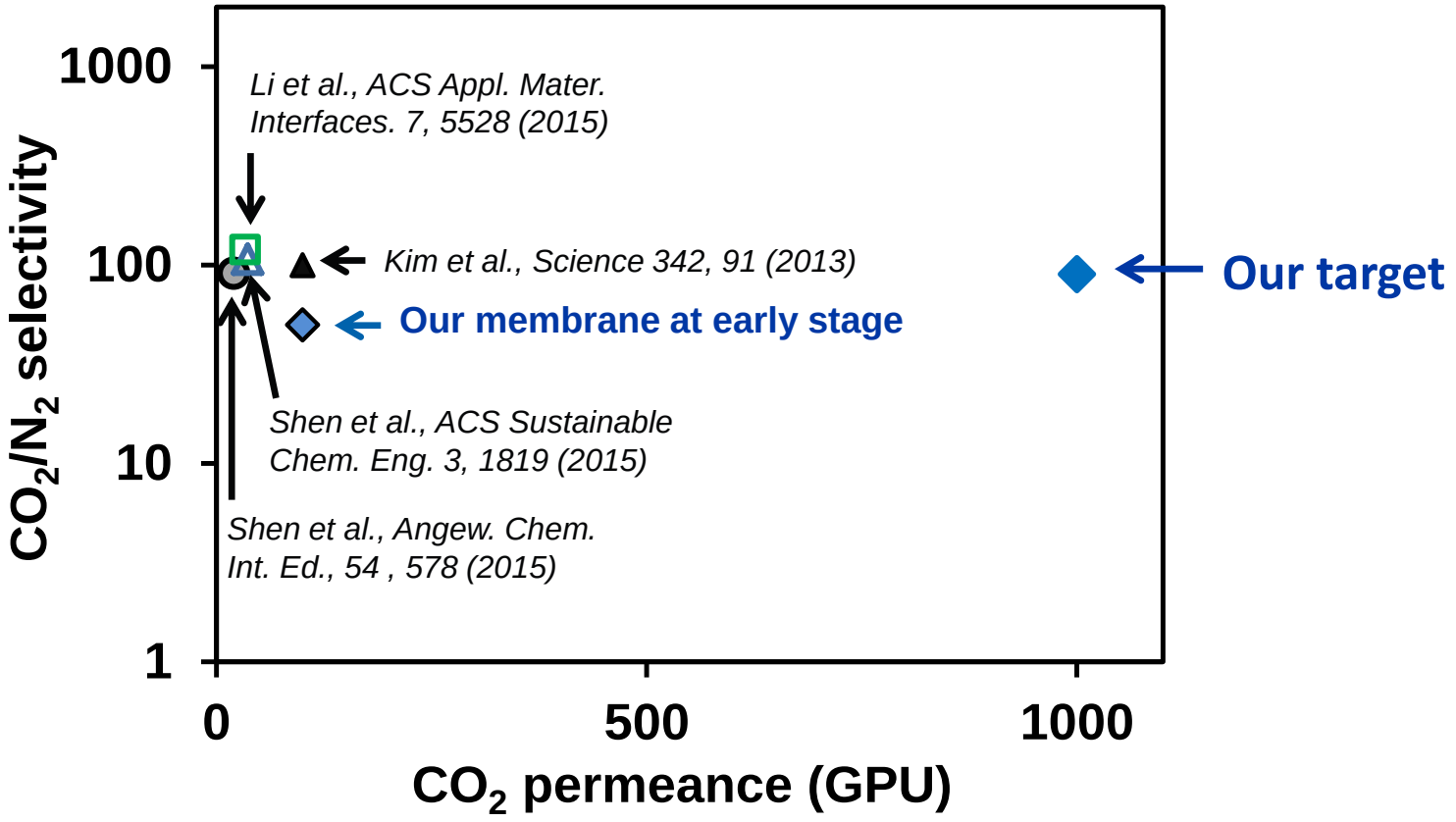
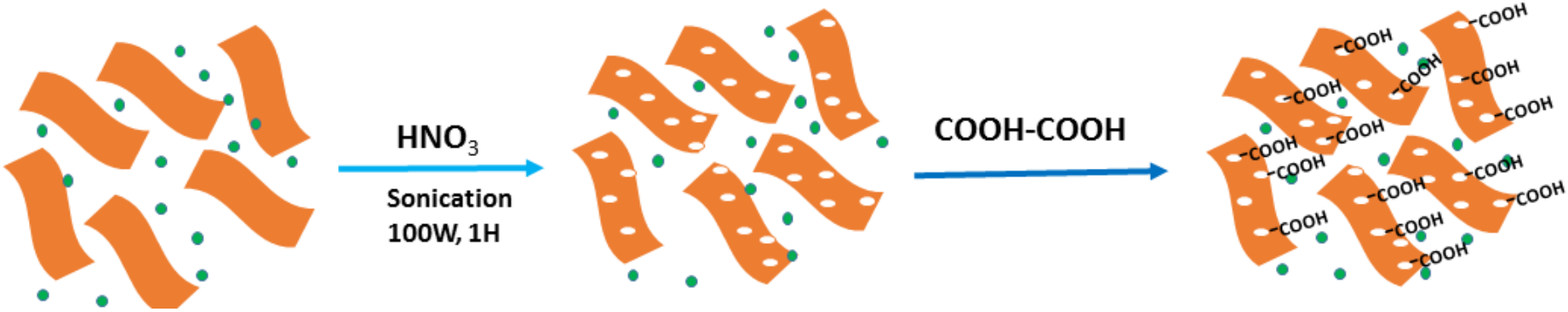
Challenge: initial GO membrane performance needed significant improvement

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



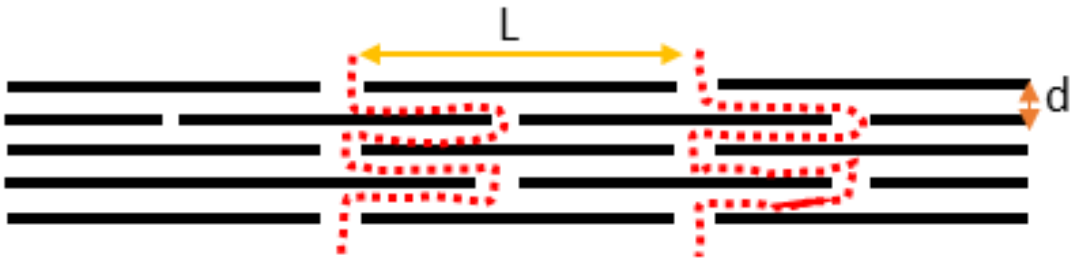
Approaches to improve CO_2 permeance

- Create more structural defects on GO flake by HNO_3 etching

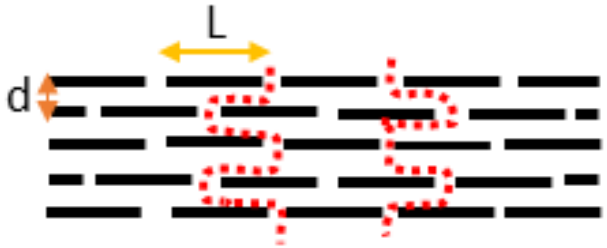


- Reduce GO flake lateral size by ultra-sonication

W/O ultra-sonication

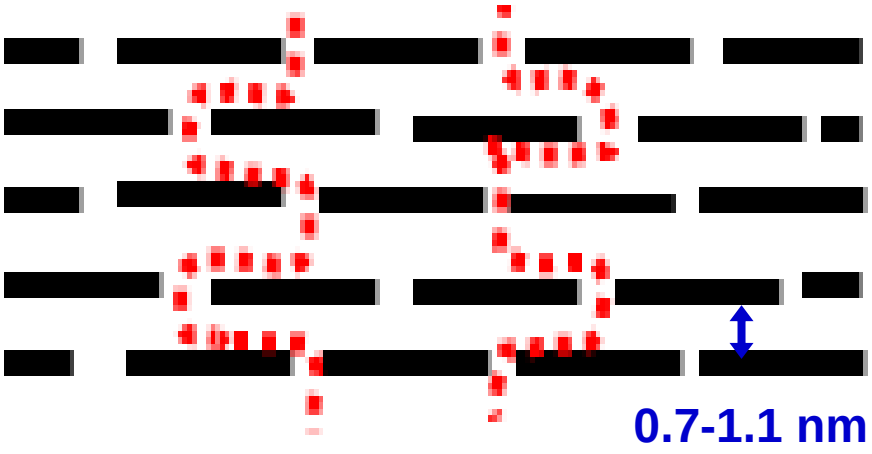


W/ ultra-sonication

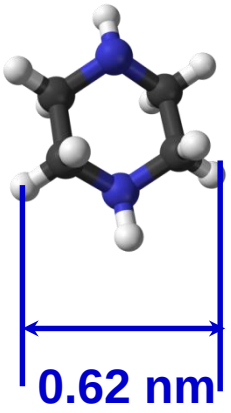


Approach to improve CO_2/N_2 selectivity: fill the space between GO layers with CO_2-philic agent

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

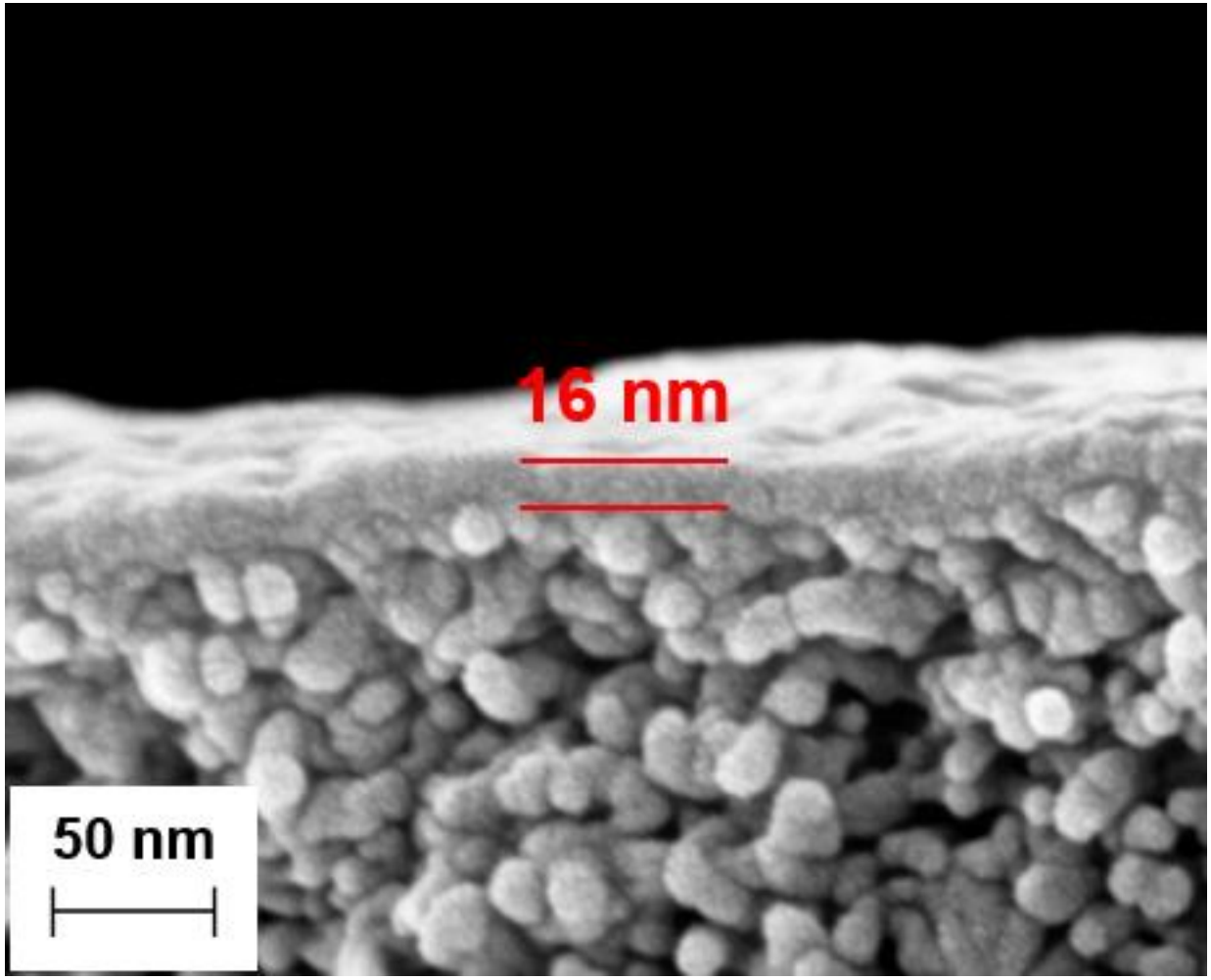


CO_2-philic agent example: piperazine (PZ)



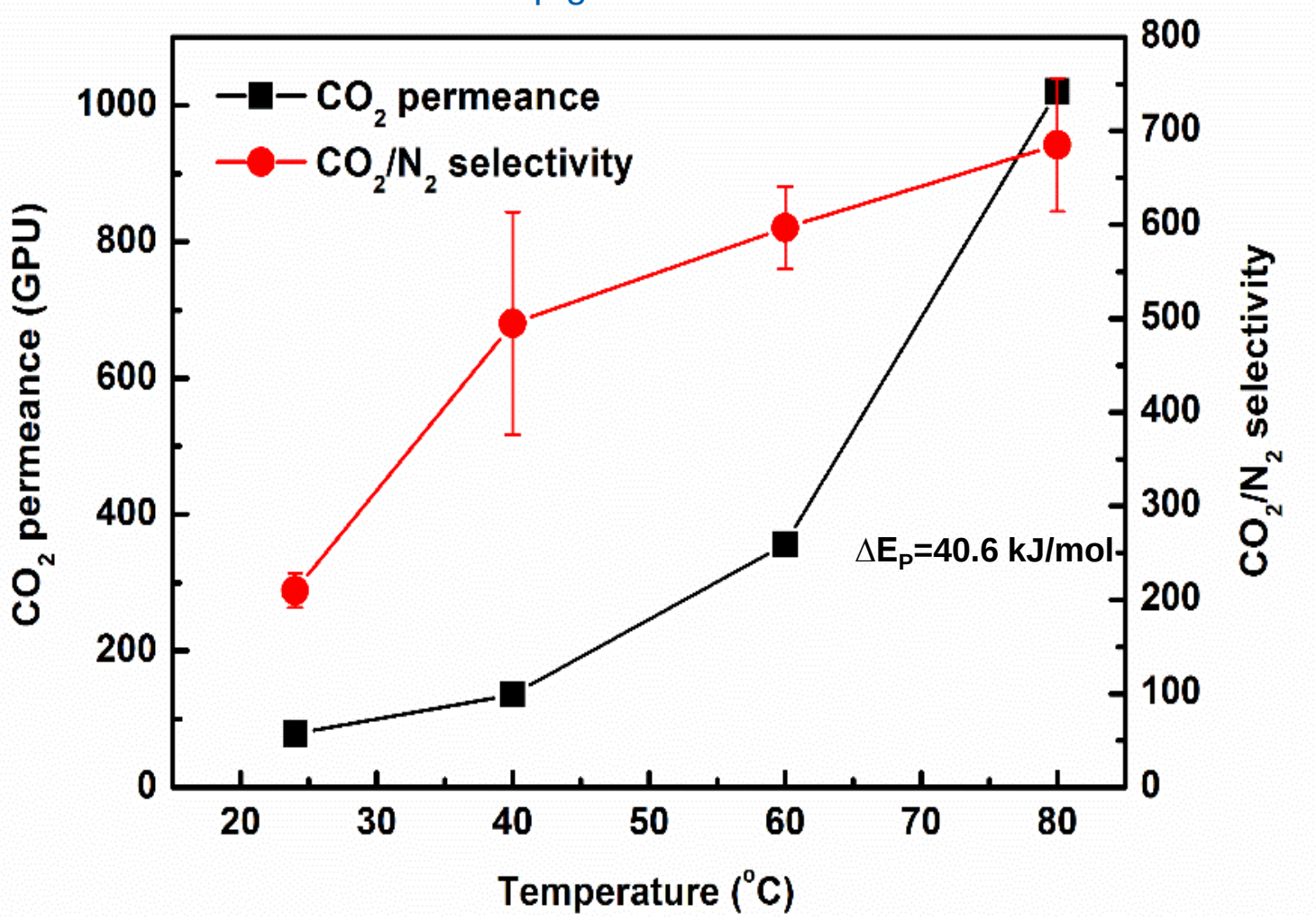
- XPS and FTIR analysis confirmed the crosslinking of PZ with GO sheets

Cross-sectional SEM of the PZ filled GO membrane



GO-PZ membrane separation performance

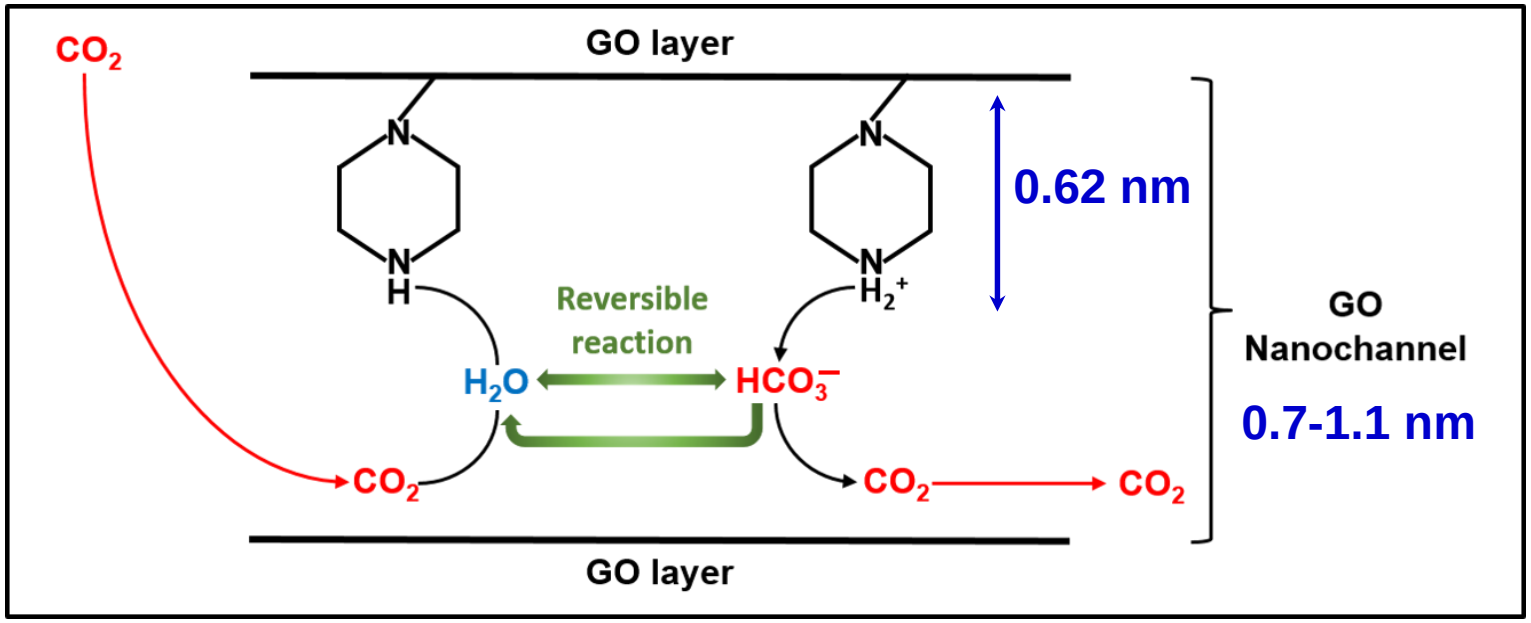
Feed: 15% CO_2/85%N_2 with saturated water vapor
Permeate: with sweep gas



Facilitated transport mechanism

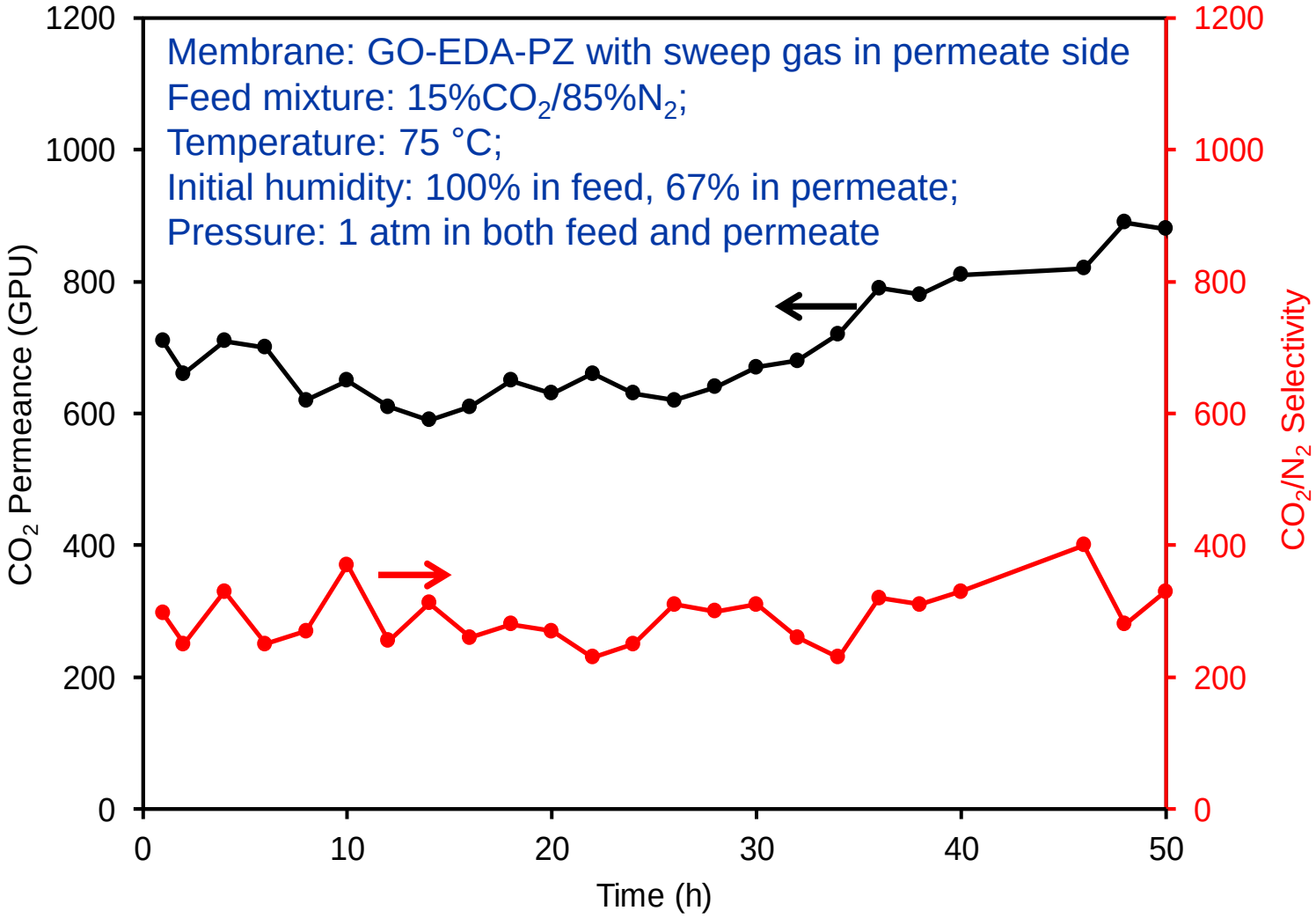
- **CO_2**: $2CO_2+2RR'NH+H_2O \leftrightharpoons RR'NCOOH+RR'NH_2^+ +HCO_3^-$

$$CO_2+RR'R''N+H_2O \leftrightharpoons RR'R''NH^+ +HCO_3^-$$



- **N_2** has no enhancements and moves only by diffusion

50-h testing showed variation of performance: humidity may be controlled to achieve the best performance



Membrane stable during 50-h testing

EDA = Ethylenediamine; PZ = Piperazine

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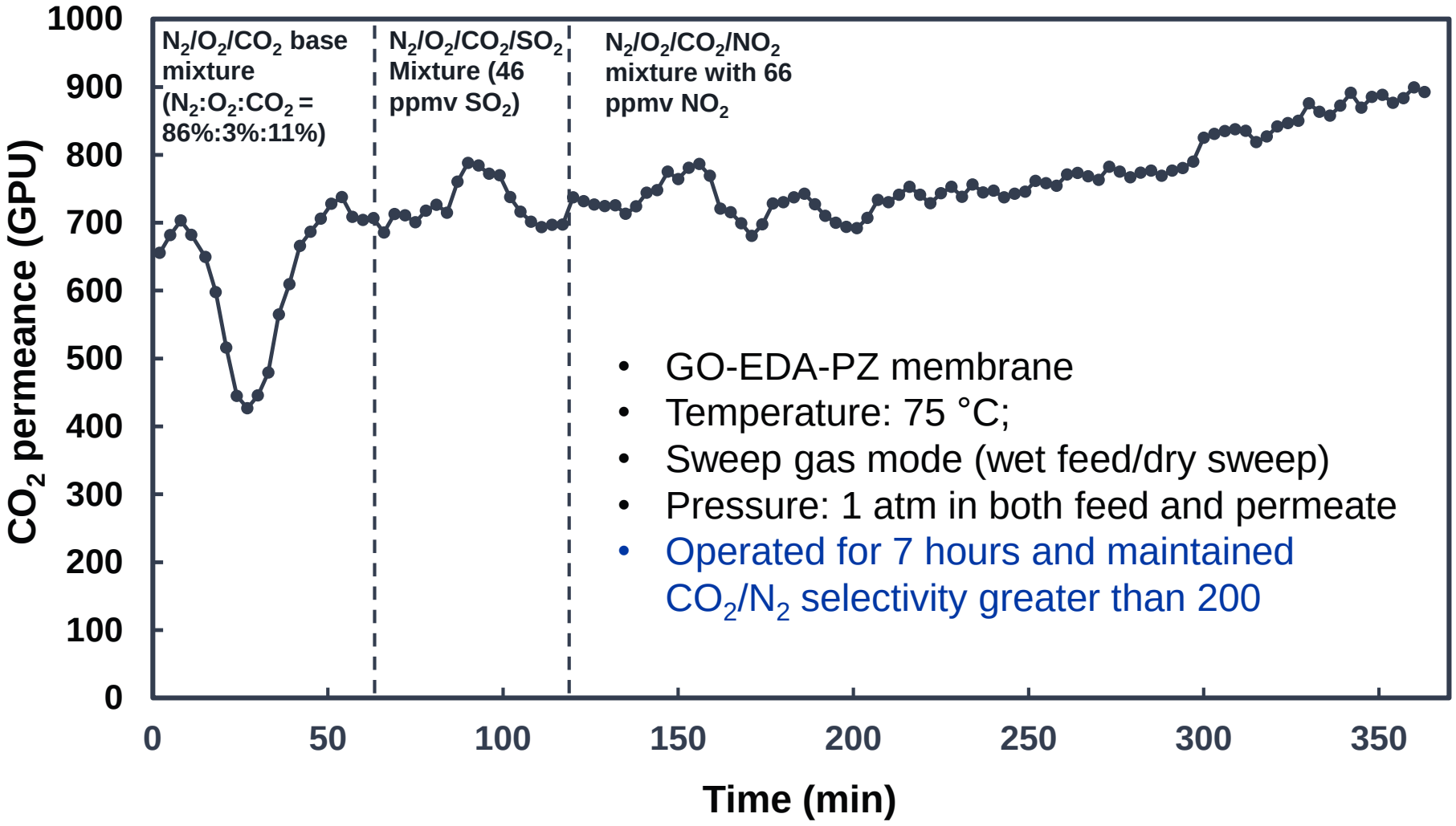
GO-based membranes showed good stability in the presence of flue gas contaminants

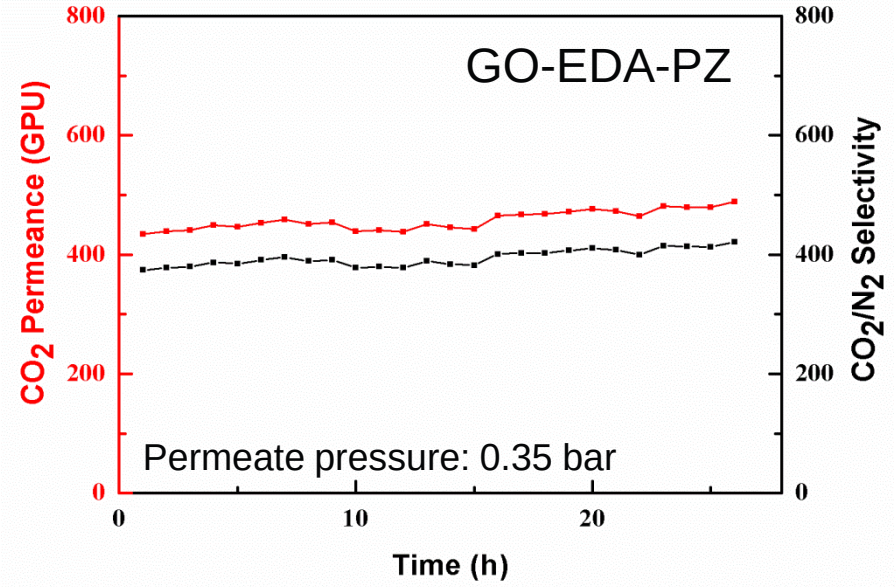


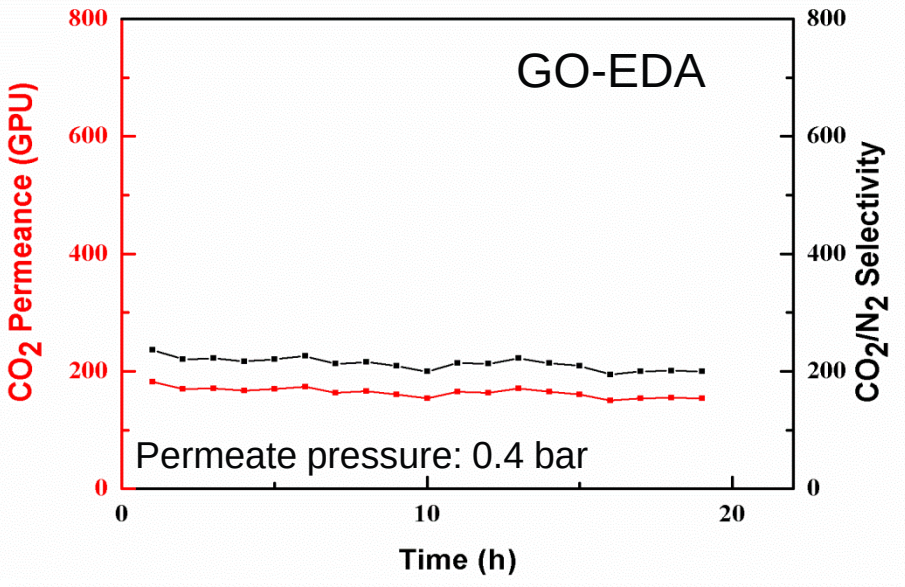
- GO-EDA-PZ membrane
- Temperature: 75 °C;
- Sweep gas mode (wet feed/dry sweep)
- Pressure: 1 atm in both feed and permeate
- Operated for 7 hours and maintained CO_2/N_2 selectivity greater than 200

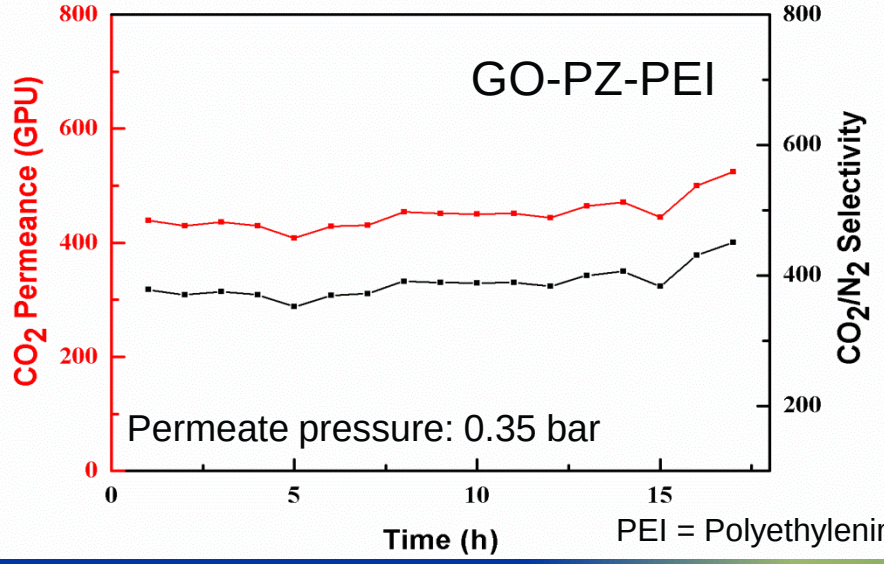
- GO-PZ and GO-EDA membranes also stable in the presence of flue gas contaminants

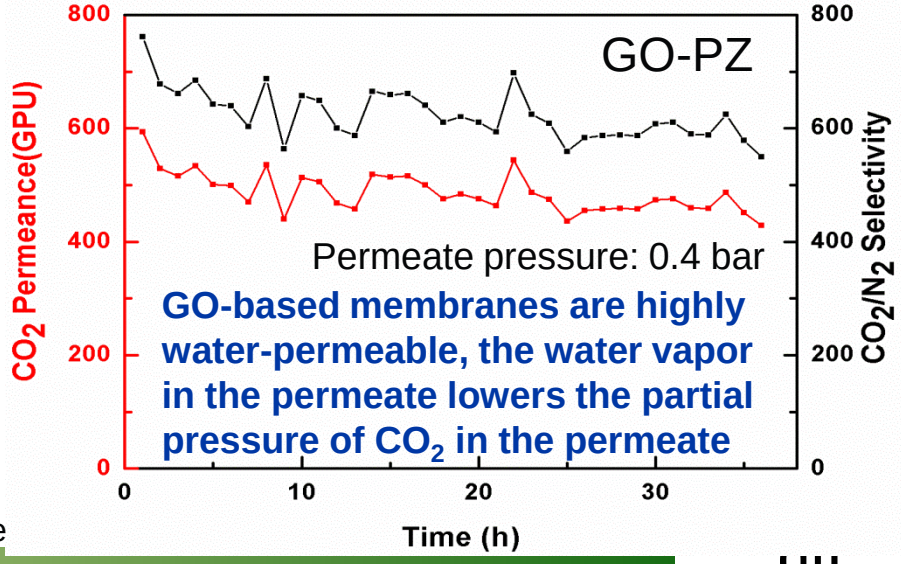
In addition to sweep gas mode, we also tested GO-based membranes with permeate side under vacuum

Feed mixture: 15%CO_2/85%N_2 saturated with H_2O vapor; temperature: 75 °C









PEI = Polyethylenimine

>1,000 GPU CO_2 permeance achieved in vacuum mode with improved membrane and optimized humidity

Membrane	Improved GO-PZ membrane
Temperature	75 °C
Humidity	85%
Feed gas	15% CO_2/85% N_2
CO_2 permeance, GPU	**1080 ± 55**
CO_2/N_2 selectivity	**650 ± 31**

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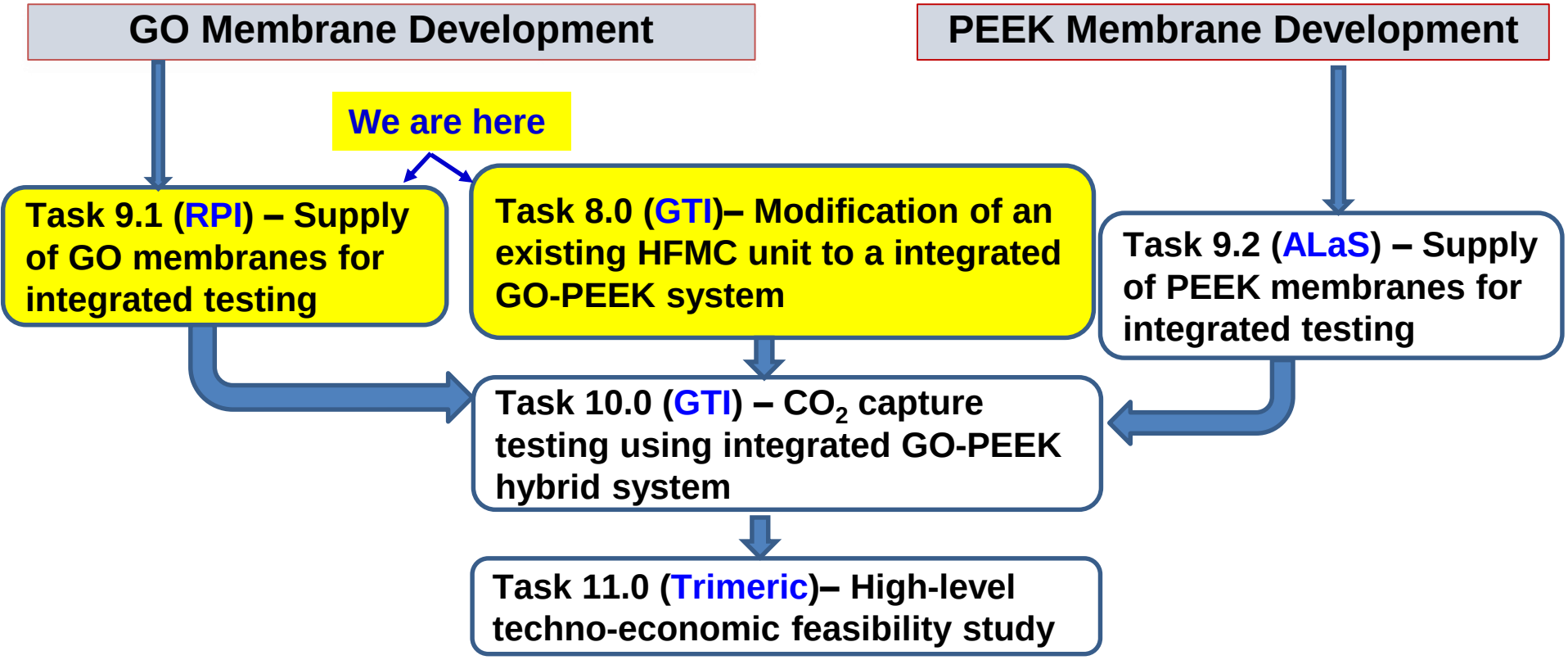
Future work overview/roadmap

- **In this project**



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

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Summary

- We are developing a transformational hybrid process for CO_2 capture combining a conventional gas membrane unit and a HFMC unit
- **The 3rd Generation PEEK fiber** developed to date
  - Fibers with intrinsic CO_2 permeance >3,000 GPU at 25˚C demonstrated in 2-inch-diameter modules
  - A 2-inch-diameter module containing 3rd generation fibers effective in capturing CO_2 from low CO_2-concentration feeds with aMDEA solvent
- **GO-based membrane** developed to date
  - CO_2 permeance > 1,000 GPU and α_{CO_2/N_2} > 600 achieved both in sweep gas and vacuum permeation modes using simulated coal flue gas
  - Good stability in the presence of flue gas contaminants
- Future work will focus on integrated GO-PEEK process testing and TEA

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  - **Huynh Ngoc Tien**
  - **Jarvis Chen**
  - **Mahdi Fathizadeh**

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