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U.S. DEPARTMENT OF ENERGY

DE-FE0031598

Bench-scale Development of a Transformational Graphene Oxide-based Membrane Process for Post-combustion CO_2 Capture

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Technology based on our work published in *Science*, *Nature Communications*, and *Journal of Membr. Sci.*

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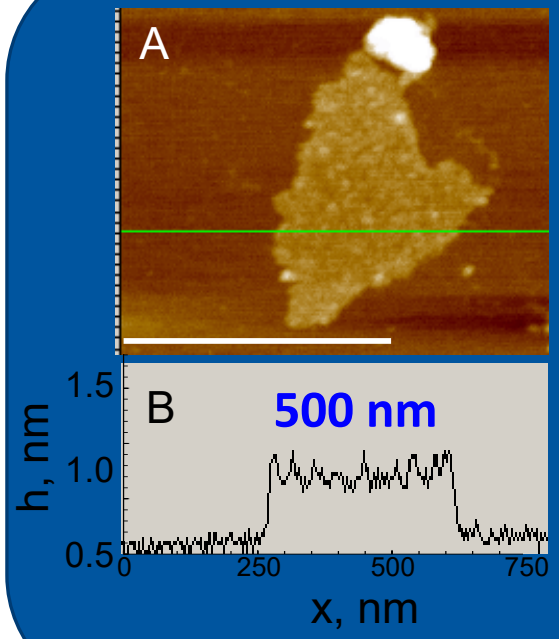
Science
AAAS

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

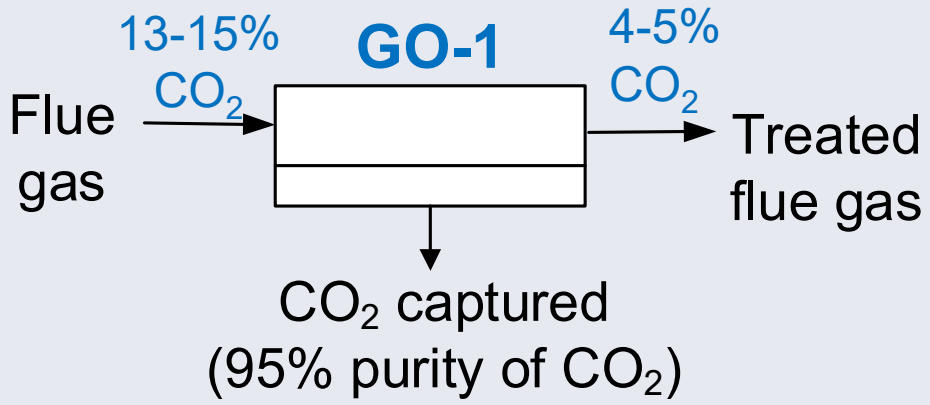
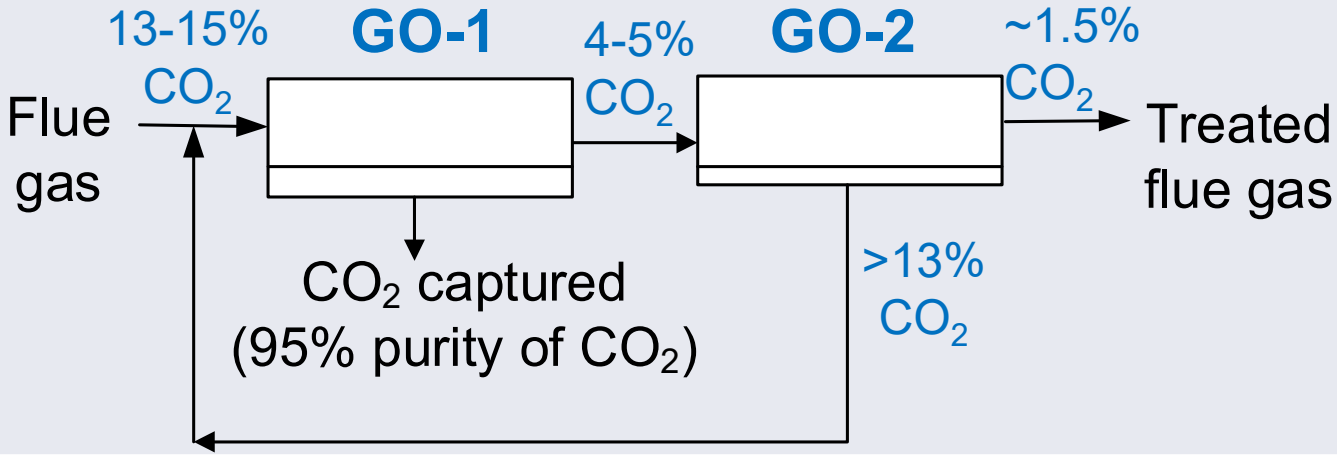
Project overview

- **Performance period**: June 1, 2018 – May 31, 2023
- **Funding**: $2,914,074 from DOE; $728,738 cost share
- **Objective**: Develop a transformational graphene oxide (GO)-based membrane process (**GO²**) for CO_2 capture with 95% CO_2 purity and a cost of electricity (COE) at least 30% lower than DOE amine reference baseline SC PC plant case.
- **Team:**

Member	Roles
GTI ENERGY	▪ Project management and planning ▪ CO_2 capture process development and testing
Rensselaer	▪ GO membrane development and scale-up
NATIONAL CARBON CAPTURE CENTER	▪ Site host
TRIMERIC CORPORATION	▪ Technical & economic analysis

GO = graphene oxide

Process description

CO_2 capture	Diagram	Description
50–70% removal		**Single stage**
70–90% removal or NGCC flue gases		**GO^2 process** integrates a high-selectivity GO-1 membrane and a high-flux GO-2 membrane for optimal performance

GO = graphene oxide

An innovative membrane structure: N-GOQD infiltrated SWCNT network with CO_2-philic agents

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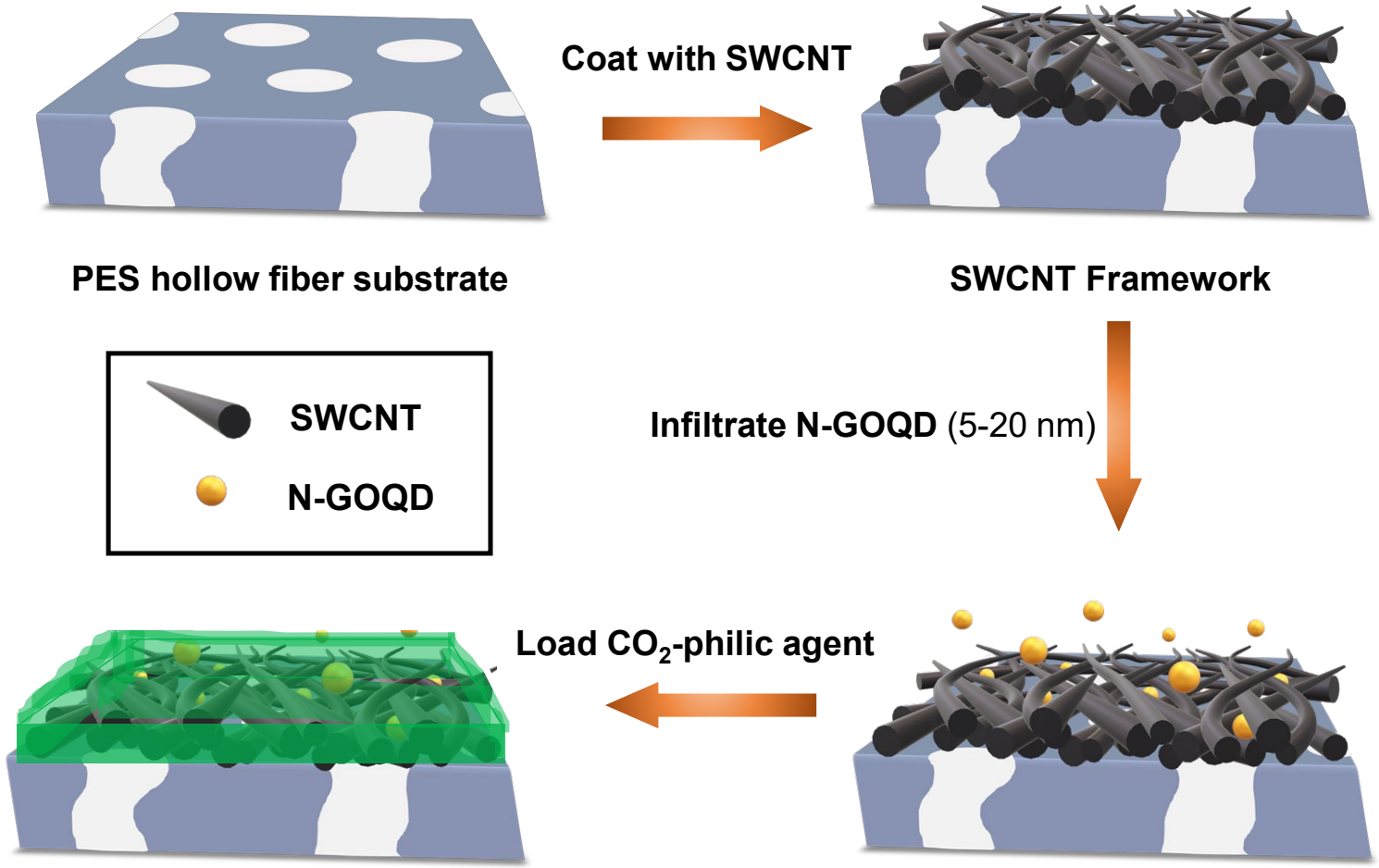
- **What does this structure look like?**



- **Why this structure?**
  - SWCNTs narrow surface pore size close to N-GOQD size
  - Infiltrated N-GOQDs pack densely with SWCNTs to form a framework with nano-confined space
  - CO_2-philic agents (e.g., amines) enhance CO_2 transport

PES = polyether sulfone; SWCNT = single-walled carbon nanotube; N-GOQD = nitrogen-doped graphene oxide quantum dot

High-quality GO-based membranes prepared on commercially available PES hollow fiber substrate

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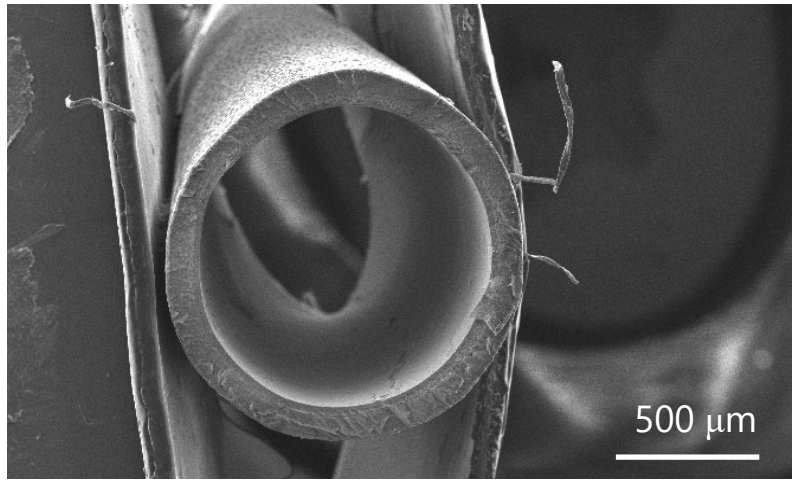
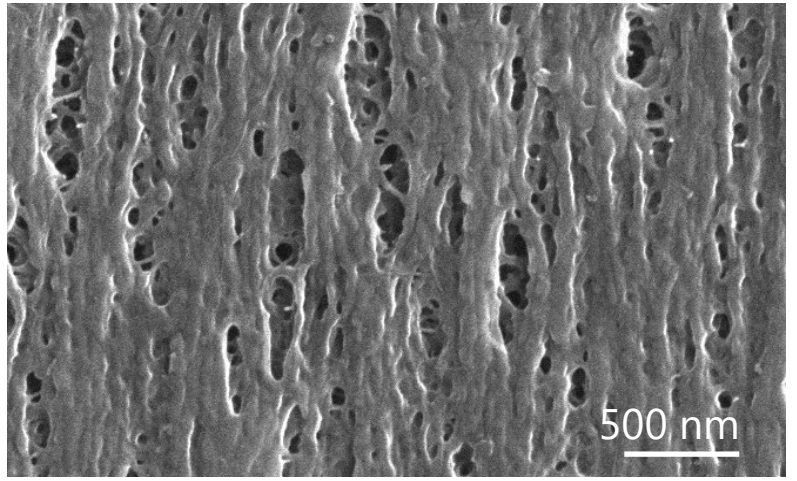
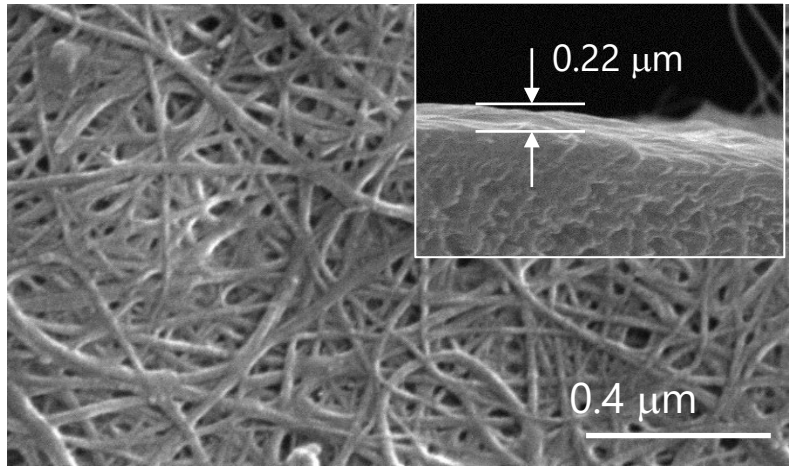
Hollow fiber inner diameter: 1 mm

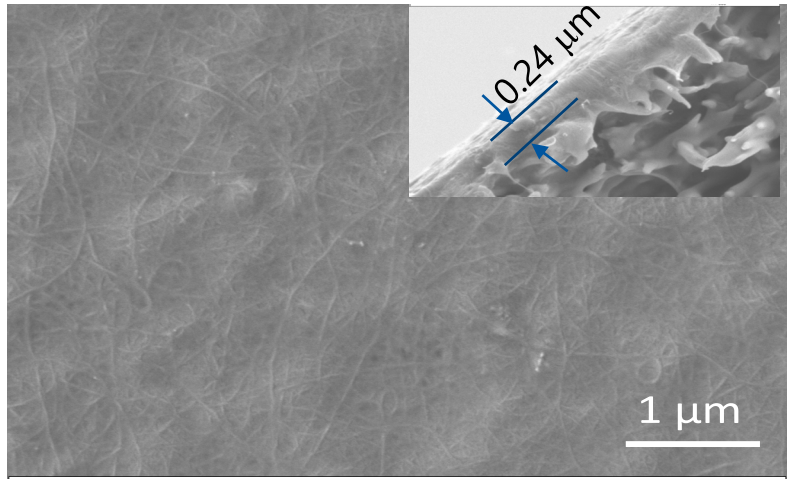




Surface of the substrate: skin layer with pore size of 50-200 nm

Surface and cross section of the SWCNT layer





Surface and cross section of the N-GOQD/ SWCNT/ CO_2-philic agent membrane

PES = polyether sulfone; SWCNT = single-walled carbon nanotube;
N-GOQD = nitrogen-doped graphene oxide quantum dot; IL = Ionic Liquid

GO-1 and GO-2 membranes (area: ~50 cm^2) achieved performance goals under no stage-cut test condition

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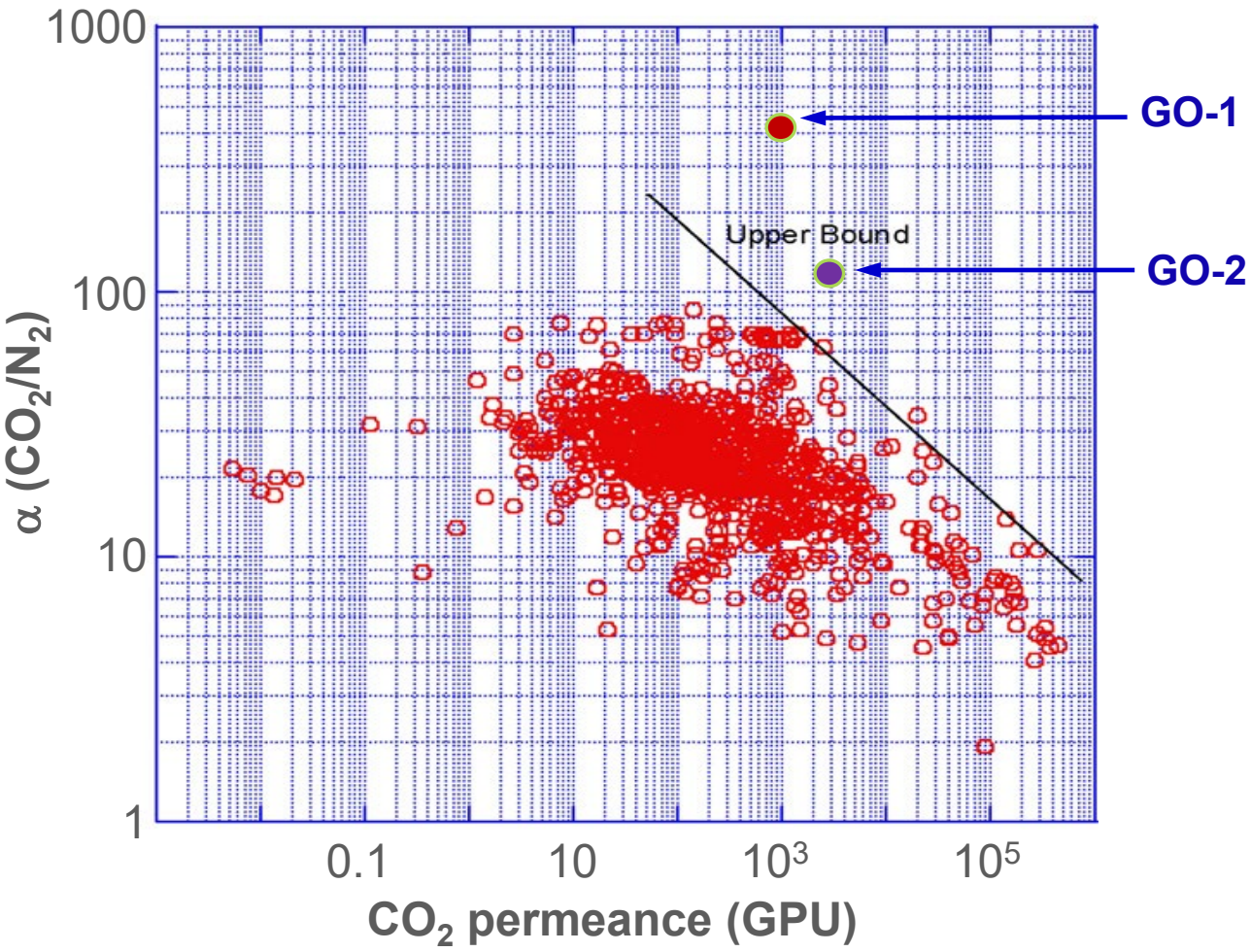
	CO_2 permeance (GPU)	CO_2/N_2 selectivity
GO-1 goal	1,000	200
GO-1 developed	1,100	300
GO-2 goal	2,500	20
GO-2 developed	2,600	120

- Feed: mixed simulated flue gases
  - GO-1: 8-12 vol% CO_2
  - GO-2: ~4 vol% CO_2
- Temperature: 80°C
- Feed pressure: ~1.0 bara
- Permeate side pressure: 0.2-0.4 bara



Robeson, J. Membrane Sci. ***2008****, Vol. 320, p390*
Note: Polymer data points (red): 100 nm membrane thickness assumed

GO-1 stage-cut tests with simulated coal flue gas: good stability, dry-base CO_2 purity as high as 98 vol%

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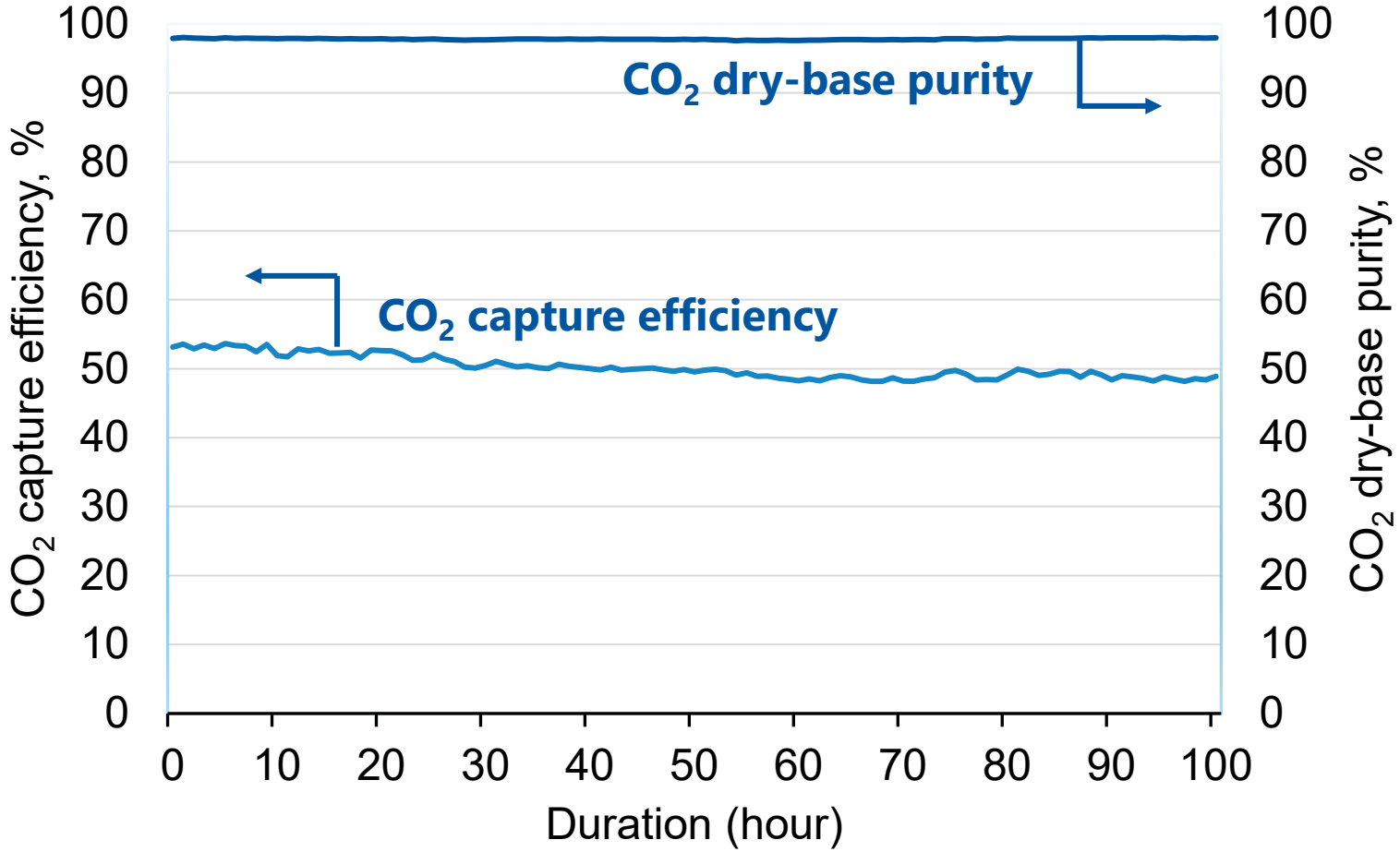
Testing conditions

Membrane area, cm^2	75
Temperature, °C	65
Feed CO_2 concentration, vol%	12
Feed pressure, bara	1.0
Permeate pressure, bara	0.15
Relative humidity, %	100



GO-1 stage-cut tests with simulated NGCC flue gas: good stability, dry-base CO_2 purity as high as 96 vol%

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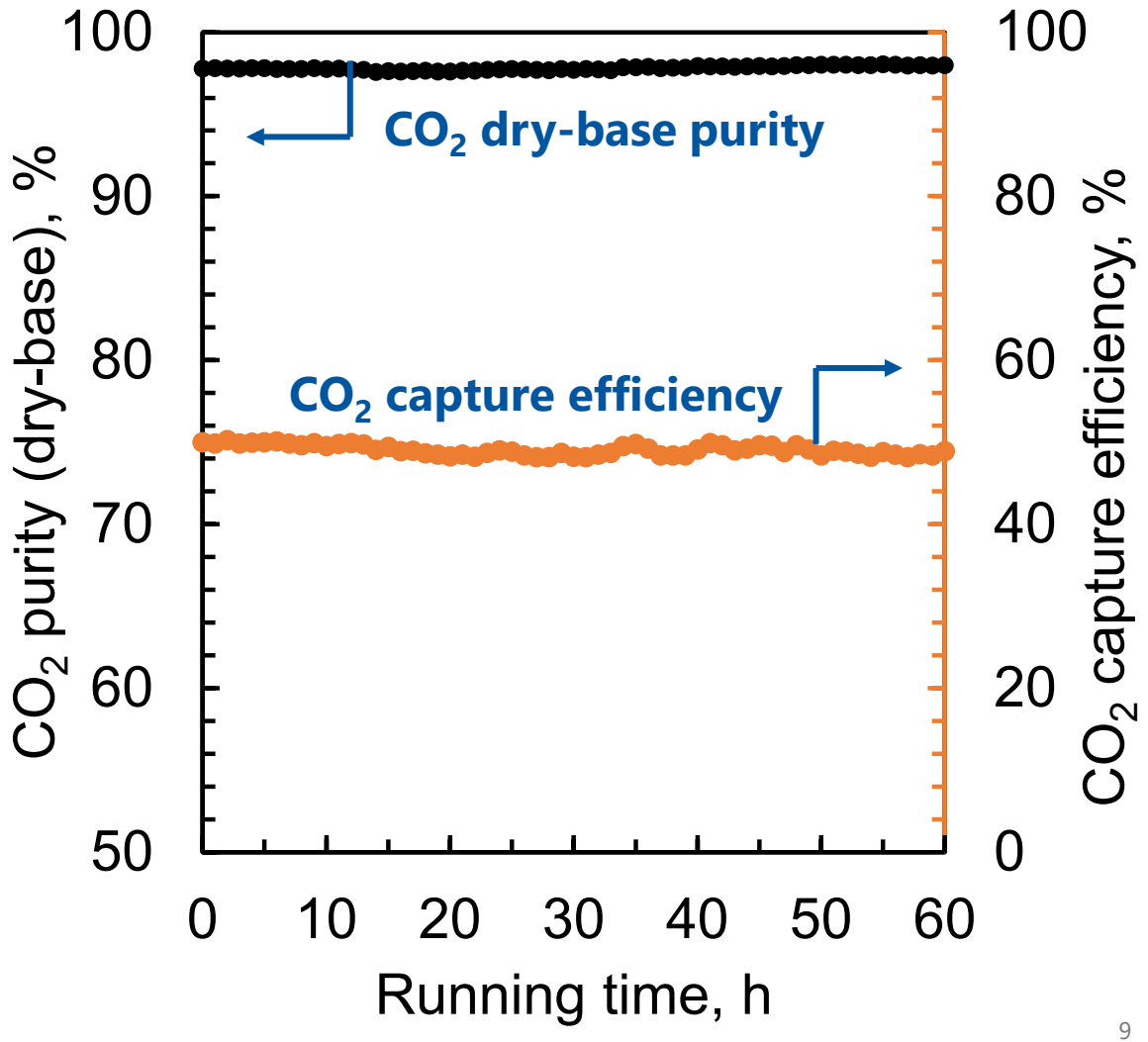
Testing conditions

Membrane area, cm^2	75
Temperature, °C	70
Feed CO_2 concentration, vol%	4.2
Feed pressure, bara	1.0
Permeate pressure, bara	0.15
Relative humidity, %	100

Testing results

CO_2 permeance (GPU)	CO_2/N_2 selectivity	CO_2 capture efficiency (%)
2,400	2,100	50-81



GO-2 stage-cut tests using 5 vol% CO_2 feed: good stability and desired CO_2 permeate concentration

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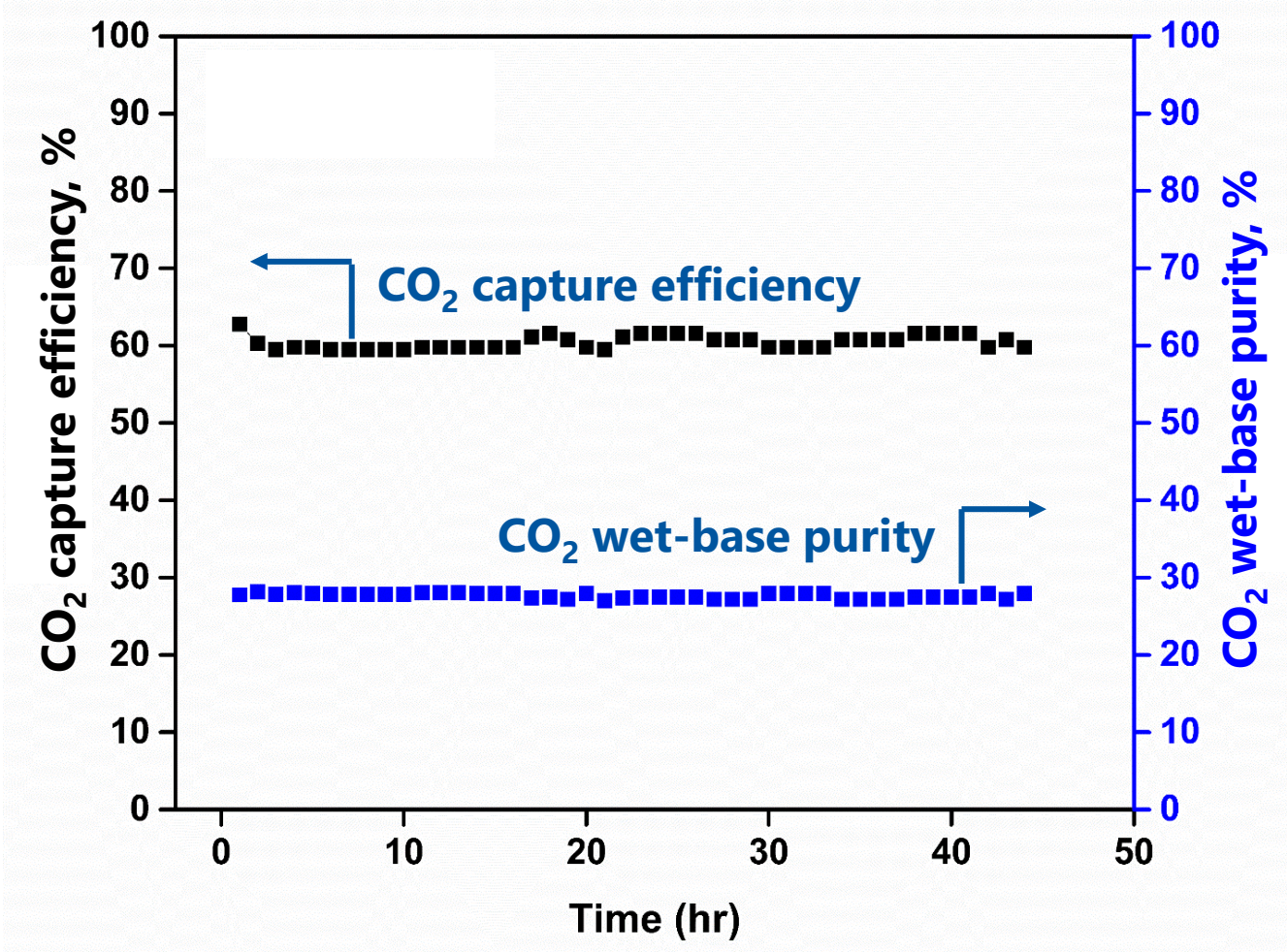
Testing conditions

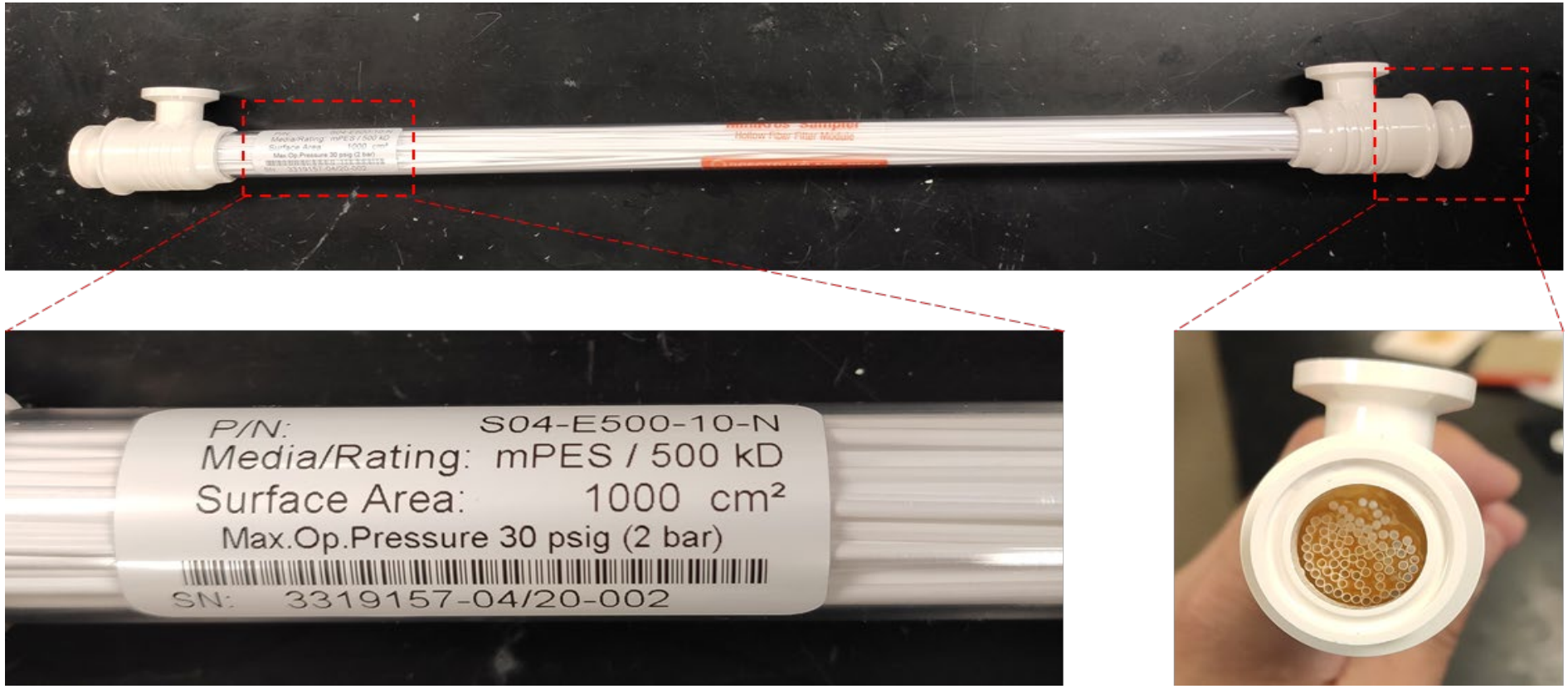
Membrane area, cm^2	115
Temperature, °C	70
Feed CO_2 concentration, vol%	5
Feed pressure, bara	1.0
Permeate pressure, bara	0.15-0.3
Relative humidity, %	100

Testing results

CO_2 permeance (GPU)	CO_2/N_2 selectivity	CO_2 capture efficiency (%)
2,900	190	61



Scaleup of membranes on commercially available 1,000 cm² hollow fiber substrates



Material	Fiber ID (mm)	Module Length (cm)	Effective Length (cm)	Number of Fibers	Effective surface Area (cm²)
PES	1.00	47	41.5	78	1,000

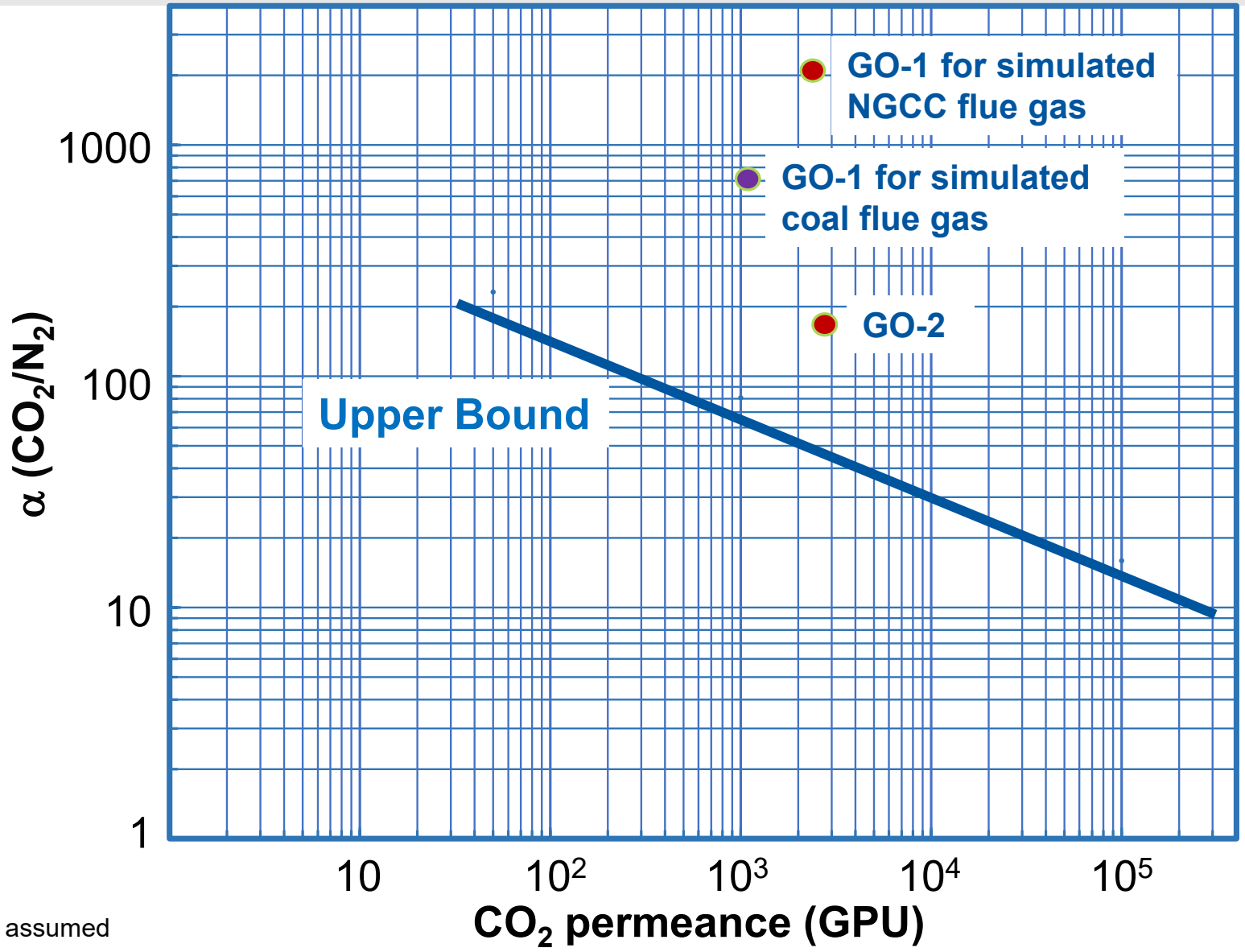
GO-1 membrane successfully scaled to 1,000 cm²; scaleup of GO-2 ongoing

Membrane type	GO-1
Membrane area, cm^2	1,000
Temperature, °C	70
CO_2 feed concentration, vol%	12

Testing conditions			**Separation performance**			
Permeate side pressure (bara)	Feed pressure (bara)	Feed H_2O concentration (%)	CO_2 permeance (GPU)	CO_2/N_2 selectivity	CO_2 capture efficiency (%)	CO_2 dry-base purity (vol.%)
0.175	1.2	23.5	460	530	52.6	96.7
0.17	1.35	20.8	660	490	61.6	95.4
0.15	1.05	27.8	1,100	760	56.2	96.3

Where do our recent membranes fall on the Robeson plots?

- **GO-1 and GO-2 performances shown here are results obtained from stage-cut tests**



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

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

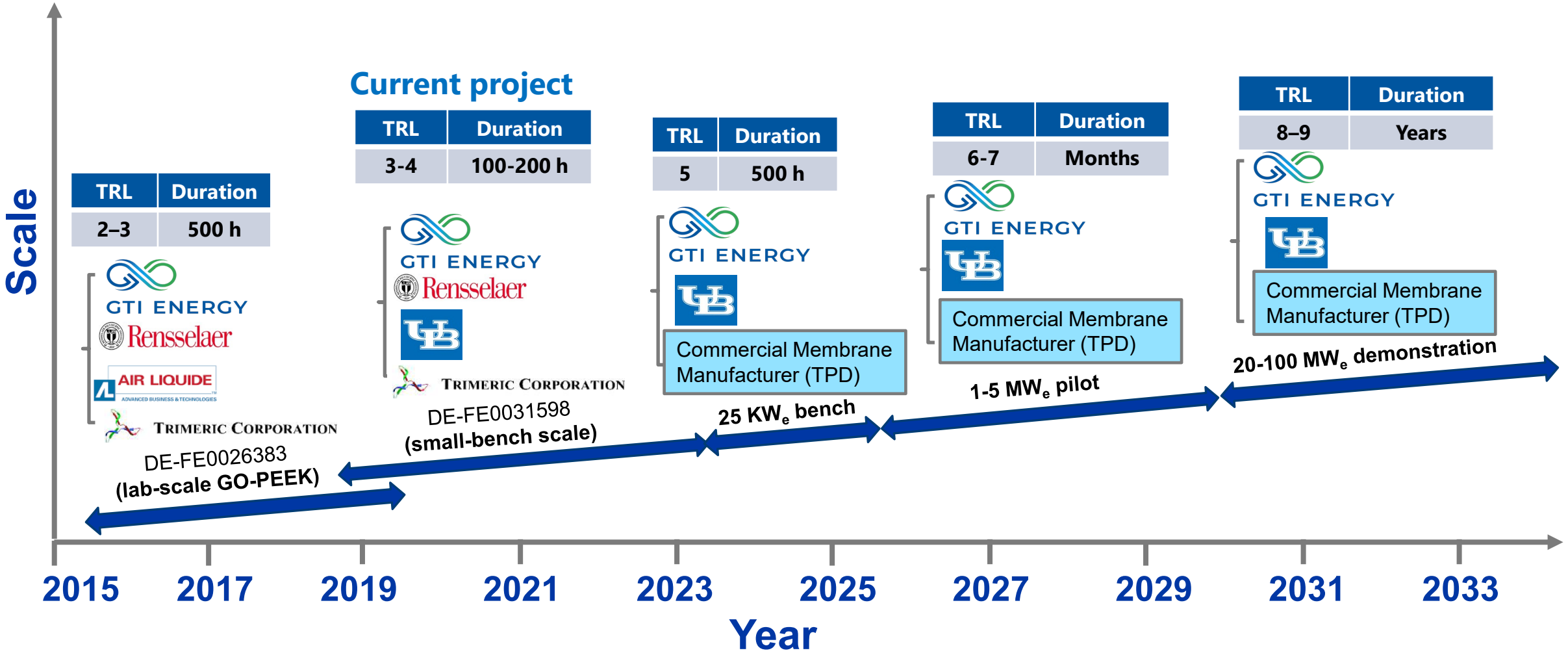
Bench-scale system designed and constructed

Commissioning tests recently completed at GTI

Tests at NCCC planed

- **Testing site**: the Lab-Scale Test Unit (LSTU) at NCCC
- **Objectives**:
  - Achieve 60-90% CO_2 capture and CO_2 purity of >95%
  - Collect date for TEA and validate cost targets
- **Projected timeline**: February 1 to April 30, 2023
- **Activities**:
  - Installation of skid
  - Commissioning testing
  - Parametric tests with coal flue gas and simulated NGCC flue gas
  - Stability test for 200 h with coal flue gas
  - Decommissioning

Technology development path



Summary

- We are developing a transformational graphene oxide-based membrane process for post-combustion CO_2 capture
  - **Single stage** for 50–70% removal from coal flue gas
  - **GO² process** integrating a high-selectivity GO-1 membrane and a high-flux GO-2 membrane for 70–90% removal from coal or natural gas flue gases
- An innovative membrane structure developed
  - Recently optimized GO-1 and GO-2 membranes showed high CO_2 capture performance and good stability during stage-cut tests
- GO-1 membranes successfully scaled to 1,000 cm^2 surface area; scaleup of GO-2 membranes ongoing
- Bench-scale system constructed, and will be tested at NCCC in 2023

NCCC = National Carbon Capture Center

Acknowledgements

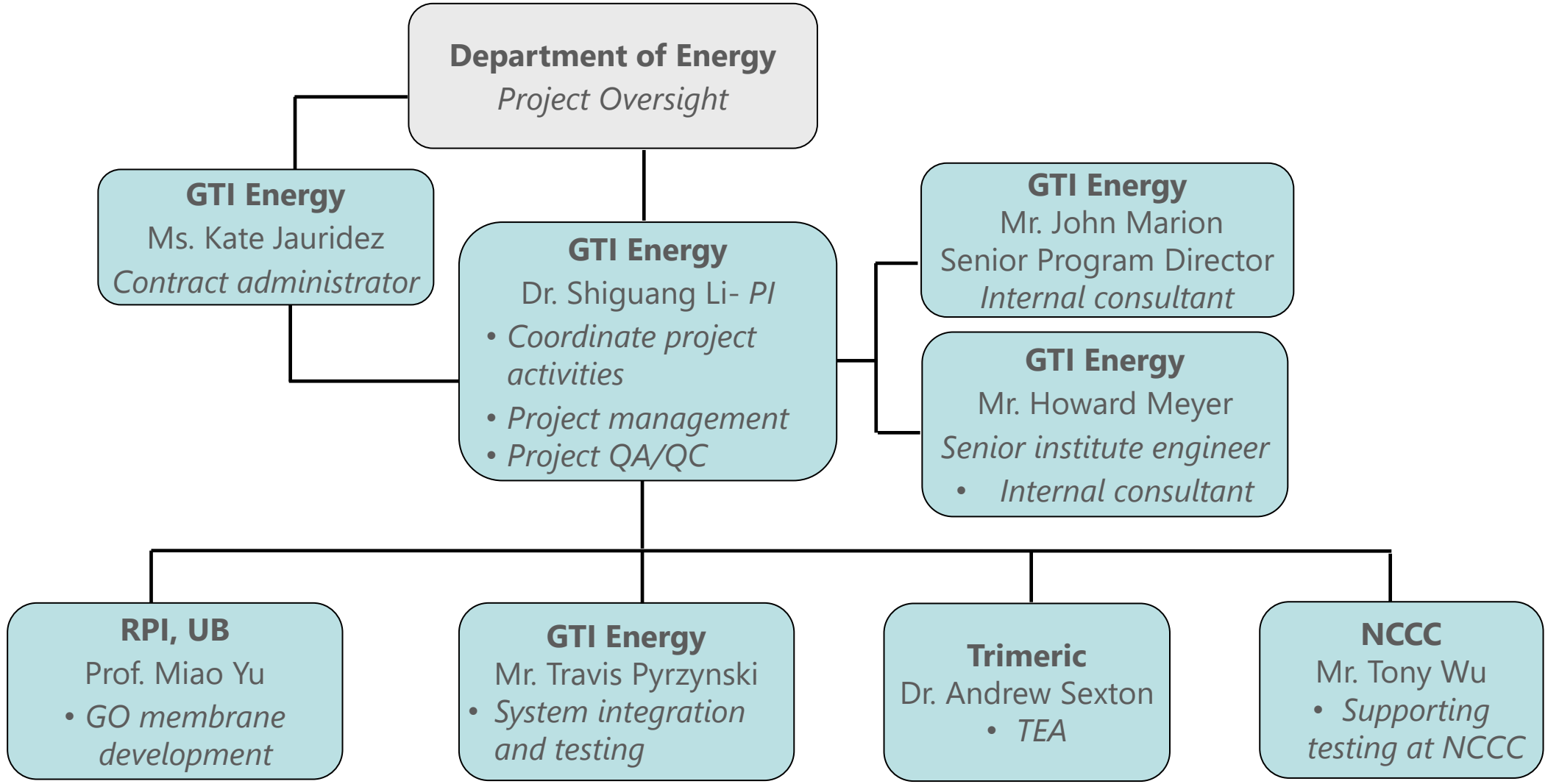
- Financial and technical support

DE-FE0031598

CO_2 Capture Project - Phase 4

- DOE NETL: Dustin Brown, Andrew O'Palko, José Figueroa, Dan Hancu and Lynn Brickett
- The CCP4: Betty Pun and technical team
- NCCC: Frank Morton and Tony Wu

Appendix – Organization Chart



Appendix – Gantt Chart

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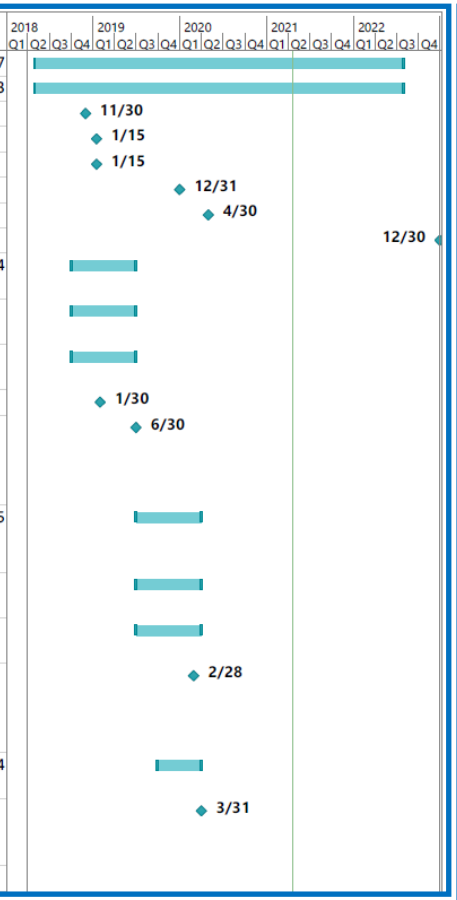
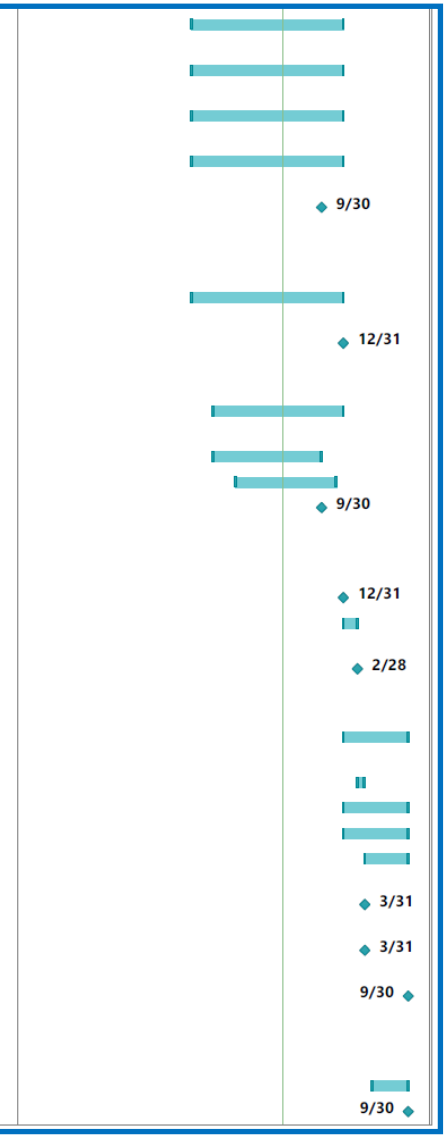
BP1

ID	Task	Sub-T	MS	Task or Milestone Description	Start	Finish	Task Total
1				Total Project	Tue 5/1/18	Mon 8/1/22	$3,642,857
2	1.0			Project management and planning	Tue 5/1/18	Mon 8/1/22	$286,973
3			1.1	Updated Project Management Plan	Mon 10/1/18	Fri 11/30/18	
4			1.2	Kickoff Meeting	Mon 10/1/18	Tue 1/15/19	
5			1.3	Technology maturation plan submitted to DO	Mon 10/1/18	Tue 1/15/19	
6			1.4	Continuation applicatoin for BP2 submitted	Sun 12/1/19	Tue 12/31/19	
7			1.5	Submit BP1 report	Wed 4/1/20	Thu 4/30/20	
8			1.6	Submit final technical report	Fri 10/1/21	Fri 12/30/22	
9	2.0			Development of GO membrane with area of 50-100 cm2	Mon 10/1/18	Sun 6/30/19	$358,884
10		2.1		Fabrication of GO hollow fiber membranes by vacuum filtration	Mon 10/1/18	Sun 6/30/19	
11		2.2		Fabrication of flat sheet GO membranes by printing	Mon 10/1/18	Sun 6/30/19	
12			2.1	50-100 cm2 GO membranes prepared	Mon 10/1/18	Wed 1/30/19	
13			2.2	For 50-100 cm2 area membranes, GO-1 exhibits CO2/N2 selectivity ≥ 100 and CO2 permeance ≥ 1,000 GPU and GO-2 exhibits CO2/N2 selectivity ≥ 10 and CO2 permeance	Fri 2/1/19	Sun 6/30/19	
14	3.0			Improvement of preparation conditions for 50-100 cm2 GO membranes towards higher selectivities	Mon 7/1/19	Tue 3/31/20	$550,225
15		3.1		Fabrication of GO hollow fiber membranes by vacuum filtration	Mon 7/1/19	Tue 3/31/20	
16		3.2		Fabrication of flat sheet GO membranes by printing	Mon 7/1/19	Tue 3/31/20	
17			3.1	For 50-100 cm2 area membranes, GO-1 exhibits CO2/N2 selectivity ≥200 and CO2 permeance ≥1,000 GPU and GO-2 exhibits CO2/N2 selectivity ≥20 and CO2 permeance	Mon 7/1/19	Fri 2/28/20	
18	4.0			Performance stability testing of GO membranes at near realistic flue gas	Tue 10/1/19	Tue 3/31/20	$207,864
19			4.1	Stability testing shows the CO2 permeances and CO2/N2 selectivities decreased by less than 10% in the presence of flue gas	Tue 10/1/19	Tue 3/31/20	
20				End of BP1 (5/1/18-3/31/20)			



BP2

21	5.0			Scale-up of GO membrane modules to effective areas of 1000 cm2	Wed 4/1/20	Fri 12/31/21	$572,444
22		5.1		Fabrication of GO hollow fiber membranes by vacuum filtration	Wed 4/1/20	Fri 12/31/21	$159,626
23		5.2		Fabrication of flat sheet GO membranes by printing	Wed 4/1/20	Fri 12/31/21	$272,204
24		5.3		Fabrication of spiral-wound GO membrane modules	Wed 4/1/20	Fri 12/31/21	$140,614
25			5.1	For 1000 cm2 area membranes, GO-1 exhibits CO2/N2 selectivity ≥200 and CO2 permeance ≥1,000 GPU and GO-2 exhibits CO2/N2 selectivity ≥20 and CO2 permeance	Wed 4/1/20	Thu 9/30/21	
26	6.0			100-h stability tests for GO membranes developed under task 5	Wed 4/1/20	Fri 12/31/21	$221,276
27			6.1	CO2 permeances and CO2/N2 selectivities decrease by less than 10% during a 100-h continuous testing	Wed 4/1/20	Fri 12/31/21	
28	7.0			Design and construction of two-stage GO membrane skid	Wed 7/1/20	Fri 12/31/21	$341,140
29		7.1		Process simulation and design of system	Wed 7/1/20	Thu 9/30/21	$60,548
30		7.2		Construction of membrane skid	Thu 10/1/20	Wed 12/1/21	$280,592
31			7.1	Complete process design for low and high CO2 flue gas conditions; and process simulation indicates that the CO2 capture system can achieve >95% CO2 purity	Wed 7/1/20	Thu 9/30/21	
32			7.2	Constructed skid ready for testing	Wed 7/1/20	Fri 12/31/21	
33	8.0			Testing of GO system at GTI using natural gas-fired flue gas	Sat 1/1/22	Mon 2/28/22	$91,035
34			8.1	95% CO2 purity achieved when testing the constructed GO system using natural gas-fired flue gas	Sat 1/1/22	Mon 2/28/22	
35	9.0			Skid installation, commissioning and testing at NCCC using actual flue gas	Sat 1/1/22	Fri 9/30/22	$879,833
36		9.1		Skid installation and commissioning at NCCC	Tue 3/1/22	Wed 3/30/22	$160,427
37		9.2		GO membrane support from RPI	Sat 1/1/22	Fri 9/30/22	$281,555
38		9.3		GO membrane support from OSU	Sat 1/1/22	Fri 9/30/22	$82,565
39		9.4		CO2 capture testing of the GO2 system at NCCC using actual flue gas	Fri 4/1/22	Fri 9/30/22	$355,286
40			9.1	Commissioning complete and system ready for testing at NCCC	Tue 3/1/22	Thu 3/31/22	
41			9.2	1000 m2 GO membrane modules shipped to NCCC	Tue 3/1/22	Thu 3/31/22	
42			9.3	Skid testing at NCCC complete, 70-90% CO2 removal rate achieved, 95% CO2 purity validated, and membrane shows good stability during a 200-h continuous testing	Sun 5/1/22	Fri 9/30/22	
43	10.0			Technical and economic study	Sun 5/1/22	Fri 9/30/22	$133,183
44			10.	Issue TEA report	Sun 5/1/22	Fri 9/30/22	



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