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

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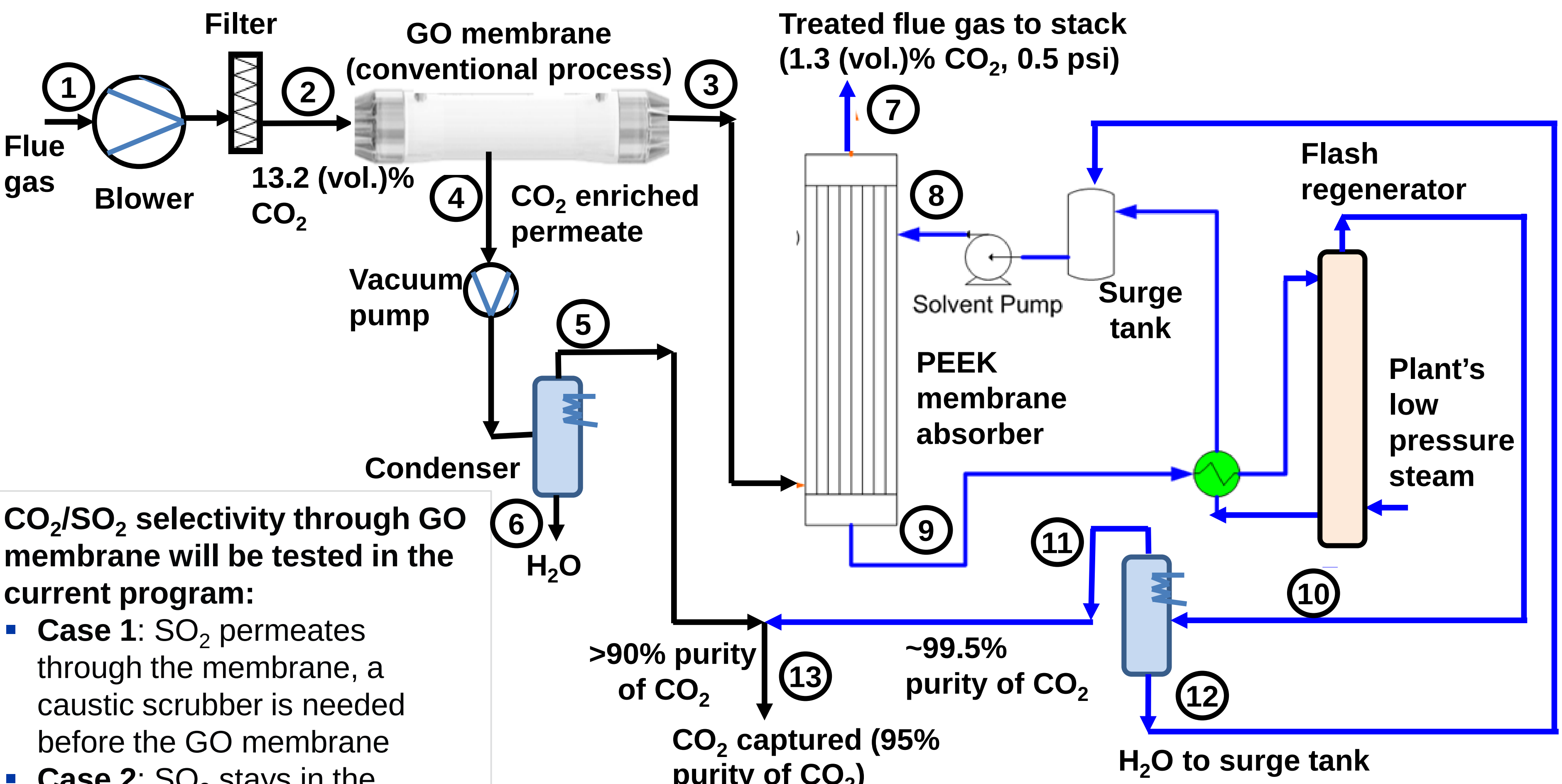
Project overview

- **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

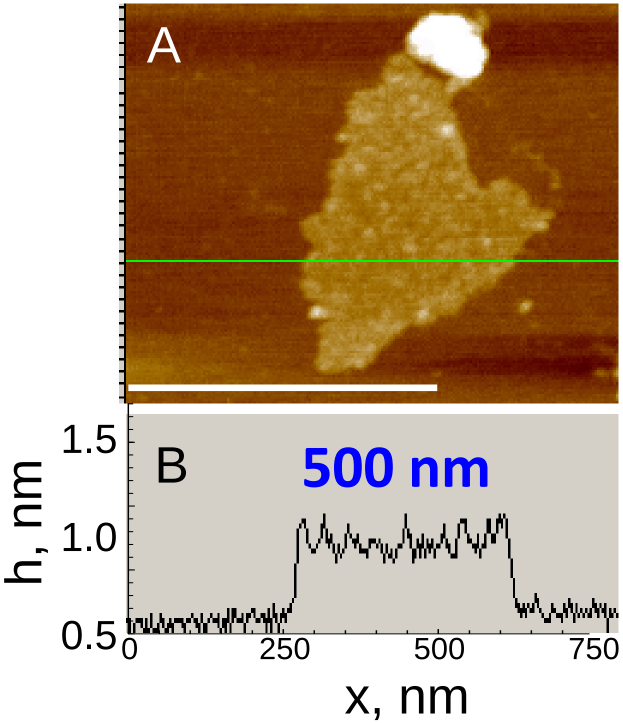


CO_2/SO_2 selectivity through GO membrane will be tested in the current program:

- **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 unneeded; HFMC can handle 150 ppmv SO_2 (DE-FE-0004787)

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

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

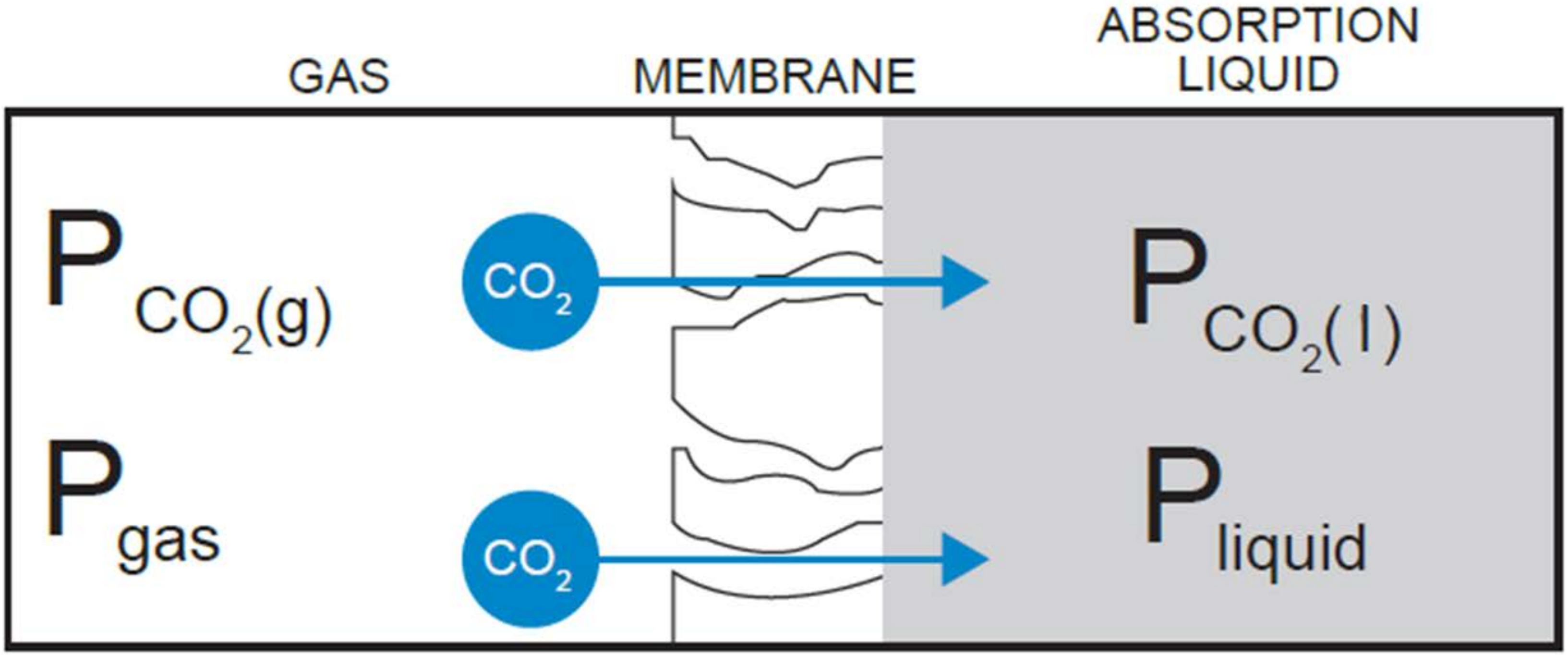


Single-layered GO flake prepared as thin as 1 nm

- **Contribution of the paper**:
  - Structure defect-free GO membrane is impermeable to gas
  - Structural defects on GO flakes can be controlled as transport pathway for selective gas separations

What is a membrane contactor?

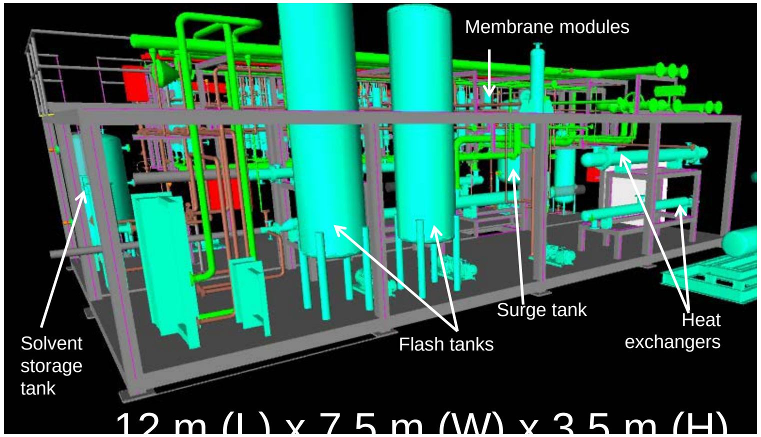
- High surface area membrane device that facilitates mass transfer
- Gas on one side, liquid on other side



- Membrane does not wet out in contact with liquid
- **Separation mechanism**: CO_2 permeates through membrane, reacts with the solvent; N_2 does not react and has low solubility in solvent

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

Commercial-sized modules

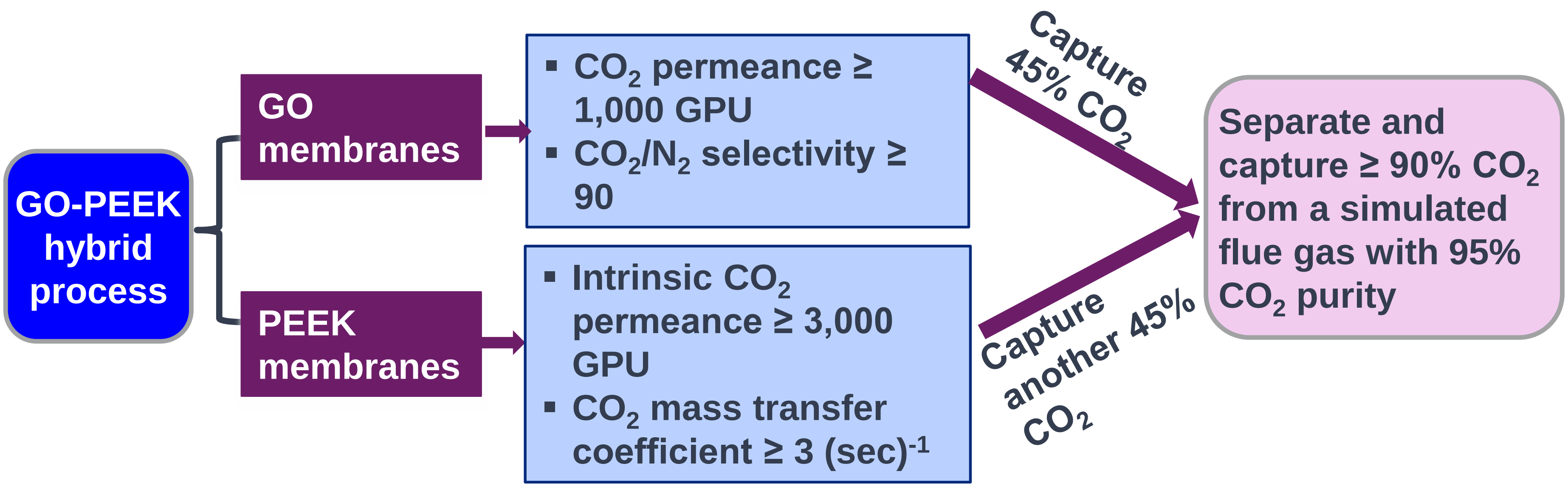


3D model of the 0.5 MW_e plant

Pilot plant construction to be completed by 9/30/16

To be tested at NCCC in 2017

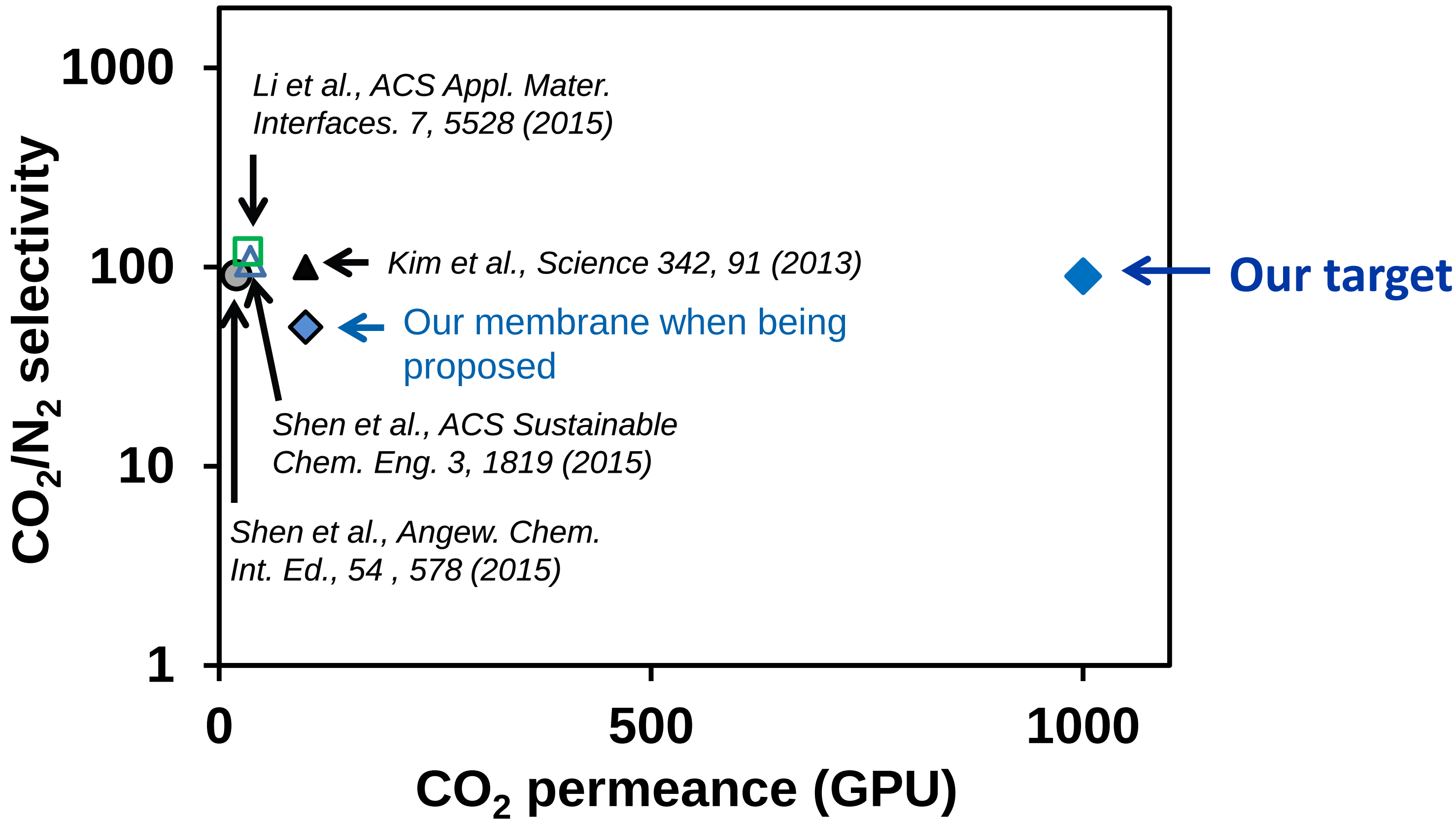
GO-PEEK technical goals



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

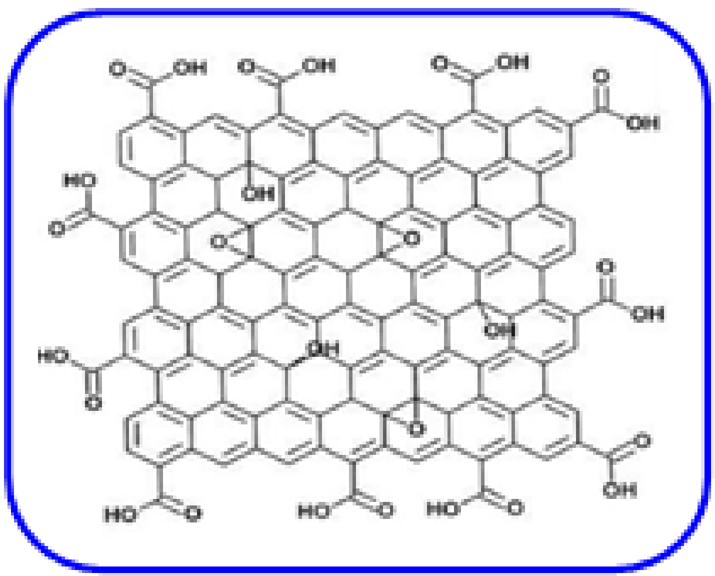
Technical challenges of applying GO-PEEK process to existing coal-fired plants

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



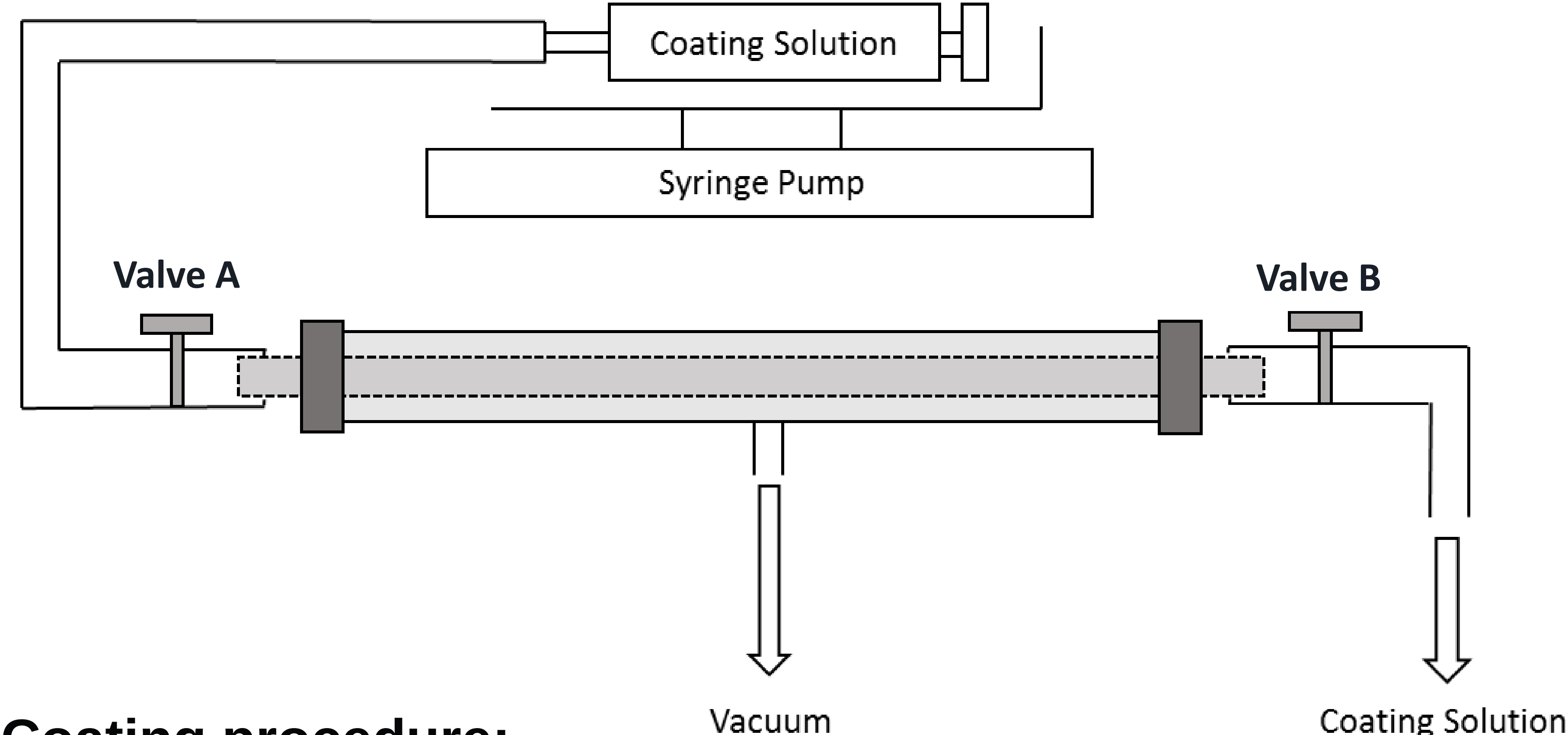
- **Durability** – Long-term stability of both GO and PEEK membranes
- **Scale-up and cost reduction** – Both membranes in hollow fiber format

Progress on GO Membranes



GO: single-atomic layered, oxidized graphene

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



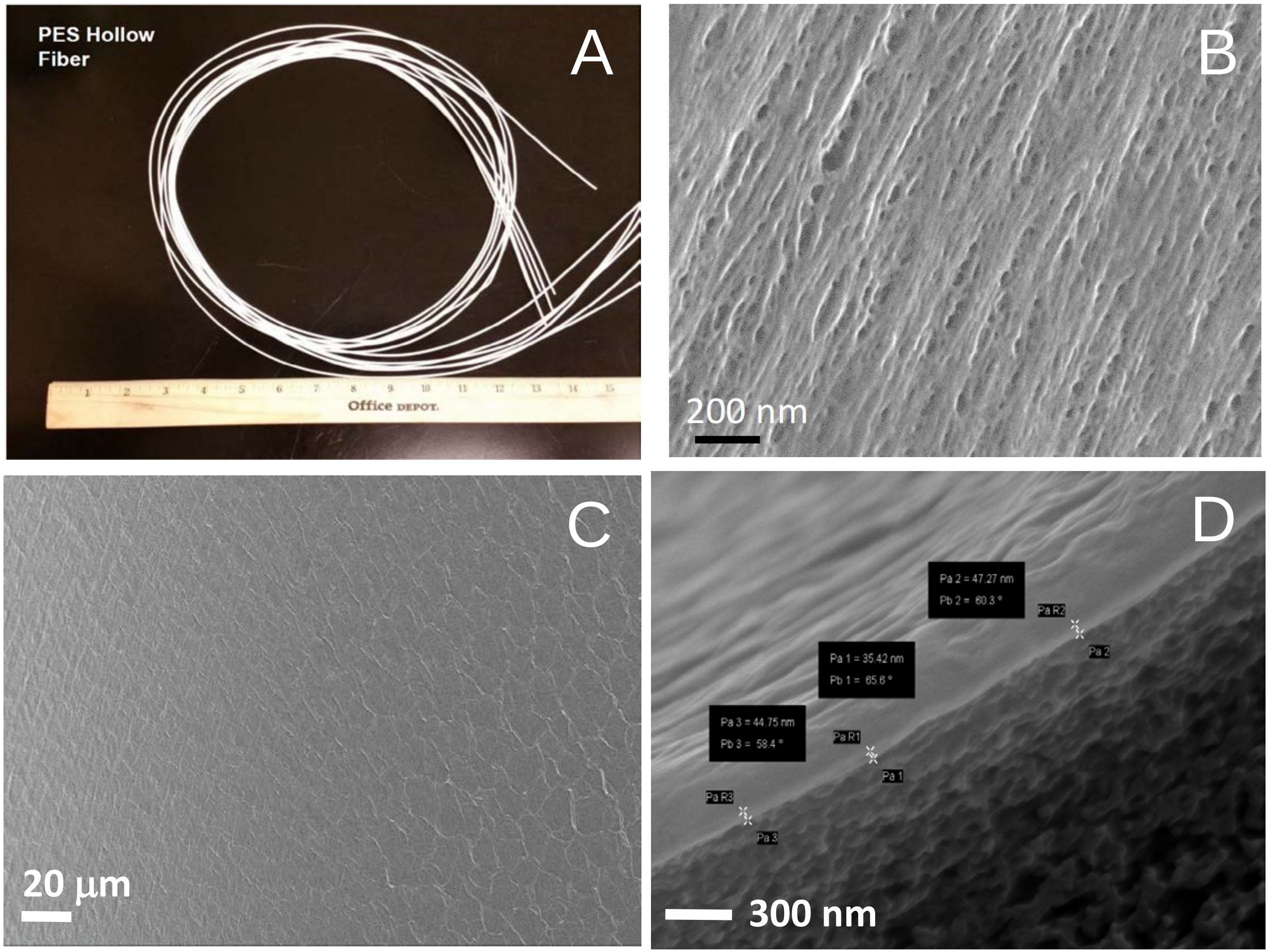
Coating procedure:

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. Close valves A and B, leave the coated fiber under vacuum for a controlled time

GO membrane (thickness: ~40 nm) supported on polyethersulfone (PES) hollow fiber

PES fiber

Uncoated fiber surface

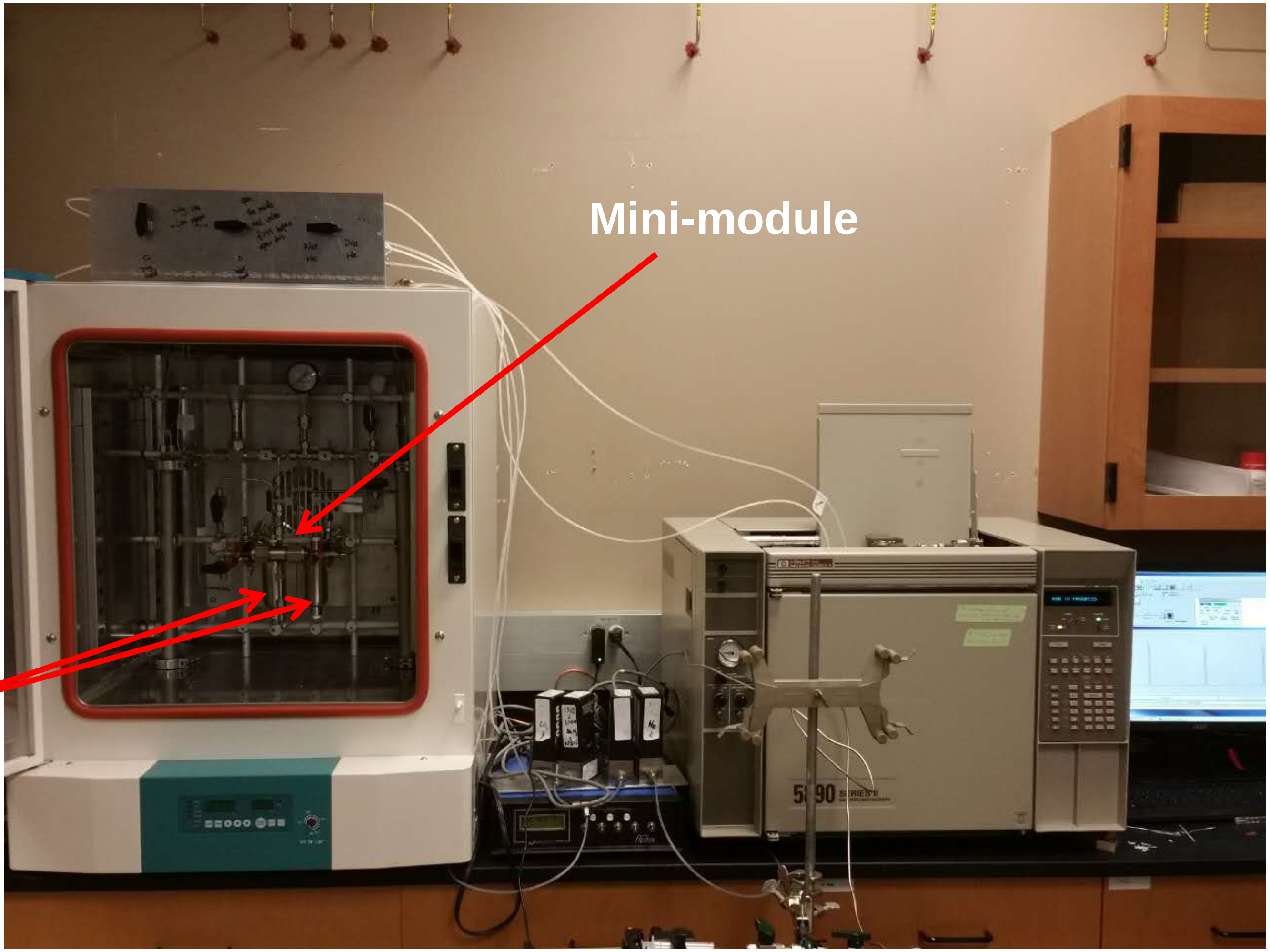


Coated fiber surface

Coated fiber cross section

Coated fiber sealed in a mini-module for gas permeation testing

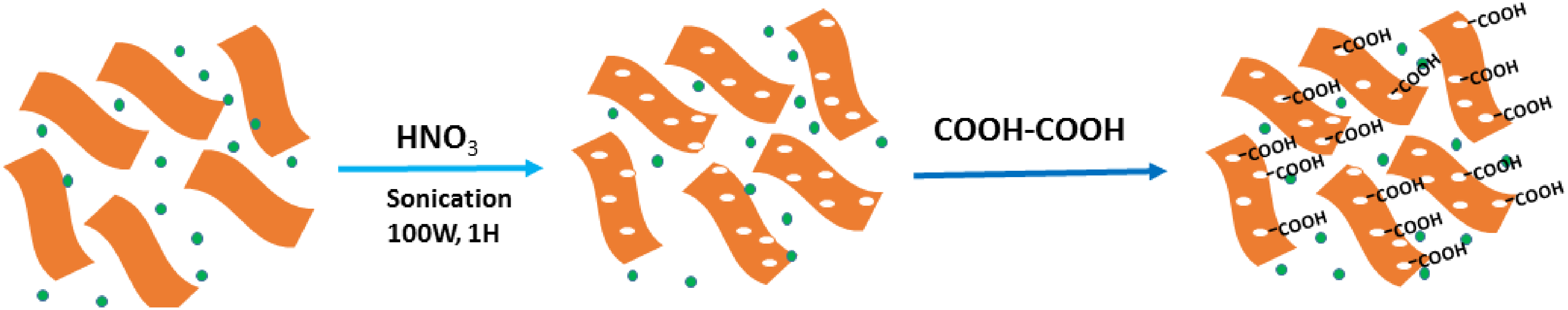
Permeation testing unit



Water bubbler and knockout vessel

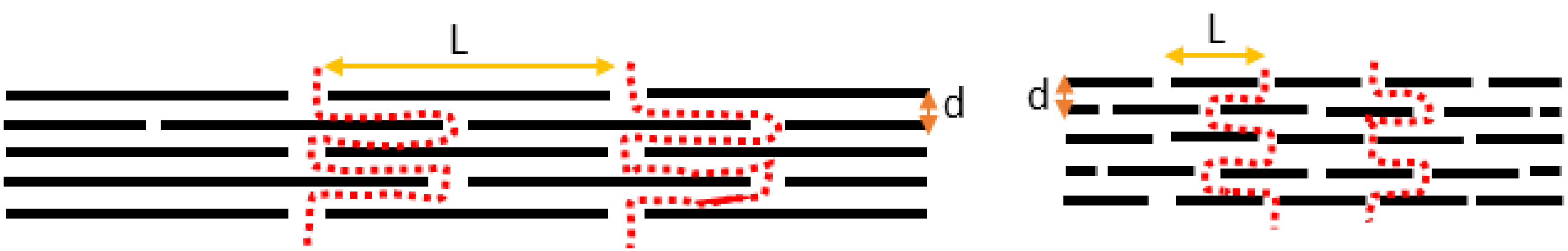
Approaches to improve membrane performance

- Create more structural defects on GO flake by HNO_3 etching

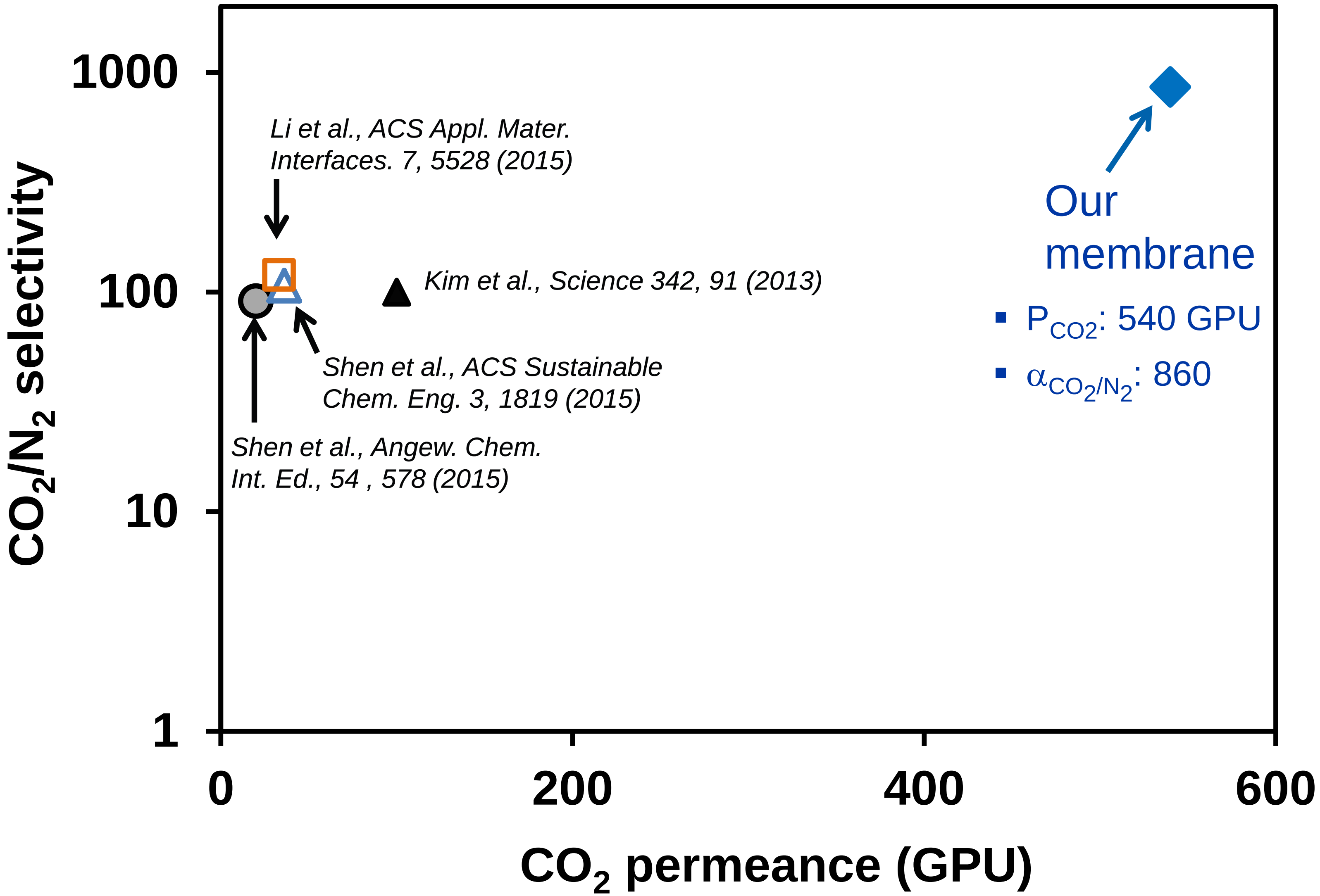


- Reduce GO flake lateral size by ultra-sonication

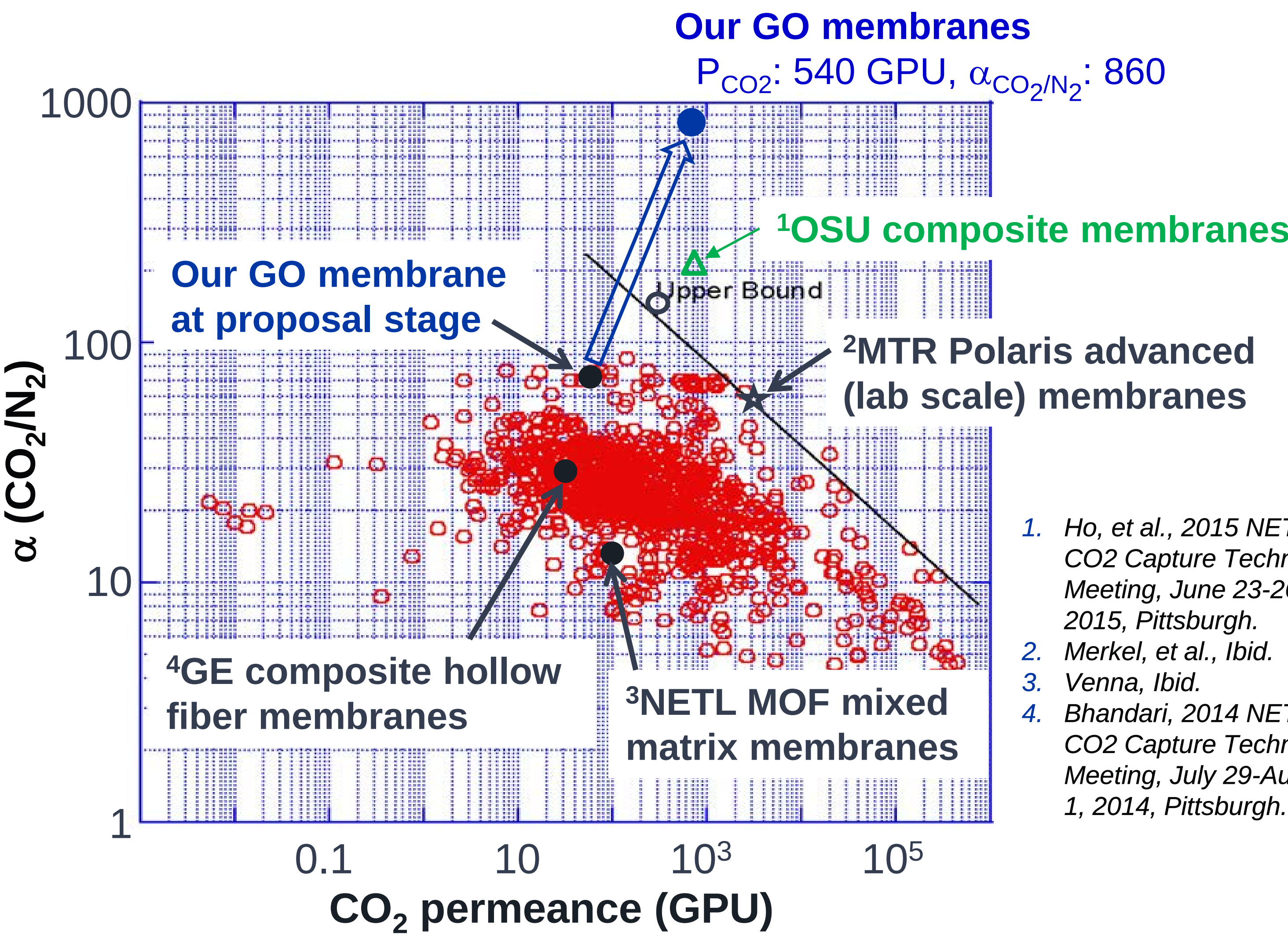
W/O ultra-sonication | **W/ ultra-sonication**



Optimized membranes showed superior performance to GO-based membranes reported in the literature



Comparison to other CO_2/N_2 separation membranes

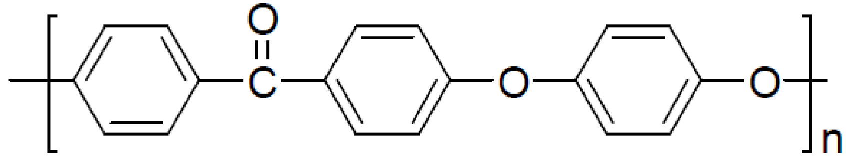


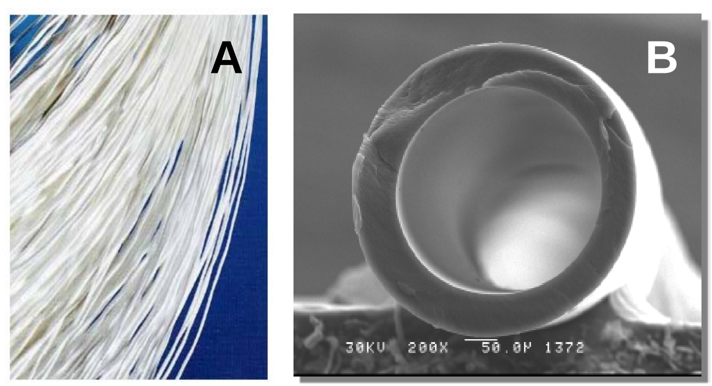
1. *Ho, et al., 2015 NETL CO2 Capture Technology Meeting, June 23-26, 2015, Pittsburgh.*
2. *Merkel, et al., Ibid.*
3. *Venna, Ibid.*
4. *Bhandari, 2014 NETL CO2 Capture Technology Meeting, July 29-August 1, 2014, Pittsburgh.*

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

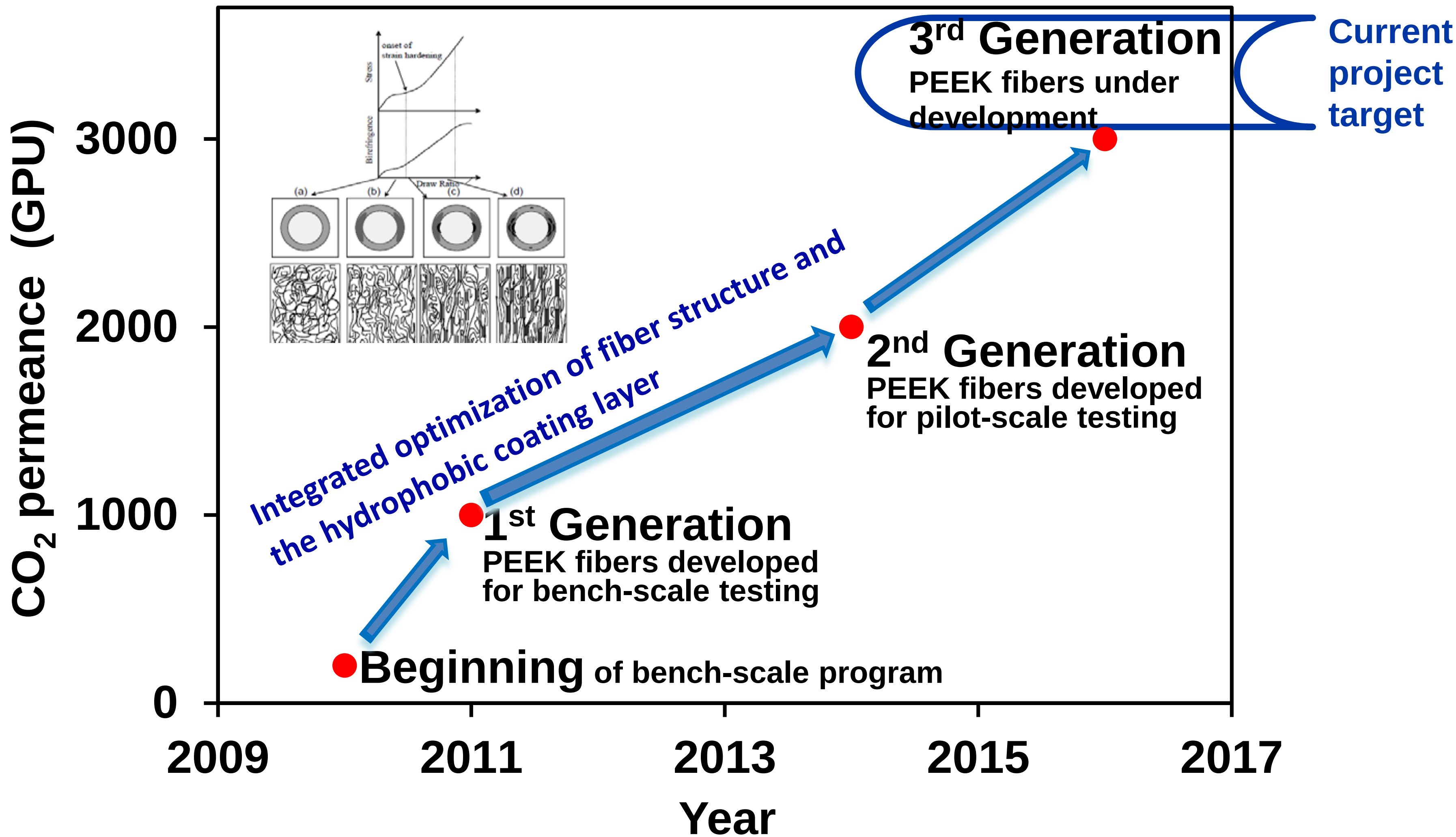
Note: Polymer data points (red): 100 nm membrane thickness assumed

Progress on PEEK Membranes





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

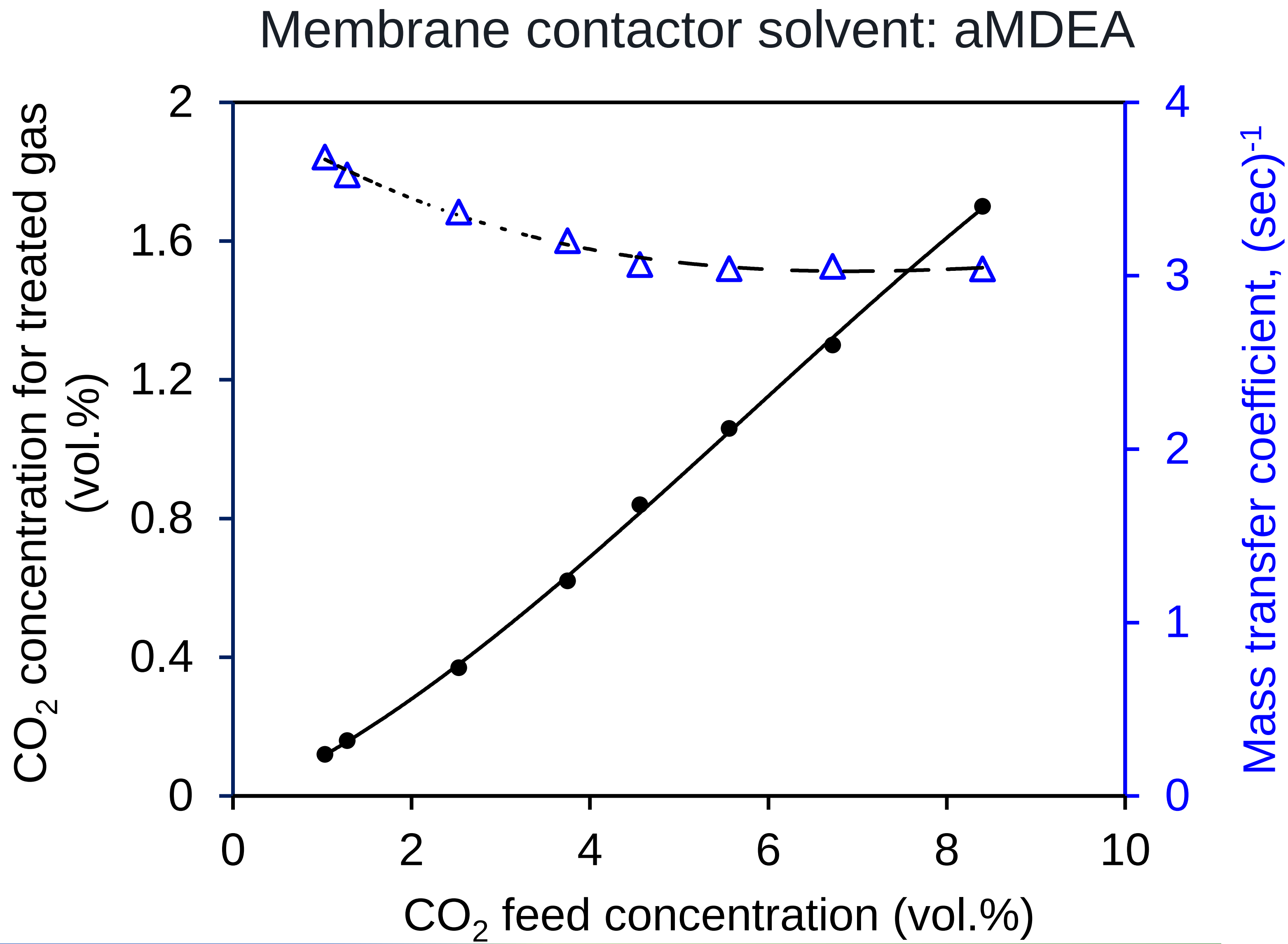


1 GPU = 1 x 10^6 cm^3 (STP)/cm^2 • s • cmHg

To date, intrinsic CO_2 permeance of 2,500 GPU obtained for a new 2-inch module

Test number	Temperature (°C)	Feed inlet pressure (psig)	Retentate pressure (psig)	Permeate pressure (psig)	CO_2 permeance (GPU)
1	22	5.35	2.7	0.27	2,500
2	22	4.31	2.4	0.18	2,400

This module showed mass transfer coefficient > 3.0 $(sec)^{-1}$ in capturing CO_2 from low CO_2-concentration feeds



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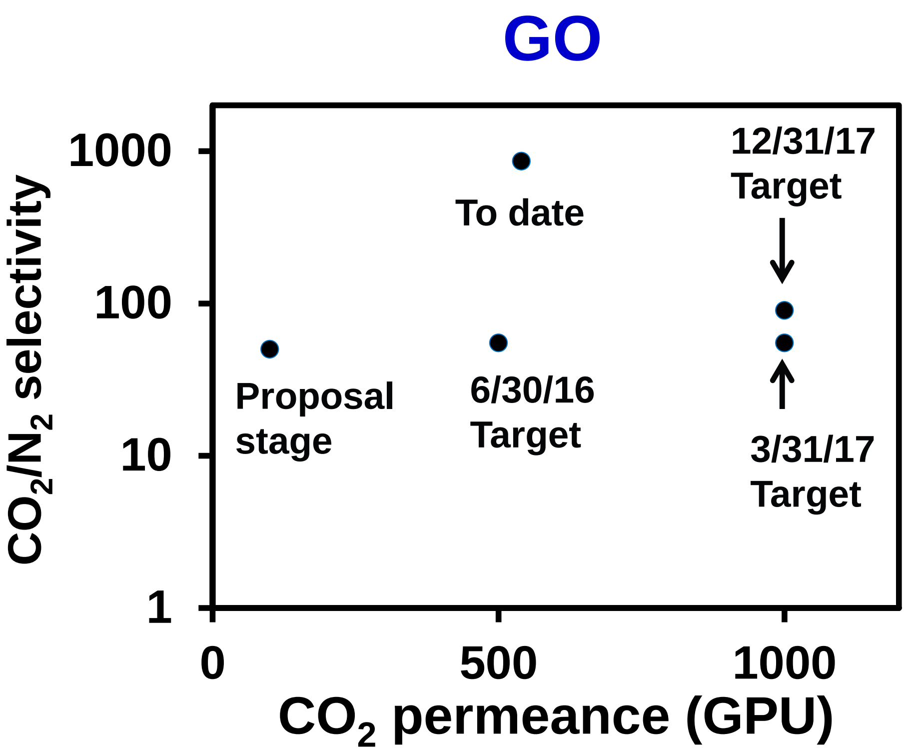
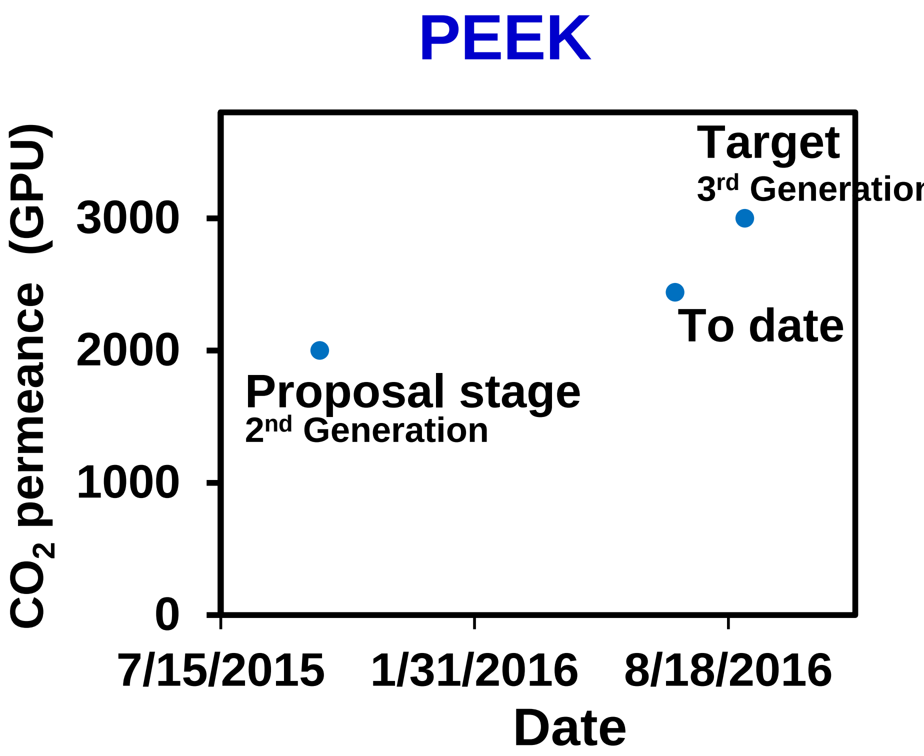
Plans for future development in this project

- Further development for GO and PEEK membranes





- **Integrated GO-PEEK** process tests to achieve technical goal

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

- Increase CO_2 permeance for both GO and PEEK membranes
- 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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Summary

- 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 of 540 GPU and α_{CO_2/N_2} of 860 obtained at 80°C for a humidified CO_2/N_2 mixture
  - Superior performance to GO-based membranes reported in the literature
  - Selectivity higher than other CO_2/N_2 separation membranes
- **PEEK membrane** developed to date
  - Intrinsic CO_2 permeance of 2,500 GPU obtained
  - Mass transfer coefficient > 3.0 $(sec)^{-1}$ in capturing CO_2 from low CO_2-concentration feeds with aMDEA solvent

Acknowledgements

- **Financial support**

ALaS

- **DOE NETL José Figueroa**