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

DOE Contract No. DE-FE0026383

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BP1 Review Meeting (NETL-Pittsburgh)
March 22, 2017

Project at a glance

- **Status**: Currently in BP1 (October 1, 2015 – March 31, 2017) with a budget of $814,748 from DOE ($255,624 cost share)
- **Accomplishments**:
  - Graphene oxide (GO) membranes developed: CO_2 permeance > 1,000 GPU, α_{CO_2/N_2} > 600 for simulated flue gas at 80°C
  - The 3rd generation polyether ether ketone (PEEK) fibers developed: intrinsic CO_2 permeance > 3,000 GPU at 22-60°C
- **Schedule and budget:** All BP1 Milestones and Success Criteria met
  - Ahead of schedule (under budget) to complete BP1 work
  - **Overall, we are ready for BP2 starting April 1, 2017**
- **Issue(s):**
  - PEEK: no major issues identified
  - GO: stability needs to be improved through optimization of membrane preparation and operation conditions (major scope of the BP2)

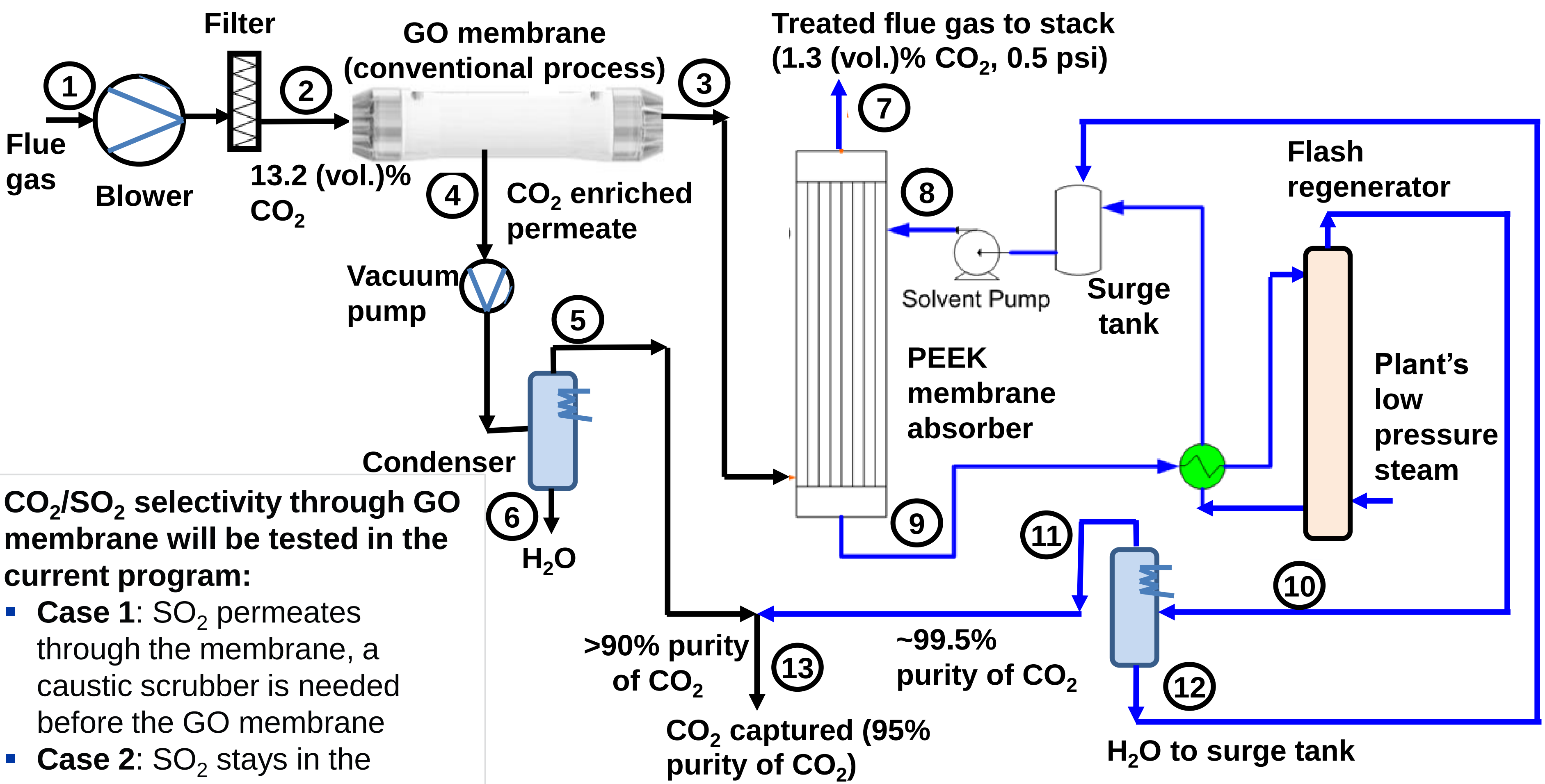
GPU= **G**as **P**ermeation **U**nit

Project overview

- **Performance period**: Oct. 1, 2015 – Sep. 30, 2018
- **Funding**: \$1,999,995 from DOE; \$500,000 cost share
- **Objectives**: Develop a hybrid membrane process combining a graphene oxide (GO) gas separation membrane configuration 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	• GO membrane development
Air Liquide Advanced Business & Technologies ALaS	• PEEK membrane development
Trimeric Corporation	▪ High-level technical & economic feasibility study

Process description



CO_2/SO_2 selectivity through GO membrane will be tested in the current program:

- **Case 1**: SO_2 permeates through the membrane, a caustic scrubber is needed before the GO membrane
- **Case 2**: SO_2 stays in the retentate, scrubber not needed; HFMC can handle 150 ppmv SO_2 (DE-FE-0004787)

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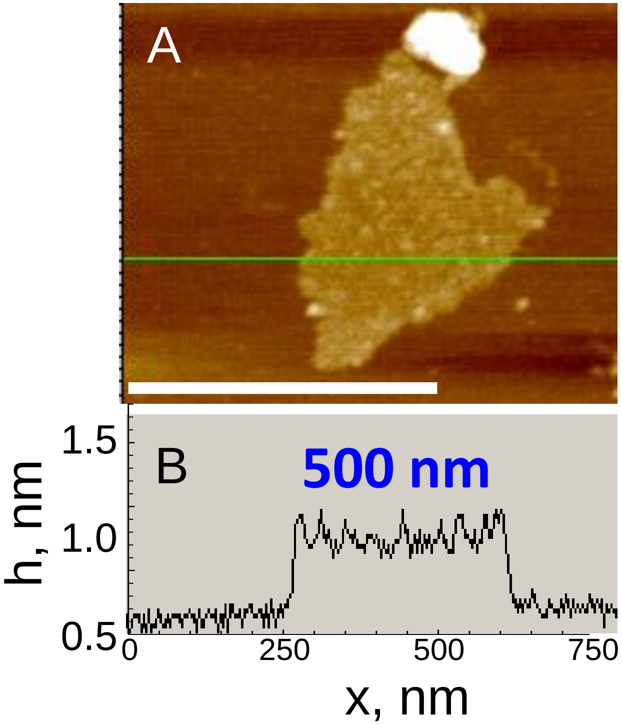
GO membrane technology based on our pioneering work published in *Science (2013, 342 (6154) 95)*

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



Single-layered GO flake prepared as thin as 1 nm

- **<u>Contribution of the paper</u>**:
  - Structural defects on GO flakes can be controlled as transport pathway for selective gas separations

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GO-PEEK technical goals

GO-PEEK hybrid process

GO membranes

- CO_2 permeance ≥ 1,000 GPU
- CO_2/N_2 selectivity ≥ 90

PEEK membranes

- Intrinsic CO_2 permeance ≥ 3,000 GPU
- CO_2 mass transfer coefficient ≥ 3 $(sec)^{-1}$

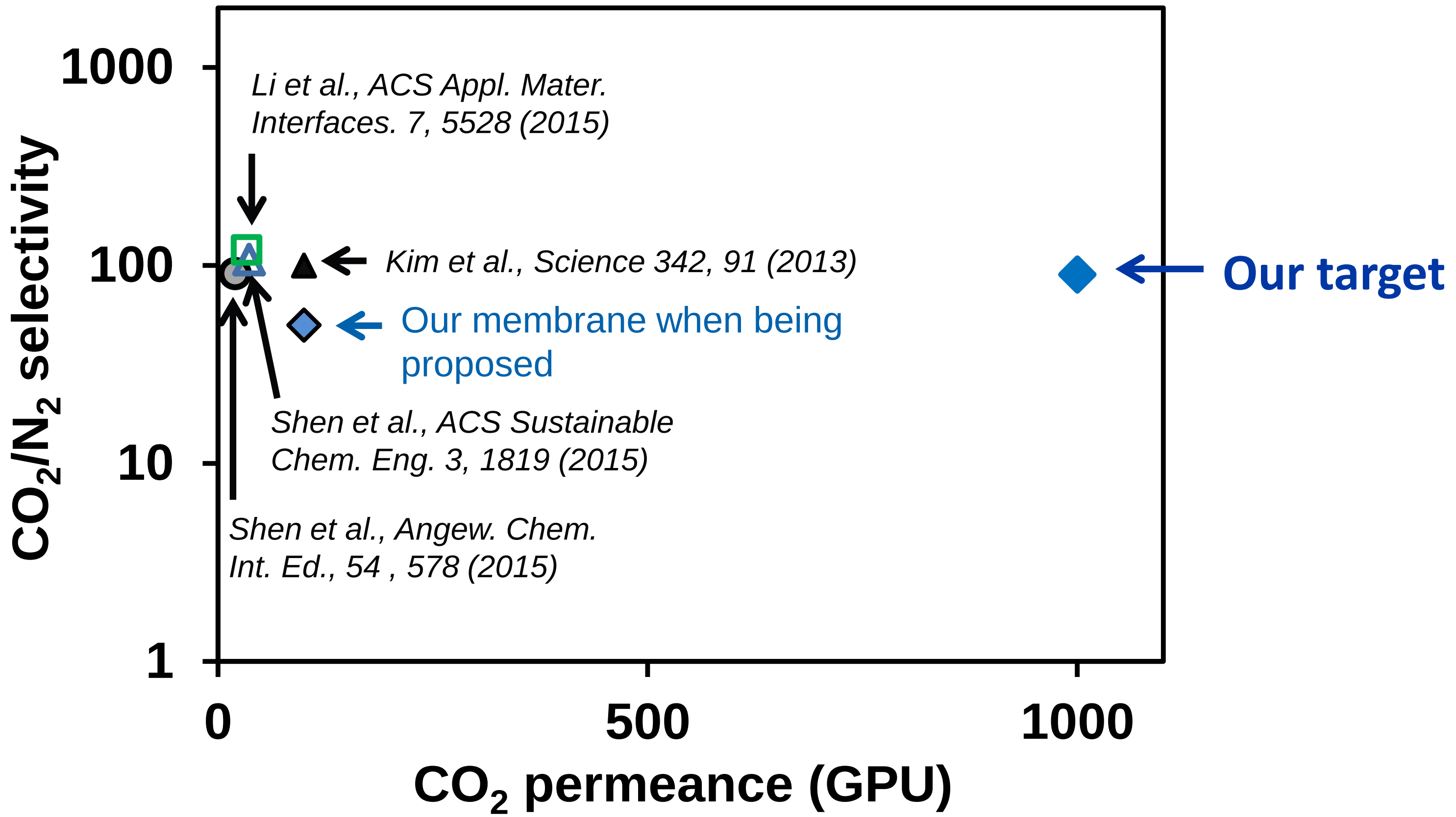
Capture 45% CO_2

Capture another 45% CO_2

Separate and capture ≥ 90% CO_2 from a simulated flue gas with 95% CO_2 purity

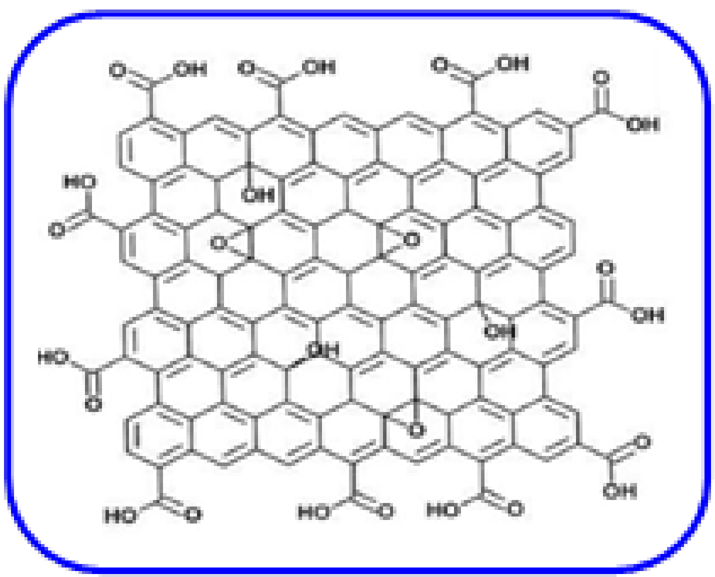
Technical challenges of applying GO-PEEK process to existing coal-fired plants

- **GO membrane performance** – Needs significant improvement



- **Durability** – Long-term stability of both GO and PEEK membranes
- **Scale-up and cost reduction** – Both membranes in hollow fiber format

Progress on GO Membranes

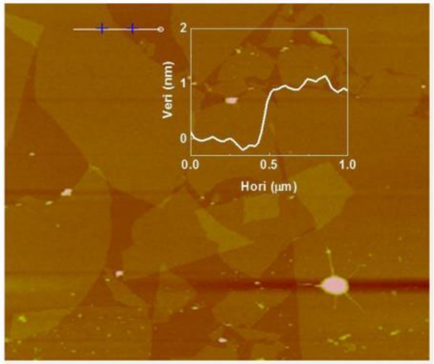


GO: single-atomic layered, oxidized graphene

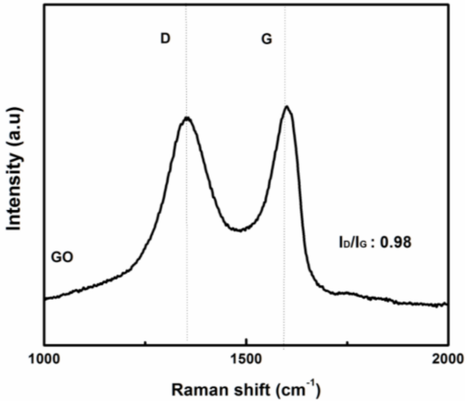
Large quantity of GO prepared, characterizations confirmed morphology, composition and structure

- Typical membrane preparation: 50 mL dispersion with 0.5 mg GO is needed

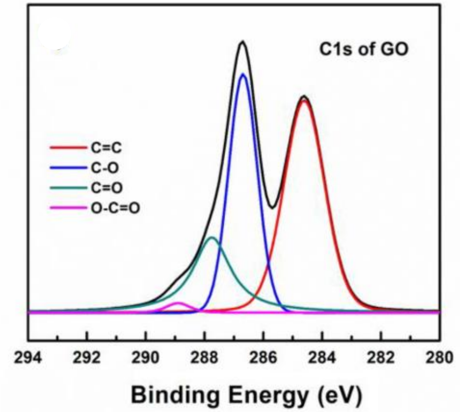
AFM



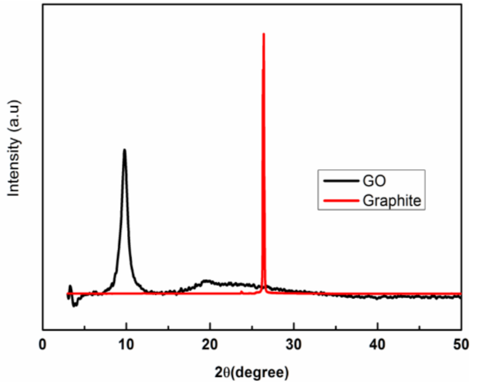
Raman



XPS

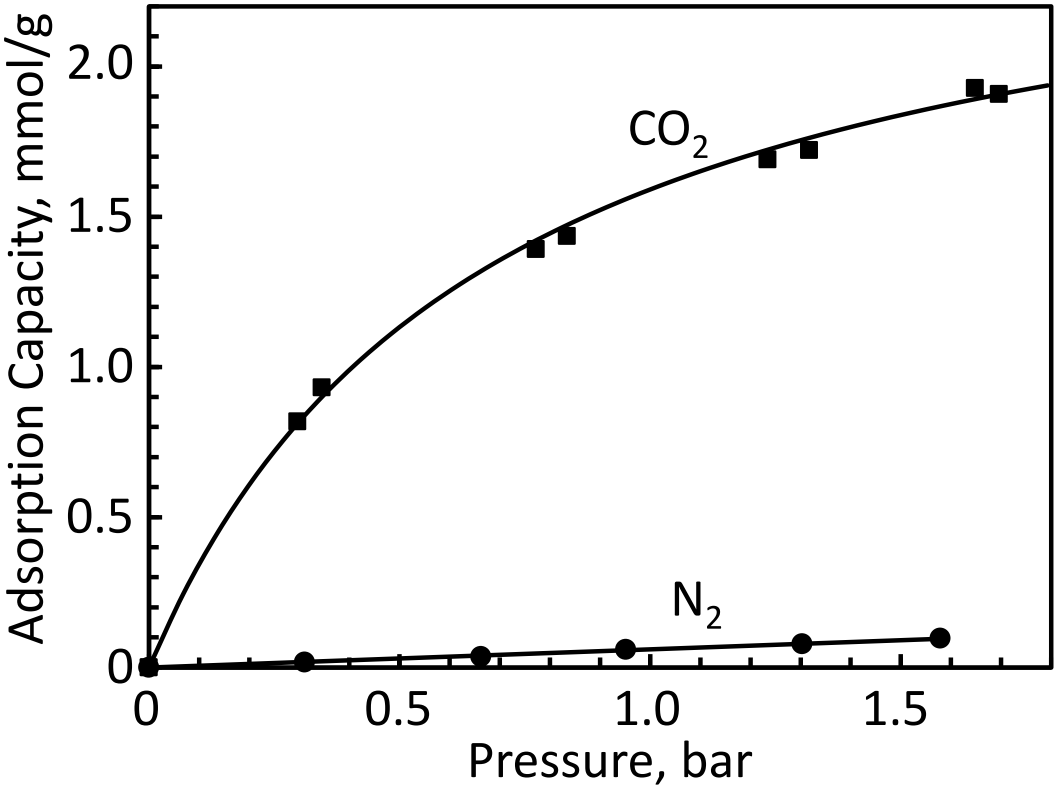


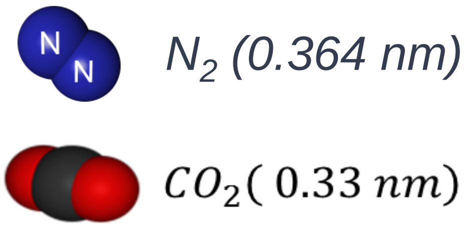
XRD



- Confirmation: power prepared is single layered GO with various functional groups

What is the separation mechanism?

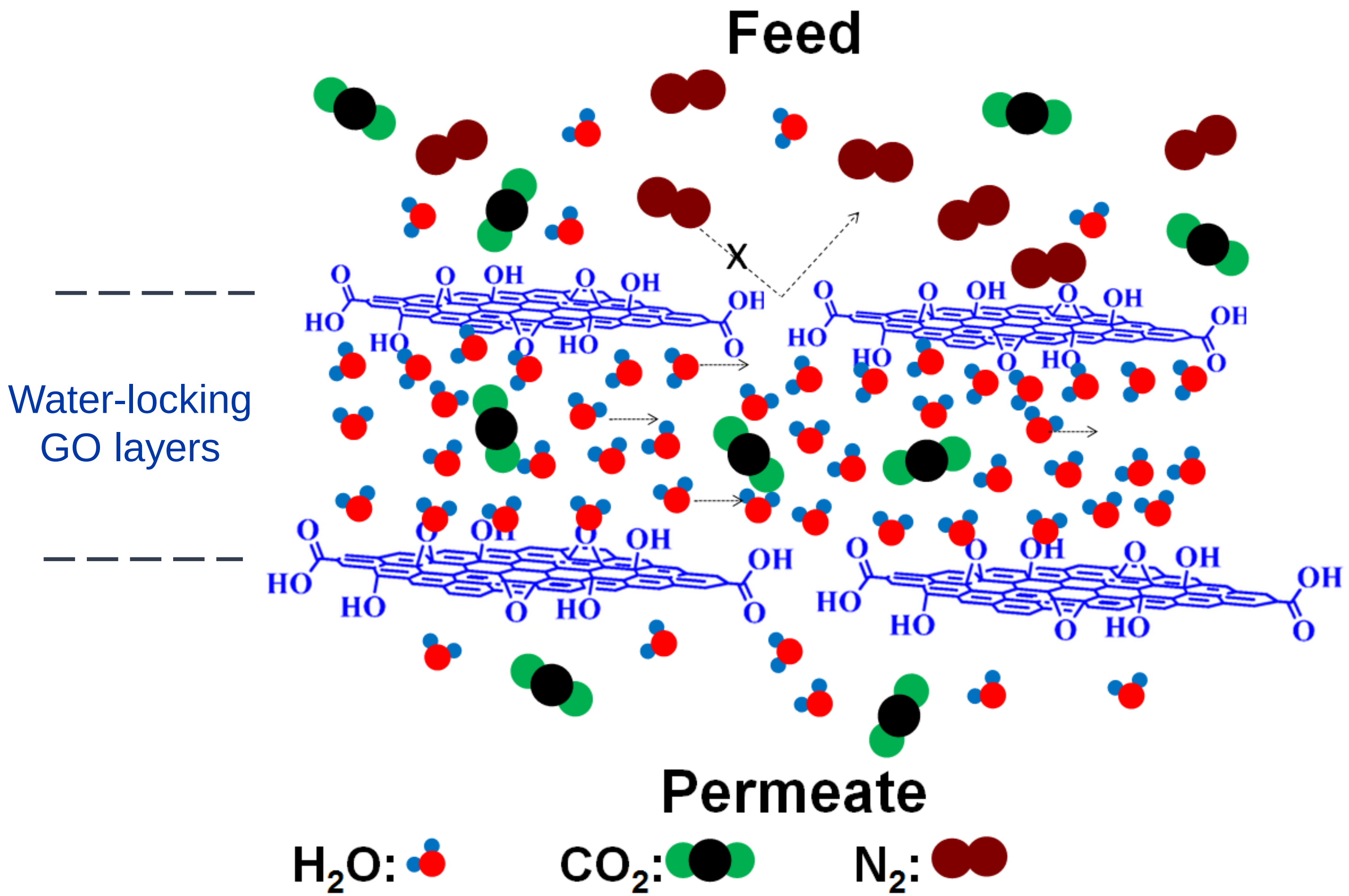




- **The smaller molecule CO_2 diffuses faster than the larger molecule N_2 which also favors the separation of CO_2 over N_2**

- **Preferential adsorption of CO_2 over N_2 would favor separating CO_2 over N_2**

$CO_2/N_2/H_2O$ transport mechanism through layered GO membrane: solution diffusion



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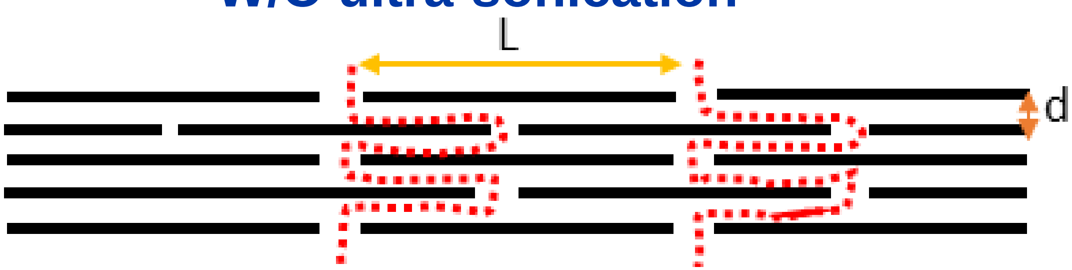
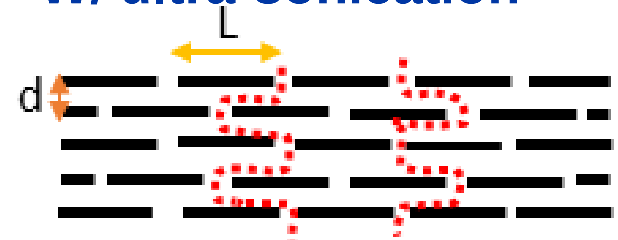
Approach 1 for improvement of membrane performance: reducing GO flake lateral size by ultra-sonication

GO type	Description
I	**Original GO prepared by modified Hummers method**
IA	*GO-COOH (GO functionalized with COOH group)*
II	**GO with enlarged structural defects etched by HNO_3 oxidation**
III	**GO with reduced lateral size by ultra-sonication**
IIIA	*Prepared by 1 h ultra-sonication*
IIIB	*Prepared by 2 h ultra-sonication*
IIIC	*Prepared by 3 h ultra-sonication*
IIID	*Prepared by 4 h ultra-sonication*
IIIE	*Prepared by 5 h ultra-sonication*
IIIF	*Prepared by 6 h ultra-sonication*

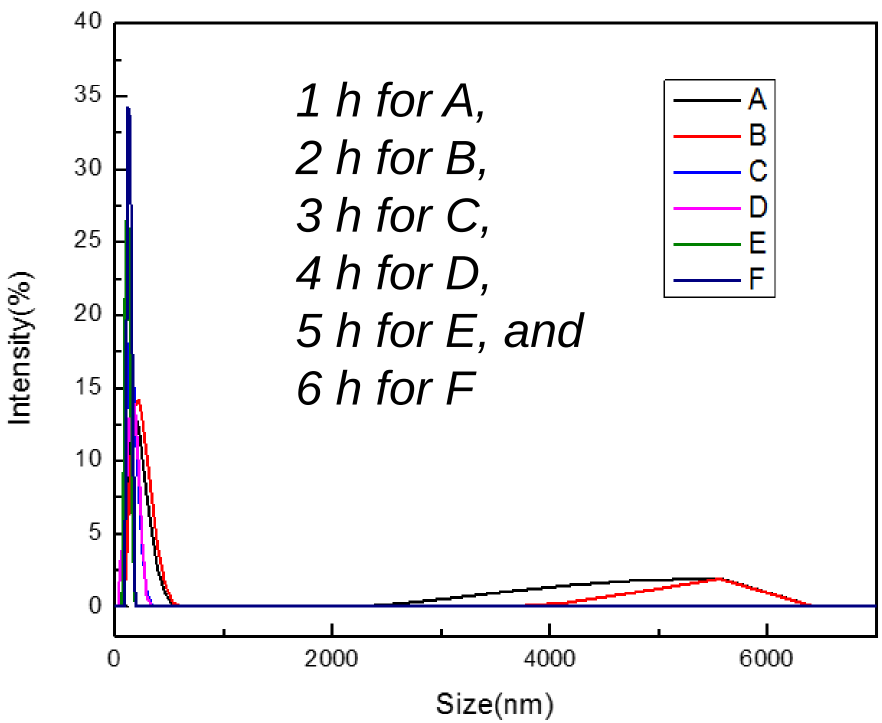
W/O ultra-sonication

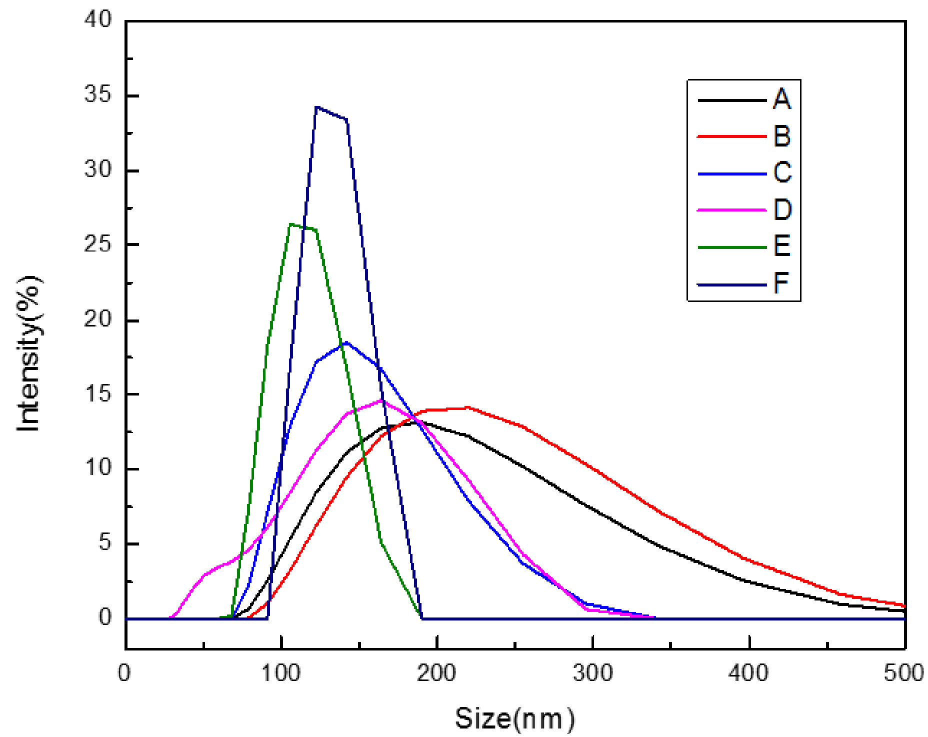


W/ ultra-sonication



Dynamic light scattering showed sonication effectively reduces GO size

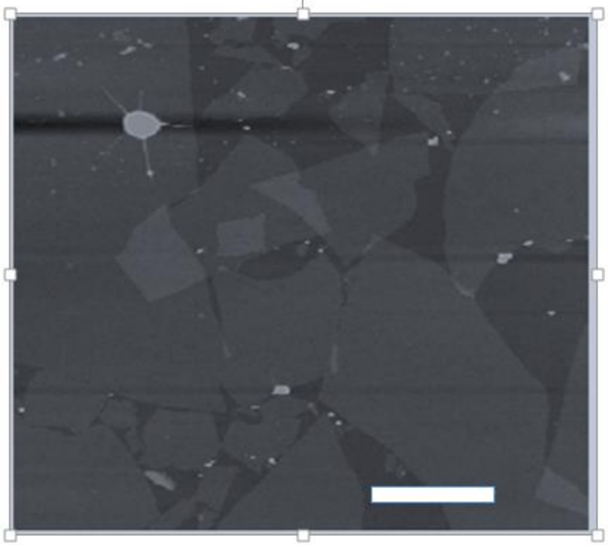




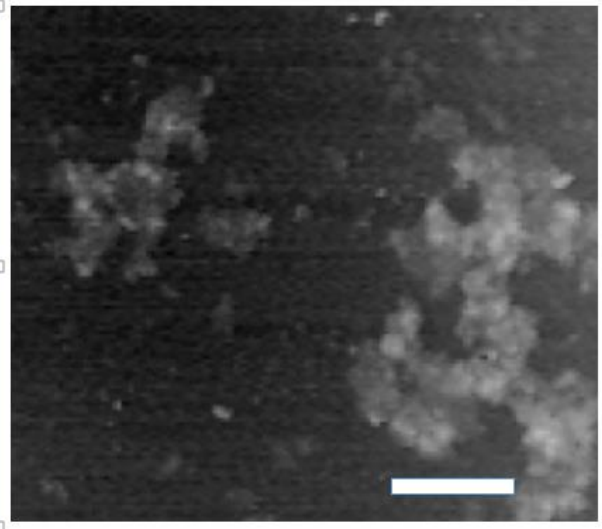
GO after 1-h sonication had a dual size distribution with two peaks centered at 200 and 5,000 nm. After 3-h sonication, the large-size GO disappeared and the GO particle sizes were smaller than approximately 150 nm. Further sonication led to a slight decrease in GO particle size.

AFM images (Type I, Type IIIA and Type IIIE) confirmed the reduced GO size

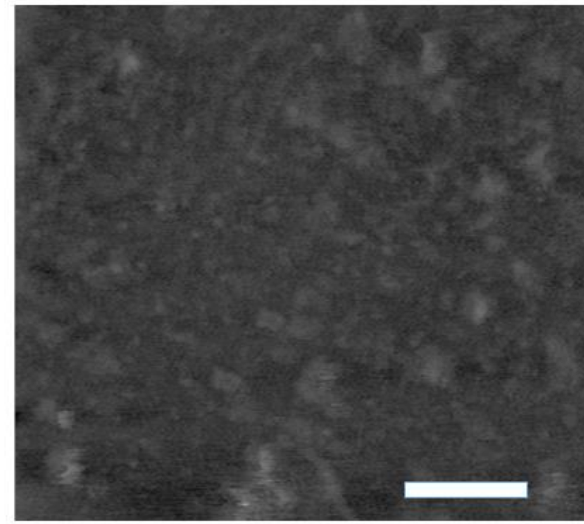
The scale bar is 1 μm



GO-Type I



GO-Type IIIA



GO-Type IIIE

Approach 2: PES support pre-washing to remove agents (mainly glycols) and thus reduce resistance from substrate

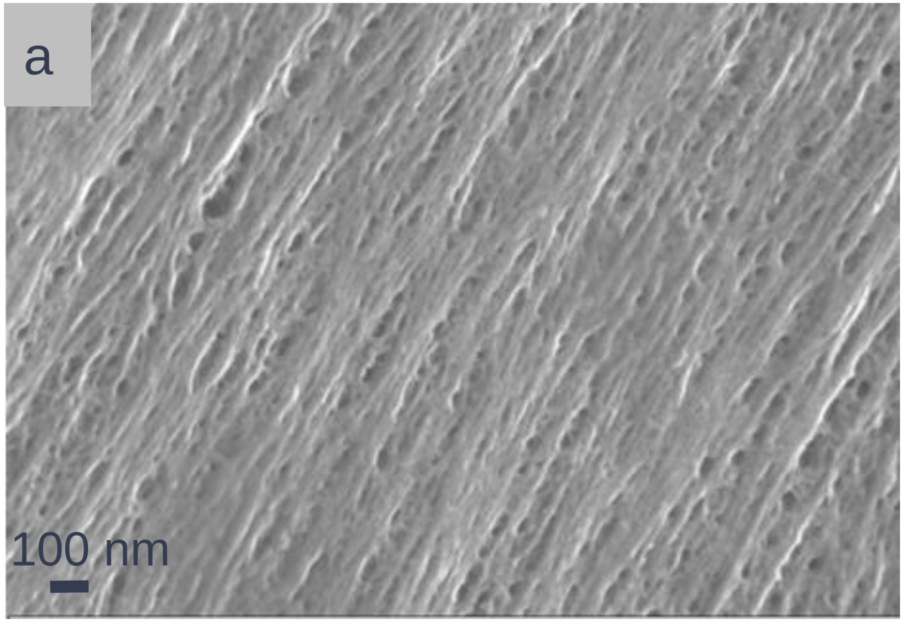
Permeance for the PES substrate

Support	Permeance* (GPU)	
	N_2	CO_2
Untreated support	480	530
Pretreated support	3,400	3,400

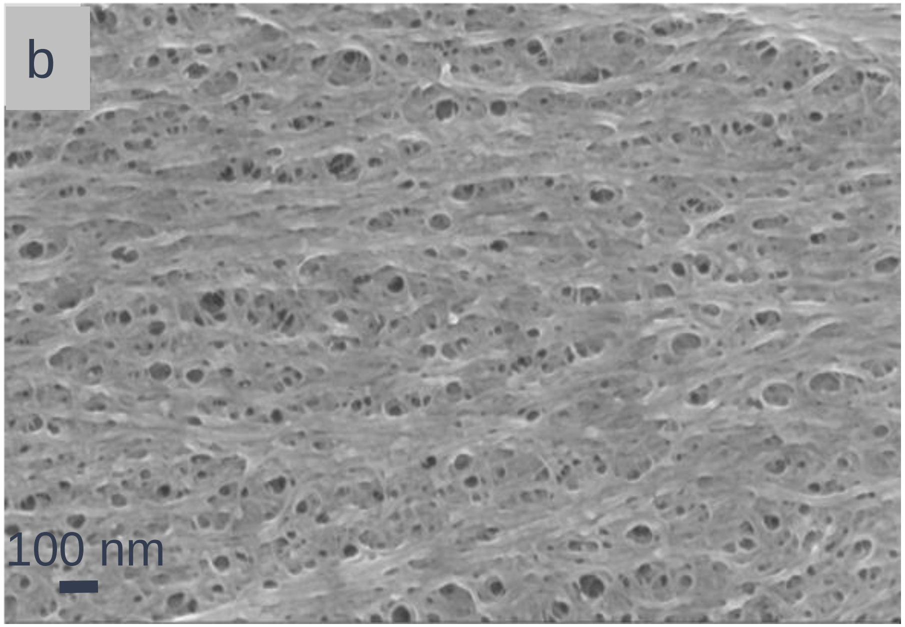
*Feed condition: 15% CO_2/85%N_2 with saturated water vapor at 24 °C; ΔP across the membrane was 1 to 5 psi.

PES = polyethersulfone

Field emission scanning electron microscope images showed support pores became larger after washing

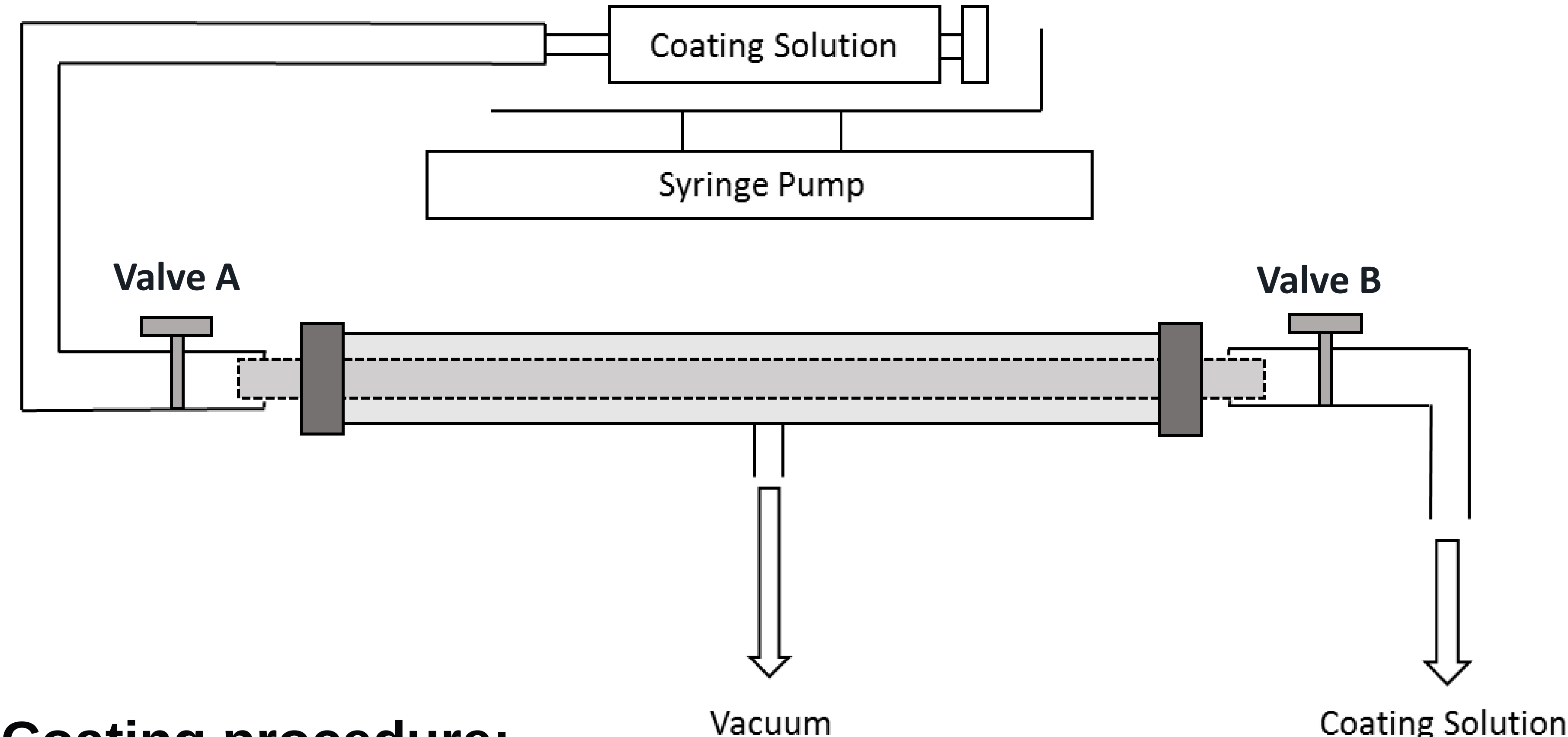


Support before washing



Support after washing

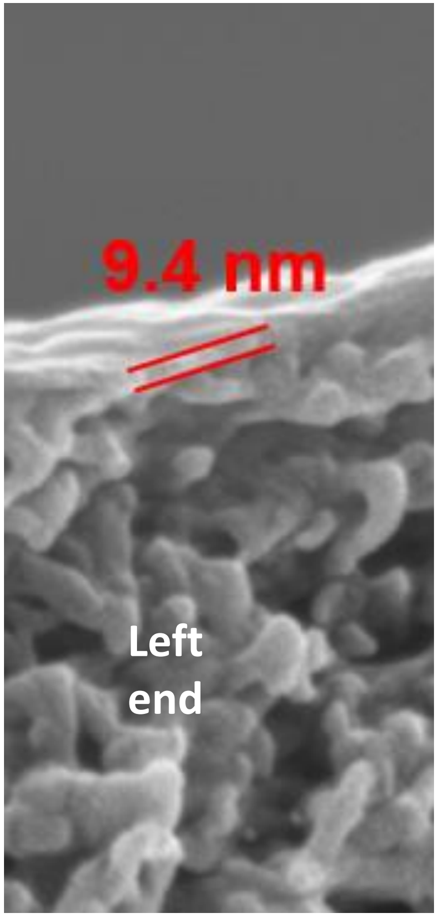
Procedure developed for coating GO-based membrane on hollow fiber (HF) support

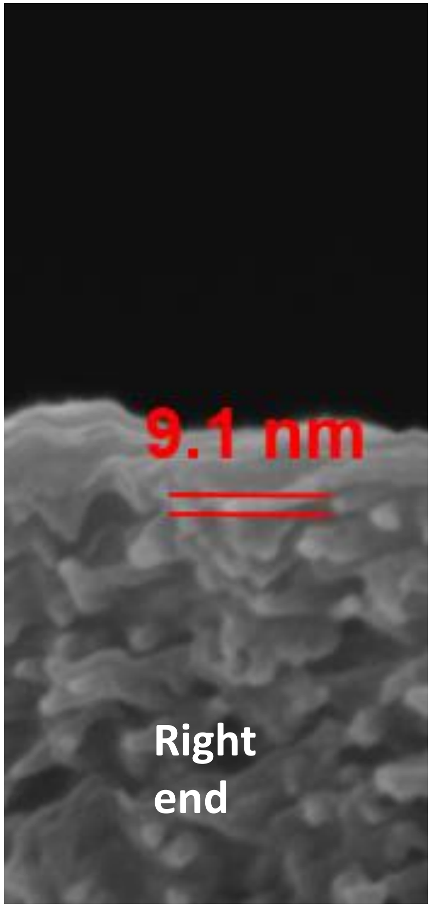


Coating procedure:

1. Valves A and B are open, GO dispersion flows continuously in hollow fiber
2. Vacuum filtration is conducted for a controlled time; and
3. Valves A and B are closed; coated fiber stays under vacuum for a controlled time

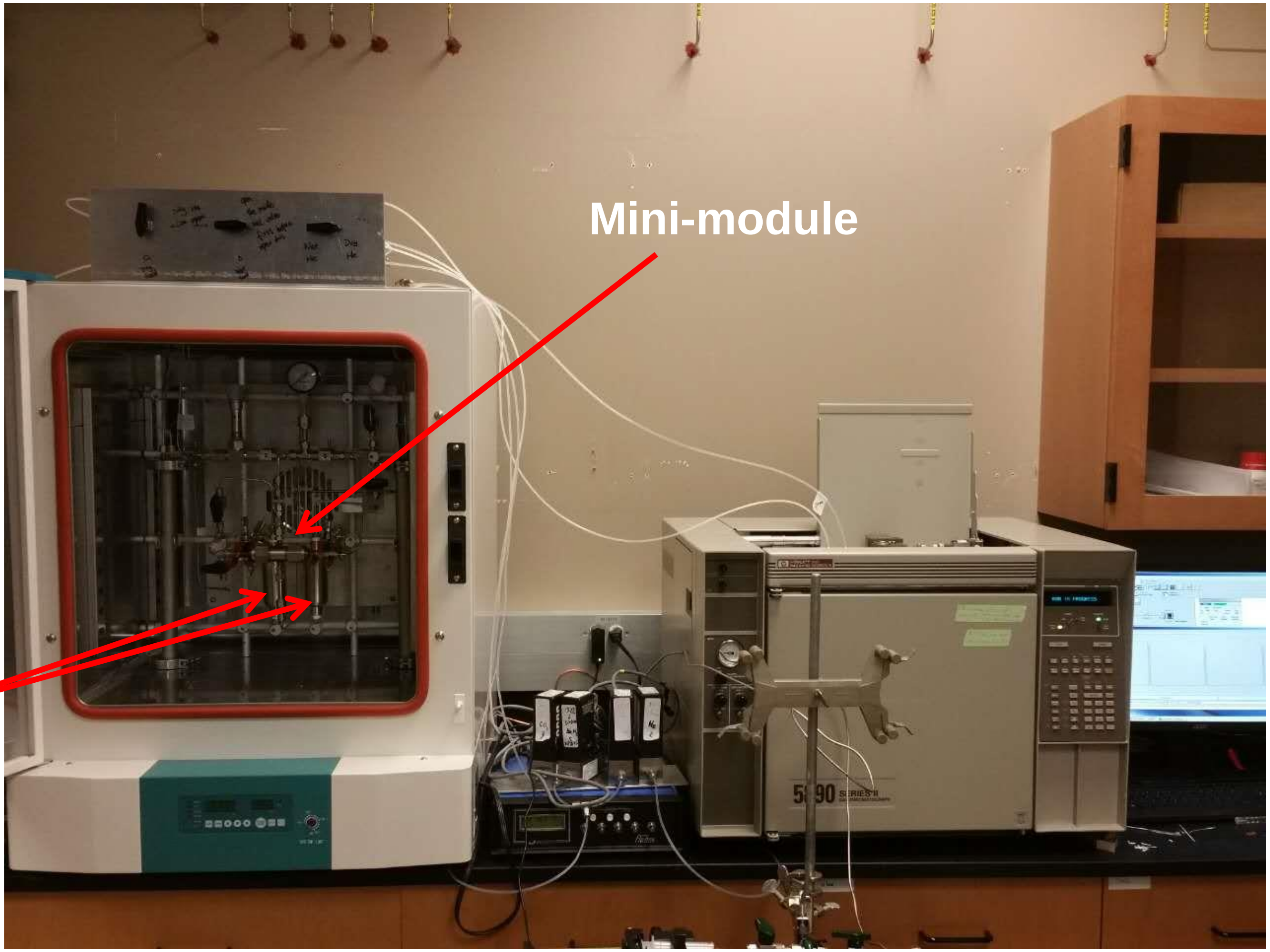
GO-based membranes as thin as 9 nm





GO-based membranes sealed in a mini-module for gas permeation testing

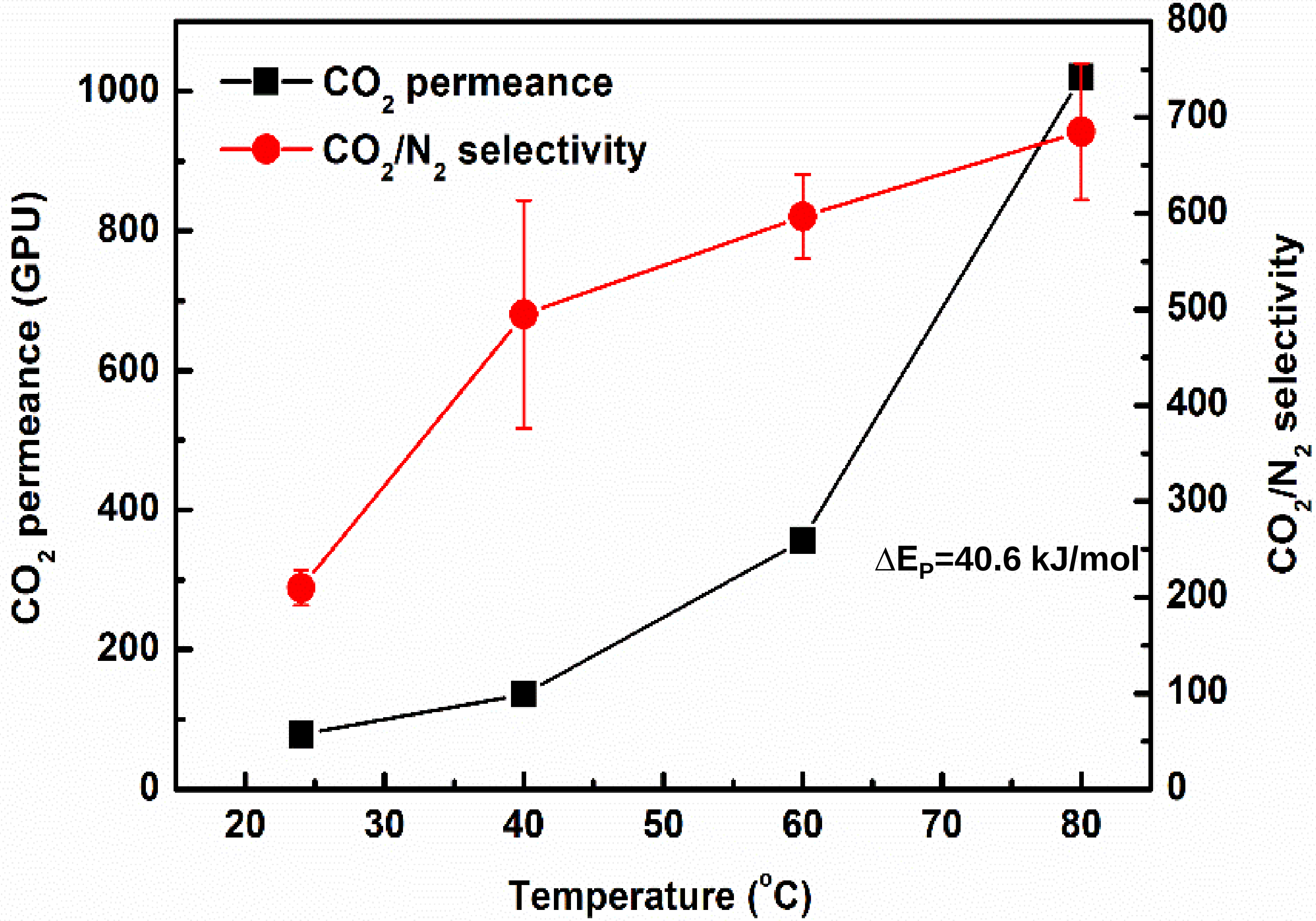
Permeation testing unit



Water bubbler and knockout vessel

GO-based membranes for CO_2/N_2 mixture separation under wet condition

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



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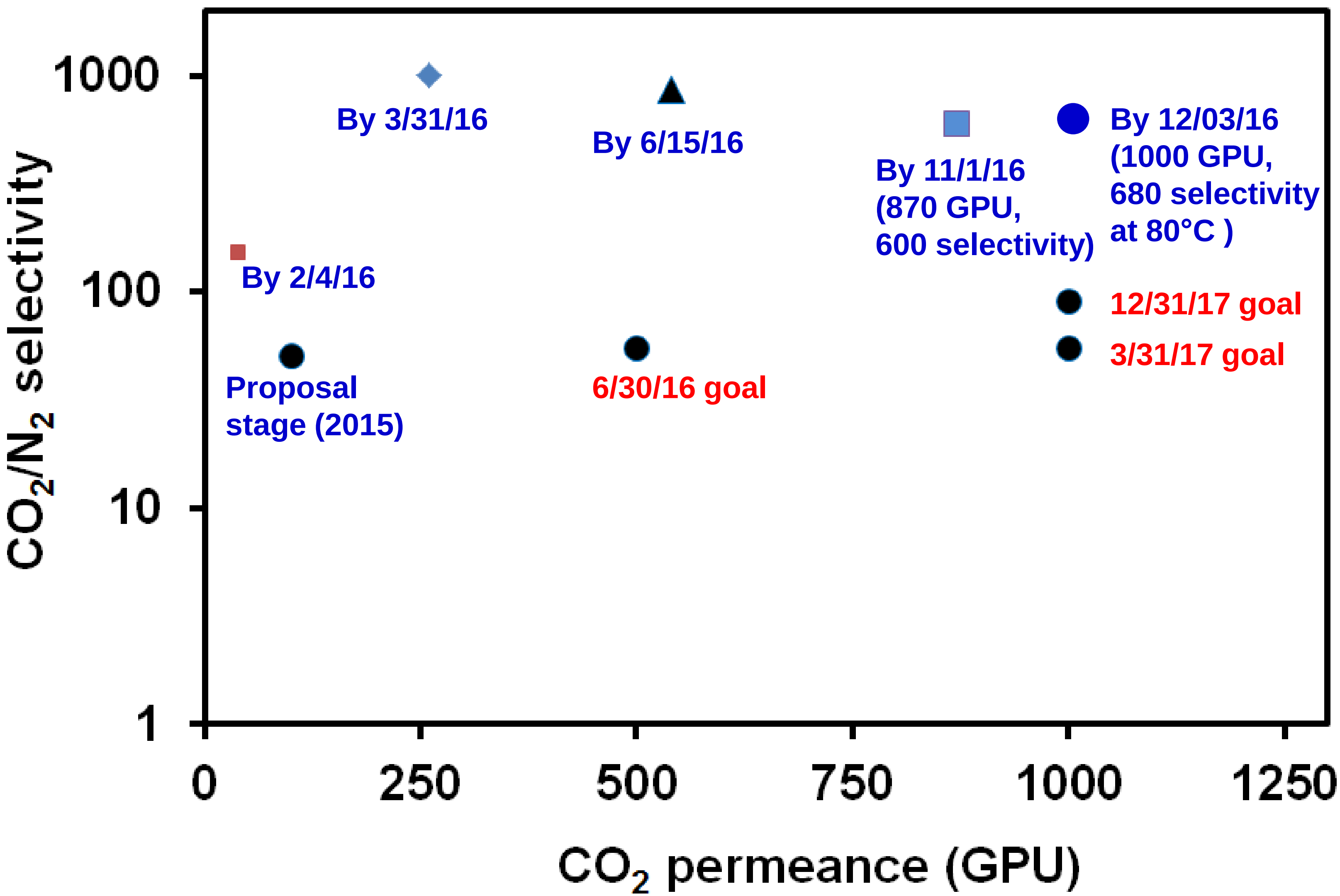
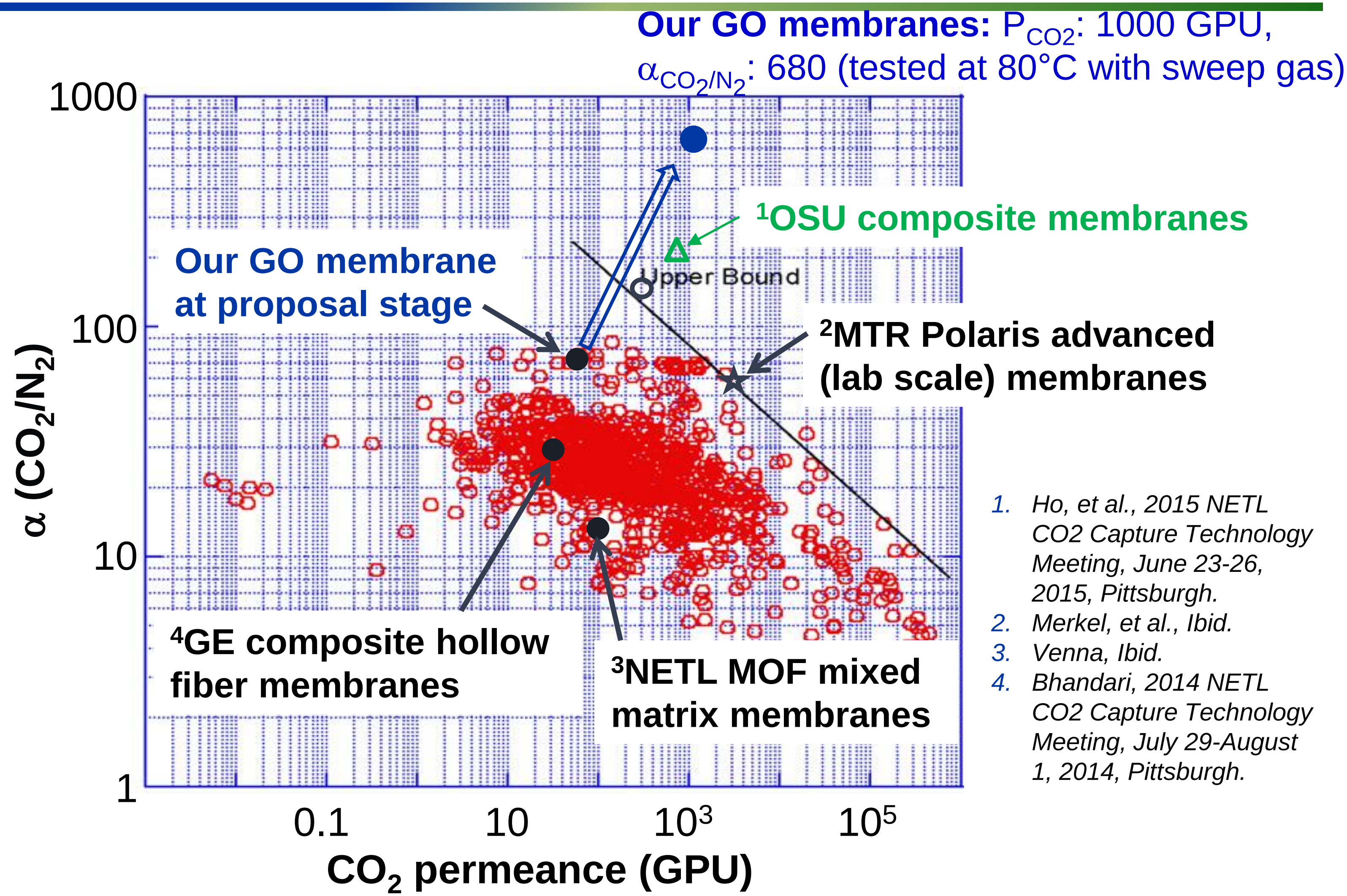
Progression of GO membrane development



Comparison to other CO_2/N_2 separation membranes



1. *Ho, et al., 2015 NETL CO2 Capture Technology Meeting, June 23-26, 2015, Pittsburgh.*
2. *Merkel, et al., Ibid.*
3. *Venna, Ibid.*
4. *Bhandari, 2014 NETL CO2 Capture Technology Meeting, July 29-August 1, 2014, Pittsburgh.*

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

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

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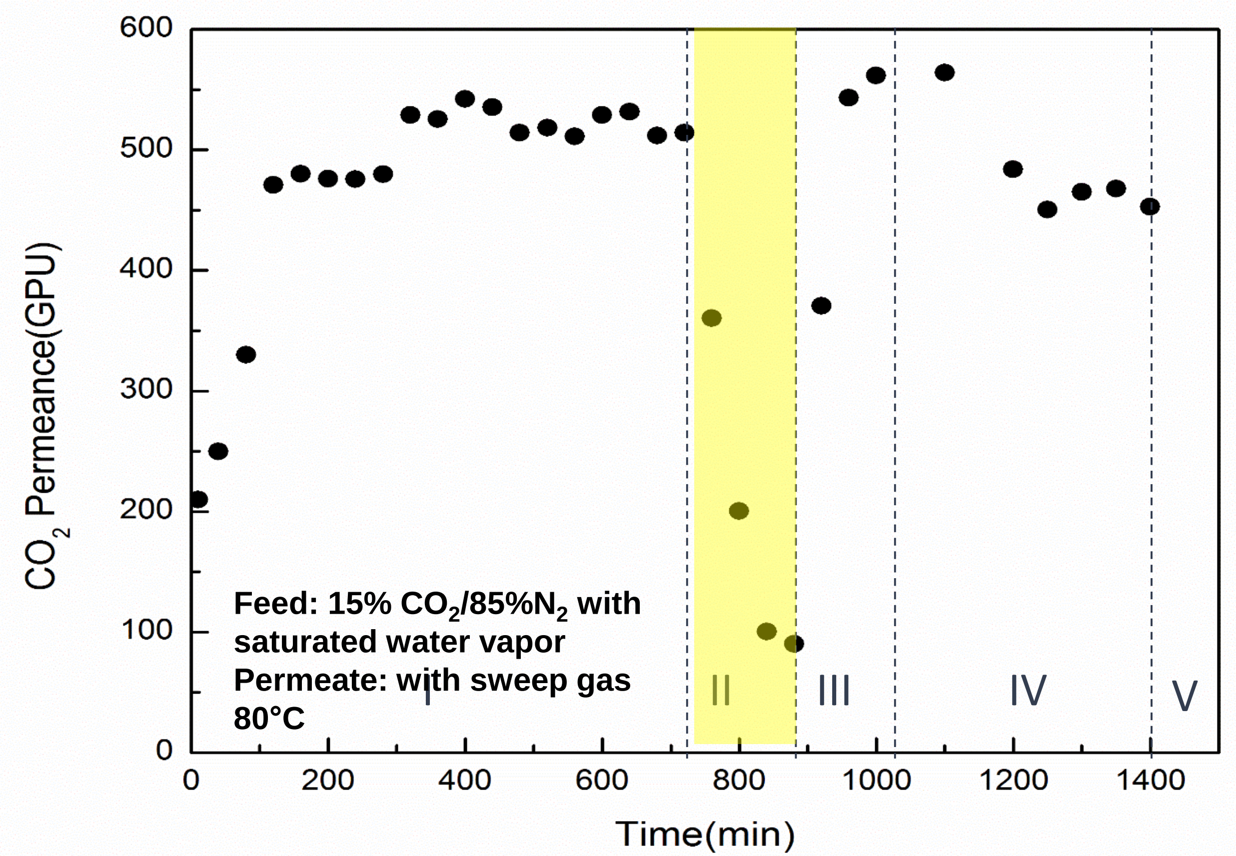
Preliminary stability testing indicated operation condition needs to be optimized during BP2



Area	CO_2/N_2 Selectivity	RH (feed)
I	>400	100
II	<200	100
III	<20	0
IV	>400	100
V	Stop	Stop

Area II: water condensation in membrane due to a low temperature of sweep helium

Scaleup consideration

This scale of module to be used in large bench scale and to be tested at NCCC

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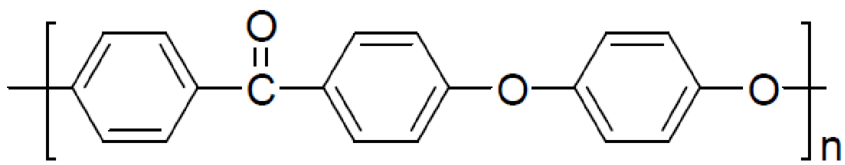
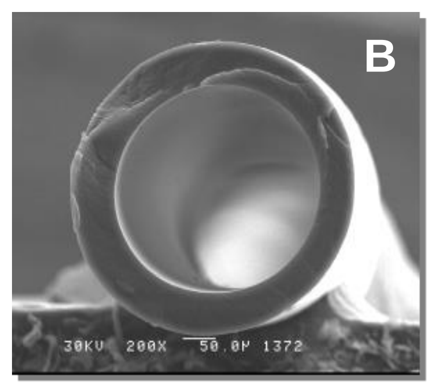
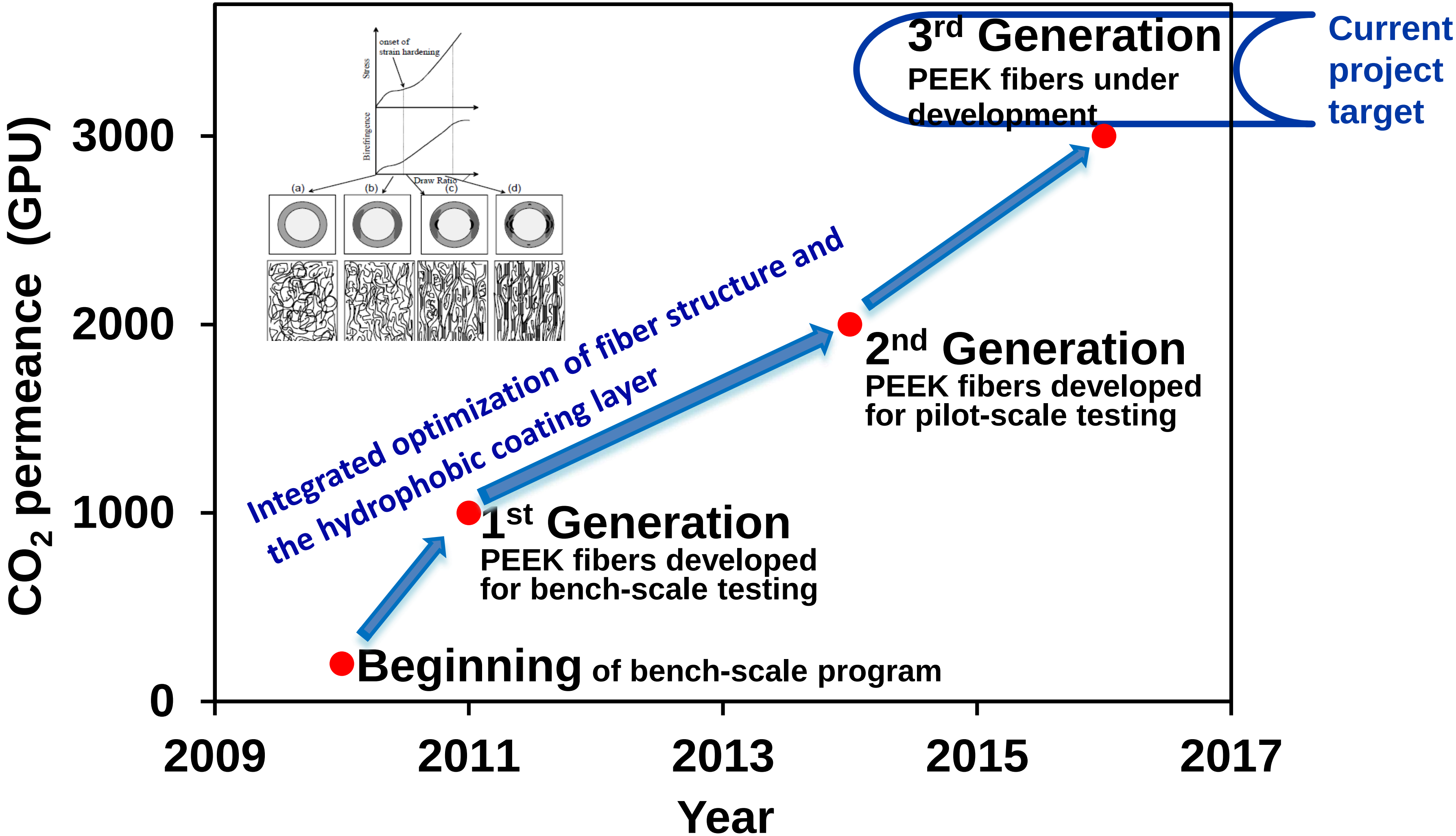
Progress on PEEK Membranes





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



1 GPU = 1 x 10^{-6} cm^3 (STP)/cm^2 • s • cmHg

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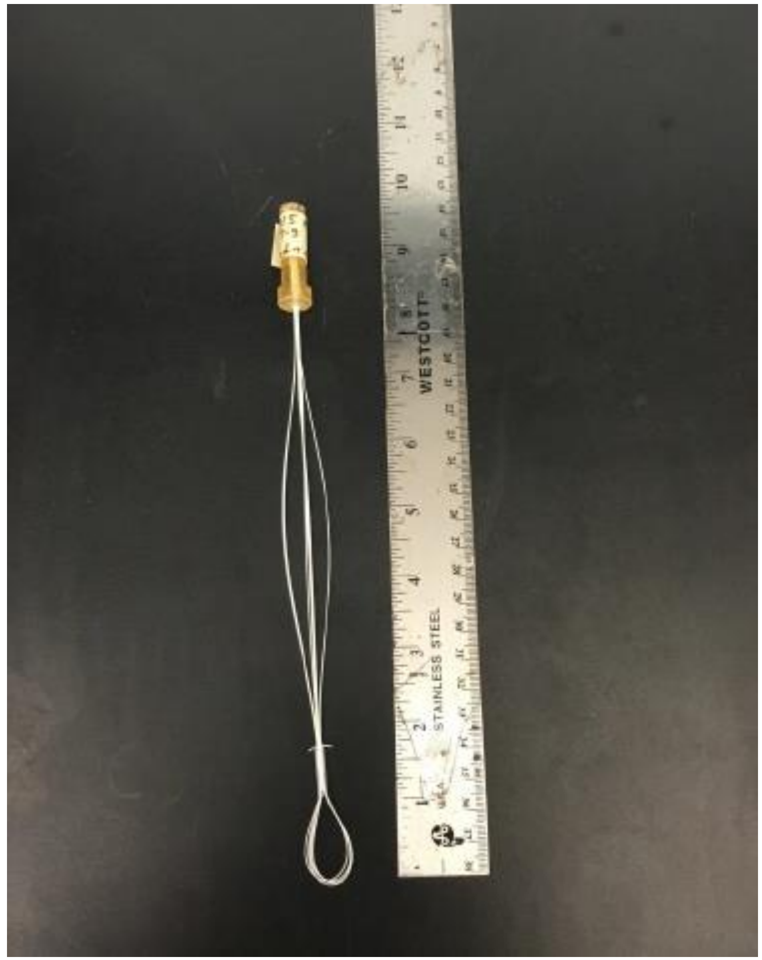
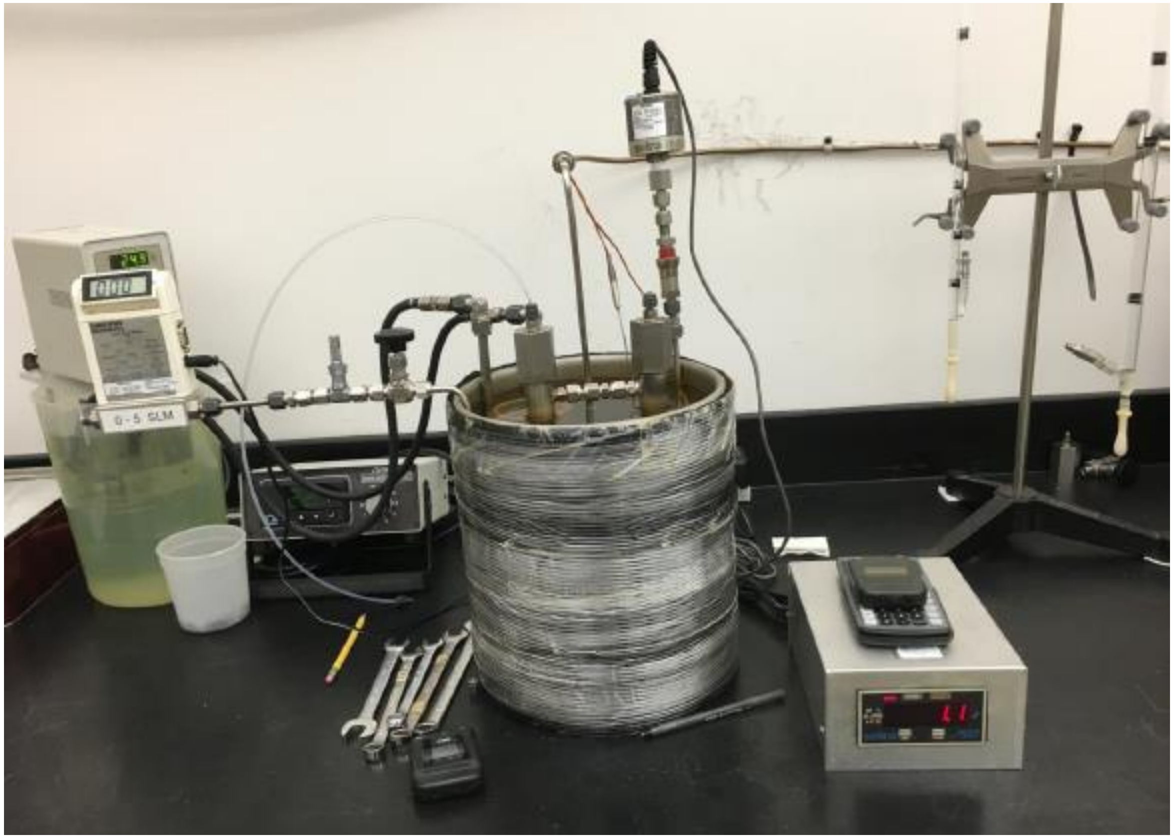
Air Liquide's micro module lab testing



Air Liquide's lab testing system



Eight types of fibers were investigated

Sample No.	Fiber OD (Micron)	Fiber ID (Micron)	CO_2 permeance* (GPU)
78-33-3A	582	350	2,300
78-33-3B	582	350	2,500
78-118-3A	569	358	2,300
78-118-3B	569	358	2,800
78-117-5A	569	353	3,400
78-117-5B	569	353	3,400
78-117-5C	569	353	3,700
78-117-5D	569	353	3,800

Temperature: 25°C, feed pressure: ~ 5 psig

2-inch module 2PG809 containing 78-117-5A fibers (CO_2 permeance of 3,400 GPU)

Single gas permeances for CO_2 at 25°C

Feed pressure (psig)	Retentate side pressure (psig)	Permeate side pressure (psig)	Intrinsic CO_2 permeance (GPU)
12	11.4	0.43	2,750
15	14.3	0.65	2,750

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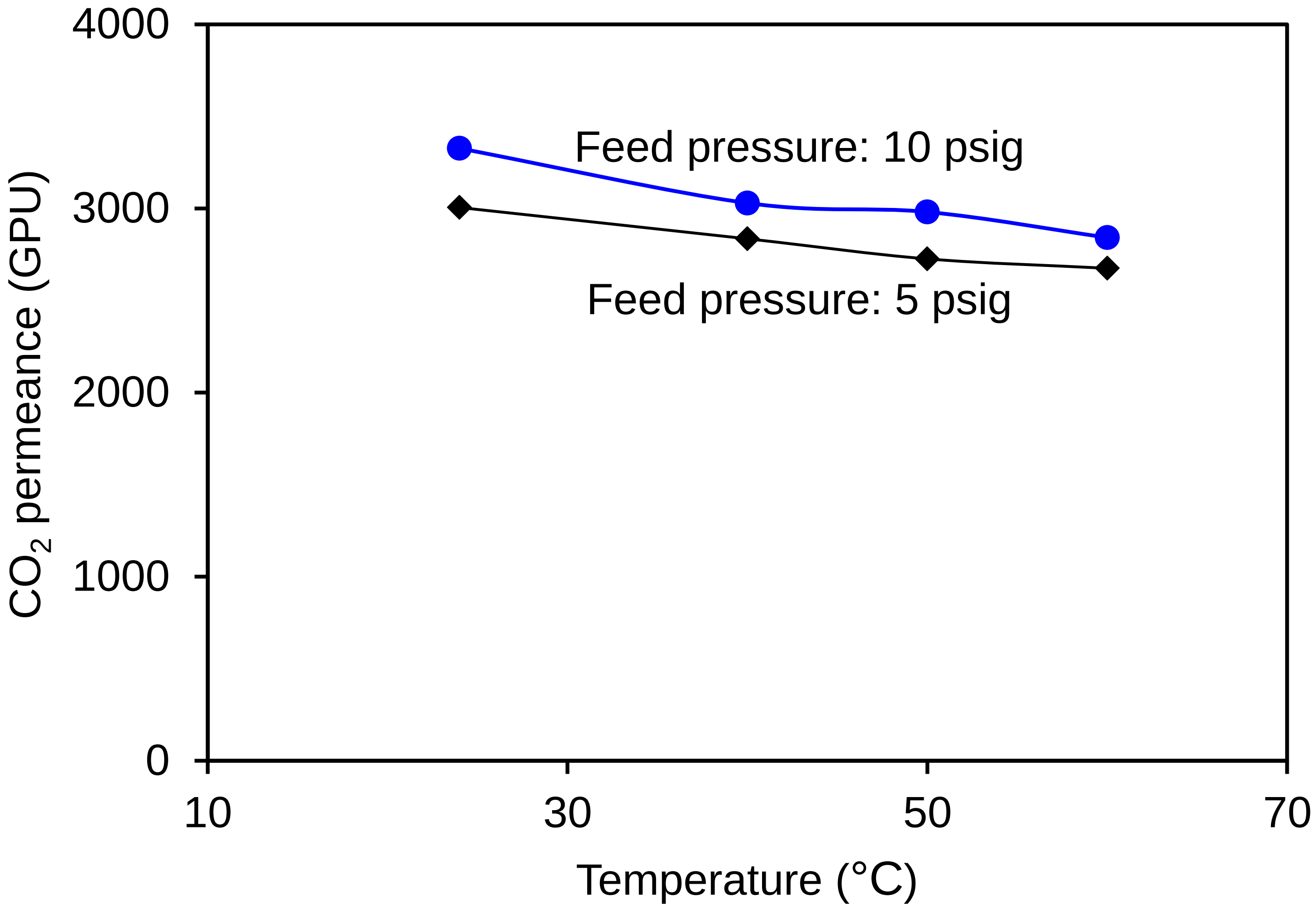
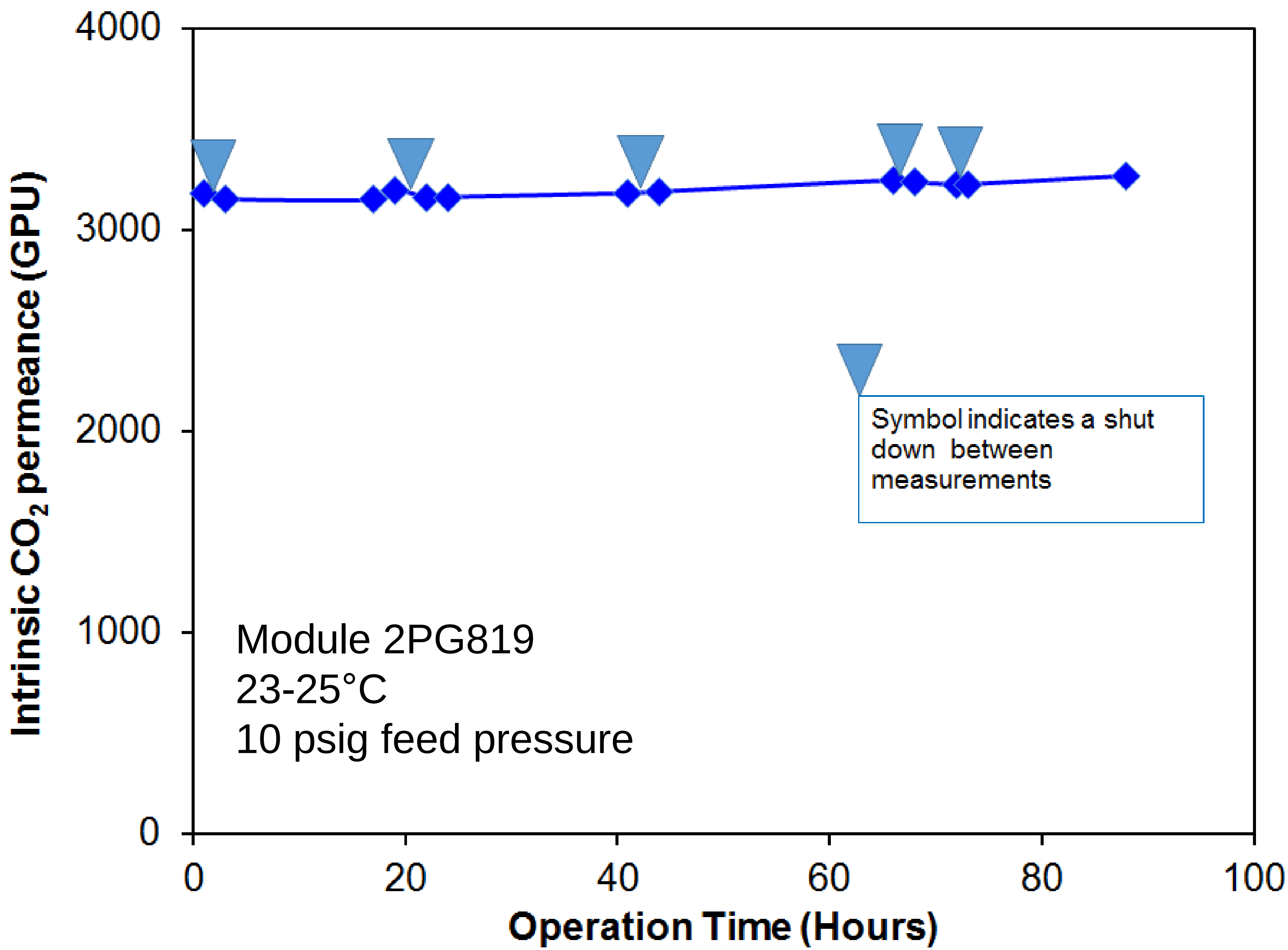
Another 2-inch module 2PG818 containing 78-117-5C fibers (CO_2 permeance of 3,700 GPU)

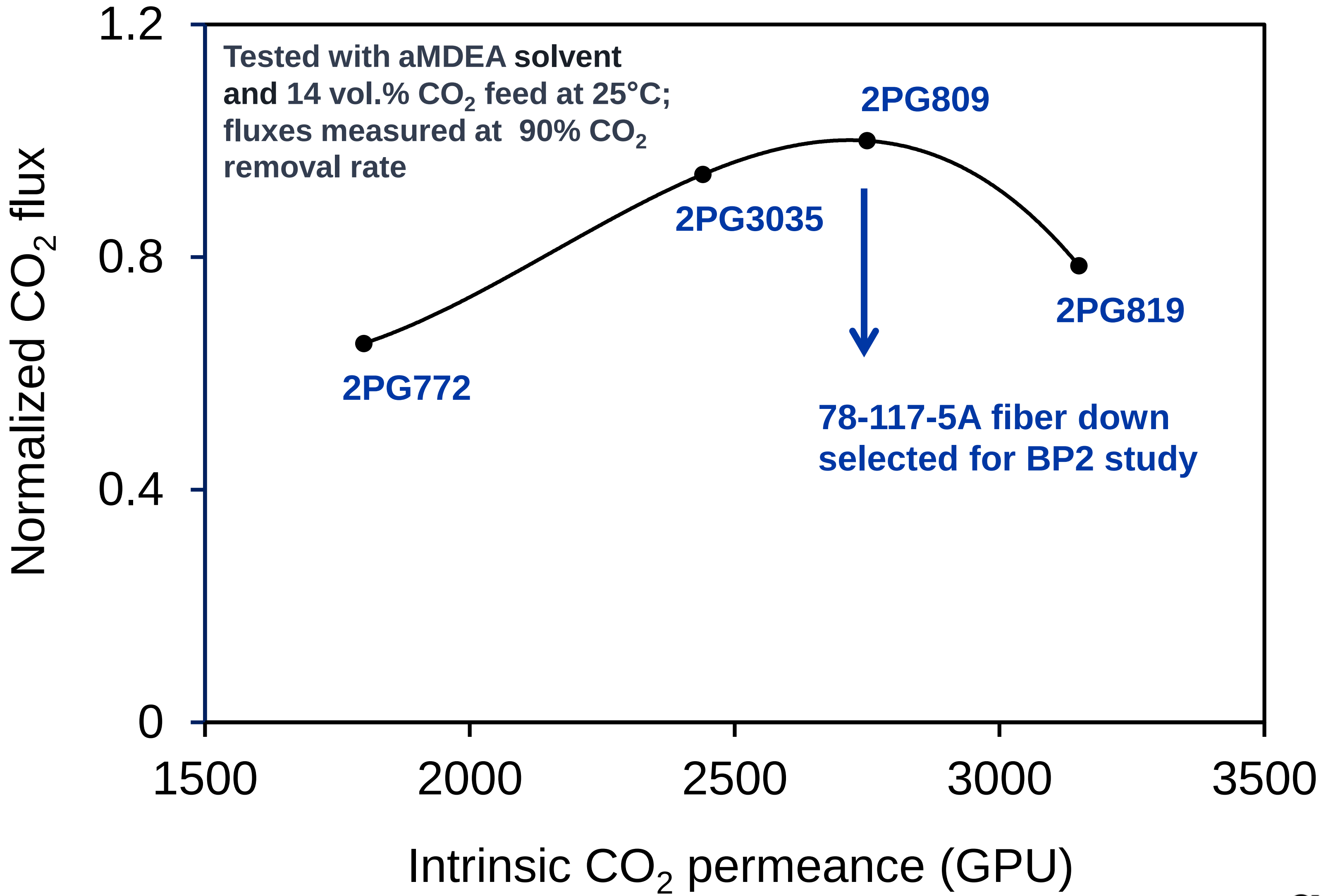


Intrinsic CO_2 permeance as high as 3,000-3,300 GPU at 25°C, meeting our goal of 3,000 GPU

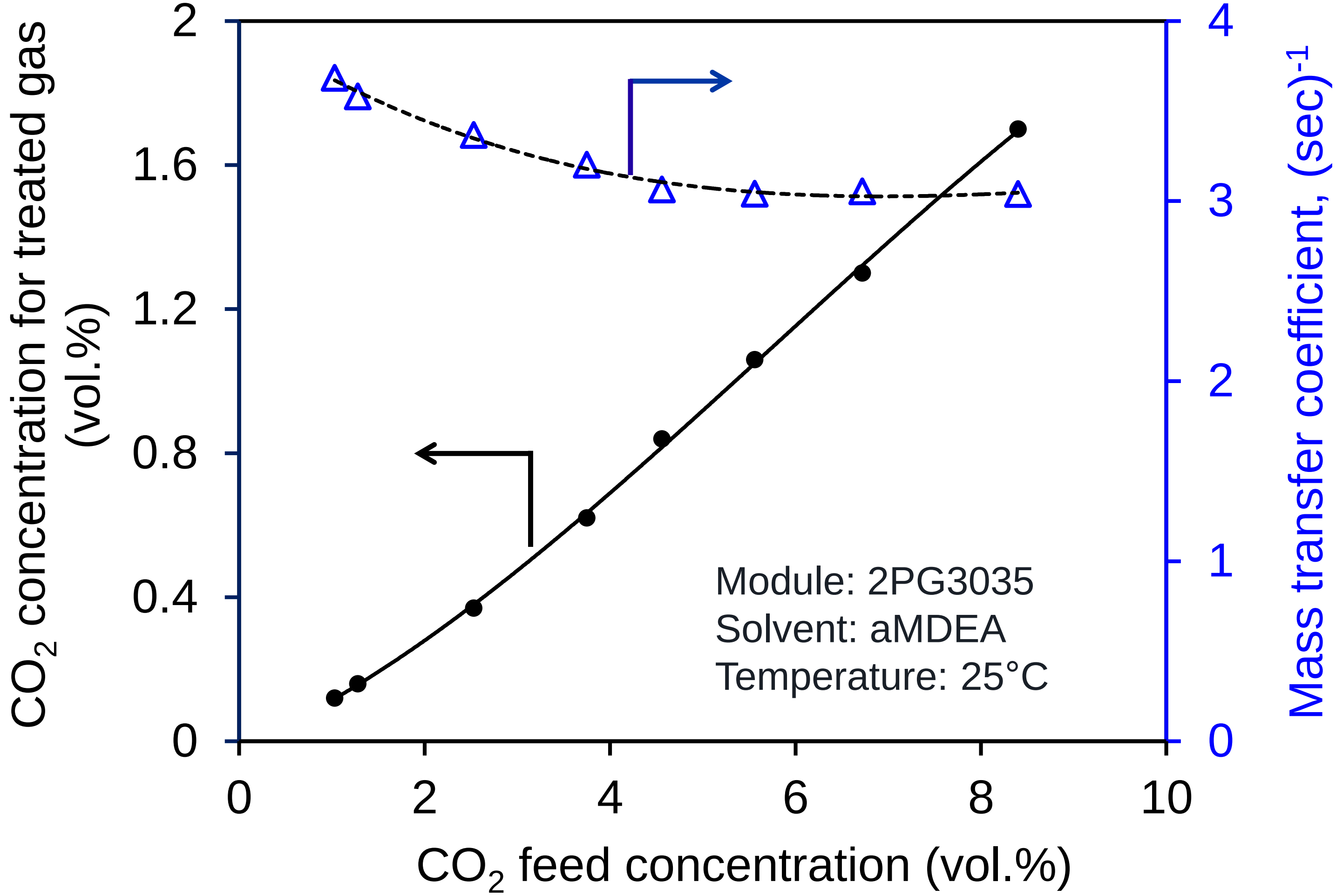
Intrinsic CO_2 permeance stable



CO_2 flux in contactor vs. intrinsic CO_2 permeance



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



BP1 success criteria met

1) GO membranes exhibit CO_2/N_2 selectivity ≥55 and CO_2 permeance ≥1,000 GPU; and
2) PEEK hollow fiber membrane intrinsic CO_2 permeance of 3,000 GPU achieved.

BP1 all milestones met

Milestone	Milestone Title/Description	Planned Completion Date	Actual Completion Date
1.1	Updated Project Management Plan	11/30/15	11/25/15
1.2	Kickoff Meeting	12/31/15	12/07/15
2.1	GO membranes with thickness <50 nm successfully prepared on porous hollow fiber supports	02/28/16	02/20/16
4.1	Achieve membrane intrinsic CO_2 permeances of 3,000 GPU for PEEK hollow fiber modules	08/31/16	10/24/16
5.1	GO membranes with thickness <25 nm successfully prepared on porous hollow fiber supports	12/31/16	12/03/16
5.2	GO membranes exhibit CO_2/N_2 selectivity ≥55 and CO_2 permeance ≥1,000 GPU	03/30/17	12/03/16

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Summary for BP1 study

- We are developing a novel CO_2 capture process combining a conventional gas membrane unit and a HFMC unit
- **GO membrane** developed to date
  - CO_2 permeance > 1,000 GPU and α_{CO_2/N_2} > 600 obtained at 80°C for a humidified CO_2/N_2 mixture
  - Superior performance to GO-based membranes reported in the literature
- **The 3rd Generation PEEK fiber** developed to date
  - Fibers with intrinsic CO_2 permeance >3,000 GPU at 25°C
  - 78-117-5A fiber down selected for BP2 study
  - Membrane module effective in capturing CO_2 from low CO_2-concentration feeds with aMDEA solvent
- Ahead of schedule (under budget) to complete BP1 work
  - All milestone and success criteria met
  - **Ready for BP2 starting April 1, 2017**

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BP2 overview/roadmap

GO Membrane Development

Task 6.0 (USC) – Further GO optimization

Task 7.0 (GTI) – Performance stability testing of GO membranes using simulated flue gases

Task 9.1 (USC) – GO membrane support for integrated testing

PEEK Membrane Development

Task 9.2 (ALaS) – PEEK membrane support for integrated testing

Integrated GO-PEEK Hybrid System

Task 8.0 (GTI)– Modification of an existing HFMC apparatus to GO-PEEK system

Task 10.0 (GTI) – CO_2 capture testing using integrated GO-PEEK hybrid system

Task 11.0 (Trimeric)– High-level techno-economic feasibility study

Requesting…

- Continuation of BP2
- BP2 budget of $1,185,247
  - GTI’s team to provide $244,376 cost share

After the current project, steps can be taken to further reduce capture cost

- Increase CO_2 permeance for GO membrane
- Improve manufacture process to lower membrane costs
- Use advanced solvents instead of aMDEA
- Use novel process for solvent regeneration
  - e.g. gas pressurized stripping reported by Carbon Capture Scientific[1]
  - e.g. advanced flash regeneration by UT [2]

1: Scott Chen et al., Ibid
2. Gary Rochelle, 2016 NETL CO2 Capture Technology Meeting, August 8-12, 2016, Pittsburgh.

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Acknowledgements

- **Financial support**

ALaS

- **DOE NETL José Figueroa**