GTI ENERGY

U.S. DEPARTMENT OF ENERGY

DE-FE0031598

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

Shiguang Li, Weiwei Xu, Qiaobei Dong, Howard Meyer, *GTI Energy*
Miao Yu, Fan Wang, Dinesh Behera, *The State University of New York at Buffalo (UB)*

2024 FECM/NETL Carbon Management Research Project Review Meeting
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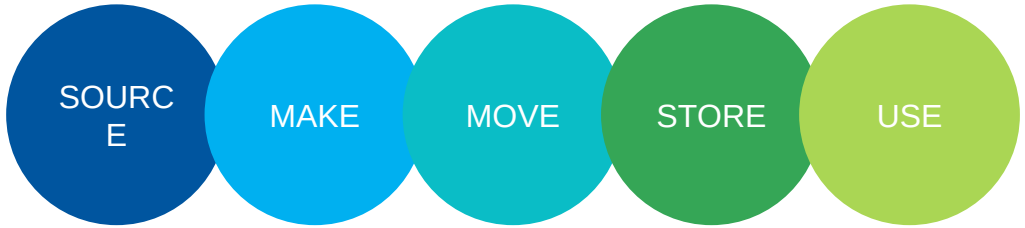
GTI Energy: 80-year history of turning raw technology into practical energy solutions

GTI Energy is a leading energy research and training organization



Across the entire energy value chain

World-class facility in Chicago area

500+ Enterprise Employees

CCUS is one of GTI strategic focus areas

Active DOE Projects

- **Carbon capture**
  - **FE0031946**: 20 TPD facilitated transport membrane (FTM) for power plant application
  - **FE0032466**: 3 TPD ROTA-CAP for steel plant application
  - **FE0032463**: 3 TPD FTM for cement plant (sub to OSU)
  - **FE0031598**: Bench-scale GO-based membrane
  - **FE0032215**: Nano-confined ionic liquid membrane
  - **FE0031730**: Size-sieving adsorbent (sub to UB)
- **Carbon conversion**
  - **FE0031909:** Membrane reactors for conversion of CO_2 to fuels/chemicals
  - **FE0032246:** Converting CO_2 to alternative cement (sub to WashU)
- **Carbon dioxide removal (CDR)**
  - **FE0031969**: Trapped small amines in capsules (sub to UB)
- **Carbon transport and storage**
  - **FE0032239**: CarbonSAFE Phase II

Technology based on our work published in *Science* and *Nature Communications*

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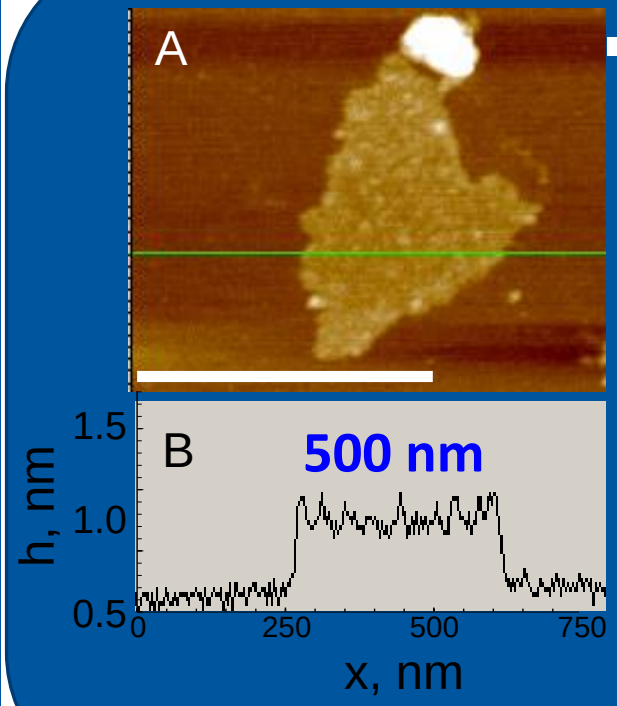
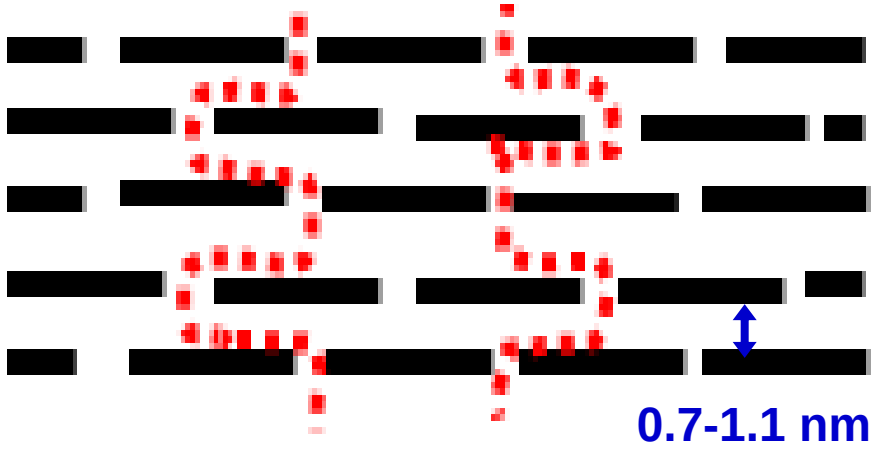
Science AAAS

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



- **Contribution**:
  - Structural defects on GO flakes can be controlled as transport pathway for selective gas separations

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



nature COMMUNICATIONS

CO_2 permeance: 1,000 GPU
CO_2/N_2 selectivity: 680

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

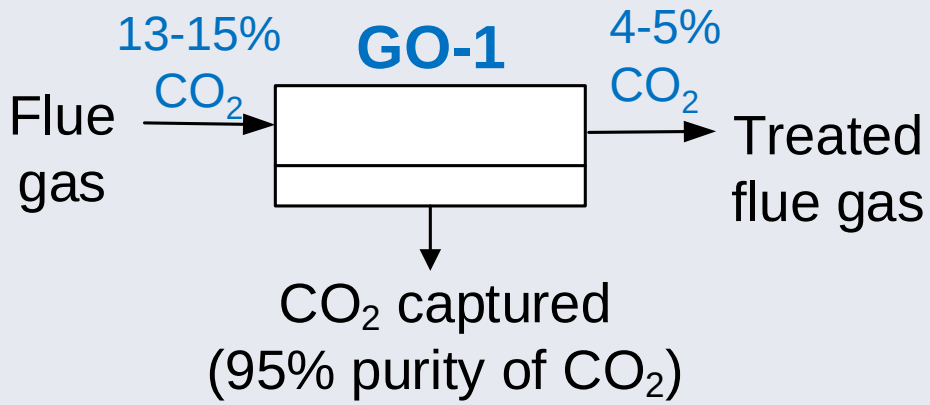
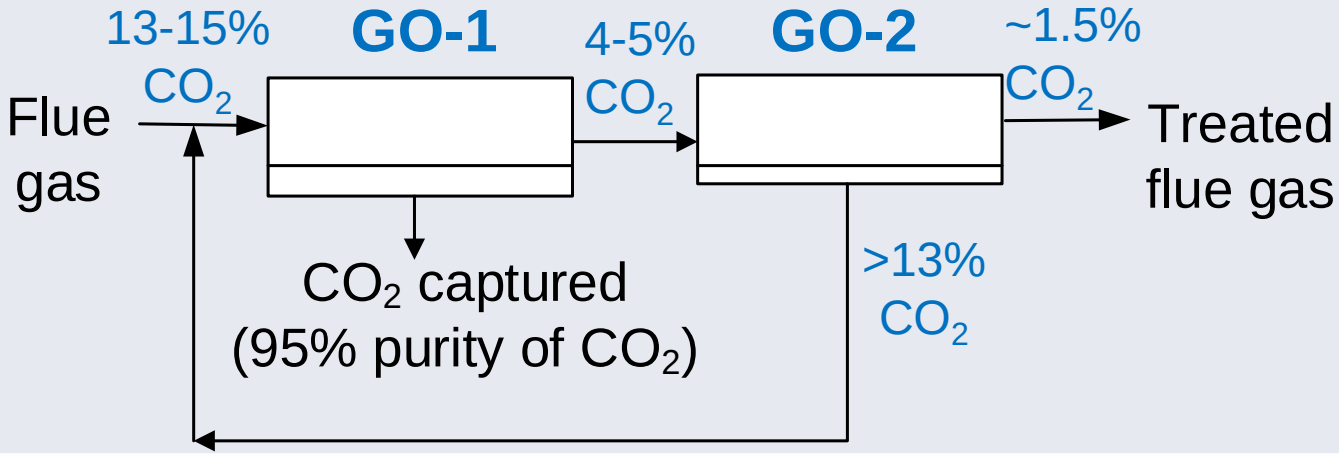
Project overview

- **Performance period**: June 1, 2018 – October 30, 2024
- **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, UB	▪ GO membrane development and scale-up
NATIONAL CARBON CAPTURE CENTER	▪ Site host
TRIMERIC CORPORATION	▪ Technical & economic analysis

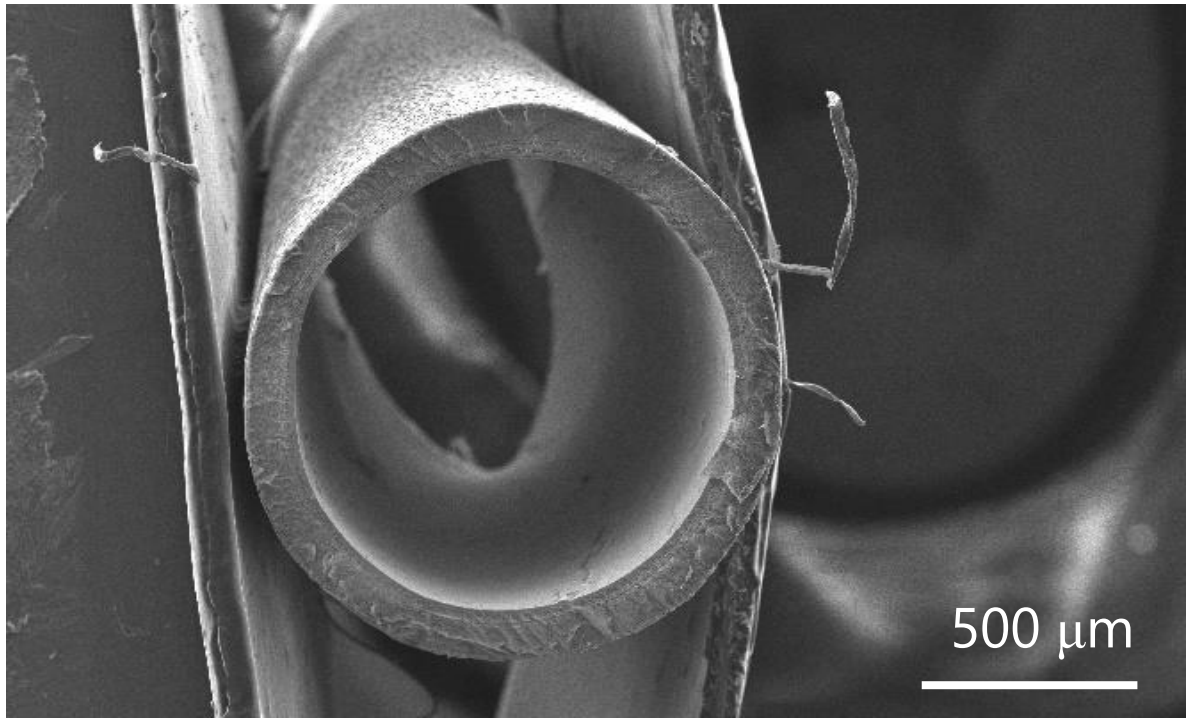
GO = graphene oxide

Process description

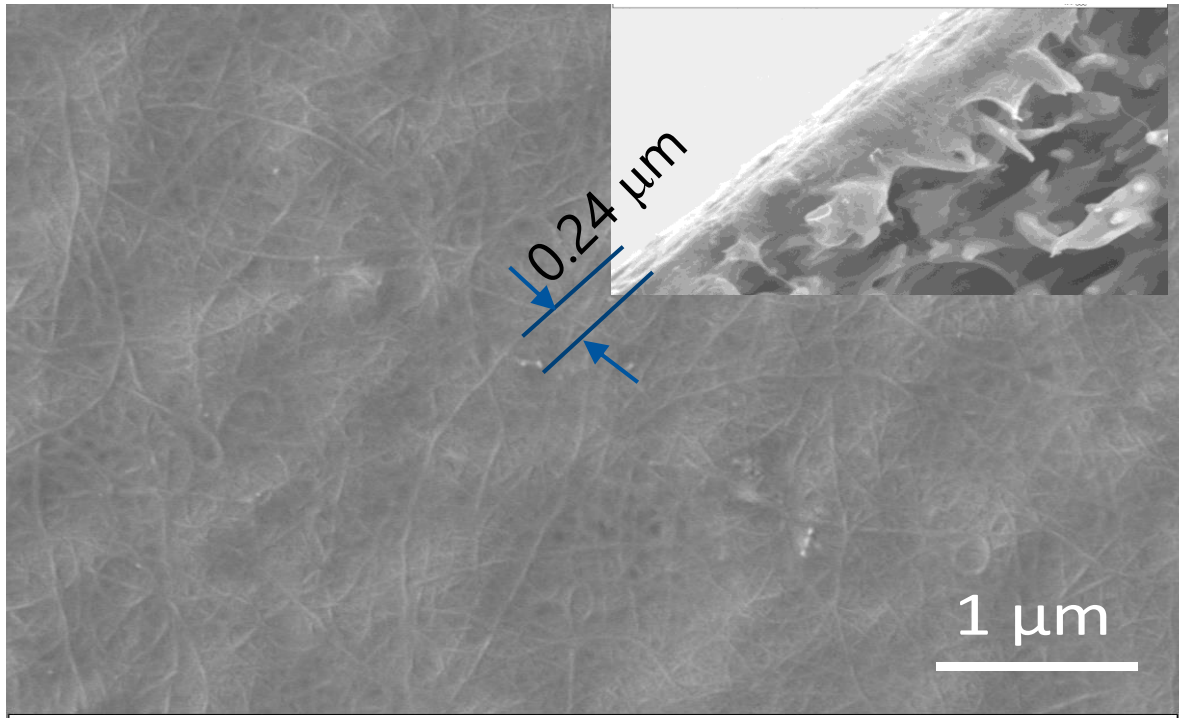
CO_2 capture	Diagram	Description
50–70% capture		**Single stage**
70–90% capture		**GO^2 process** integrates a high-selectivity GO-1 membrane and a high-flux GO-2 membrane for optimal performance

GO = graphene oxide

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



Hollow fiber inner diameter: 1 mm



Membrane surface and cross section

PES = polyether sulfone

In Budget Period 1 (BP1), GO-1 and GO-2 membranes (surface area: ~50 cm²) achieved performance goals

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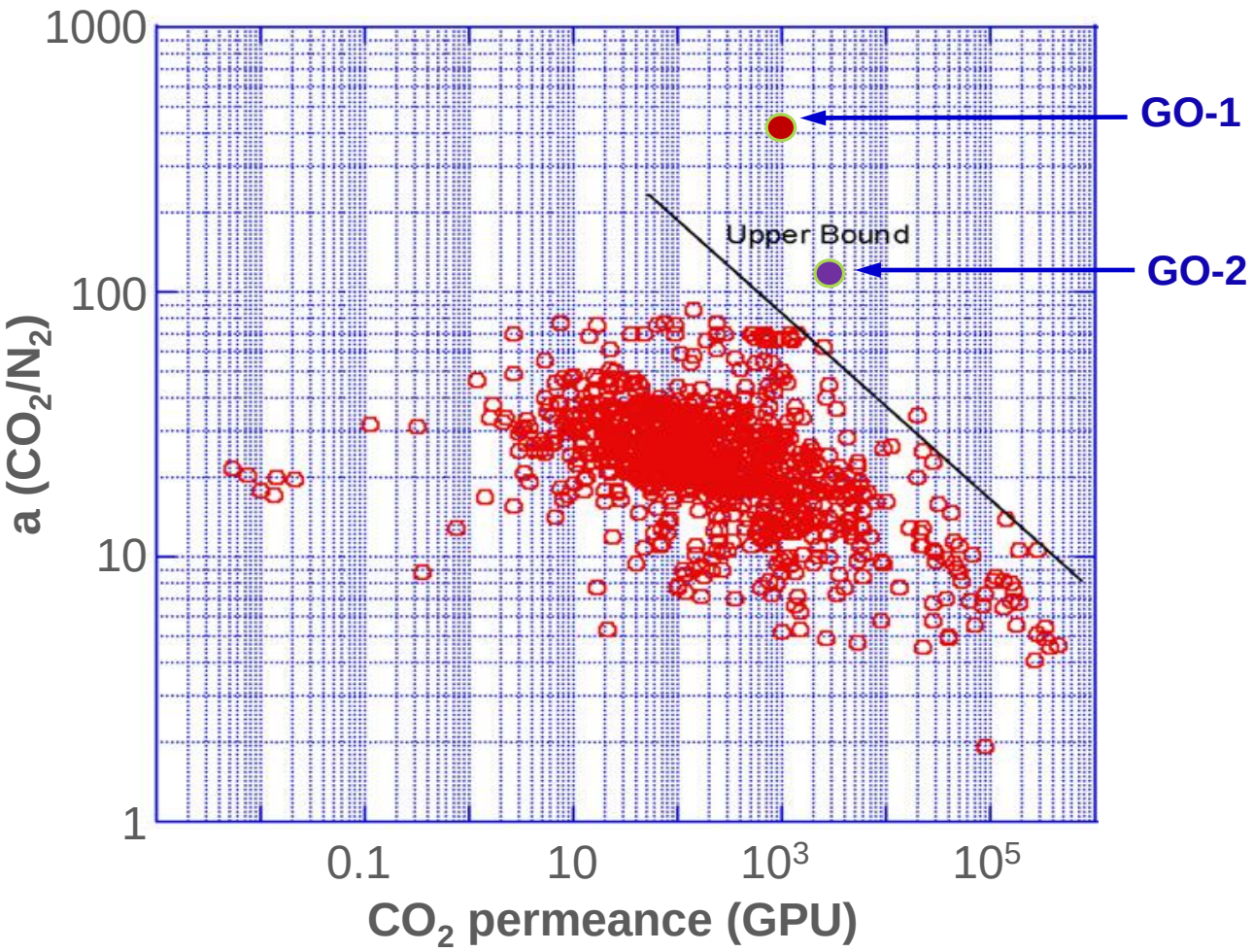
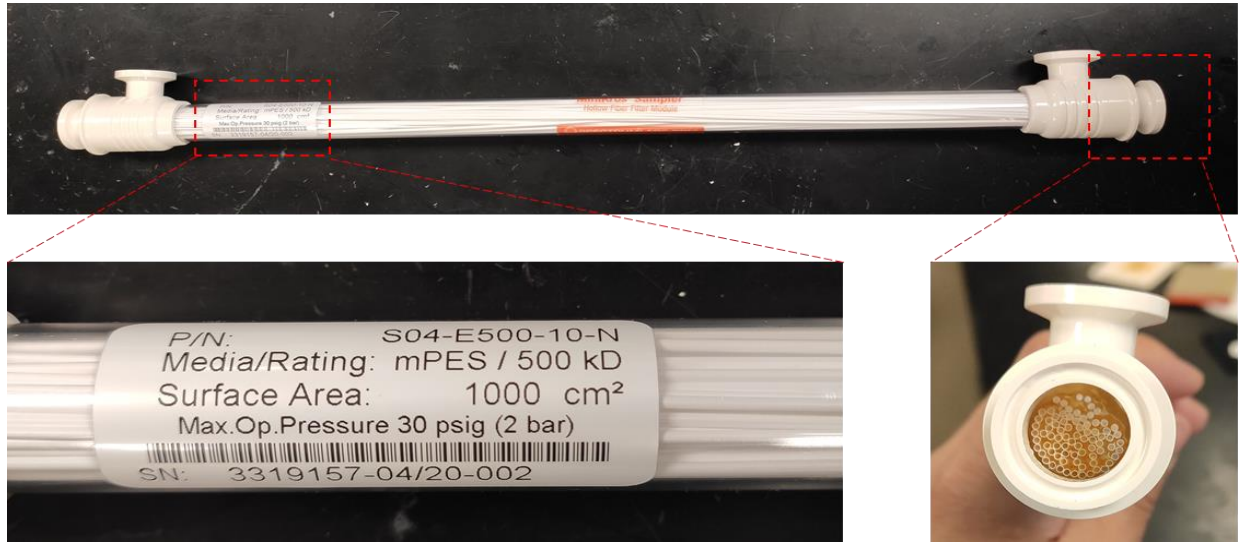
	CO_2 permeance, GPU	CO_2/N_2 selectivity
GO-1 goal	1,000	200
GO-1 developed	1,100	300
GO-2 goal	2,500	20
GO-2 developed	2,600	120

- 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

BP2: membranes scaled up to 1,000 cm^2; bench scale system constructed and installed at NCCC



Material	Fiber ID, mm	Module length, cm	Effective length, cm	# of fibers	Effective surface area, cm^2
PES	1.0	47	41.5	78	1,000

- Bench system installed at NCCC

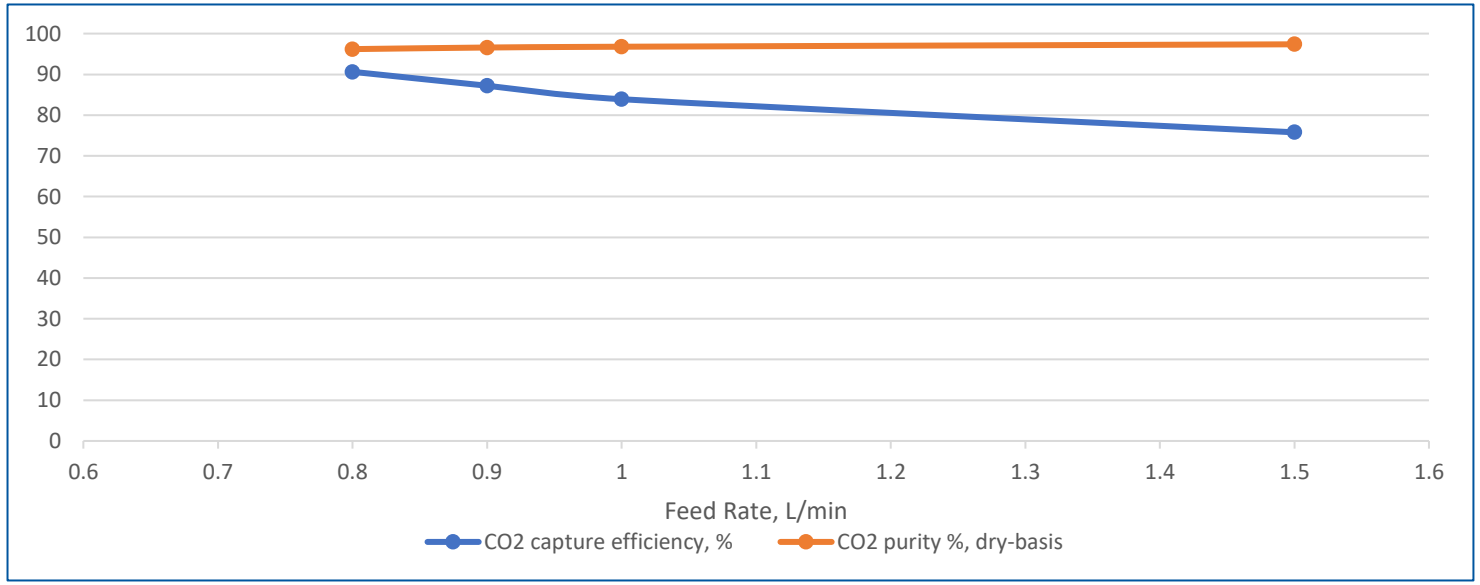
Feed gas at NCCC

- Actual natural gas boiler flue gas was modified to replicate the CO_2 concentrations found in coal flue gas

Gas	Simulated coal-fired flue gas
CO_2	12.5%-16%
O_2	3.3%-7.5%
SO_2	<1ppm
NO_2	2-3 ppm
Water	80-90% saturation
N_2	Balance

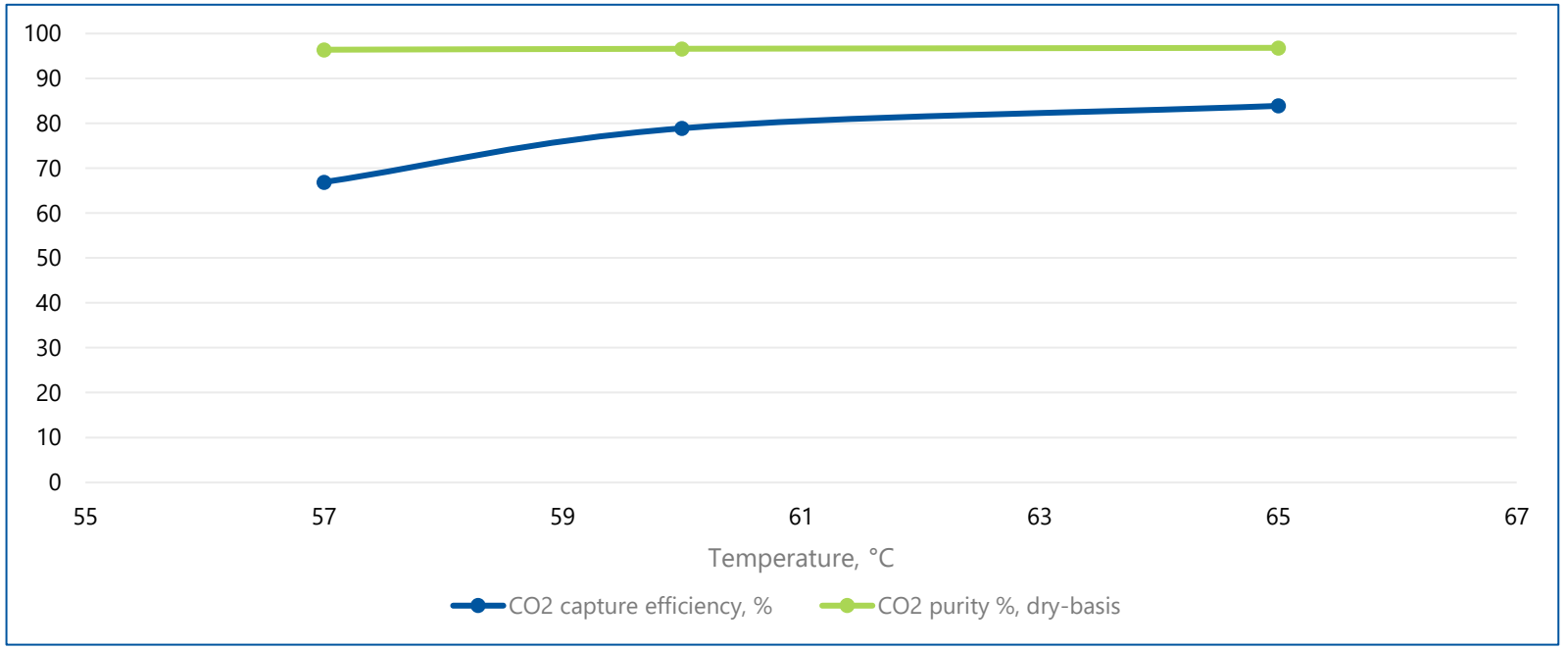
Parametric tests: As flow rate decreases, capture efficiency increases with a small effect on product purity

#	Parameters	T, °C	Pressure, bara		Feed CO_2 concentration, vol% dry-basis	Feed flow rate, L/min	CO_2 capture efficiency, %	CO_2 purity %, dry-basis
			Feed	Permeate				
1	Feed flow rate	65	1.2	0.15	15	1.5	75.8	97.4
2		65	1.2	0.15	15	1.0	83.9	96.8
3		65	1.2	0.15	15	0.9	87.2	96.6
4		65	1.2	0.15	15	0.8	90.6	96.2



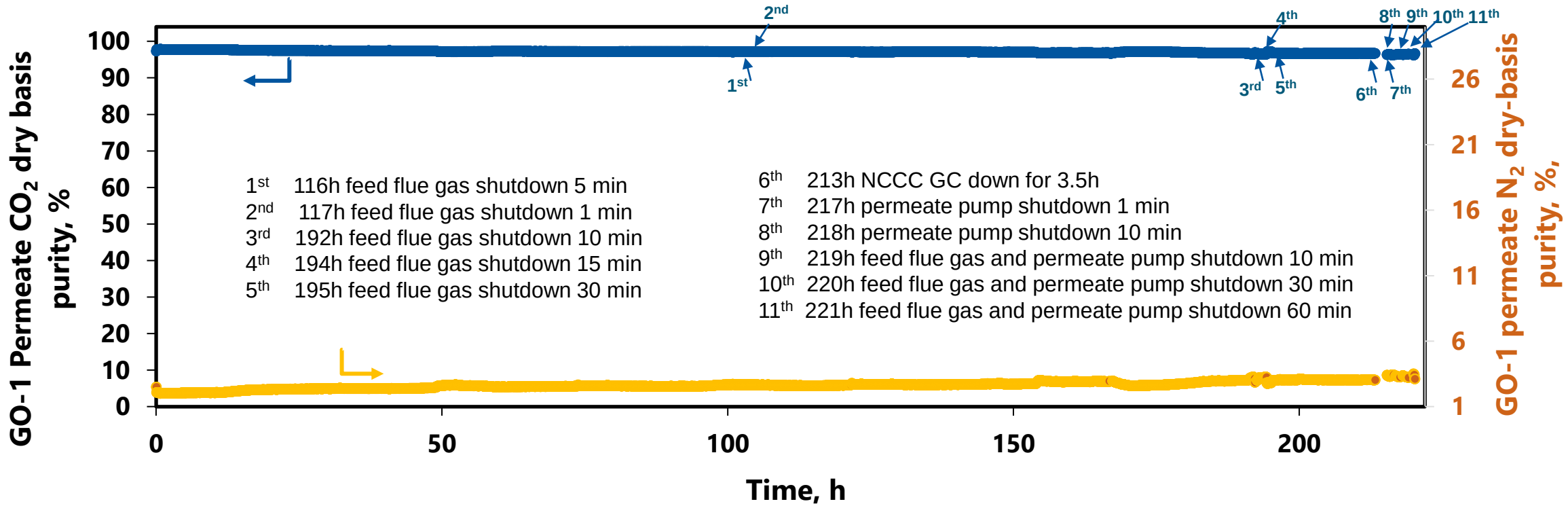
Parametric tests: Capture efficiency increases as temperature increases with a small effect on purity

#	Parameters	T, °C	Pressure, bara		Feed CO_2 concentration, vol% dry-basis	Feed flow rate, L/min	CO_2 capture efficiency, %	CO_2 purity %, dry-basis
			Feed	Permeate				
1	Operating temperature	57	1.2	0.15	15	1.0	66.9	96.4
2		60	1.2	0.15	15	1.0	78.9	96.6
3		65	1.2	0.15	15	1.0	83.9	96.8



220-h single-stage testing indicated good dynamic stability and long-term stability

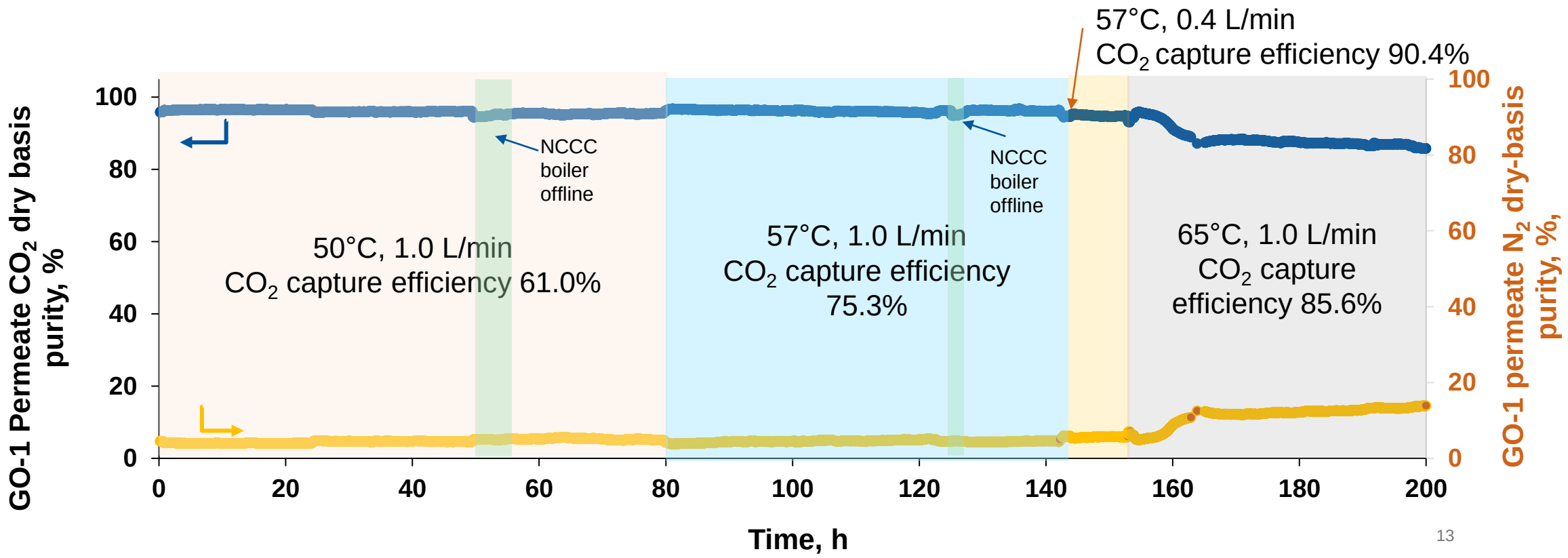
GO-1 membrane area, cm^2	Feed composition, vol%	Temperature, °C	Feed pressure, bara	Permeate pressure, bara
1,000	16% CO_2, 4% O_2, 80% N_2 dry-basis	50	1.06	0.15



200-h two-stage (GO^2 process) continuous testing showed stable performance

- Dry-basis feed mixture: 16 vol% CO_2, 4 vol% O_2, 80 vol% N_2; feed mixture is saturated with H_2O

GO-1 membrane area, cm^2	GO-2 membrane area, cm^2	GO-1 permeate pressure, bara	GO-2 permeate pressure, bara
1,000	75	0.15	0.15



Status of the milestones

Budget Period	M #	Task #	Milestone Title/Description	Planned Completion Date	Actual Completion Date
1	1.1	1	Updated Project Management Plan	11/30/18	9/6/18
1	1.2	1	Kickoff Meeting	1/15/19	2/6/19
1	1.3	1	Technology maturation plan submitted to DOE	1/15/19	12/28/18
1	2.1	2	50-100 cm^2 GO membranes prepared	1/30/19	1/15/19
1	2.2	2	For 50-100 cm^2 area membranes, GO-1 exhibits CO_2/N_2 selectivity ≥100 and CO_2 permeance ≥1,000 GPU and GO-2 exhibits CO_2/N_2 selectivity ≥10 and CO_2 permeance ≥2,500 GPU	6/30/19	6/11/19
1	1.4	1	Continuation application for BP2 submitted	12/31/19	12/28/19
1	3.1	3	For 50-100 cm^2 area membranes, GO-1 exhibits CO_2/N_2 selectivity ≥200 and CO_2 permeance ≥1,000 GPU and GO-2 exhibits CO_2/N_2 selectivity ≥20 and CO_2 permeance ≥2,500 GPU	2/28/20	12/18/20
1	4.1	4	Stability testing shows the CO_2 permeances and CO_2/N_2 selectivities decreased by less than 10% in the presence of flue gas contaminants	3/31/20	11/23/20
2	1.5	1	Submit BP1 Report	4/30/20	4/15/20
2	5.1	5	For 1,000 cm^2 area membranes, GO-1 exhibits CO_2/N_2 selectivity ≥200 and CO_2 permeance ≥1,000 GPU and GO-2 exhibits CO_2/N_2 selectivity ≥20 and CO_2 permeance ≥2,500 GPU	5/31/22	8/25/22
2	6.1	6	CO_2 permeances and CO_2/N_2 selectivities decrease by <10% during a 100-h continuous testing	2/28/23	2/28/23
2	7.1	7	Complete process design for low and high CO_2 flue gas conditions; and process simulation indicates that the CO_2 capture system can achieve ≥95% CO_2 purity	9/30/21	9/20/21
2	7.2	7	Constructed skid ready for testing	12/31/21	12/31/21
2	8.1	8	95% CO_2 purity achieved when testing the constructed GO^2 system using simulated flue gas	5/30/23	4/12/23
2	9.1	9	Commissioning complete and system ready for testing at NCCC.	6/30/23	8/19/23
2	9.2	9	1,000 cm^2 GO membrane modules shipped to NCCC	6/30/23	8/15/23
2	9.3	9	Skid testing at NCCC complete, 70-90% CO_2 removal rate achieved, 95% CO_2 purity validated, and membrane shows good stability during a 200-h testing	6/30/24	6/3/24
2	10.1	10	Issue technoeconomic analysis (TEA) report	7/31/24	7/31/24
2	1.6	1	Submit Final Technical Report	1/29/25	

Summary

- GTI and UB have developed a transformational graphene oxide-based membrane process for post-combustion CO_2 capture
- Membranes successfully scaled to 1,000 cm^2 surface area
- Bench-scale system designed, constructed and tested at NCCC
- 220-h single-stage testing indicated good dynamic stability and long-term stability
- 200-h two-stage (GO^2 process) continuous testing showed stable performance, 70-90% CO_2 removal rate achieved, 95% CO_2 purity validated

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

Disclaimer