DOE Contract No. DE-FE0031598

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

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U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings, August 16, 2021

Project overview

- **Performance period**: June 1, 2018 – September 30, 2022
- **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:**

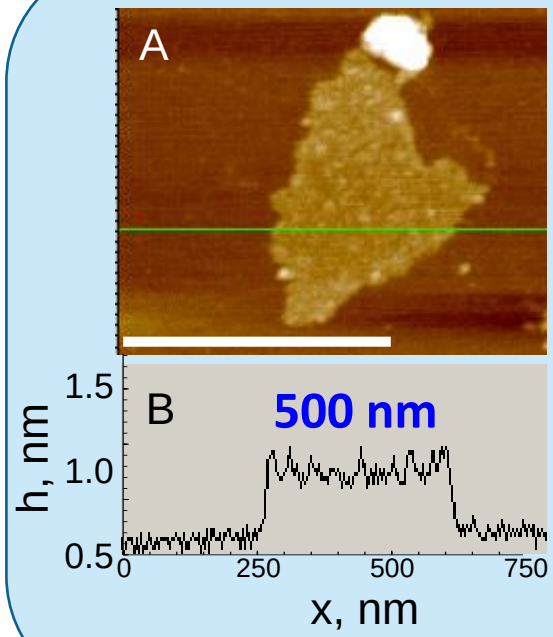
Member	Roles
gti	• Project management and planning • Quality control • CO_2 capture performance tests
Rensselaer / UB	• GO membrane development and scale-up • Process design and optimization
NC National Carbon Capture Center	• Site host
Trimeric Corporation	▪ Technical & economic study

GO = graphene oxide

GO membrane technology based on our work published in *Science, Nature Communications, and Journal of Membrane Science*

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

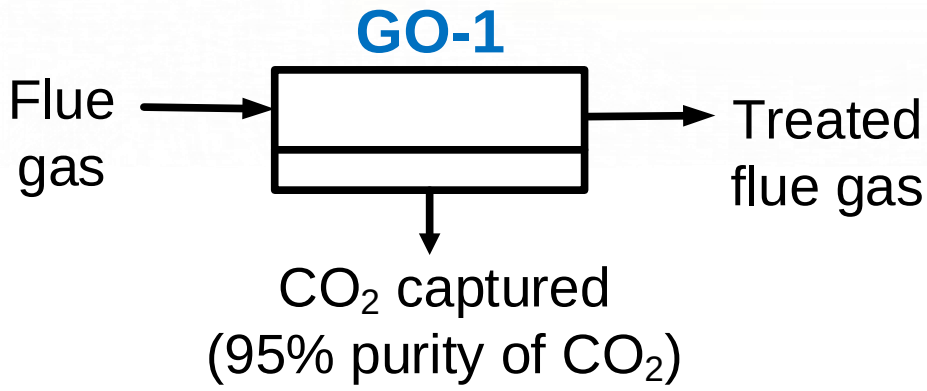
Journal of Membrane Science
Volume 573, 1 March 2019, Pages 184-191

Ultrathin, ethylenediamine-functionalized graphene oxide membranes on hollow fibers for CO_2 capture

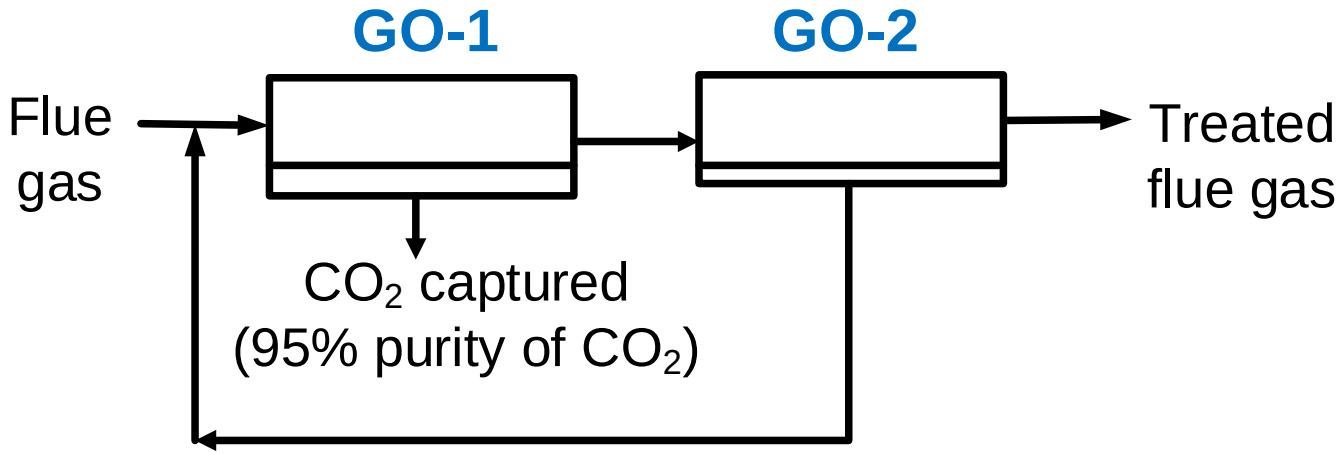
gti

Process description

- 50–70% removal from coal flue gas: **single stage**



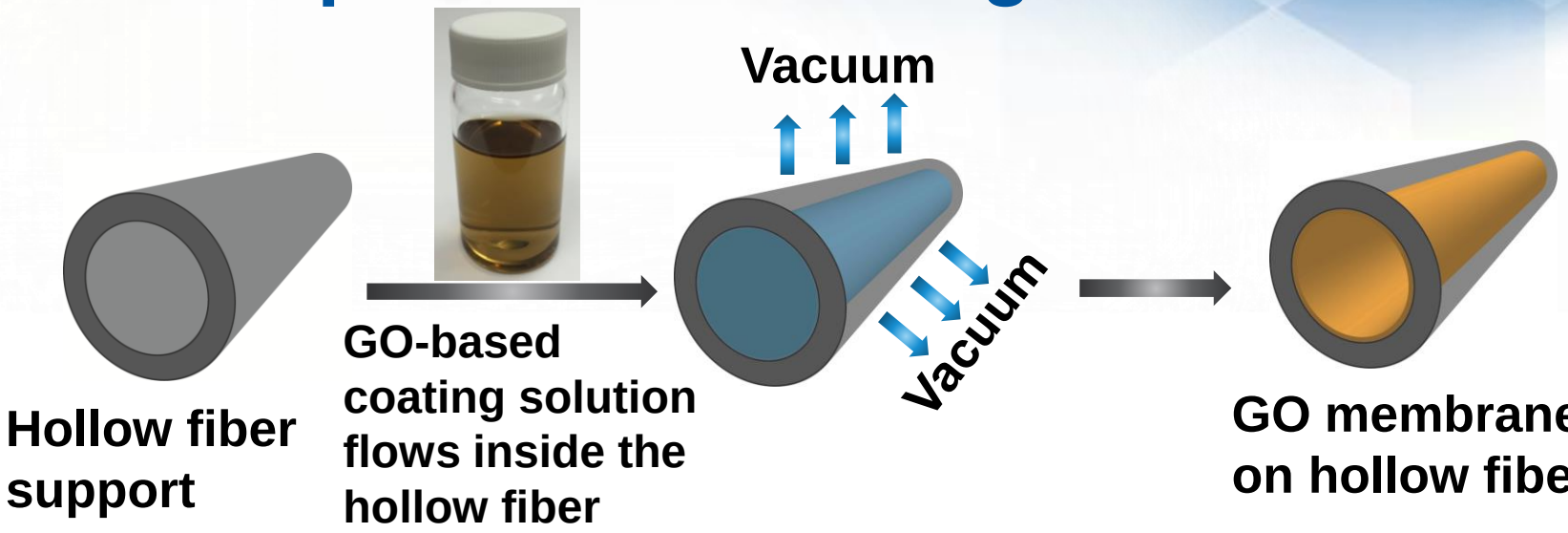
- 70–90% removal from coal or natural gas flue gases: a proprietary **GO^2 process** integrates a high-selectivity GO-1 membrane and a high-flux GO-2 membrane for optimal performance



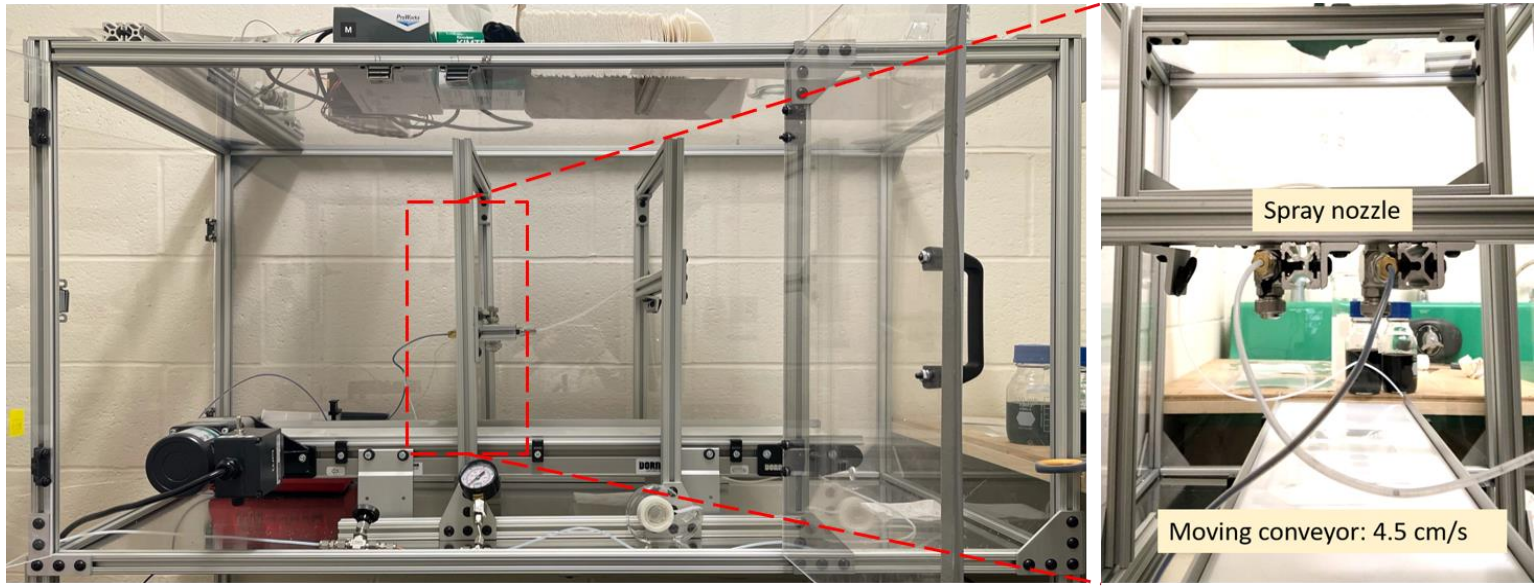
GO = graphene oxide

Scalable procedures developed for fabricating GO membranes

Hollow fiber membranes:
Vacuum filtration



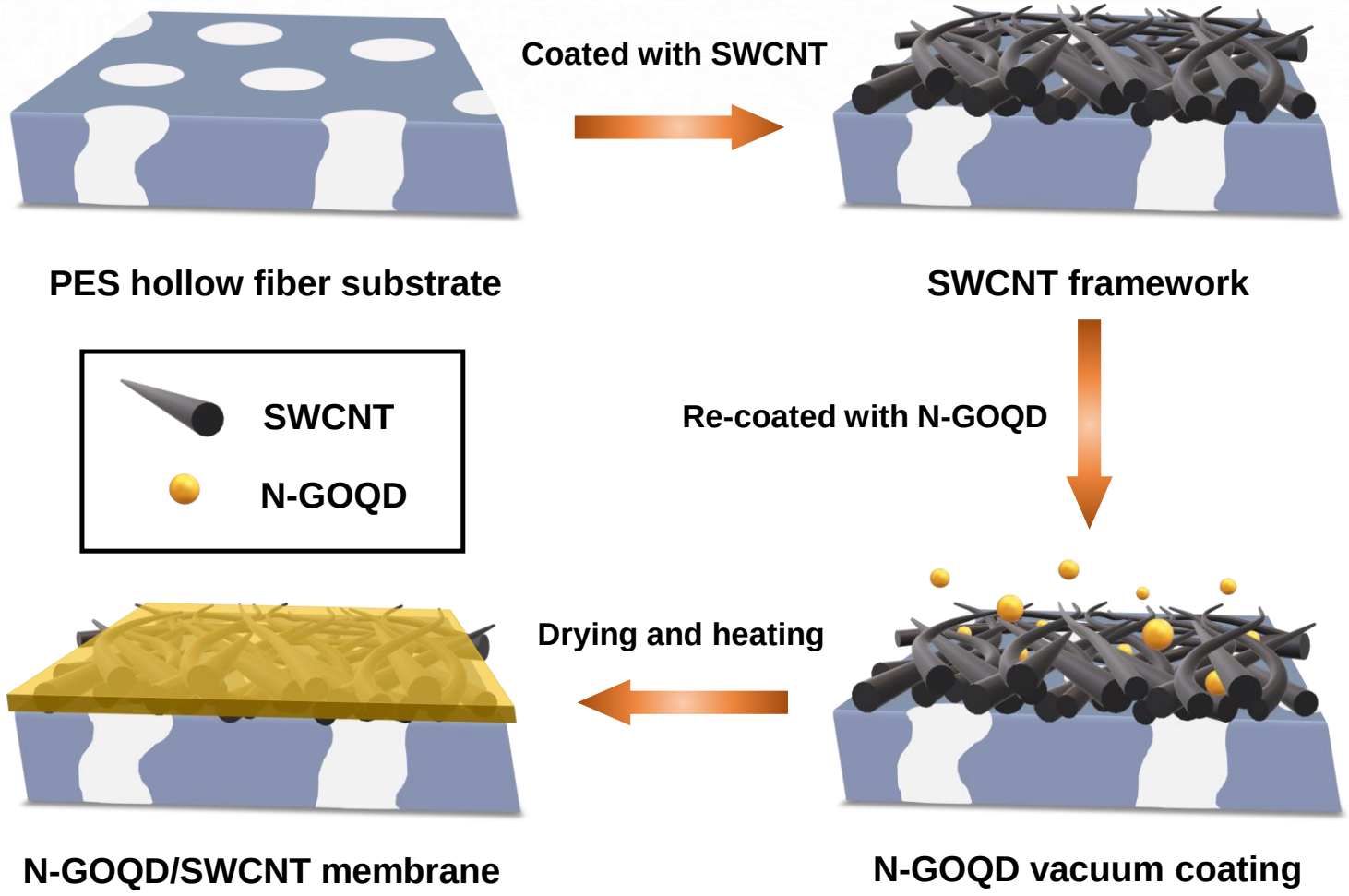
Flat sheet membranes:
Spray coating



Substrate: PES (polyethersulfone)

An innovative membrane structure: GO nanochannels intercalated by single-walled carbon nanotubes

- What does this structure look like?

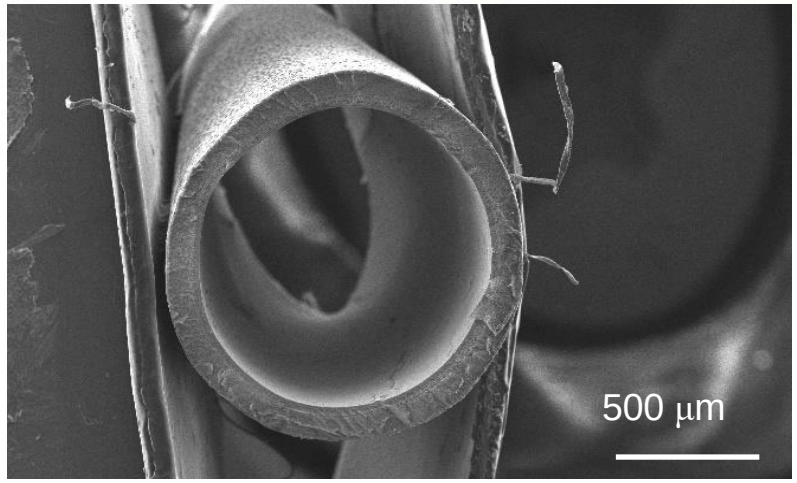


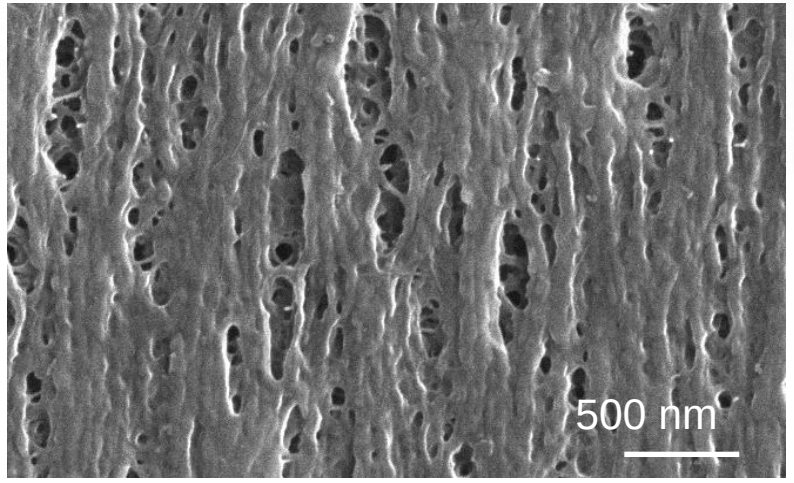
- Why this structure?
  - SWCNTs narrow surface pore size below GOQD size
  - Infiltrated GOQDs pack densely with SWCNTs to form a carbon-based hybrid membrane

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

High-quality GO-based membranes prepared on the commercial available PES hollow fiber substrates

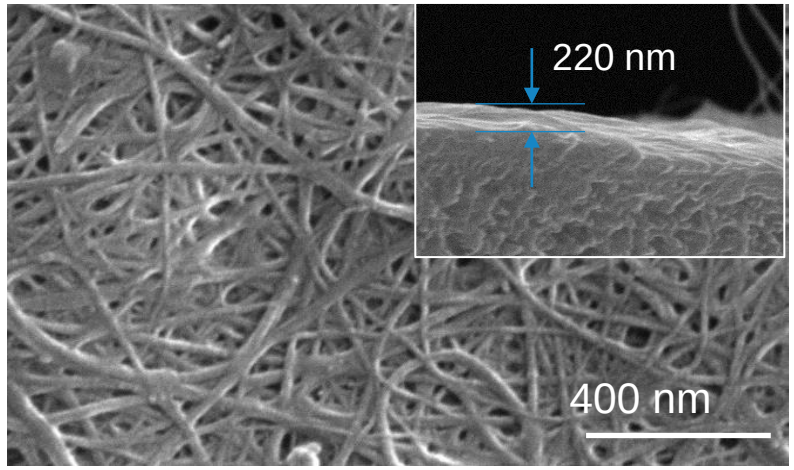
Hollow fiber inner diameter: 1 mm

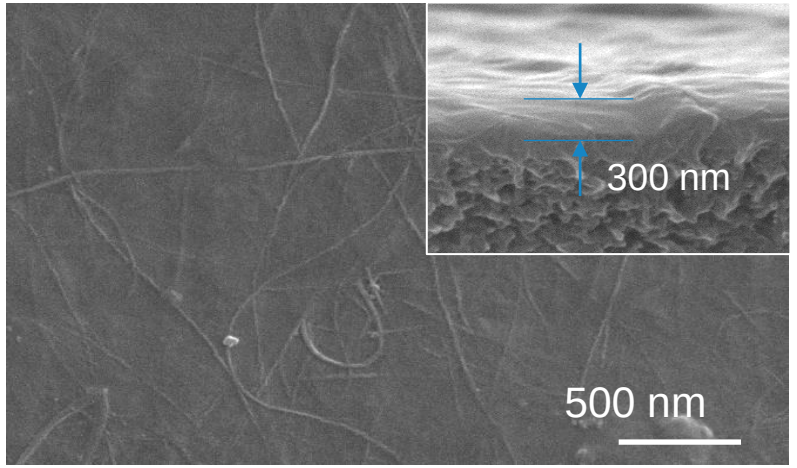




Surface of the substrate: skin layer with pore size of 50-200 nm

Surface and cross section of the SWCNT layer



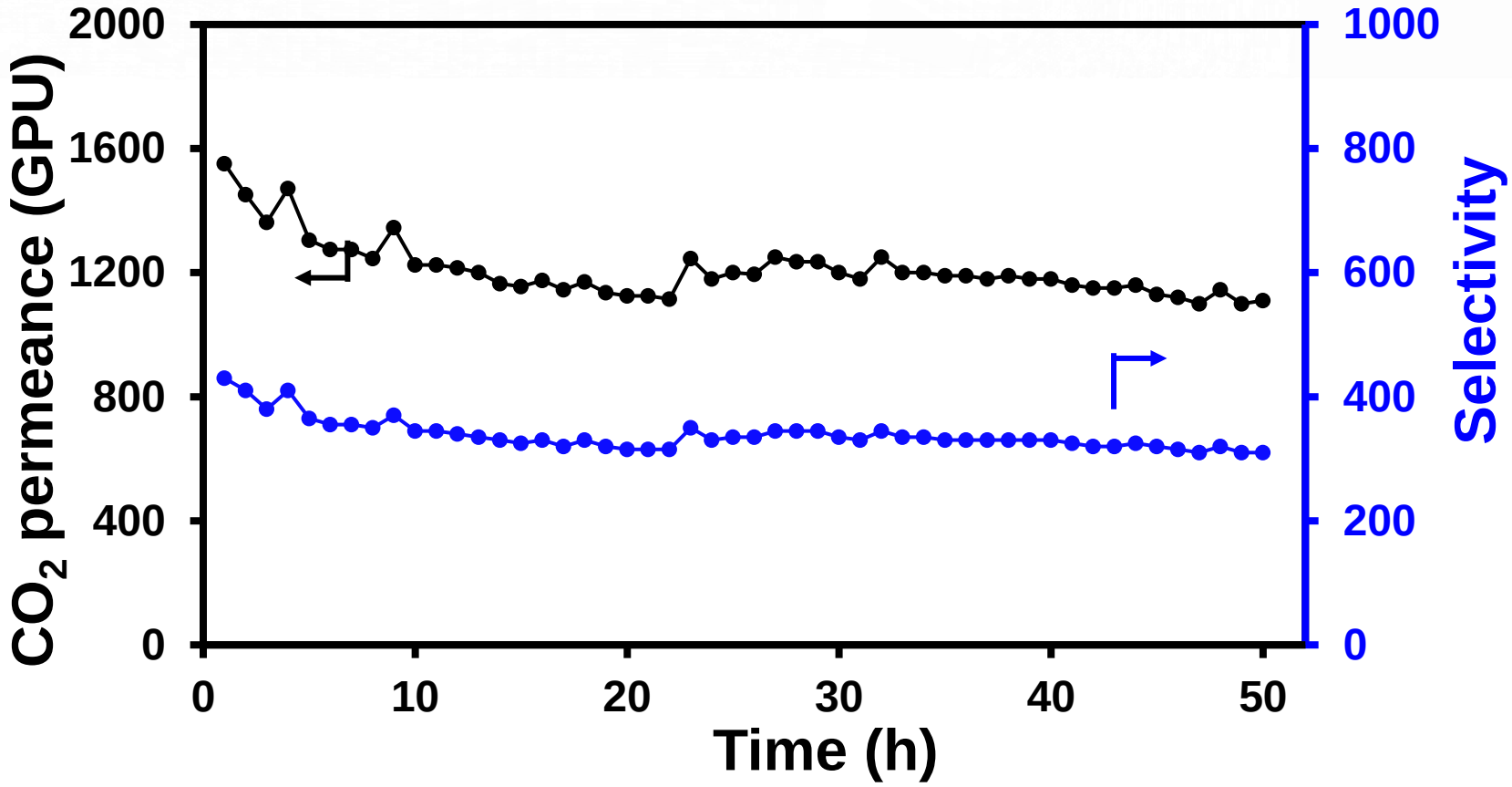


Surface and cross section of the N-GOQD/SWCNT/ DETA membrane

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

GO-1 membrane showed CO_2/N_2 selectivity of 300 with CO_2 permeance of 1,100 GPU at 80°C during 50-h testing

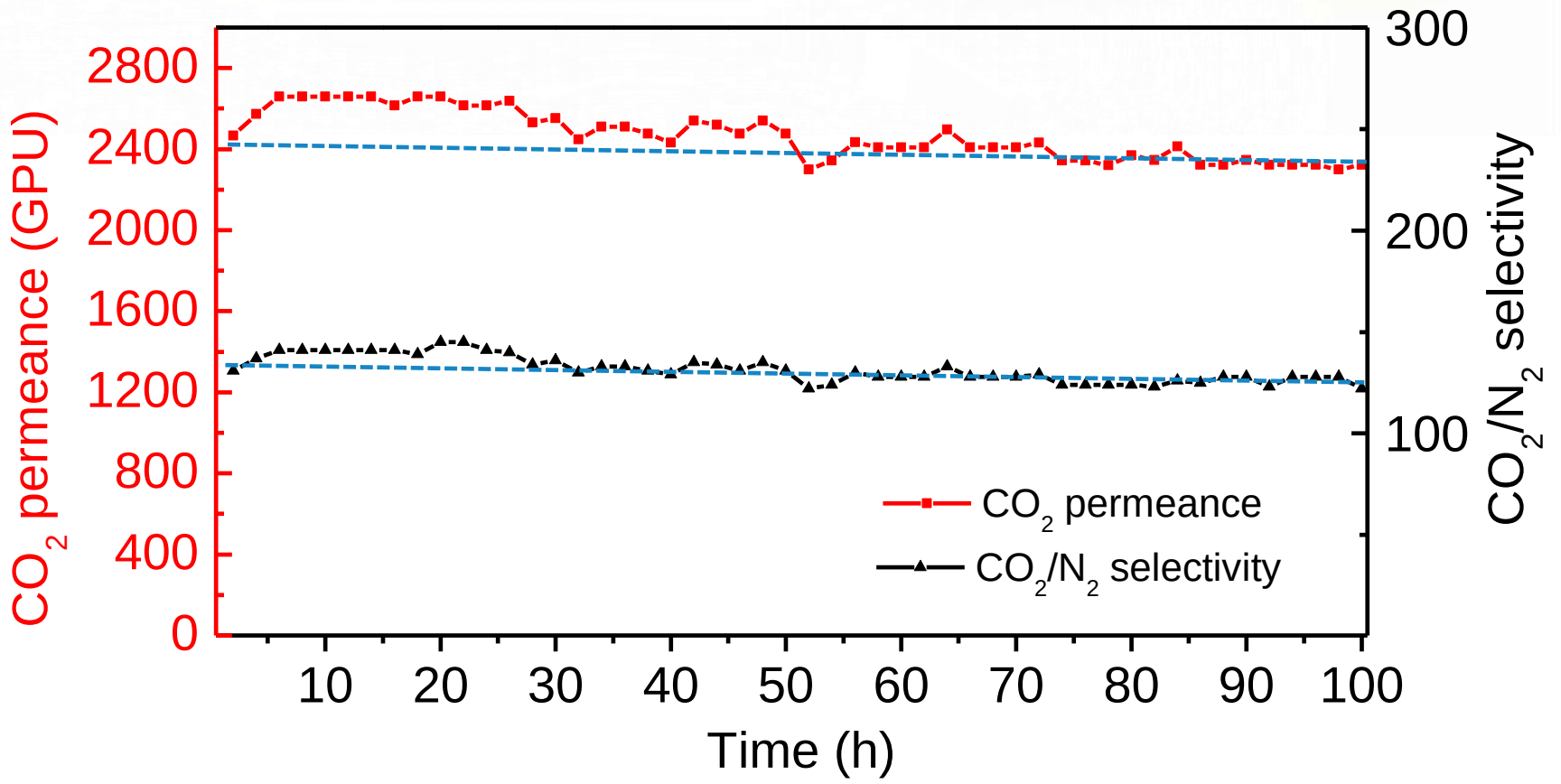
- Flat sheet membrane
- Membrane: GO/PEI/DETA
- Testing conditions:
  - Feed mixture: 8.0 vol% CO_2, 45.2 vol% N_2, and 46.8 vol% H_2O
  - Temperature: 80°C
  - Feed pressure: ~1.0 bara
  - Permeate side pressure: 0.40 bara



GO = graphene oxide; PEI = polyethylenimine; DETA = diethylenetriamine
GPU = Gas Permeation Unit (1 GPU = 3.348 x 10^{-10} mol/m^2/s/Pa)

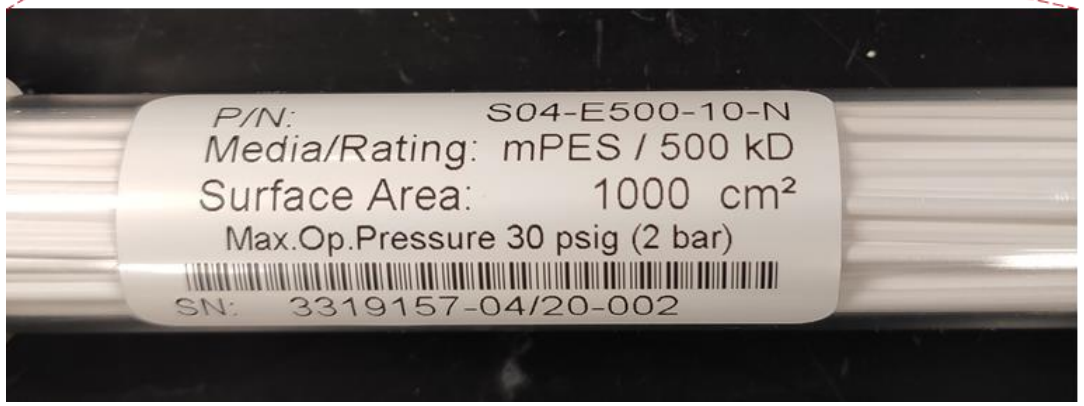
GO-2 membrane showed CO_2 permeance of 2,400 GPU with CO_2/N_2 selectivity of 125 at 80°C during 100-h testing

- Flat sheet membrane
- Membrane: GOQD/CNT/DETA
- Testing conditions:
  - Feed mixture: 4.0 vol% CO_2, 49.2 vol% N_2, and 46.8 vol% H_2O
  - Temperature: 80°C
  - Feed pressure: ~1.0 bara
  - Permeate side pressure: 0.30 bara



GOQD = graphene oxide quantum dot; CNT = carbon nanotube; DETA = diethylenetriamine;
GPU = Gas Permeation Unit (1 GPU = 3.348 x 10^{-10} mol/m^2/s/Pa)

Scaleup of GO-based 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

1,000 cm^2 membrane showed CO_2 permeance of 984 GPU with CO_2/N_2 selectivity of 330 during a stage-cut testing

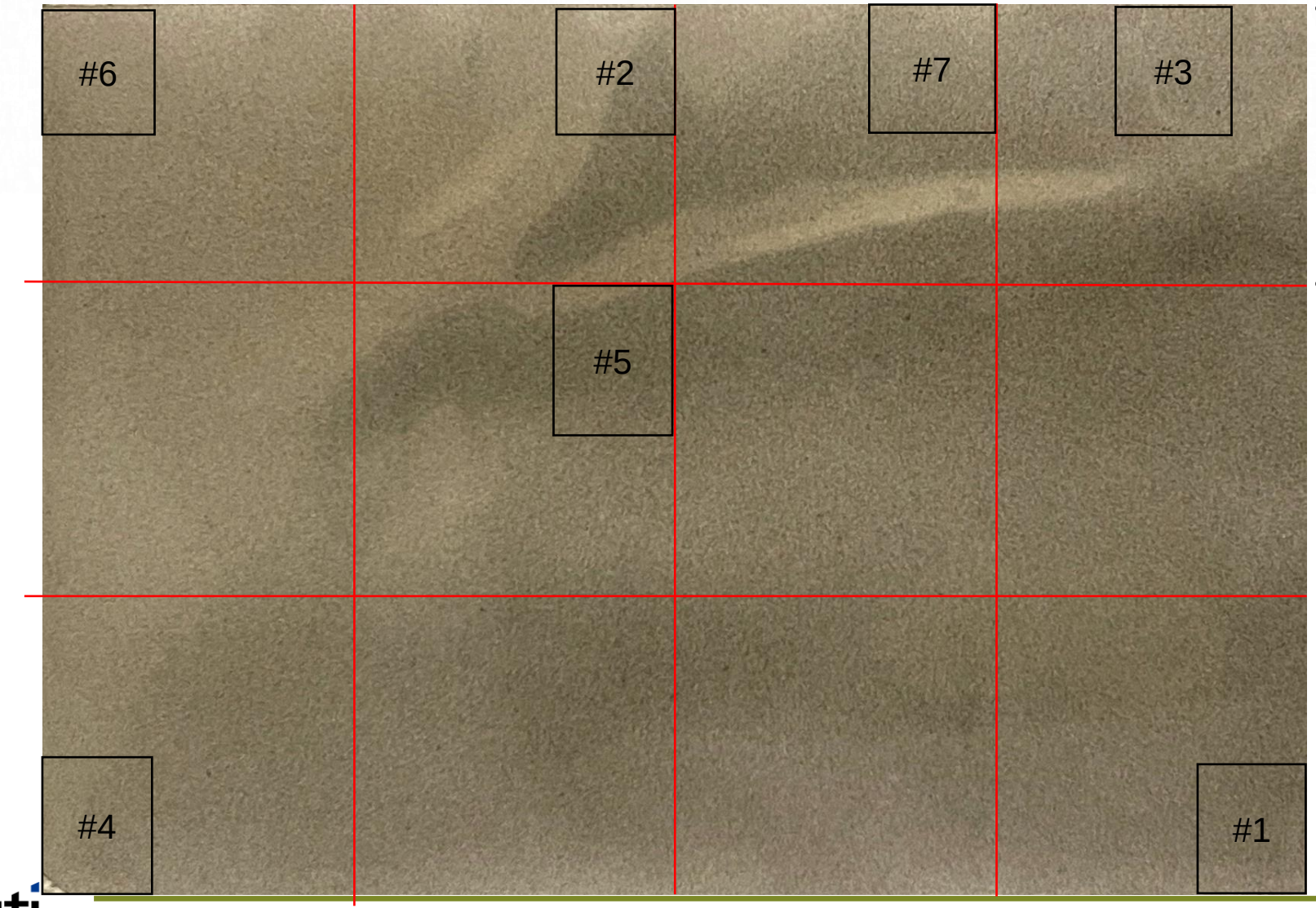
- Membrane: GOQD/CNT/DETA
- Testing condition:
  - Feed mixture: CO_2 9.1 vol%; N_2 50.8 vol%; H_2O 40.1 vol%
  - Temperature: 80°C
  - Feed pressure: ~1 bara
  - Permeate side pressure: 0.40 bara
- CO_2 capture performance:

CO_2 permeance (GPU)	CO_2/N_2 selectivity	Permeate side CO_2 purity (dry base)	CO_2 capture rate
984	330	96.6 vol%	40.3%

GOQD = graphene oxide quantum dot; CNT = carbon nanotube; DETA = diethylenetriamine

Scaleup of GO-based flat sheet membranes by spray coating

145 cm^2 (14.5 cm x 10 cm) coated



- Membrane: GOQD/CNT/PSS/DETA
- Testing condition:
  - Feed mixture: 15 vol%CO_2/85 vol%N_2 (saturated with H_2O)
  - 80°C
  - Feed pressure: ~ 1 bara
  - Permeate pressure: 0.40 bara
- CO_2 capture performance

Sample	CO_2 permeance, GPU	$\alpha_{CO2/N2}$
#1	997	240
#2	1,310	240
#3	998	120
#4	1,020	300
#5	1,030	310
#6	1,240	360
#7	1,130	340
Average	1,100 ± 127	272 ± 81

Lab testing indicates the presence of NO_2 and O_2 does not affect the CO_2 capture performance of the GO membrane

- Membrane: GOQD/CNT/TEPA-PEI-DETA, area: 51.6 cm^2
- Testing conditions:

Feed mixture	CO_2 (vol%)	N_2 (vol%)	H_2O (vol%)	O_2 (vol%)	NO_2 (ppmv)	Feed Pressure (bara)	Permeate pressure (bara)	T (°C)
$CO_2/N_2/H_2O$	8.0%	45.3%	46.7%	0	0	1	0.4	80
$CO_2/N_2/H_2O/O_2/NO_2$	8.0%	43.7%	46.7%	1.6%	35	1	0.4	80

- Testing results:

Feed mixture	CO_2 permeance (GPU)	CO_2/N_2 selectivity
$CO_2/N_2/H_2O$	1,490 ± 34	200 ± 10
$CO_2/N_2/H_2O/O_2/NO_2$	1,450 ± 29	190 ± 3.0

CNT = carbon nanotube; GOQD = graphene oxide quantum dot; TEPA: tetraethylenepentamine; PEI = polyethylenimine; DETA = diethylenetriamine
GPU = Gas Permeation Unit (1 GPU = 3.348×10^{-10} $mol/m^2/s/Pa$)

Preliminary testing data indicate membrane performance not affected by SO_2

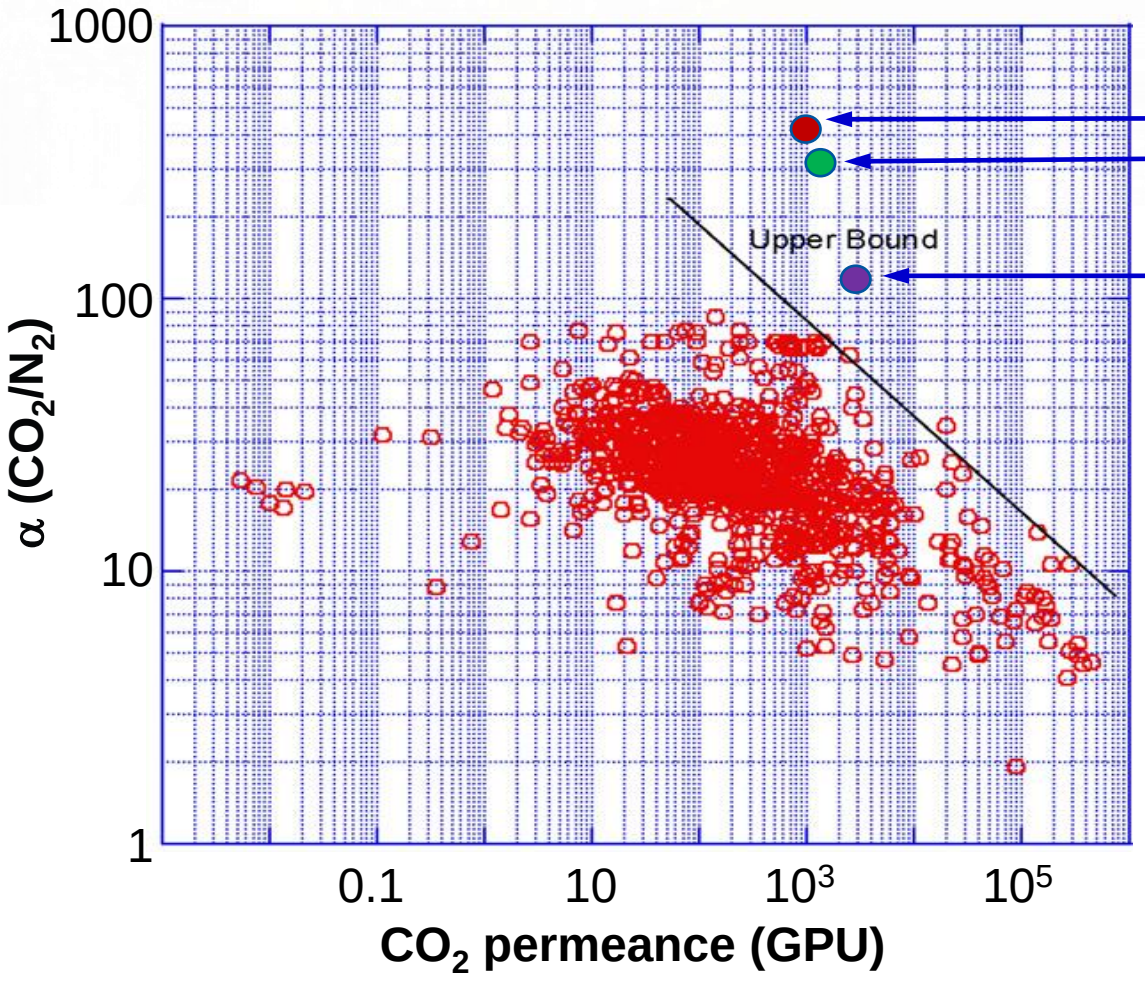
- Tests conducted with two fresh membranes: one with SO_2 in feed, another without SO_2 in feed
  - Feed mixture: CO_2 : N_2: O_2: H_2O = 12.8 %: 38.9%: 1.6%: 46.7% in vol%; SO_2: 46 ppm
  - Temperature: 80°C; Feed pressure: ~1 bara; Permeate side pressure: 0.44 bara
- Similar transient permeation behavior: membrane performance reached steady state in ~2 h after vacuum was introduced to the permeate
- Taking into account of membrane variations and testing error bar (±10%), CO_2 permeances and CO_2/N_2 selectivities calculated from two tests (with and without SO_2) were identical

Test condition	CO_2 permeance (GPU)	N_2 permeance (GPU)	CO_2/N_2 selectivity
Without SO_2	961	4.68	205
With SO_2	1060	5.19	204

- Steady-state stability (≥100 h) will be further investigated under Task 6 with scaled membranes (500-1,000 cm^2)

GPU = Gas Permeation Unit (1 GPU = 3.348 x 10^{-10} mol/m^2/s/Pa)

Where do our membranes fall on the Robeson plots?



GO-1 hollow fiber membrane (1,000 cm^2) at 80°C

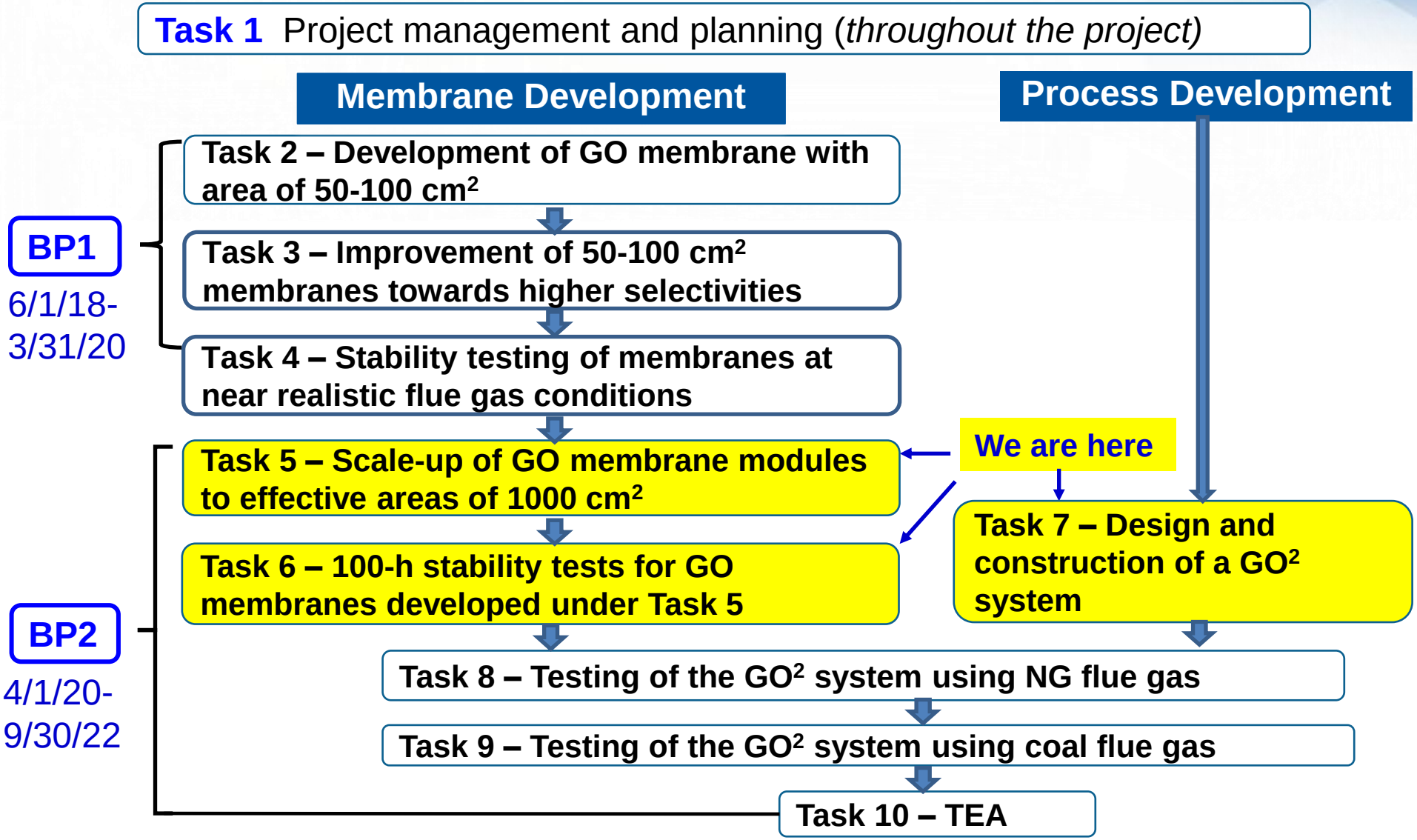
GO-1 flat sheet membrane at 80°C

GO-2 flat sheet membrane at 80°C

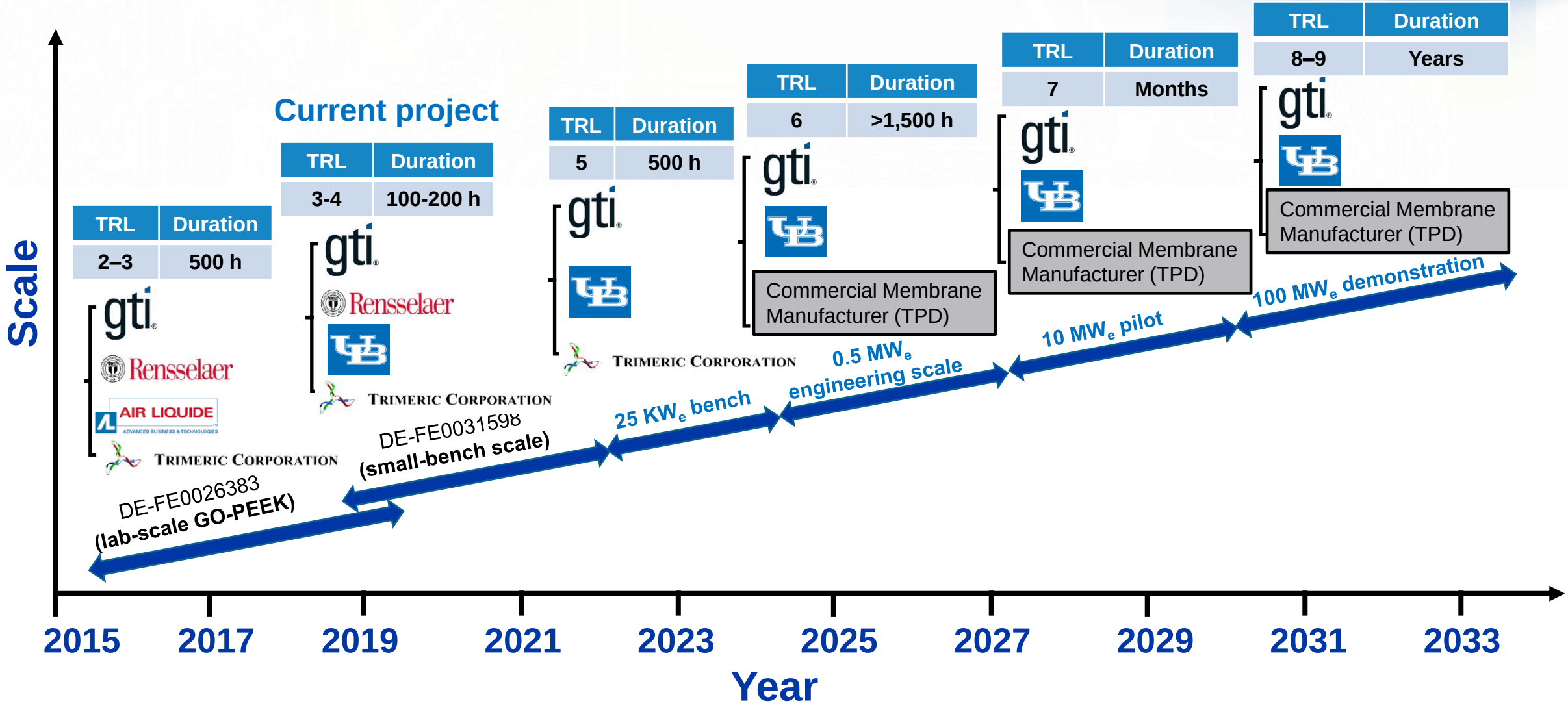
Robeson, J. Membrane Sci. ***2008****, Vol. 320, p390*

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

Future work of this project



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 was developed and showed high CO_2 capture performance and good stability
- Preliminary lab tests indicated GO-based membranes stable in the presence of O_2, NO_2 and SO_2
- Membranes scaled to 1,000 cm^2 surface area. The performance of the scaled membranes achieved technical goals
- A bench-scale system is under design and will be tested at NCCC

NCCC = National Carbon Capture Center

Acknowledgements

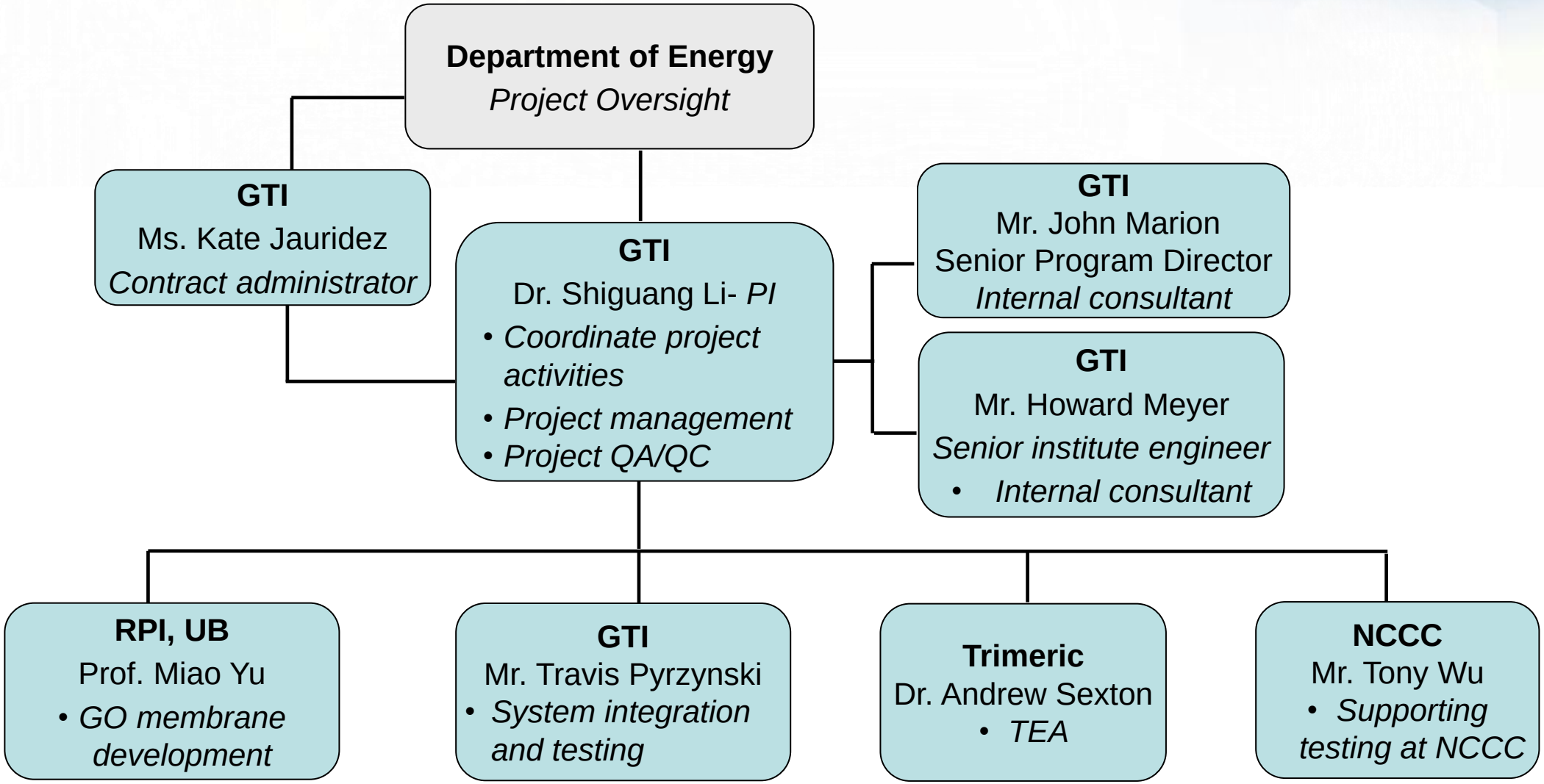
- Financial and technical support

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 Mark Crombie
- NCCC: Frank Morton and Tony Wu

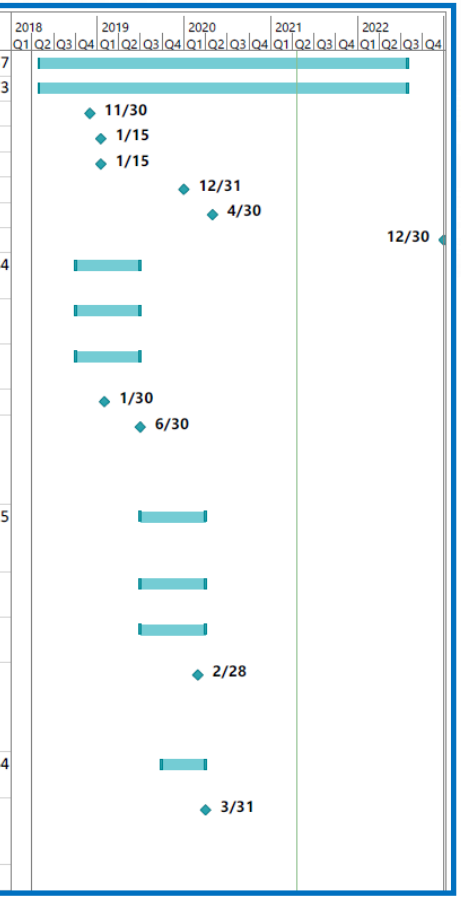
Appendix – Organization Chart



Appendix – Gantt Chart

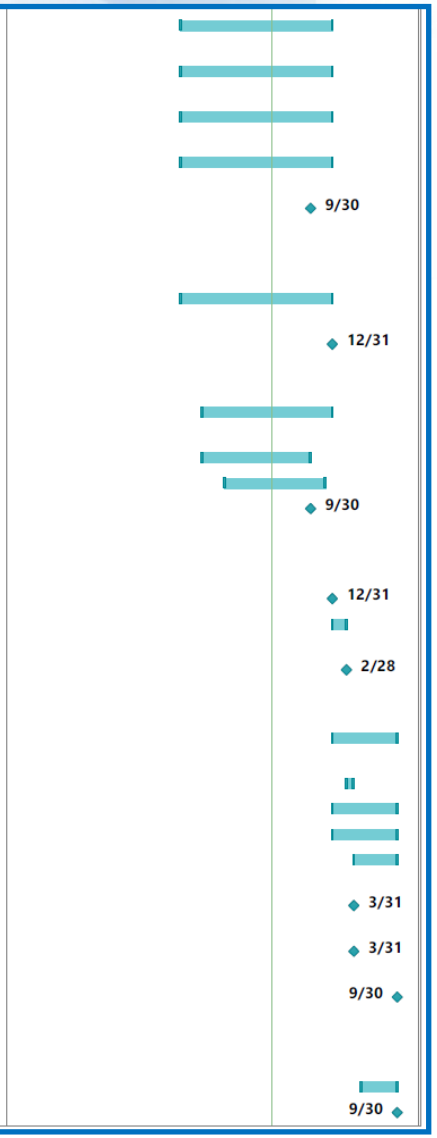
BP1

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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