

**REPORT**  
GTI ENERGY PROJECT 22345

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**Bench-scale Development of a  
Transformational Graphene Oxide-based  
Membrane Process for Post-combustion  
CO<sub>2</sub> Capture**

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## 1. Executive Summary

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Graphene-based materials, such as graphene and graphene oxide (GO), have been considered as next-generation membrane materials<sup>[1-5]</sup>. GTI Energy and The State University of New York at Buffalo (UB) have been developing a transformational GO-based membrane process (designated as GO<sup>2</sup>) that integrates a high CO<sub>2</sub>/N<sub>2</sub> selectivity membrane (GO-1) and a high CO<sub>2</sub> flux membrane (GO-2) for post-combustion CO<sub>2</sub> capture<sup>[6-8]</sup>. In the process, flue gas is first sent to the GO-1 membrane. A vacuum pump is used on the membrane permeate side to provide sufficient driving force for CO<sub>2</sub> permeation. The CO<sub>2</sub>-depleted residue leaving the GO-1 membrane is then sent to the GO-2 membrane, which also utilizes a vacuum on the permeate side to generate the necessary driving force for separation. The permeate from the GO-2 membrane is recycled back to the feed of the GO-1 membrane. The CO<sub>2</sub>-enriched permeate from the GO-1 membrane is cooled to remove most of the water, resulting in a CO<sub>2</sub> dry-basis purity of  $\geq 95$  vol%.

This report summarizes the bench-scale testing conducted by GTI Energy and UB under award "DE-FE0031598: Bench-scale Development of a Transformational Graphene Oxide-based Membrane Process for Post-combustion CO<sub>2</sub> Capture" sponsored by the Department of Energy (DOE). The objective of this project is to develop a GO-based membrane process that can be installed in a new pulverized coal (PC) plant or retrofitted into an existing plant for CO<sub>2</sub> capture with CO<sub>2</sub> dry-basis purity over 95 vol% and a levelized cost of electricity (COE) at least 30% lower than a supercritical PC power plant utilizing a conventional CO<sub>2</sub> capture process.

The GO-based membrane technology was tested for post-combustion CO<sub>2</sub> capture at the National Carbon Capture Center (NCCC). During the tests at NCCC, a 1,000 cm<sup>2</sup> GO-1 membrane was installed for single-stage testing. This membrane achieved a CO<sub>2</sub> dry-basis purity of >95 vol% and exhibited good long-term and dynamic stability during 220 hours (h) of single-stage testing. Subsequently, a 1,000 cm<sup>2</sup> GO-1 membrane and a 75 cm<sup>2</sup> GO-2 membrane were installed for the integrated two-stage test. During the parametric testing, four different feed flow rates (1.5, 1.0, 0.9, and 0.8 L/min) were tested at 65°C, resulting in CO<sub>2</sub> capture efficiency of 75.8%, 83.9%, 87.2%, and 90.6%, respectively. Additionally, two tests were conducted under operating temperatures of 57 and 60°C, achieving CO<sub>2</sub> capture efficiency of 66.9% and 78.9%, respectively. All parametric tests showed CO<sub>2</sub> dry-basis purity above 96 vol%. Finally, a 200-h stability test was performed for the integrated two-stage GO<sup>2</sup> process during which 95.6 vol% CO<sub>2</sub> dry-basis purity and 90.4% CO<sub>2</sub> capture efficiency were achieved.

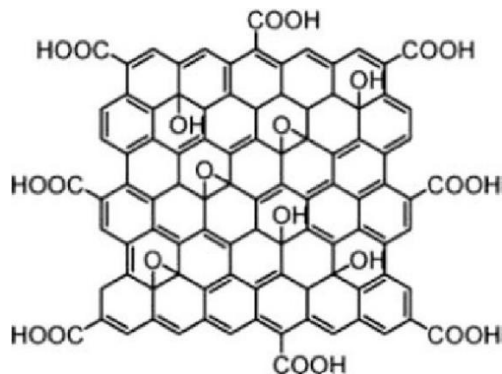
Following these tests at NCCC, GTI Energy plans to leverage the lessons learned to further improve membrane fabrication and process design, advancing this technology to higher technology readiness level.

## 2. Introduction

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The objective of this project is to develop a transformational GO-based membrane process that can be installed in new PC or natural gas power plants or retrofitted into existing plants. This GO-based membrane process aims to achieve CO<sub>2</sub> dry-basis purity on a dry-basis above 95 vol% while reducing the COE by at least 30% compared to a supercritical PC power plant using conventional carbon capture technology. Building on a previous laboratory-scale project supported by DOE under DE-FE0026383, this transformational GO-based membrane process (designated as GO<sup>2</sup>) combines two specialized membranes: a high CO<sub>2</sub>/N<sub>2</sub> selectivity membrane (GO-1) and a high CO<sub>2</sub> flux membrane (GO-2). This integrated membrane technology targets efficient, post-combustion CO<sub>2</sub> capture to help meet ambitious emissions reduction goals.

Graphene-based materials, such as GO (see Figure 1), have emerged as promising candidates for next-generation membrane technologies. Due to its sub-nanometer thickness, GO enables the fabrication of ultrathin membranes, significantly reducing transport resistance and enhancing overall efficiency in gas separation applications.



**Figure 1.** Chemical structural of GO.

In the GO<sup>2</sup> process, the GO-1 and GO-2 membranes are integrated to achieve cost-effective CO<sub>2</sub> capture. Flue gas first enters the GO-1 membrane, where a portion of CO<sub>2</sub> permeates through the membrane. The retentate from the GO-1 membrane is directed to the GO-2 membrane. Here, the permeate from the GO-2 membrane is recycled back to the feed of the GO-1 membrane, while the retentate from the GO-2 membrane is released to the atmosphere. The final product, a CO<sub>2</sub>-rich permeate stream from the GO-1 membrane, achieves a dry-basis purity of  $\geq 95$  vol%.

In Budget Period 1, GO-based membranes were successfully scaled up to an effective area of 50-100 cm<sup>2</sup>. The GO-1 membranes showed a CO<sub>2</sub>/N<sub>2</sub> selectivity  $\geq 200$  and a CO<sub>2</sub> permeance  $\geq 1,000$  GPU (GPU: Gas permeation Unit; 1 GPU =  $1 \times 10^{-6}$  cm<sup>3</sup>(STP) cm<sup>-2</sup> s<sup>-1</sup> cm Hg<sup>-1</sup> =  $3.348 \times 10^{-10}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>). The GO-2 membranes showed a CO<sub>2</sub>/N<sub>2</sub> selectivity  $\geq 20$  and a CO<sub>2</sub> permeance  $\geq 2,500$  GPU.

In Budget Period 2, the GO-based membranes were further scaled up to 1,000 cm<sup>2</sup>. Simultaneously, a bench-scale GO<sup>2</sup> skid was designed, constructed, and initially tested at GTI Energy's laboratory using simulated coal-fired flue gas. After validating the performance of the GO<sup>2</sup> skid, the skid was shipped to NCCC for further testing.

This report focuses on the field test results obtained at NCCC. The main activities conducted at NCCC included the following:

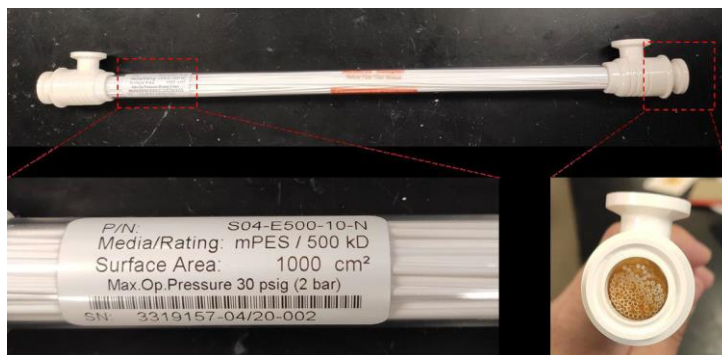
- Installing the GO<sup>2</sup> skid and conducting commissioning testing.
- Performing parametric tests to determine the optimal operational conditions for long-term steady-state operation.
- Completing a single-stage steady-state test for  $\geq 200$  hours.
- Completing a two-stage steady-state test for  $\geq 200$  hours, gathering essential data for further process scale-up.

### 3. Experimental

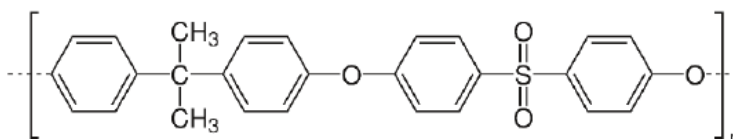
#### 3.1 Membrane Materials

##### 3.1.1 Polyether Sulfone Substrate

The commercially available polyether sulfone (PES) substrate used in the membrane preparation is shown in Figure 2, featuring a surface area of 1,000 cm<sup>2</sup>. The structural composition of PES is shown in Figure 3.



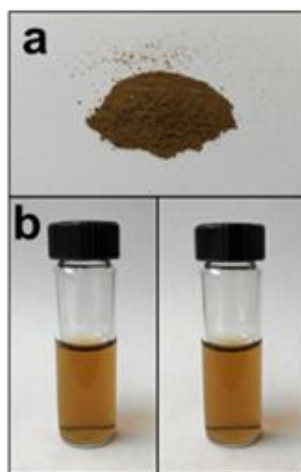
**Figure 2.** Photographs of PES substrate.



**Figure 3.** Structural composition of PES.

##### 3.1.2 Graphene Oxide Quantum Dots

Figure 4a shows the dark yellow color of the graphene oxide quantum dots (GOQDs) powder, while Figure 4b shows the GOQDs in a water solution. The super hydrophilic properties of the GOQDs facilitate the formation of a well-dispersed and stable suspension.

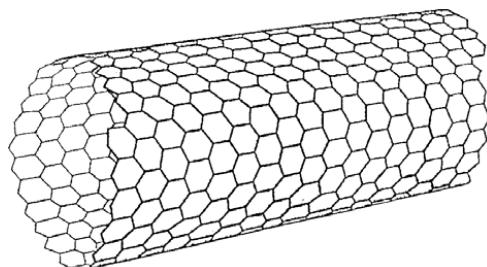


**Figure 4.** Photographs of GOQDs powder and solution.



### 3.1.3 Single-Wall Carbon Nanotubes

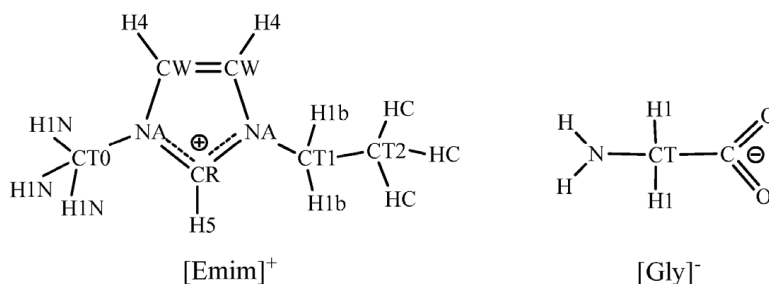
Single-wall carbon nanotubes (SWCNTs) have been extensively investigated for membrane fabrication, both as free-standing membranes and as inorganic fillers in mixed matrix membranes, due to their porous structure and exceptional mechanical properties. The structure of SWCNTs is shown in Figure 5.



**Figure 5.** Structure of SWCNTs.

### 3.1.4 Ionic Liquid

Ionic liquids, known for their low vapor pressure, high thermal and chemical stability, and excellent CO<sub>2</sub> affinity, were employed as a promising membrane material. Specifically, the ionic liquid [EMIM][GLY], was used in the preparation of GO-based membranes, and its structure is shown in Figure 6.



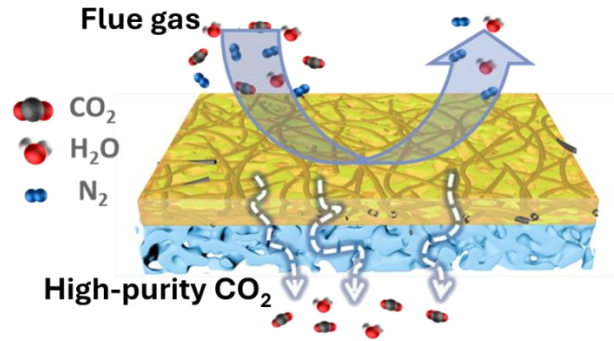
**Figure 6.** Structure of ionic liquid [EMIM][GLY].

## 3.2 Membrane Preparation

For the preparation of GO-based membranes, an ultrathin layer of SWCNTs is deposited onto a PES substrate, serving as the structural skeleton. Subsequently, a mixture of GOQDs and ionic liquid is infiltrated into the nanomaterials skeleton layer using a vacuum-assisted deposition method. Following infiltration, heat treatment is applied to promote the formation of a dense and uniform layer, optimizing the structure for efficient gas separation. Note that the GO-1 and GO-2 membranes were made using the same materials, but they differ in the amounts of SWCNTs and ionic liquid used, resulting in different gas permeation properties.

Figure 7 shows the membrane structure scheme, where the blue section indicates the structural skeleton, and the yellow section represents the dense layer of GOQDs and ionic liquid. Under a transmembrane pressure difference, CO<sub>2</sub> molecules from the feed side react with CO<sub>2</sub> carriers within the selective layer. The resulting reaction products then diffuse across the membrane and revert to CO<sub>2</sub> molecules through a reverse reaction, ultimately being released to the low-

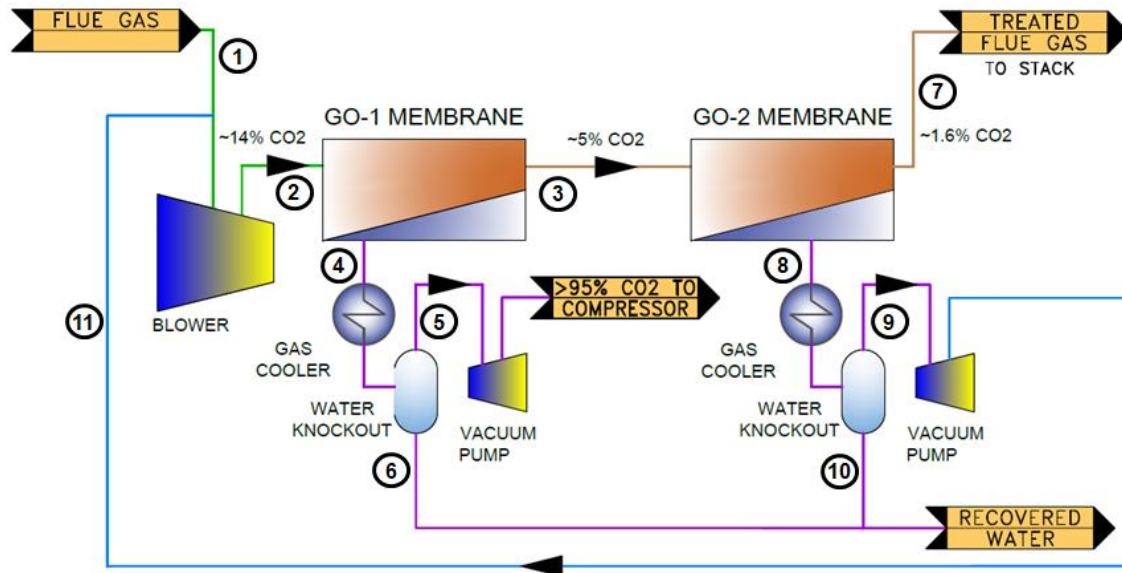
pressure side. In contrast, the permeation of nitrogen is relatively sluggish due to limited molecular diffusion and the absence of reactive diffusion.



**Figure 7.** Structure of the GO-based membrane.

### 3.3 GO<sup>2</sup> Skid

The process flow diagram of the GO<sup>2</sup> process is shown in Figure 8. In this setup, a blower boosts the pressure of the incoming flue gas before it enters the GO-1 membrane. On the permeate side, a vacuum pump maintains a vacuum of 0.1 bara to 0.2 bara. Due to the high water permeability of the GO-based membranes, water vapor from the flue gas permeates through the membrane, lowering the partial pressure of CO<sub>2</sub> on the permeate side. The applied vacuum provides sufficient driving force for CO<sub>2</sub> permeation. The CO<sub>2</sub>-depleted residue exiting the GO-1 membrane is directed to the GO-2 membrane, which also uses a vacuum on the permeate side to enhance separation. The permeate from the GO-2 membrane is cooled down to recover water, and the dried permeate is subsequently recycled to the feed side of the GO-1 membrane. The treated flue gas exiting the GO-2 membrane is sent to the stack. The CO<sub>2</sub>-enriched permeate from the GO-1 membrane is cooled to remove most of the water. In the commercial embodiment, the remaining non-condensable stream would be compressed and sent for sequestration. In this GO<sup>2</sup> process, the GO-1 membrane functions as a high-selectivity membrane, whereas the GO-2 membrane functions as a high-flux membrane, optimizing the efficiency of CO<sub>2</sub> capture.



**Figure 8.** Process flow diagram of the GO<sup>2</sup> process for CO<sub>2</sub> capture.

Figure 9 shows the setup of the integrated GO<sup>2</sup> skid at NCCC's Lab-Scale Testing Unit (LSTU). A slipstream of flue gas from the natural gas boiler was directed to the skid as the feed gas. Pure CO<sub>2</sub> and N<sub>2</sub> were mixed with natural gas boiler flue gas to create simulated coal-fired flue gas. Utility connections, including demineralized water, electricity, and analytical gases for gas chromatography (GC) analysis, were established. Additionally, NCCC electricians ensured that all equipment was properly grounded. The system was equipped with a 1,000 cm<sup>2</sup> GO-1 membrane as the first stage, followed by a 75 cm<sup>2</sup> GO-2 membrane as the second stage. A commissioning test was subsequently conducted to confirm that the skid was operating correctly.



**Figure 9.** GO<sup>2</sup> skid installed in NCCC's LSTU lab.

### 3.4 Simulation of Coal-Fired Flue Gas via CO<sub>2</sub> and N<sub>2</sub> Blending at NCCC

This project was initially intended to test coal-fired flue gas. However, due to the unpredictable availability of coal-fired flue gas at NCCC, an alternative approach was implemented. NCCC can provide natural gas boiler flue gas, which is diluted with air to reach a CO<sub>2</sub> concentration of approximately 4.5 vol% (dry basis). After discussions with DOE, a decision was made to inject pure CO<sub>2</sub> and N<sub>2</sub> into the diluted natural gas boiler flue gas to create simulated coal-fired flue gas. The gas compositions of NCCC's natural gas boiler flue gas and the simulated coal-fired flue gas are shown in Table 1.

**Table 1.** Composition of NCCC's diluted natural gas boiler flue gas and simulated coal-fired flue gas.

Gas	NCCC diluted natural gas boiler flue gas	Simulated coal-fired flue gas
CO <sub>2</sub>	~4.5 vol%	12.5 vol%-13 vol%
O <sub>2</sub>	~13.5 vol%	3.3 vol%-7.5 vol%
SO <sub>2</sub>	< 1 ppm	<1 ppm
NO <sub>2</sub>	2-3 ppm	1.1-1.7 ppm
H <sub>2</sub> O	None	80-90% saturation
N <sub>2</sub>	Balance	Balance

### 3.5 Gas Separation Performance Measurement at NCCC

Gas mixture separation tests were conducted to evaluate the CO<sub>2</sub> separation performance of the GO-based membranes using the GO<sup>2</sup> skid. The gas permeance, defined as the pressure normalized flux, was calculated using Equation 1:

$$P_i = \frac{J_i}{\Delta P_i} \quad (1)$$

Where  $P_i$  is the permeance of gas species  $i$ ,  $J_i$  is the flux of gas species  $i$ , and  $\Delta P_i$  is partial pressure difference of gas species  $i$  between feed and permeate sides. The flux of each gas species was calculated based on its composition, as measured by GC analysis, and the total gas mixture flow rate on the permeate side. The perm-selectivity, defined as the ratio of the permeance of two different gas species, was calculated using Equation 2:

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad (2)$$

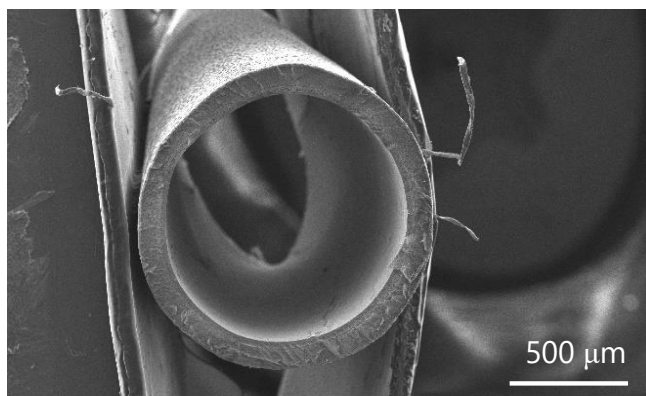
Where  $i$  and  $j$  represent different gas species.

## 4. Results and Discussion

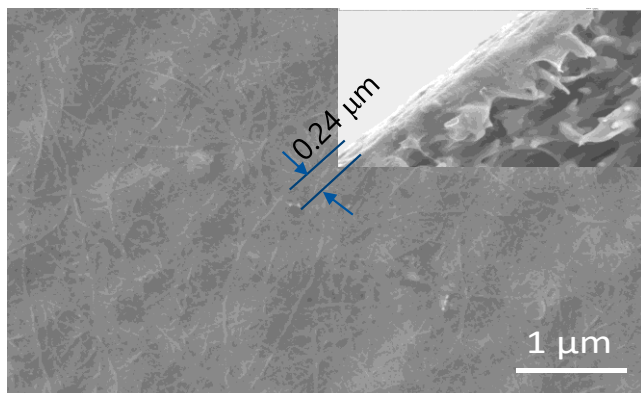
### 4.1 Membrane Properties

#### 4.1.1 Scanning Electron Microscope

The surface and cross-sectional morphologies of the membranes were characterized using a Carl Zeiss AURIGA Cross-Beam Focused Ion Beam Scanning Electron Microscope (FIB-SEM). Cross-sectional SEM images were obtained by freeze-fracturing samples in liquid nitrogen, preserving their microstructure. Figure 10 shows an SEM image of the PES hollow fiber substrate, revealing an inner diameter of 1 mm. The surface SEM image of the GO-based membrane (Figure 11) indicates the quality of membrane coating, showing a smooth and defect-free GO layer with no visible holes or cracks. The cross-sectional SEM image, also shown in Figure 11, reveals a thin membrane layer with an approximate thickness of 0.24  $\mu\text{m}$ .



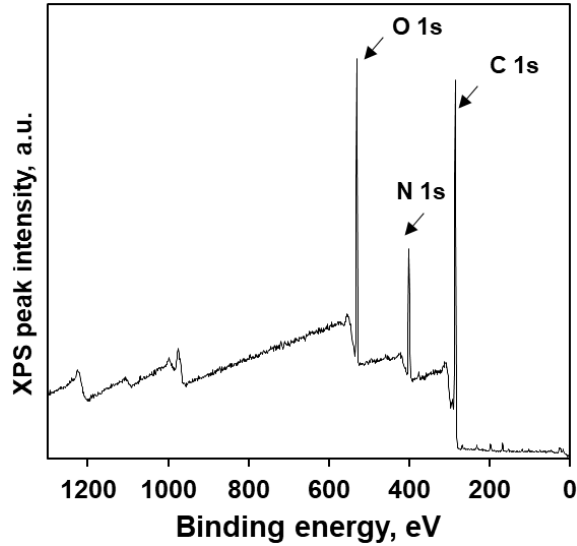
**Figure 10.** SEM image of hollow fiber PES substrate.



**Figure 11.** Surface and cross-sectional (inserted) SEM images of GO-based membrane.

#### 4.1.2 X-ray Photoelectron Spectroscopy

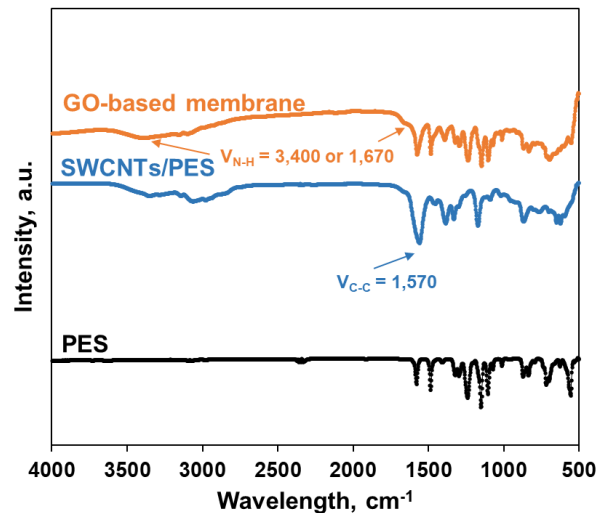
The surface chemistry and composition of the membranes were analyzed using X-ray photoelectron spectroscopy (XPS). As shown in Figure 12, XPS characterization confirmed the successful incorporation of ionic liquid into the GO-based membrane. An intensified nitrogen XPS characteristic peak around 400 eV was observed in the [EMIM][GLY] loaded membrane, which is attributed to the nitrogen introduced by the imidazole and amine functional groups in the ionic liquid.



**Figure 12.** XPS spectra of GO-based membrane.

#### 4.1.3 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) characterization revealed intensified peaks at  $3,400\text{ cm}^{-1}$  and  $1,670\text{ cm}^{-1}$  in the GO-based membrane compared to the plain PES substrate and SWCNTs loaded PES membrane, as shown in Figure 13. These peaks correspond to the primary and secondary amines and the C-N bond from  $[\text{GLY}]^{-}$  anion, indicating the successful incorporation of the ionic liquid into SWCNTs mesh.



**Figure 13.** FTIR spectra of PES substrate, SWCNTs/PES, and GO-based membrane.

#### 4.2 Membranes QA/QC Testing

GO-1 membranes were prepared, followed by quality assurance/quality control (QA/QC) testing. The membranes were tested using a simulated flue gas composed of 10.0 vol%  $\text{CO}_2$ , 28.1 vol%  $\text{H}_2\text{O}$ , 5.0 vol%  $\text{O}_2$ , and balance  $\text{N}_2$ . The feed side and permeate side pressures were set at 1 bara and 0.15 bara, respectively. Under these conditions, the membranes exhibited consistent  $\text{CO}_2$

capture performance, as shown in Table 2, indicating good reproducibility in both membrane quality and performance.

**Table 2.** Performance of GO-1 membranes.

Membrane #	CO <sub>2</sub> capture efficiency, %	CO <sub>2</sub> dry-basis purity, vol%
1	40.2	96.5
2	44.1	95.5
3	46.5	97.4
4	41.5	96.4

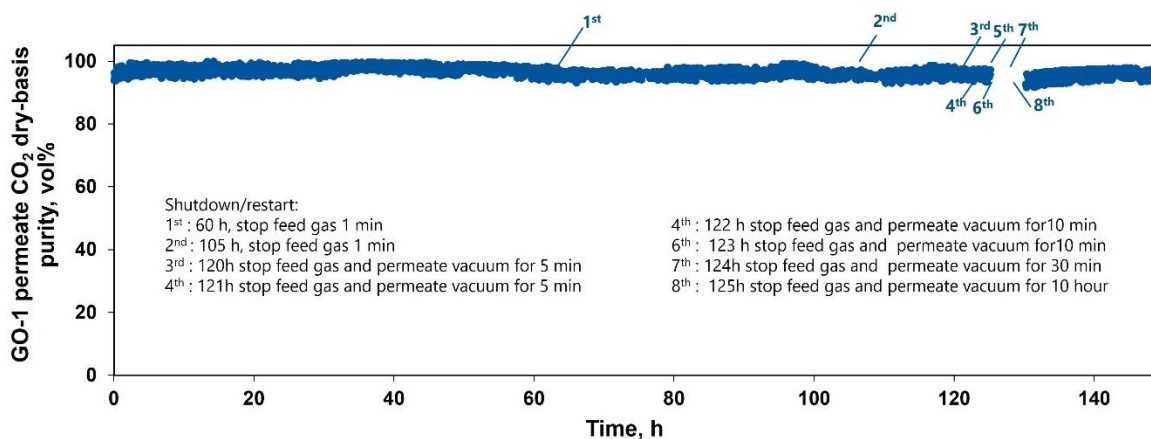
GO-2 membranes were also fabricated, followed by QA/QC testing. The test results are summarized in Table 3. The feed gas for the GO-2 membrane consisted of 4.8 vol% CO<sub>2</sub>, 13.5 vol% H<sub>2</sub>O, and balance N<sub>2</sub>, closely matching the retentate gas composition of the GO-1 membrane. The feed side and permeate side pressures were maintained at 1 bara and 0.15 bara, respectively. These conditions reflect the operational parameters used to evaluate the performance of the GO-2 membrane.

**Table 3.** Performance of GO-2 membranes.

Membrane #	CO <sub>2</sub> capture efficiency, %	CO <sub>2</sub> wet-basis purity, vol%
1	45	25
2	47	29

### 4.3 Validation Testing of the Bench Scale System at GTI Energy

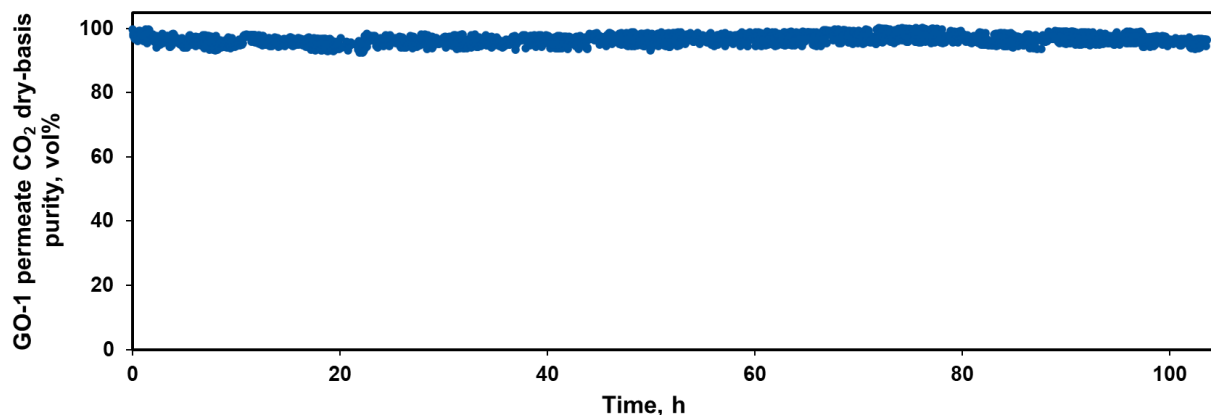
A stability test was conducted for the GO-1 membrane using a simulated flue gas mixture composed of 15.0 vol% CO<sub>2</sub>, 24.1 vol% H<sub>2</sub>O, and balance N<sub>2</sub>. The feed side and permeate side pressures were maintained at 1.2 bara and 0.15 bara, respectively, with an operating temperature of 65°C. Throughout the test, the membrane underwent eight shutdown/startup cycles. As shown in Figure 14, the CO<sub>2</sub> dry-basis purity on the permeate side remained stable during the 150-hour testing period, indicating the membrane’s robust performance under cyclic operation and extended testing conditions.



**Figure 14.** Long-term testing of a 1,000 cm<sup>2</sup> GO-1 membrane with eight shutdowns/startups.



A 100-hour integrated test was conducted using one 1,000 cm<sup>2</sup> GO-1 membrane and three 75 cm<sup>2</sup> GO-2 membranes with simulated coal-fired flue gas. As shown in Figure 15, the CO<sub>2</sub> dry-basis purity on the GO-1 permeate side stabilized at approximately 96 vol% during the test period while achieving a CO<sub>2</sub> capture efficiency of 71%. These results indicate the system's effectiveness in achieving high CO<sub>2</sub> purity and consistent capture performance under integrated operation conditions.



**Figure 15.** Long-term testing of the integrated system using simulated coal-fired flue gas.

#### 4.4 Parametric Testing of the GO<sup>2</sup> Skid at NCCC

Following the completion of the skid commissioning at NCCC, parametric testing was conducted using simulated coal-fired flue gas. This gas mixture comprised 12.5 vol%-13.0 vol% CO<sub>2</sub>, 3.3 vol%-7.5 vol% O<sub>2</sub>, was 80%-90% water-saturated, and balance N<sub>2</sub>. SO<sub>2</sub> levels were maintained below 1 ppm, while NO<sub>2</sub> concentrations were kept between 1.1 and 1.7 ppm.

Firstly, the effect of feed flow rate on CO<sub>2</sub> capture performance was investigated. The tests were conducted at an operating temperature of 65°C, with the feed and permeate side pressures set at 1.2 bara and 0.15 bara, respectively. The CO<sub>2</sub> concentration was 15.0 vol% on a dry basis. The results are summarized in Table 4. As the feed flow rate decreased, a slight decline in CO<sub>2</sub> dry-basis purity was observed, while the CO<sub>2</sub> capture efficiency showed a significant increase. At a feed flow rate of 0.8 L/min, a CO<sub>2</sub> capture efficiency of 90.6% and a CO<sub>2</sub> dry-basis purity of 96.2 vol% were achieved. The permeate stream contains 3.0 vol% N<sub>2</sub> and 0.8 vol% O<sub>2</sub>. To meet the oxygen purity specification for the CO<sub>2</sub>, a further purification step (e.g. liquefaction and distillation) will be needed to decrease the oxygen concentration to be below 10 ppmv.

**Table 4.** Effect of feed flow rate on CO<sub>2</sub> capture performance.

Test #	Feed flow rate, L/min	CO <sub>2</sub> capture efficiency, %	CO <sub>2</sub> dry-basis purity, vol%
1	1.5	75.8	97.4
2	1.0	83.9	96.8
3	0.9	87.2	96.6
4	0.8	90.6	96.2

The effect of operating temperature on CO<sub>2</sub> capture performance was also investigated. The operating temperatures were 57°C, 60°C and 65°C. As shown in Table 5, the CO<sub>2</sub> capture



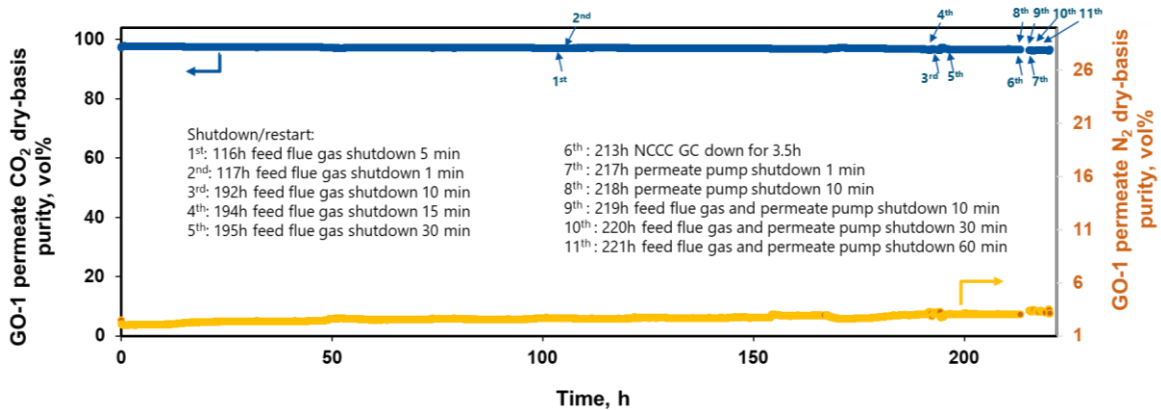
efficiency increased with rising temperature, while the CO<sub>2</sub> dry-basis purity remained above 96 vol% throughout the temperature range tested.

**Table 5.** Effect of operating temperature on CO<sub>2</sub> capture performance.

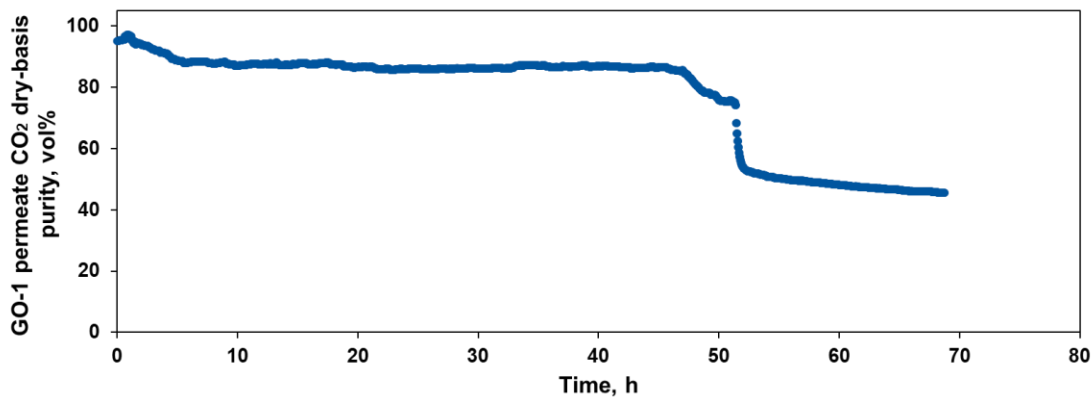
Test #	Operating temperature, °C	CO <sub>2</sub> capture efficiency, %	CO <sub>2</sub> dry-basis purity, vol%
1	57	66.9	96.4
2	60	78.9	96.6
3	65	83.9	96.8

#### 4.5 Long-term Testing at NCCC

A long-term, single-stage test over 220 h was conducted using a 1,000 cm<sup>2</sup> GO-1 membrane at 50°C. The feed flue gas contained dry-basis concentrations of 16.0 vol% CO<sub>2</sub> and 4.5 vol% O<sub>2</sub>, with the feed and permeate pressures set at 1.06 bara and 0.15 bara, respectively. The test results are shown in Figure 16. Initially, a CO<sub>2</sub> capture efficiency of 47.0% and a CO<sub>2</sub> dry-basis purity of 98.0 vol% were achieved. Throughout the test, the CO<sub>2</sub> dry-basis purity consistently remained at 98.0 vol%. Notably, the membrane underwent eleven shutdowns and startups during the testing period, indicating its robustness under operational fluctuations.



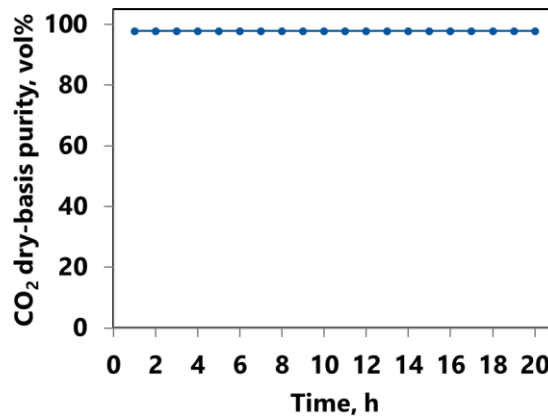
**Figure 16.** Single-stage long-term testing results at NCCC.



**Figure 17.** Integrated testing results at NCCC.

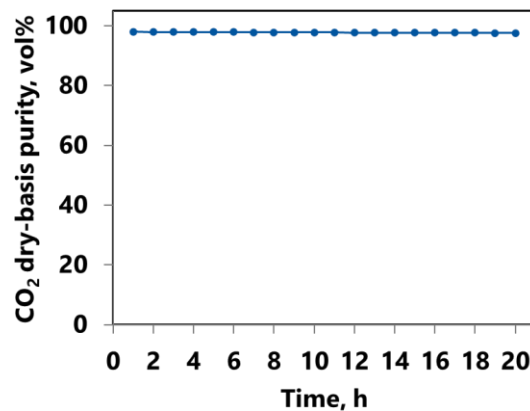
An integrated test was conducted at NCCC using one 1,000 cm<sup>2</sup> GO-1 membrane and one 75 cm<sup>2</sup> GO-2 membrane at 50°C. The feed flue gas contained dry-basis concentrations of 16.0 vol% CO<sub>2</sub> and 4.0 vol% O<sub>2</sub>, with the feed and permeate pressures set at 1.06 bara and 0.15 bara, respectively. The test results are shown in Figure 17. Initially, a CO<sub>2</sub> capture efficiency of 75.4% and a CO<sub>2</sub> dry-basis purity of 98.0 vol% were achieved. However, as the testing time increased, the CO<sub>2</sub> dry-basis purity gradually declined, eventually dropping to 43.0 vol% at 68 hours.

Upon investigation in the lab, it was determined that the decline in performance was due to improper storage of the ionic liquid, which led to its degradation. To address this issue, a new batch of ionic liquid was procured, and a new 1,000 cm<sup>2</sup> GO-1 membrane was prepared using this freshly acquired ionic liquid. This newly prepared membrane was tested at 70°C with a simulated coal-fired flue gas composed of 11.9 vol% CO<sub>2</sub>, 20.8 vol% H<sub>2</sub>O, 5.0 vol% O<sub>2</sub> and balance N<sub>2</sub>. The test was conducted under a feed pressure of 1.0 bara and a permeate side pressure of 0.15 bara. The membrane maintained a stable CO<sub>2</sub> dry-basis purity of 97.0 vol% over a period of 20 hours (Figure 18), indicating good stability and performance of this membrane.



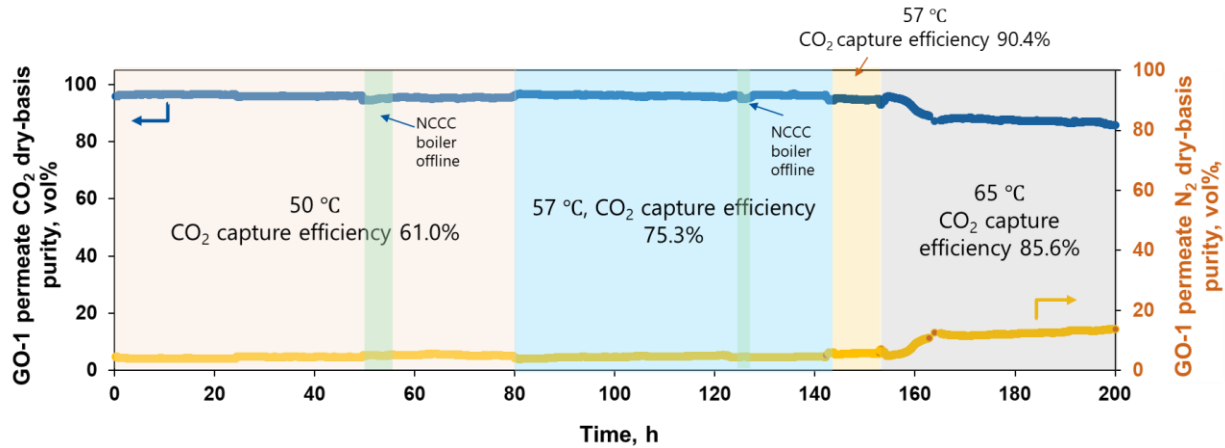
**Figure 18.** Testing results of 1,000 cm<sup>2</sup> GO-1 membrane using new ionic liquid.

To confirm the results and ensure reproducibility, an additional 1,000 cm<sup>2</sup> GO-1 membrane was prepared using this freshly acquired ionic liquid. This membrane was tested under the same conditions as the previous one. Figure 19 shows that this membrane also maintained a stable CO<sub>2</sub> dry-basis purity of 97.0 vol% over a period of 20 hours, confirming both the good stability and reproducibility of the membrane.



**Figure 19.** Testing results of repeated 1,000 cm<sup>2</sup> GO-1 membrane using new ionic liquid.

An additional integrated test was conducted at NCCC using a 1,000 cm<sup>2</sup> GO-1 membrane and a 75 cm<sup>2</sup> GO-2 membrane. The feed flue gas contained dry-basis concentrations of 16.0 vol% CO<sub>2</sub> and 4.0 vol% O<sub>2</sub>, with feed and permeate side pressures of 1.06 bara and 0.15 bara for both the GO-1 and GO-2 membranes. The results are shown in Figure 20.



**Figure 20.** Repeated integrated testing results at NCCC.

Initially, at an operating temperature of 50°C, the system achieved a stable CO<sub>2</sub> capture efficiency of 61.0 % and a CO<sub>2</sub> dry-basis purity of 96.0 vol% for over 80 hours. When the operating temperature was increased to 57°C, the CO<sub>2</sub> capture efficiency improved to 75.3%, while the CO<sub>2</sub> dry-basis purity remained at 96.0 vol% for 63 hours. Subsequently, reducing the feed flow rate between 145 and 153 hours resulted in a significant increase in CO<sub>2</sub> capture efficiency to 90.4%, with a CO<sub>2</sub> dry-basis purity of 95.6 vol%, successfully meeting the project targets of over 90.0% efficiency and 95.0 vol% dry-basis purity. Finally, at an elevated temperature of 65°C, the CO<sub>2</sub> capture efficiency was recorded at 85.6%, although CO<sub>2</sub> dry-basis purity dropped to 83.0 vol%. Overall, the membranes indicated good stability at both 50°C and 57°C, achieving a CO<sub>2</sub> capture efficiency ranging from 70% to 90% and validating that a CO<sub>2</sub> dry-basis purity greater than 95.0 vol% is achievable.

## 5. Summary

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- GTI and UB have developed a transformational graphene oxide-based membrane process for post-combustion CO<sub>2</sub> capture.
- GO-based membranes were successfully scaled to 1,000 cm<sup>2</sup> surface area. Good stability was achieved during an integrated testing with GO-1 and GO-2 membranes using simulated flue gas.
- A bench-scale system was designed, constructed, and tested at NCCC.
- Good stability was achieved during testing of a single-stage process with > 10 shutdowns/startups at NCCC.
- During the integrated testing, the membranes showed good stability at 50°C and 57°C. 70-90% CO<sub>2</sub> removal efficiencies and ≥95% CO<sub>2</sub> purity were validated during the steady state operation at NCCC.

## 6. Reference

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- [1] H. Li et al., Ultrathin, Molecular-Sieving Graphene Oxide Membranes for Selective Hydrogen Separation. *Science*, 342, 95-98 (2013).
- [2] F. Zhou et al., Ultrathin graphene oxide-based hollow fiber membranes with brush-like CO<sub>2</sub>-philic agent for highly efficient CO<sub>2</sub> capture. *Nature Communications*, 8, 2107 (2017).
- [3] F. Zhou et al., Ultrathin, ethylenediamine-functionalized graphene oxide membranes on hollow fibers for CO<sub>2</sub> capture. *Journal of Membrane Science*, 573, 184-191 (2019).
- [4] F. Zhou et al., Novel carbon-based separation membranes composed of integrated zero- and one-dimensional nanomaterials. *Journal of Materials Chemistry A*, 8, 1084-1090 (2020).
- [5] F. Zhou et al., Printed graphene oxide-based membranes for gas separation and carbon capture. *Chemical Engineering Journal*, 430, 132942, (2022).
- [6] D. Behera et al., A facilitated transport membrane composed of amine-containing ionic liquid confined in a GO/CNT network for highly efficient carbon capture. *Journal of Membrane Science*, 712, 123177 (2024).
- [7] H. Li, et al., Ultra-selective membrane composed of charge-stabilized fixed carrier and amino acid-based ionic liquid mobile carrier for highly efficient carbon capture. *Chemical Engineering Journal*, 453, 139780, (2023).
- [8] H. Li, et al., Two-stage membrane-based process utilizing highly CO<sub>2</sub>-selective membranes for cost and energy efficient carbon capture from coal flue gas: A process simulation study. *Journal of Membrane Science*, 669, 11259, (2023).

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## 8. List of Acronyms

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<b>Acronym</b>	<b>Description</b>
CCP4	Carbon Capture Project Phase 4
COE	Cost of electricity
DOE	Department of Energy
FIB-SEM	Focused Ion Beam Scanning Electron Microscope
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GO	Graphene oxide
GOQDs	Graphene oxide quantum dot
GPU	Gas permeation unit
h	Hour
LSTU	Lab-Scale Testing Unit
NCCC	National Carbon Capture Center
PC	Pulverized coal
PES	Polyether sulfone
QA/QC	Quality assurance/quality control
SWCNTs	Single-wall carbon nanotube
UB	The State University of New York at Buffalo
XPS	X-ray photoelectron spectroscopy

**END OF REPORT**