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Demonstration of high-performance CO_2-selective graphene membranes for energy-efficient carbon capture

EfficientCapture

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Zusammenfassung

Die erfolgreiche Umsetzung des vom Schweizer Bundesrat festgelegten Null-Emissionsziels erfordert eine rasche Entwicklung einer energieeffizienten Technologie zur CO2-Abscheidung. Dieses Projekt baut auf der neuartigen zweidimensionalen (2D) Membrantechnologie der EPFL auf, bei der ein atomar dicker, poröser Graphenfilm als CO2-selektive Schicht verwendet wird. Das Projekt zielt darauf ab, die Technologie zu vergrössern (Membran im Metermassstab) und die Abscheidung von 10 kg CO2/Tag zur Reinigung von Rauchgas und Biogas zu demonstrieren.

Im ersten Jahr des Projekts haben wir erfolgreich einen hochskalierten Reaktor in Betrieb genommen, der in der Lage ist, eine Graphenschicht im Metermaßstab in einer einzigen Charge zu synthetisieren. Der Reaktor kann eine kontrollierte Oxidation von Graphen durchführen, um hochdichte Poren im Å-Maßstab für die CO2-Abscheidung zu bilden. Außerdem haben wir Polymerbeschichtungssysteme zur mechanischen Verstärkung von großflächigem Graphen in Betrieb genommen und validiert. Wir haben ein neuartiges Modul für 2D-Membranen entwickelt und dabei die Konzentrationspolarisation und die Druckabfall-Effekte optimiert. Wir haben Modulprototypen mit zunehmendem Maßstab (10 cm2, 100 cm2) hergestellt und erfolgreiche Dichtungsmembranen hergestellt. Schließlich haben wir den Membranprozess optimiert, um eine CO2-Reinheit von 98 % zu erreichen, die die Integration eines nachgeschalteten CO2-Umwandlungsprozesses ermöglicht.

Résumé

Pour atteindre l'objectif de zéro émission fixé par le Conseil fédéral suisse, il faut développer rapidement une technologie de capture du carbone efficace sur le plan énergétique. Ce projet s'appuie sur la nouvelle technologie de membrane bidimensionnelle (2D) de l'EPFL, qui utilise un film de graphène poreux de l'épaisseur d'un atome comme couche sélective du CO2. Le projet vise à mettre à l'échelle la technologie (membrane à l'échelle du mètre) et à démontrer la capture de 10 kg de CO2/jour pour nettoyer les gaz de combustion et purifier le biogaz.

Au cours de la première année du projet, nous avons mis en service avec succès un réacteur à grande échelle capable de synthétiser un film de graphène à l'échelle du mètre en un seul lot. Le réacteur peut effectuer une oxydation contrôlée du graphène pour former des pores de haute densité à l'échelle Å pour la séparation du CO2. Nous avons également mis en service et validé des systèmes de revêtement en polymère pour renforcer mécaniquement le graphène sur de grandes surfaces. Nous avons développé un nouveau module pour la membrane 2D tout en optimisant la polarisation de la concentration et les effets de chute de pression. Nous avons fabriqué des prototypes de modules à échelle croissante (10 cm2, 100 cm2) et avons réalisé avec succès des membranes d'étanchéité. Enfin, nous avons optimisé le processus membranaire pour obtenir une pureté de CO2 de 98 % et permettre l'intégration d'un processus de conversion du CO2 en aval.

Summary

A successful realization of the zero-emission target set by the Swiss Federal Council requires a rapid development of energy-efficient carbon capture technology. This project builds up on the EPFL's novel two-dimensional (2D) membrane technology using atom-thick, porous graphene film as CO_2-selective layer. The project aims to scale-up the technology (meter-scale membrane) and demonstrate capture of 10 kg CO_2/day to clean flue gas and purify biogas.

In the first year of the project, we have successfully commissioned a scaled-up reactor capable of synthesizing meter-scale graphene film in a single batch. The reactor can carry out controlled oxidation

of graphene to form high-density Å-scale pores for CO_2 separation. We have also commissioned and validated polymer coating systems to mechanically reinforce large area graphene. We have developed a novel module for 2D membrane while optimizing concentration polarization and pressure drop effects. We have fabricated module prototypes with increasing scale (10 cm^2, 100 cm^2) and have carried out successful sealing membranes. Finally, we have optimized the membrane process to yield CO_2 purity of 98% to allow the integration of downstream CO_2 conversion process.

Contents

Abbreviations

2D: Two-dimensional

CVD: Chemical Vapor Deposition

GPU: Gas permeation unit (1 GPU = 3.35×10^{-10} mol m^{-2} s^{-1} Pa^{-1})

SLG: Single-layer graphene

NSLG: Nanoporous single-layer graphene

1 Introduction

1.1 Background information and current situation

The sixth assessment report by the Intergovernmental Panel on Climate Change highlights the necessity to restrict the global temperature rise to within 1.5 ºC from the pre-industrial levels, which requires the reduction of CO_2 emissions from industrial point sources as well as atmosphere (negative emission).[1]

Among the point sources, power plants are the largest emitters with CO_2 concentration in flue gas amounting to 7-14%. There is also an intrinsic need to remove CO_2 from the raw biogas (with CO_2 concentration near 45%) which has started to play an important role in the Swiss gas grid. The captured CO_2 can be then converted into CH_4 using renewable electricity. This can be added to the gas grid leading to a reduction of overall carbon emission. Naturally, for the successful implementation of capture while realizing energy needs of Switzerland, the development and deployment of energy- and cost-efficient capture technology is of paramount importance.

The need for energy-efficient technology comes from high cost of capture from the currently commercially available technology which is based on absorption of CO_2 in amine-based solvent. Here, the high cost (>CHF 50-110/ton$_{CO2}$) mainly arises from the requirement to regenerate liquid amines by thermal treatment. [2] High-performance-membrane-based capture processes can cut down the capture penalty because they do not rely on the expensive thermal energy but instead on the electrical energy (compression/vacuum) to create a concentration gradient across the membrane. The current membrane-based capture technology is based on the dense polymeric films as the selective layer. The state-of-the-art polymeric films have shown promising CO_2/N_2 performance.[3] However, there is an opportunity (i) to significantly improve separation performance especially the CO_2 permeance which affects the needed membrane area and, therefore, the capital cost, and (ii) to improve the operational life of the membranes. Thermally and chemically stable nanoporous inorganic material based selective layer has an intrinsic advantage of high CO_2 permeance and improved thermal and chemical stability.

The Laboratory of Advanced Separations (LAS) at EPFL has developed extremely thin nanoporous inorganic film, composed of an atom-thick porous graphene layer for high-performance carbon capture. We have demonstrated record-high carbon capture performance with CO_2 permeance reaching 10000 GPU and CO_2/N_2 and CO_2/CH_4 selectivities reaching 30 and 20, respectively. The CO_2 permeance, which determines the needed membrane area, is an order of magnitude better than that from commercial membranes. Our laboratory has been producing centimeter-scale coupons of NSLG membranes (technology readiness of 4-5).

1.2 Purpose of the project

Our technoeconomic analysis indicates that a double stage membrane module fitted with high-performance graphene membranes with only a small membrane area of 0.4 m^2 is sufficient for capturing 10 kg$_{CO2}$/day (our target rate) in an energy-efficient manner with capture penalty in the range of 30-40 CHF/ton$_{CO2}$.[4] Given the high potential of this technology in addressing the important issue of global warming, its further scale-up and demonstration is attractive. Therefore, the project will seek to scale-up the production of nanoporous graphene films, membrane elements and membrane modules. Subsequently, the project will build two-stage membrane process to capture CO_2 from flue gas and biogas with the help of our industrial collaborators.

1.3 Objectives

This project aims to scale-up porous graphene films hosting Å-scale pores for gas separation to meter-scale. The project then intends to develop membrane element and module using graphene film as selective layer. The membrane will be implemented in two-stage membrane process to capture CO_2 at the rate of 10 kg/day from flue gas and biogas.

Overall, by testing high-performance membranes, we aim to validate the analysis from our technoeconomic analyses:

Feed Condition	Recovery	Purity	Specific Energy Demand ($GJ/tonCO_2$)	Capture Cost ($/tonCO_2$)	Membrane Lifespan (year)
Flue gas (12% CO_2)	90% CO_2	90% CO_2	1.5	41	5
Biogas (45% CO_2)	96% CO_2, 91% CH_4	90% CO_2, 96% CH_4	0.7	38	5

Our specific objectives are:

1. Scale-up production of high-performance graphene membranes (target area 1 m^2) using intrinsically-scalable fabrication methods that are capable of yielding m^2 graphene membranes in a single synthesis batch.

2. Develop compact plate and frame membrane modules that have low volume footprint and high packing density (100-300 m^2/m^3) but low pressure drop while avoiding concentration polarization.

3. Build membrane skids consisting of double stage membrane process with recycle, and demonstrate its efficacy for capturing 10 kg CO_2 from two distinct sources (biogas and waste incineration) with recovery of 90% and purity of 90% for flue gases. In the case of biogas, demonstrate purification of biogas to achieve CH_4 concentration of 96% by the double-stage membrane process.

4. Demonstrate membrane stability by continuous online monitoring the performance data.

2 Description of facility

As a part of the project, we have built a dedicated scale-up laboratory to produce high-quality films in clean environment. The equipment includes a homemade reactor to produce porous graphene at meter-scale allowing CVD and oxidation of graphene within the same reactor (Figure 1). The CVD system contains a 2 m long, 20 cm in diameter quartz tube and consists of mechanical support, concentric alumina tube (to prevent silica contamination from quartz tube), radiation shield, and automated control and pumping system (Figure 2). The corresponding process flow diagram is shown in Figure 3.

Figure 1: The membrane scale-up laboratory at EPFL

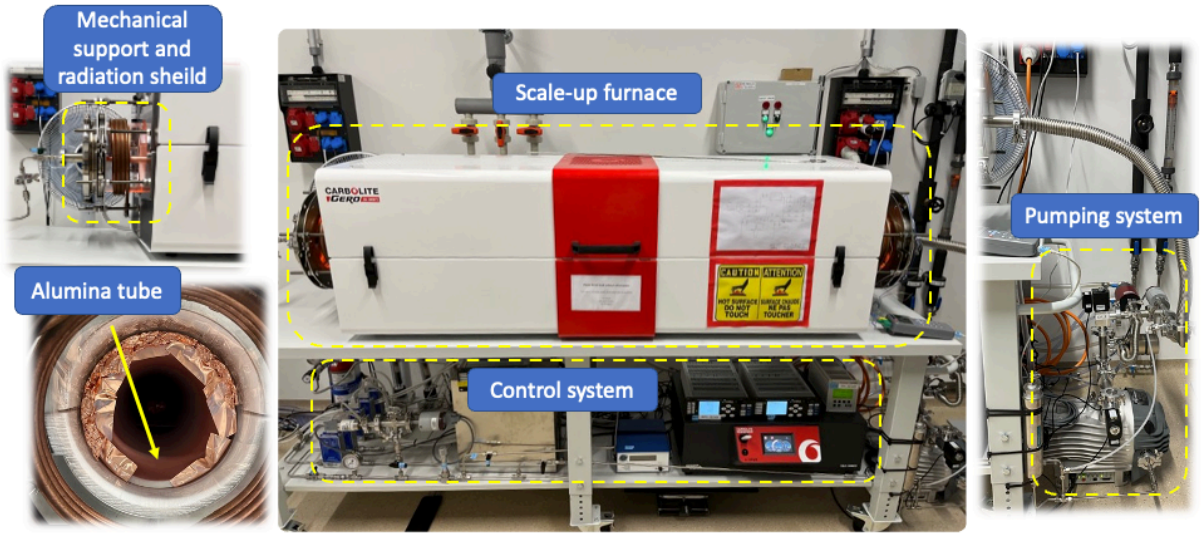

Figure 2: Large-scale CVD furnace for graphene synthesis.

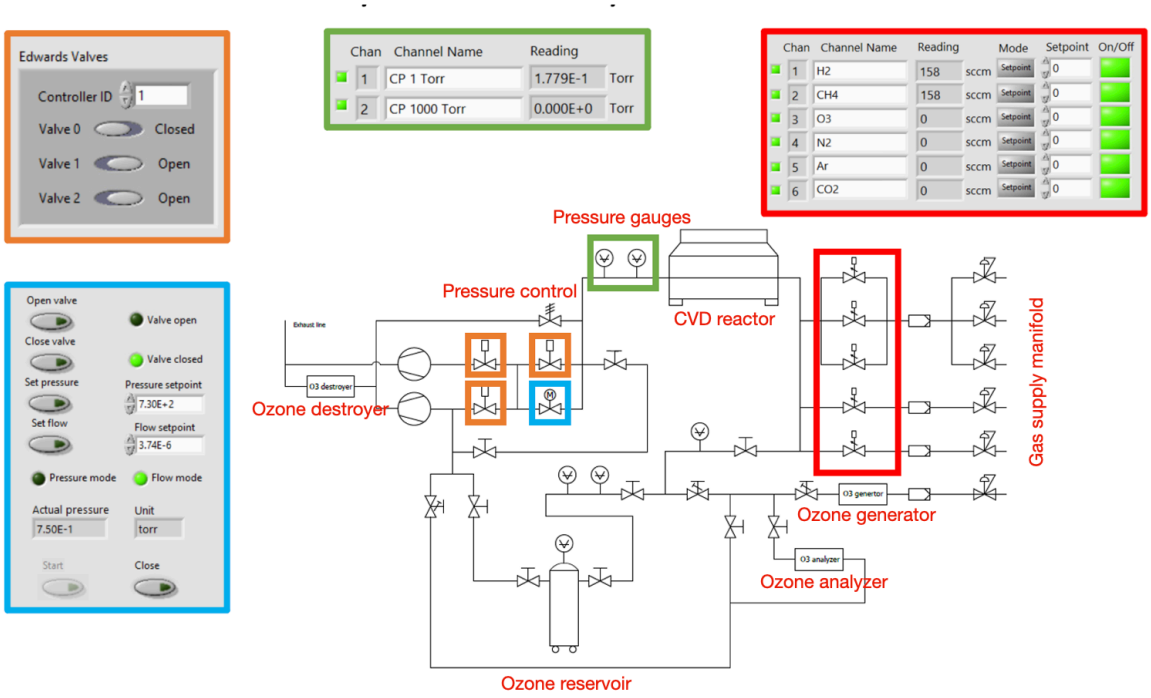

Figure 3: Process flow diagram for the large-scale CVD reactor for producing nanoporous graphene.

We have also installed a spin coater capable of coating thin polymeric film for large substrate (up to 30 cm diameter coupons, Figure 4). For meter-scale graphene membrane, this is sufficient and convenient route to reliably coat a thin polymeric film.

Figure 4: Large-area spin coater hosted inside a fume hood.

EPFL in collaboration with HES-SO is building a demonstration site on campus which is expected to be ready in 2023. The membrane skid will be commissioned at this demonstration site.

3 Procedures and methodology

3.1 Synthesis of single-layer graphene

Before synthesis, Cu foil is cut into desired sizes and undergoes an acid treatment to remove the surface coatings or impurities, which can be preserved after graphene synthesis. The acid treatment is done by first immersing Cu foil into 4 wt% nitric acid (HNO_3) for 10 min and then washing it in deionized (DI) water for 4 times.

The procedure for the synthesis of high-quality single-layer graphene (SLG) in the scale-up CVD furnace consists of four steps, CO_2 cleaning, H_2 annealing, graphene synthesis, and cooling (Figure 5). CO_2 cleaning is done below 1020 ℃ under ambient pressure, after which the atmosphere is changed to H_2/Ar for annealing. The annealing procedure is optimized close to the melting point of Cu, followed by a stepwise cooling to the CVD growth temperature (1020 ºC). The synthesis is done at 190 mTorr maintained by flowing 3 and 9 sccm of H_2 and CH_4, respectively. After 30 min of synthesis, the furnace is cooled down naturally.

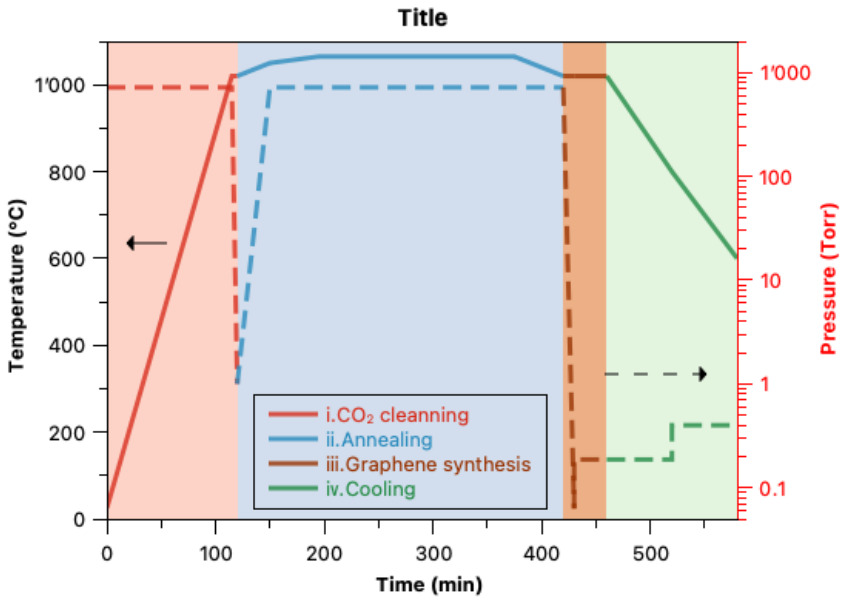

Figure 5. Large-scale CVD protocol for graphene synthesis.

3.2 Procedures for ozone treatment

To synthesize nanoporous single-layer graphene (NSLG), an ozone gasification process is applied after synthesizing graphene directly inside the CVD furnace. First, the ozone is produced and stored in a 250 L reservoir (Figure 6). After stabilizing the temperature of the CVD furnace, ozone is quickly injected into the evacuated furnace within 2 min. The reaction continues for a certain time with a continuous ozone flow, and ozone is then evacuated when the reaction is done. Finally, the furnace is heated up to promote pore formation in graphene.

Figure 6. Ozone reservoir for a quick injection of ozone into the CVD furnace.

3.3 Procedures for membrane preparation

NSLG membrane is fabricated using different reinforcement layers and assembled in a customized module with a 1 cm diameter membrane area (Figure 7). First, NSLG with Cu substrate is spin-coated with a 1-µm-thick layer of poly(1-trimethylsilyl-1-propyne) (PTMSP, 3 wt%). After drying, the membrane is placed on the mechanical support consisting of a commercial polyethersulfone (PES) and metal mesh layer. The membrane is sandwiched by two rubber gaskets and sealed by an outer O-ring by tightening the module with screws. To expose the NSLG membrane, the Cu foil is etched with $FeCl_3$ solution.

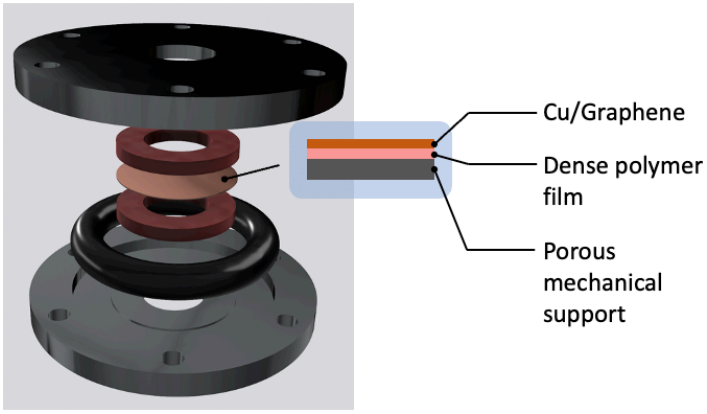

Figure 7. Schematic of NSLG membrane assembly.

Overall, the activity in this period focused on preparing a low-cost Cu foil for graphene synthesis, assembling a large-scale CVD reactor, developing transfer protocols for preparing crack-free large area membranes (10 cm^2) packed in a novel membrane module and improved process configuration to achieve the target recovery and purity.

For the Cu foil, the activity focused on ensuring highly smooth and contamination free surface of Cu to synthesize graphene to achieve parity results with higher cost counterparts. For this foil preparation techniques were optimized.

For the CVD reactor, the process focused on developing protocols which minimize contamination in graphene during graphene, allowing the synthesis of high-quality polycrystalline film, allowing operation in a safe and controllable manner especially limiting the heating of end connections for CVD to 100 ºC. For this novel radiation shields were designed, and water cooling was implemented (Figure 2).

Module was designed to reduce nonideal effects of concentration polarization and pressure drop. For this, flow channel width was optimized.

Technoeconomic calculations focused on reducing the capture penalty for achieving target purity and recovery.

4 Activities and results

Preparation of low-cost Cu foil

Our proof-of-principle results on high-performance graphene membranes were obtained on expensive Cu foil with cost over 8000 CHF/m^2. To decrease this cost, we developed lower purity Cu foil alternates (Table 1).

Table 1. Comparison of the Cu substrate used in this work and the market.

Supplier	Carl Roth® (used in this work)	Alfa Aesar®	Alfa Aesar®	Strem®
Thickness (µm)	100	25	127	50
Price/m^2 (CHF)*	87	241	650	8013

*Note: the price is sensitive to market dynamics.

100 µm-thick Cu foil from Carl Roth® with a cost of 87 CHF/m^2 was chosen because it fits the cost projected in the technoeconomic analysis. We chose a thicker foil because it is easier to handle (lesser degree of bending and folding which is good for graphene transfer). The Cu foil is processed reduce surface roughness and contamination (Figure 8, detailed description can be made available on request).

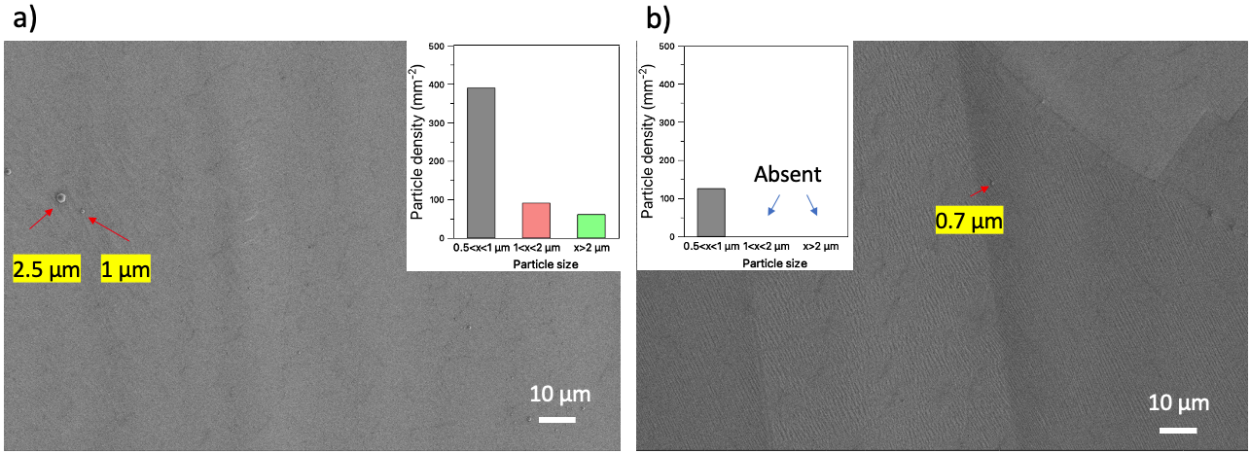

Figure 8. SEM image of graphene surface synthesized on a) as-received Cu and b) treated Cu. The inset is the contamination particle density after graphene synthesis.

High-quality, large area graphene synthesis:

The procedure for the synthesis of high-quality single-layer graphene (SLG) in the scale-up CVD furnace consists of four steps, CO_2 cleaning, H_2 annealing, graphene synthesis, and cooling (Figure 9). CO_2 cleaning is done below 1020 ℃ under ambient pressure, after which the atmosphere is changed to H_2/Ar for annealing. The annealing procedure is optimized close to the melting point of Cu, followed by a stepwise cooling to the CVD growth temperature (1020 ºC). The synthesis is done at 190 mTorr pressure maintained by flowing 3 and 9 sccm of H_2 and CH_4, respectively. After 30 min of synthesis, the furnace is cooled down naturally. Large area graphene could be successfully synthesized (Figure 10).

The high-quality of graphene is evident by the Raman spectroscopy. The spectrum shows a negligible defect peak (*D* peak), and a map of peak intensity ratio (*D*/*G*) shows that the quality of graphene is uniform (Figure 11).

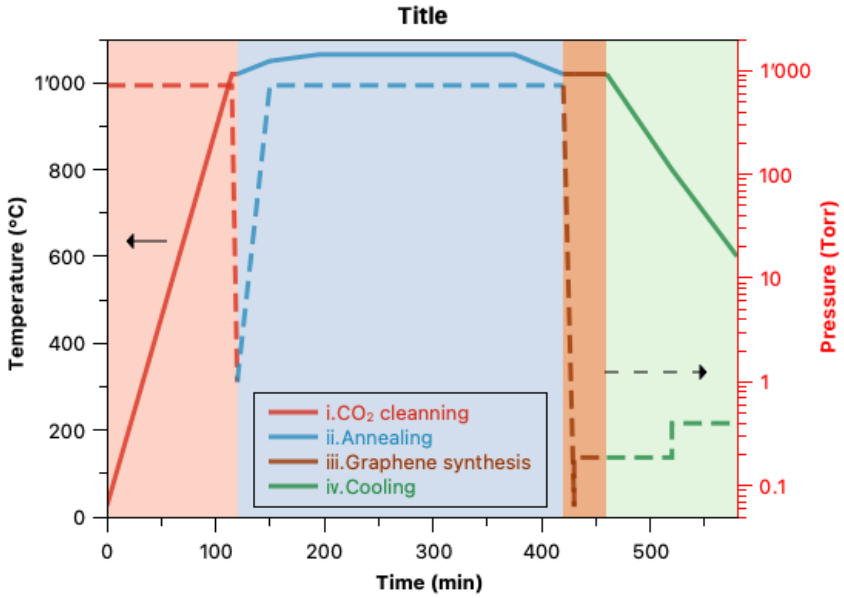

Figure 9. Large-scale CVD protocol for graphene synthesis.

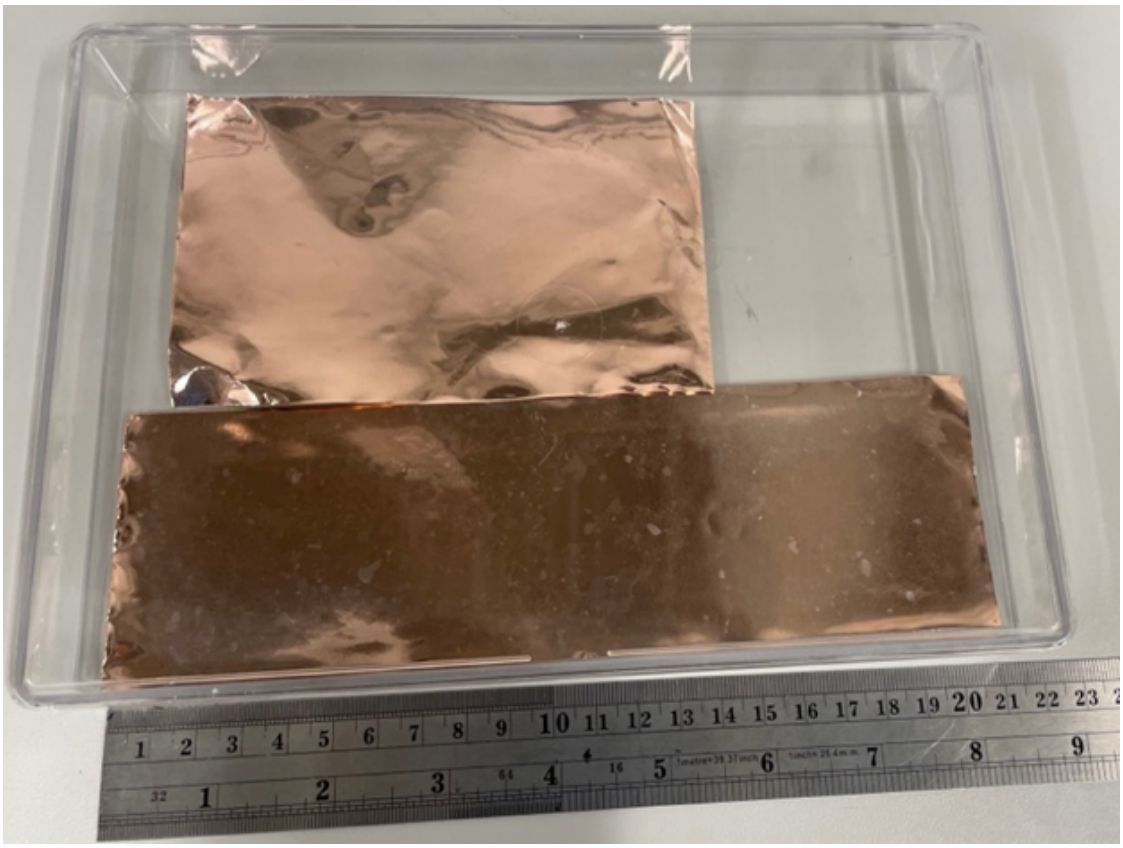

Figure 10. Large coupons of graphene synthesized in the large-scale CVD furnace.

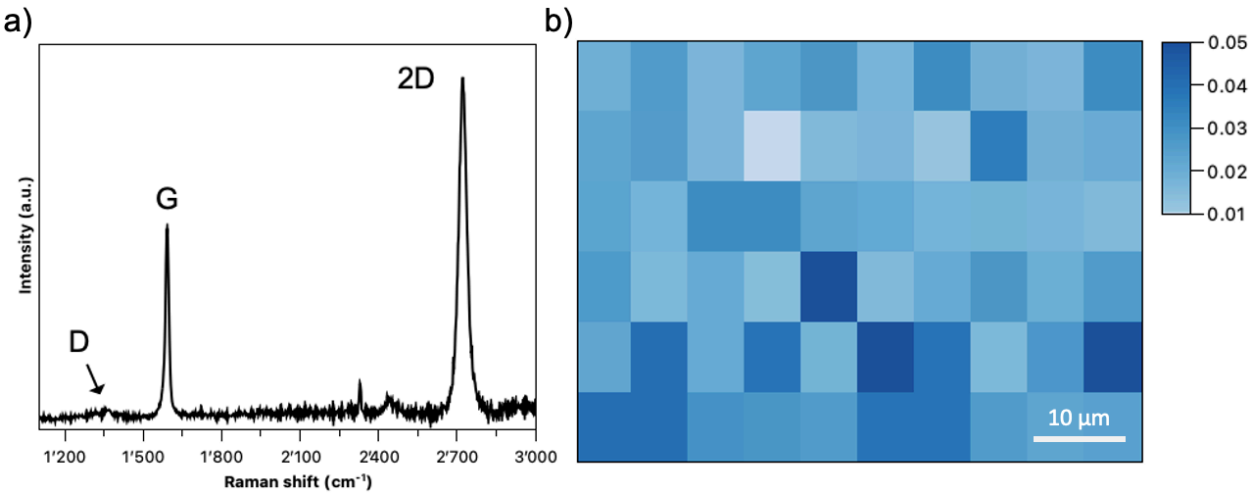

Figure 11. a) Raman spectrum of SLG, and b) the color map of I_D/I_G ratio on a 60 x 40 µm area.

Oxidation to prepare porous graphene with Å-scale pores

To synthesize nanoporous single-layer graphene (NSLG), an ozone gasification process is applied after the synthesis of graphene, directly inside the CVD furnace. First, the ozone is produced and stored in a 250 L reservoir (Figure 12). After stabilizing the temperature of the CVD furnace, ozone is quickly injected into the evacuated furnace within 2 min. The reaction continues for a certain time with a continuous ozone flow, and ozone is then evacuated when the reaction is done. Finally, the furnace is heated up promote pore formation in graphene.

Figure 12. Ozone reservoir for a quick injection of ozone into the CVD furnace.

By applying 10 min of O_3 treatment at 50 ℃ under 720 Torr directly inside the scale-up CVD reactor as freshly synthesized graphene, the graphene lattice reveals defects incorporation (Figure 13). After O_3 etching, an increase in both CO_2 permeance and CO_2/N_2 ideal selectivity is observed from the 1 cm scale graphene membranes. The O_3 etching condition is still under optimization to reach the target area, as shown in the figure 14.

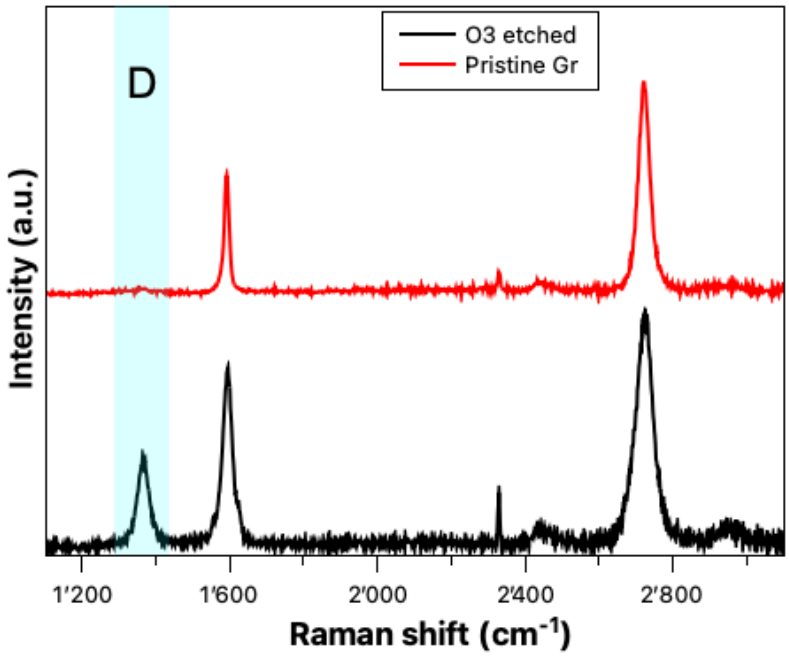

Figure 13. Raman spectra of pristine graphene and O_3 etched graphene showing defect formation by O_3.

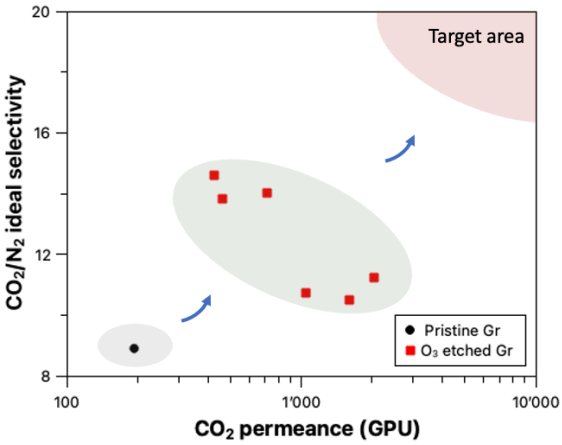

Figure 14. CO_2 permeance and CO_2/N_2 ideal selectivity from 1 cm scale pristine and O_3 etched graphene membranes.

Module design for pilot plant – selection of channel thickness

The module contains two membrane sheets which are separated by a small distance. The selection of the distance between the sheets inside the module is important because this distance corresponds to the thickness of the feed channel, and therefore, it affects the velocity of the stream. The channel thickness is designed in order to reduce two non-ideal effects of the membrane process connected to velocity, i.e., concentration polarization and pressure drops.

With concentration polarization, the concentration of the permeable component at the membrane interface is lower than in the bulk and this reduces the driving force across the membrane. The concentration profile along the thickness direction depends on the transport of the component in the channel and on the transport of the component through the membrane. To reduce concentration polarization, we would need a channel as thin as possible, since ideally, the concentration profile in one section should be flat to maximize the driving force. On the other hand, a thinner channel brings to higher velocity and higher pressure drops.

When the transport coefficient through the membrane (permeance) is higher, the concentration at the membrane interface is depleted and the concentration polarization is stronger. Therefore, with high permeance, we need to use thinner channels to reduce the concentration polarization, while when the permeance is lower, larger channels can be used.

From a practical point of view, a larger channel thickness is easier to realize and this reduces the pressure drops. Thus, the selected channel thickness is the largest thickness at which the concentration polarization is still limited. We investigated a range of thicknesses between 200 and 1500 micron for a global CO_2 recovery between 50 and 90% (fixed purity of 98%). The process presents two membrane stages, where the second is fed by the permeate produced by the first and the retentate of the second is recycled and mixed with the feed of the first stage.

We evaluated the impact of channel thickness on the membrane area of the first stage, since this typically covers most of the total membrane area (Figure 15). It is evident that the membrane area increases significantly when the channel thickness increases, and this is particularly evident at large recovery values. However, the impact of channel thickness is almost negligible at the lowest investigated recovery (50%).

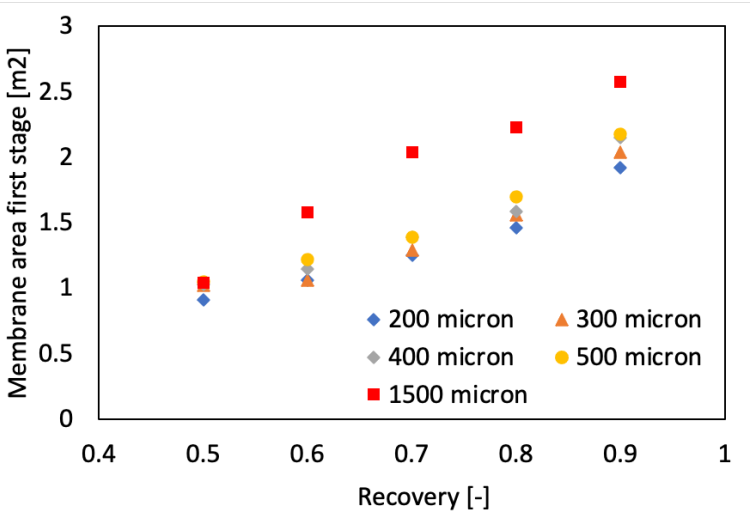

Figure 15. Membrane area in the first stage at variable global recovery and variable channel thickness. Final CO_2 purity target of 98%. Feed pressure in the first stage equal to 3 bar and permeate pressure equal to 0.01 bar. The membranes used for this plot have CO_2 permeance of 1000 GPU and CO_2/N_2 selectivity of 15.

Process design for pilot plant

We performed techno-economic analysis of double stage membrane processes for carbon capture from flue gas and from biogas. The technical model designs the process, i.e., estimates the membrane areas in each stage and the energy consumption of the vacuum pumps and the compressors, for a given target of recovery and purity. The model requires a number of inputs and parameters, such as the composition and flow rate of the inlet feed stream, the efficiency of pressure equipment and the membrane performance parameters. Then, the economic model calculates the capital and operating expenses, where the capital expenses are given by equipment cost, indirect costs and contingency and fee costs, whereas the operating expenses are given by energy costs, fixed operating costs and membrane replacement costs. The sum of the capital and operating expenses per year divided by the amount of CO_2 produced per year returns the capture penalty.

The techno-economic model can also identify the set of operating conditions (in particular, the pressures in the feed and permeate channels) that minimizes the capture penalty.

5 Evaluation of results to date

In the last year, we have successfully designed, commissioned, and validated the large-scale CVD reactor with capability of produce meter-scale graphene. We show that porosity in graphene is incorporated by ozone treatment successfully inside the reactor making it convenient to prepare large scale porous graphene films. Our success rate to produce 1 cm module is now near 100%, thanks to the novel transfer free membrane preparation step developed for larger area module. We have validated modules with area of 10 cm^2 and now optimizing 100 cm^2 module. The process for separation is being optimized inside the scale-up reactor learning from the conditions for small-scale membranes. The first set of membranes produced by the large-scale reactor show already promising performance (CO_2/N_2 selectivity of 15, CO_2 permeance of 1000 GPU). With further optimization of the etching conditions

(closely mimicking the conditions for small-scale membranes), better performance is expected. The process design will be then further optimized.

6 Next steps

In the following year, we will

1) Continue optimizing oxidation conditions for graphene with O_3, closely mimicking the conditions for small-scale reactors. We have some very exciting chemistry which we have demonstrated on small-scale membranes. This reaction parameters will now be repeated for larger scale membranes.
2) We will continue to improve the operation of CVD furnace to make it fail proof against unexpected events (power outage, over-pressurization by valve failure etc.). Some steps being taken is backup power and improved system control.
3) We are installing a low-cost clean room (ISO-5) through additional funding by EPFL in this scale-up laboratory. This will help us reduce dust particles and improve our success rate.
4) We will validate 100 cm^2 membrane modules in coming months. After this, we will design and validate 400-500 cm^2 membrane modules based on similar design. With additional Valais and EPFL funding, we will soon as high-temperature 3D printer which will allow us to print high-temperature polymer modules rapidly increasing the pace of module development. For example, the lead time for our machine shop is 4 weeks. With 3D printer, we can print modules ourselves in a day. This will accelerate module prototyping.
5) EPFL in collaboration with HES-SO is building a demonstration site on campus which is expected to be ready in Fall 2023. The membrane skid will be commissioned at this demonstration site upon its availability.

7 National and international cooperation

8 Communication

9 Publications

Some of the results of this project toward scale-up of graphene has been published here

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11 Appendix