

Chitosan/SIFSIX-3-Cu Cryogels on Printed Laser-Induced Graphene for CO₂ Electric Swing Capture

by

Monica Man-Wah Ho

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

To achieve global net zero greenhouse gas emissions, carbon dioxide (CO₂) removal technologies (CDR) must be deployed at gigatonne scale by the end of the decade. Direct air capture (DAC) is one category of CDR technology which shows promise due to its more straightforward measurability and verifiability. Low temperature, solid sorbent-based DAC systems in particular offer a lower energy demand and when paired with renewable electrical systems, avoid the use of fossil fuels and the generation of additional CO₂ emissions in the process. Several sorbents have been investigated for electric swing adsorption (ESA) DAC, where heat generated using the Joule heating principle is used for the desorption of CO₂ from the sorbent. Most of the sorbents are carbonaceous due to their semi-conductive nature which allows for electrical current travel. However, these sorbents suffer from reduced capacity at low CO₂ partial pressures, making them less suitable for DAC.

As an alternative, we explore an indirect ESA process using laser-induced graphene (LIG) which acts as a flexible heater layer. For the adsorbent layer, chitosan (CS) cryogel with in situ synthesized SIFSIX-3-Cu metal organic framework (MOF) is fabricated for its high capacity, appreciable CO₂ selectivity, and sustainability. The pure MOF powder reached its maximum adsorption capacity of approximately 2.5 mmol g⁻¹ within just five minutes, demonstrating its exceptionally fast adsorption kinetics. In contrast, the pure chitosan (CS) cryogel required more than 30 minutes to reach the same capacity. The CS/MOF hybrid cryogel exhibited intermediate kinetics, achieving a maximum adsorption capacity of 2.92 mmol g⁻¹. It was shown that the adsorbents could be regenerated in temperature range of 70-80°C, had low N₂ uptake, and 88% of the CS/MOF cryogel capacity was maintained after 4 cycles. Patterned LIG grids were subsequently fabricated and could raise the temperature of the CS/MOF cryogel adsorbent via Joule heating to the target regeneration temperature in 66 s with only 15 V. The LIG grid could also consistently generate the desired temperature range over 4 cycles. Lastly, the chitosan cryogel was fabricated directly on a LIG grid without compromising its heating capability. This successfully demonstrates how an environmentally conscious and efficient ESA system can be engineered by combining LIG optimized for heating and eco-friendly adsorbents with high CO₂ capacity.

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Dedication

I dedicate this work to my mother, Kitty Ho, whose perseverance, intelligence and strength are my inspiration.

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Chapter 1: Introduction

1.1 Background

1.1.1 Climate Change

As global temperatures rise due to anthropogenic driven greenhouse gas (GHG) emissions in the atmosphere, all life on earth will be challenged by the increasing intensity and frequency of natural disasters, rising sea levels, ocean acidification, and inhospitable temperatures. February 2023 to January 2024 marked the first 12-month period where global average surface temperature exceeded 1.5°C above pre-industrial levels [1], illustrating the urgency of action required to meet the 2015 Paris agreement targets of limiting global temperature increase to 1.5°C by 2030 and well below 2°C by 2050. While it is critical that mankind drastically reduce energy consumption and switch to using clean and/or renewable energy sources to stop global warming, it has been recognized that these mitigations alone will not be enough to stop climate change [2]. In some industries with hard-to-abate emissions, like steel and cement manufacturing or agriculture, carbon removal may be less expensive and disruptive than emissions reductions [3]. In addition, the cessation of emitting GHGs will only stop the temperature from rising further; however, it will not decrease the temperature back to pre-industrial revolution levels. To reduce temperatures to pre-industrial revolution levels, carbon dioxide removal (CDR) technologies will be needed to capture and permanently store or convert CO₂ into other materials such that it cannot be re-emitted. Low end estimates of required annual CO₂ removal by 2050 is 1.5 to 3 gigatons, which means we need to be deploying megaton scale of CDR by 2030 [4]. While many CDR technologies are being explored (**Figure 1**), direct air capture (DAC) technology is a promising option due to its ability to be paired with long term storage options, theoretical flexibility for technology siting and easier ability to quantify and verify the amount of CO₂ being captured.

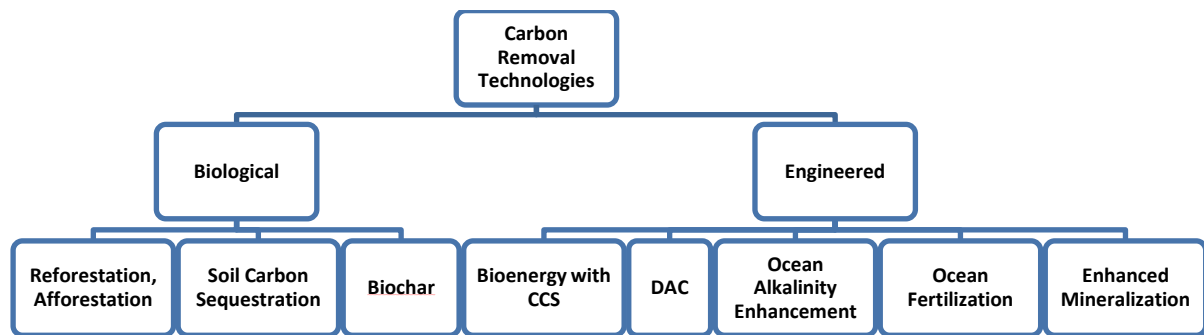


Figure 1. Summary of the different carbon dioxide removal technologies.

1.1.2 Direct Air Capture Government Policies and Incentives

There has been notable momentum in government support for carbon management and DAC in the past several years. In particular, in the U.S. the 2021 Infrastructure Investment and Jobs Act and 2022 Inflation Reduction Act triggered DAC companies around the globe to focus their efforts on the US market. Following, the DAC Prize Competitions [5], worth US 115 million in total, was launched by the U.S. Department of Energy (DOE) at the end of 2022. In 2023 the DOE announced US 1.2 billion [6] in funding for regional direct air capture hubs in addition to 19 additional [7] DAC projects selected for award negotiations to support project feasibility. The U.S. National Energy Technology Laboratory (NETL) even opened a DAC Centre [8] in May 2024 to support developers in the scale up and commercialization of DAC technology. Interestingly, NETL also announced a 4-year plan [9] to develop their own DAC system to eventually be licensed. All this is in addition to other funding for more general carbon management and removal initiatives [10]. However, with the election of the new Trump administration, it is unclear what changes will be made for funding to CDR.

In 2023, the Canadian government released its Carbon Management Strategy which projects that DAC will capture 55 Mt of CO₂ annually by 2050 in Canada to meet Canada's Net-Zero Scenario [11]. Policy support for DAC includes NRCan's Energy Innovation Program administering CAD 319 million over 7 years to support research, development, and demonstration for carbon management technologies, where two DAC projects will be receiving funding according to their February 2025 announcement [12]. CCUS Investment Tax Credits are also available for DAC at a higher rate than other project types and in February 2025 the federal government released a first draft of a GHG offset protocol to support the development of DAC projects [13]. Under the Clean Fuel Regulations there is opportunity for DAC projects to create credits, while more recently the Canadian government

expanded their CAD 135 million Low-Carbon Fuel Procurement Program to include carbon removal procurement, which could include DAC. While Canada's national policies are making progress in support of DACS (DAC with storage), provincial policies overall lack orientation towards and several opportunities exist to improve support for long-term DAC development and scale-up [14].

On the international stage, the EU finalized the Net-Zero Industry Act [15] in early 2024 which supports strategic clean energy technologies including carbon capture and storage. Notably, EU oil and gas companies are mandated to invest and support this development. The European Commission also announced US 30 million in funding for CDR projects in the EU a few months later [16].

Despite the progress, significantly more governmental support is required to scale up DAC deployment and drive down costs. Recommendations include treating DAC like a public utility [17] in terms of capital spending, careful integration into compliance carbon markets to drive long-term financing [18], streamlined permitting processes for DAC, CO₂ transport infrastructure and storage sites, while managing limited land and water supply by encouraging industrial clusters to create circular economies like the use of waste heat from other industries for DAC [19].

1.1.3 Direct Air Capture Technology

Within the DAC industry there is a suite of technologies being developed. There are a few methods of categorization including thermochemical vs. electrochemical, high vs. low temperature, and solid vs. liquid sorbent materials used to capture CO₂ from the air. Thermochemical technologies are more mature with a maximum technology readiness level (TRL) of 6 for high temperature liquid sorbent technology using natural gas and up to 9 for low temperature solid sorbent technology. Electrochemical technologies are newer with a maximum TRL of 4 [19]. **Table 1** categorizes the main DAC technologies currently being explored commercially.

Table 1. Classification of DAC Technologies [20]

	Thermochemical Technology		Electrochemical technology	
Regeneration temperature	Liquid sorbent	Solid sorbent	Liquid sorbent	Solid sorbent
High Temperature	Aqueous Alkaline Solvents	Limestone and Lime	-	-
Low Temperature	Amino Acid Solution	Solid Adsorbents: • Zeolites • Activated Carbon • Metal Organic Frameworks, etc	• Monopolar or Bipolar Membrane Electrodialysis	Electrochemically Mediated CO ₂ Capture

Considering that most DAC companies were formed in the last 6 years [21], the DAC industry is still facing several challenges including high energy consumption, where thermal requirements account for 80% and electrical energy accounts for 20% of consumption, regardless of the technology [22,23]. This energy demand feeds into its high cost, with reported and projected costs ranging up to \$1000/tCO₂ [21]. For DAC to be comparable to other waste management services in high income countries such as solid waste removal, costs need to reduce to \$100-200 by 2050 [17]. In addition, high temperature technologies which require 800-900°C during the desorption process have been relying on the burning of natural gas to generate these temperatures, highlighting the need for electricity driven solutions fueled by non-emitting energy technologies. A large part of the energy demand during DAC is due to the desorption or regeneration process where the CO₂ is separated from the sorbent that was initially used to capture the CO₂ and the sorbent is regenerated for reuse in the process. For thermochemical technologies, the regeneration process most often involves the addition of heat (temperature swing adsorption or TSA), the decrease of pressure (vacuum swing adsorption or VSA), or a combination of both. Other techniques include change in humidity (moisture swing adsorption or MSA) and electric swing adsorption (ESA), which is a subcategory of TSA where only electricity is passed through conductive material to generate heat via Joule heating principles. In traditional TSA, steam or hot gas is used as a medium for heat transfer whereas in ESA the sorbent is directly heated, making it potentially more energy efficient compared to TSA.

1.2 Project Objectives

The objective of this project is to introduce a low temperature and eco-friendly solid sorbent-based DAC system powered only by electricity. By focusing on low temperature ESA, the aim is to

introduce a system which can be powered by renewable energy systems and has reduced energy consumption for the regeneration process compared to more mature DAC technologies. In addition, materials that have a low impact on the environment such as ones that can be synthesized using minimal energy and resources were selected based on an understanding that the overall energy consumption life cycle of a DAC system is not only impacted by separation energy requirements. Hence, the bio-based polymer chitosan and SIFSIX-3-Cu metal organic framework (MOF) were chosen for the adsorbent. Chitosan is abundant, biodegradable and non-toxic. MOFs are a class of nanocrystalline materials which are promising for environmental applications including carbon capture due to their high surface area and porosity. SIFSIX-3-Cu is easily synthesized in ambient conditions and has a low global warming potential compared to several other MOFs and monoethanolamine (MEA), which is a commonly used sorbent in the carbon capture industry that requires large amounts of energy for regeneration [24]. To facilitate ESA, laser-induced graphene (LIG) was chosen for its high electrical conductivity and fast synthesis process that minimizes waste production compared to traditional chemical or electrochemical methods.

The objectives of the project can be summarized as follows

1. Develop a new adsorbent using known materials that have good CO₂ adsorption and selectivity performance, low lifecycle impact, and requires low regeneration temperature.
2. Demonstrate the ability for LIG-based Joule heaters to be used for desorption in DAC systems via ESA.

1.3 Thesis Outline

Chapter 2 provides a literature review on chitosan and chitosan/MOF-based adsorbents used for CO₂ capture. In addition, the use of LIG as flexible heaters is discussed, followed by a review of CO₂ capture systems which have used ESA.

Chapter 3 is an overview of experimental methods including material preparation, characterization techniques used, procedures for gas adsorption testing and Joule heating measurements.

Chapter 4 focuses on the adsorbents synthesized including their characterization and adsorption performance.

Chapter 5 focuses on the synthesis of LIG and its performance as a heating system for ESA DAC.

Chapter 6 provides a summary of this study and insight into potential future work on this topic to allow for real world application.

Chapter 2: Literature Review

2.1 Chitosan- and MOF-based Adsorbents

2.1.1 Chitosan-based Adsorbents

Chitosan is a polysaccharide obtained by the deacetylation of chitin, which is the second most abundant polymer found in nature [25]. Chitin can be obtained from natural sources including crustacean shells, molluscs, insects, and fungi. The process of removing the acetyl group from N-acetyl-D-glucosamine on chitin exposes amino groups for cooperative interactions with CO₂ [26] as illustrated in **Figure 2** and **Equation 1** [27].



To be considered chitosan, the degree of deacetylation (DD%) should be at least 60% [25]. Due to its biodegradability, biocompatibility, and nontoxic characteristics, chitosan has historically been popular for applications in biomedical fields. With an increasing interest in the replacement of fossil fuel-based materials for bio-based ones, chitosan has gained momentum in the field of environmental applications as well. While investigations utilizing chitosan for CO₂ capture have been published in the early 2000s, most have been within the last decade. Yoshida et al. [28] were one of the first to utilize chitosan for CO₂ capture by combining it with macroreticular anion exchange resins. They found that pure chitosan flakes could adsorb 0.1 mmol g⁻¹ but applying a thin layer of dissolved chitosan on HPA25 anion exchange resin improved the adsorption capacity by more than 3 times compared to pure HPA25. Sneddon et al. [26] reported using mesoporous silicas and mesocellular foams (MCFs) coated with chitosan to achieve a capacity of 0.98 mmol g⁻¹ at ambient conditions under 100% CO₂.

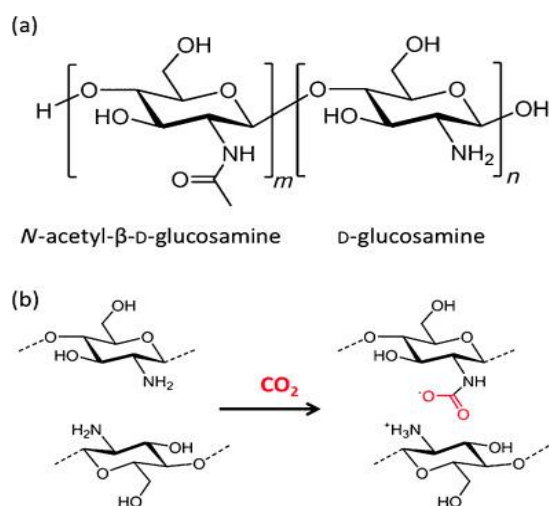


Figure 2. (a) Structure of chitosan (b) The adsorption of CO_2 by D-glucosamine units of chitosan. Reproduced under terms of the CC-BY license [26]. Copyright 2015 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA.

Others have investigated different modifications to chitosan to improve performance. For example, 4-formyltriphenylamine was grafted onto chitosan to improve its surface morphology for adsorption [29]. The amine functionalized chitosan achieved 0.85 mmol g^{-1} at 5 bar ($\sim 0.6 \text{ mmol g}^{-1}$ at 1 bar) compared to approximately 0.05 mmol g^{-1} for the prepared pure dried chitosan. The performance of chitosan beads were also enhanced by polyethylenimine (PEI) functionalization with an adsorption capacity of 2.3 mmol g^{-1} at 40°C and 0.15 bar ($\sim 2.6 \text{ mmol g}^{-1}$ at 1 bar) in dry conditions and 3.6 mmol g^{-1} (4.3 mmol g^{-1} at 1 bar) in the presence of water vapour [30]. Comparably, cross-linked chitosan beads only reached $\sim 0.5 \text{ mmol g}^{-1}$ at 1 bar. In another case, chitosan was converted to quaternized chitosan (QCS) before mixing with polyvinyl alcohol (PVA) to form cryogels. Using a CO_2 concentration of 400 ppm the composite cryogel achieved 0.18 mmol g^{-1} in a moisture swing adsorption system, but it was noted that the thermal stability of QCS was reduced compared to chitosan due to the quaternary ammonium groups [31]. Others have focused on imine functionalization of chitosan. Chitosan was prepared with meso-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) for an adsorption capacity of 0.9 mmol g^{-1} which was an improvement over the 0.05 mmol g^{-1} achieved by pure chitosan and the 0.2 mmol g^{-1} achieved by pure TPPS [32]. The performance of electrospun chitosan fibers was also improved by imination via reaction with furfural [33]. The chitosan fibers, which adsorbed $0.438 \text{ mmol g}^{-1}$ at a pressure 0.61 bar, were created using a mixture of 7/3 weight ratio of chitosan/poly(ethylene glycol) (PEG) before washing out the PEG to leave

porous chitosan fibers. The chitosan fibers which underwent a 13% imination demonstrated the greatest improvement of $0.978 \text{ mmol g}^{-1}$.

The exploration of composites containing chitosan for CO_2 capture is common. Liu et al. [34] prepared chitosan hydrogels using LiOH, KOH and urea followed by the in situ polymerization of 2-acrylamide-2-methylpropanesulfonic acid (AMPS) and acrylamide (AAM) in the chitosan hydrogel to form a double polymer network. The freeze dried chitosan/P(AMPSL-co-AAM) hydrogel which was polymerized using electron beam radiation achieved the highest CO_2 capacity of 1.54 mmol g^{-1} , followed by the chemically polymerized cryogel at 1.44 mmol g^{-1} . Lastly, the base chitosan cryogel obtained 0.88 mmol g^{-1} . Chitosan and bleaching earth clay composite beads have also been explored (**Figure 3c,d**) [35]. The cryogel composite beads adsorbed 7.84 mmol g^{-1} at a CO_2 concentration of 25%, which is the best reported performance of a chitosan-based adsorbent to date.

Combining chitosan with ionic liquids (ILs) has also been investigated. For example, chitosan ionogel droplets were encapsulated in nanoporous fumed silica to form an inverse supported ionic liquid phase material and achieved $0.1\text{-}0.8 \text{ mmol g}^{-1}$ at 1 bar and 40°C (**Figure 3b**) [36]. In another study, poly ionic liquid (PIL) chitosan aerogel beads were formed by first dissolving 2.5% w/v in 1% v/v of acetic acid, followed by the addition of PIL and glutaraldehyde crosslinker [37]. Droplets were added to a NaOH bath to induce gelation, followed by solvent exchange and supercritical drying. A capture capacity of 0.70 mmol g^{-1} at ambient conditions was reached, although notably the test was only run for 10 minutes and sorbent saturation had not been reached yet.

Zeolites are a natural aluminosilicate microporous mineral commonly investigated for separation, adsorption and catalysis [38]. Kumar et al. [38] synthesized two different zeolite-chitosan composites for CO_2 capture. At ambient conditions the ZeY@CS composite reached 1.48 mmol g^{-1} while the ZSM-5@CS reached 2.16 mmol g^{-1} with negligible hysteresis during the desorption of CO_2 for both samples. Following, Luzzi et al. [27] created chitosan-zeolite cryogel (ZX/CS) beads with the intent of using chitosan as a binder. The beads containing 90% zeolite content achieved 4.23 mmol g^{-1} of CO_2 capacity which could be fully regenerated by a vacuum swing desorption process at room temperature. The adsorption capacity increased with an increase in zeolite content but it was noted that the microstructure exposed the amino groups of chitosan for CO_2 binding to occur in addition to the zeolite activity.

Chitosan has also been used as a precursor for the synthesis of activated or porous carbons, which are highly investigated for adsorption applications due to their high porosity and stability, both thermal and chemical [39]. For example, using a freeze dried mixture of LiCl-ZnCl₂ molten salt and chitosan as a template, a nitrogen-containing activated carbon (AC) produced after undergoing 1000°C in argon gas had a CO₂ adsorption capacity of 5.6 mmol g⁻¹ at room temperature (25°C) and 7.9 mmol g⁻¹ at 0°C [39]. Very similar results were obtained when chitosan dissolved in acetic acid underwent a hydrothermal treatment at 200°C followed by activation using KOH or NaOH at 800°C [40]. KOH proved to be a slightly better activator, resulting in, 5.43 mmol g⁻¹ adsorption capacity at 25°C and 8.36 mmol g⁻¹ at 0°C at an ideal chitosan to activator ratio of 1:3 for KOH (Figure 3g). While ACs result in high adsorption capacities, the high temperatures required for the carbonization process require high energy inputs, detracting from life cycle efficiency.

Graphene and graphene oxide (GO) nanofillers have been investigated to improve the adsorption performance of chitosan through the increase of surface area, while also improving mechanical properties. A 3 wt% pure chitosan cryogel was synthesized by mixing chitosan flakes with 1% v/v aqueous acetic acid followed by 2 days of aging, freezing at -70°C, and freeze drying [41]. The pure chitosan cryogel had a capacity of 0.40 mmol g⁻¹ before calcination and reached 1.92 mmol g⁻¹ after calcination at 400°C under nitrogen. With the addition of GO, the surface area increased along with the capacity. Pre-calcination, the hybrid cryogel with 5 wt% of GO reached 0.60 mmol g⁻¹ while 4.15 mmol g⁻¹ was reached after calcination when GO made up 20 wt% of the total solid content. More recently, Hsan et al. [42] grafted chitosan with GO with the assistance of coupling reagents 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride and N-hydroxy succinimide to form cryogels that could adsorb 0.257 mmol g⁻¹ at ambient conditions. Later, they increased the number of N-groups in this cryogel by functionalizing with the amino acid arginine, which increased the adsorbed amount to 5.48 mmol g⁻¹ at 35°C after 35 min [43]. In the above studies, a lengthy chemical synthesis of the GO was first conducted. An alternative is an electrochemical process, which has been used to fabricate electrochemically exfoliated graphene (EEG) containing phosphate functional groups which could be coupled with the amine functional groups of glycosylated chitosan (GC) [44]. The hybrid cryogel (**Figure 3f**) with total solid content of 1 wt% composed of a 1:2 ratio of EEG:GC reached a maximum capacity of 2.88 mmol g⁻¹ at ambient conditions after 30 minutes. This was an improvement over pure EEG (0.16 mmol g⁻¹) and GC (0.81 mmol g⁻¹). It was also noted that the 1

wt% adsorbents performed better than the 2 wt% ones due to thicker walls and aggregation which led to decreased surface area in the latter.

2.1.2 Chitosan/MOF Adsorbents

Highly porous nanomaterials consisting of metal ion nodes connected by organic ligands are known as metal organic frameworks (MOFs). MOFs are promising for various environmental applications including CO₂ separation due to their high surface area and porosity which can be tailored by combining different metals and ligands. At a macroscale, the powder-like nature of MOFs requires it to be combined with other materials, such as polymers, to form composites for practical application.

There are a number of studies that have combined MOFs with chitosan for CO₂ adsorption. Zeolitic imidazolate framework-8 (ZIF-8) is a MOF known for its thermal, physical and chemical stability [45]. Spherical beads of chitosan/ZIF-8 were created by first dissolving zinc nitrate hexahydrate and chitosan in aqueous acetic acid [45]. It was then added dropwise to a mixture of NaOH and 2-methylimidazole to form beads. The beads were then placed in an oven at 80°C to induce MOF formation, filtered, washed, and freeze dried. The composite beads (0.679 mmol g⁻¹) were an improvement over pure CS (0.101 mmol g⁻¹), but still less than pure ZIF-8 (0.852 mmol g⁻¹). The composite beads after calcination at 500°C for 4 hours had the highest capacity of 0.990 mmol g⁻¹. After ten cycles of CO₂ sorption, the capacity decreased to 0.9133 or about a 7.7% decrease. Another ZIF family member that has been combined with chitosan is ZIF-67, a cobalt containing MOF. Cryogel beads were synthesized in a similar manner [45], however the MOF ligand was introduced after the beads were formed and dehydrated in ethanol-water baths, followed by ZIF crystallization in an oven at 80°C, freezing and lyophilization [46]. The composite beads seen in **Figure 3b** (1.21 mmol g⁻¹) performed on par with pristine ZIF-67 (1.23 mmol g⁻¹) at 0°C and it was noted that with an increase in ratio of chitosan to cobalt nitrate, the adsorption decreased. After six CO₂-sorption cycles, XRD indicated partial degradation of the beads which was attributed to Co(OH)₂ formation.

In another study, three methods of drying chitosan/HKUST-1 (Cu(II) benzene-1,3,5-tricarboxylate) beads were investigated [47]. The alcogel beads frozen with liquid nitrogen and then freeze dried had the highest capacity of 2.68 mmol g⁻¹ (**Figure 3a**), followed by the supercritically dried (73 bar, 35°C) aerogel beads at 2.54 mmol g⁻¹ and finally the room temperature vacuum dried xerogel beads at 2.28 mmol g⁻¹. For comparison, the cryogel bead capacity corresponds to 42% of pure HKUST-1 capacity of 6.44 mmol g⁻¹ and exceeds the 0.083 mmol g⁻¹ of pure chitosan cryogel beads. Instead of

fabricating beads, high surface area electrospun chitosan/PVA fibers were used as a polymer base for CuBTC MOF [48]. Initially three methods of integrating CuBTC with the fibers were investigated, however it was found that direct mixing of pre-synthesized MOF crystals or mixing of MOF precursor chemicals into the polymer solution prior to electrospinning did not yield ideal hybrid materials for adsorption. Thus, polymer fibers were first spun and then post treated via different soaking procedures in the MOF precursor solutions. Alternating soaking in first the metal ion solution, followed by soaking in the ligand solution proved to be the most effective cycle for obtaining an even dispersion of MOF crystals on the fiber surface (**Figure 3e**). After three cycles of soaking, the chitosan-MOF composite had a CO₂ capacity of 0.38 mmol g⁻¹, which was higher than the 0.08 mmol g⁻¹ obtained by the chitosan/PVA fibers alone, and more than 14 times higher than the N₂ adsorption capacity indicating good selectivity for CO₂. Rather than using chitosan as a structure for MOF impregnation as in the previously mentioned reports, Singo et al. [49] impregnated a sodalite zeolite-like MOF (sod-ZMOF) within chitosan. The sod-ZMOFs were first synthesized before being mixed in a solution containing 2 wt% chitosan in 2 wt% aqueous acetic acid and then filtered and dried. They found that their MOFs adsorbed 978 mg CO₂ g⁻¹ or ~22 mmol g⁻¹ using 15/85% CO₂ to N₂ ratio in a packed bed column, however when tested in a TGA only ~25 mg g⁻¹ (0.57 mmol g⁻¹) was adsorbed. It was also noted that with an increased gas flowrate, the adsorbed amount decreased regardless of assessment method due to the reduction in contact time between gas molecules and MOF crystals.

Lastly, while several MOFs have been investigated for CO₂ capture, SIFSIX-3-Cu (C₈N₄H₈CuSiF₆) stands out for its high uptake capacity even at low concentrations (1.24 mmol g⁻¹ at 400 ppm), unaffected performance in the presence of humidity up to 74% [50], and for its low global warming potential relative to other MOFs investigated for carbon capture and to MEA solution [24], which is one of the most commonly used sorbents in the carbon capture industry currently. Zhen et al. [51] investigated the in situ synthesis of SIFSIX-3-Cu in melamine formaldehyde sponge monoliths for CO₂ capture where PVA was used to anchor the metal salts of the MOF in the sponge, achieving 1.02 mmol g⁻¹ for a CO₂ concentration of 5000 ppm at 20°C which is below that of the pure MOF (2.26 mmol g⁻¹).

Table 2 summarizes the CO₂ adsorption measurement conditions used and capacity achieved by the above-mentioned chitosan-based and MOF-based sorbents.

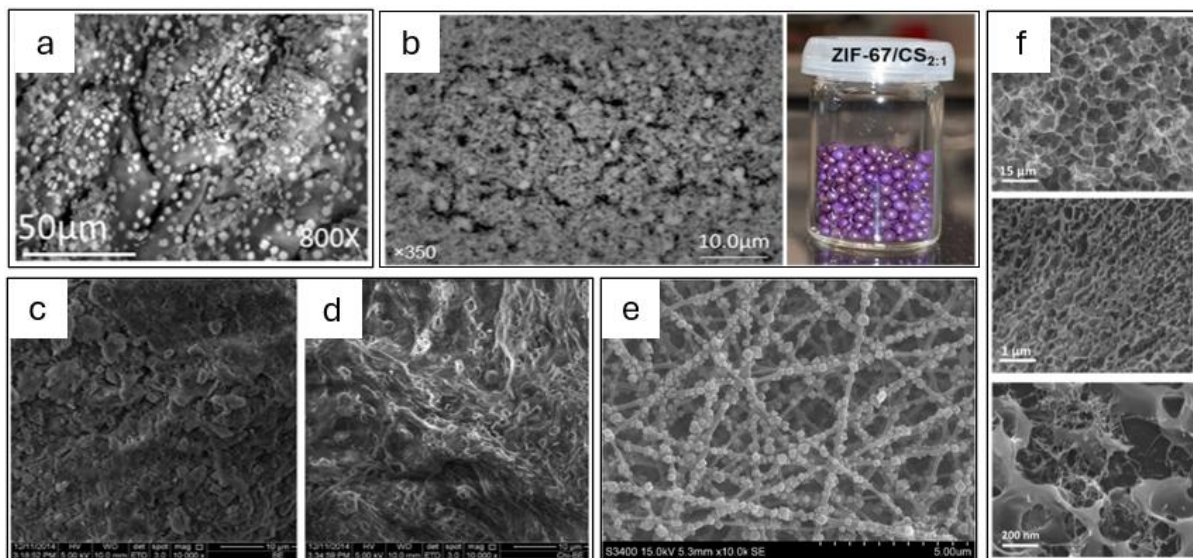


Figure 3. Digital and/or microscopic images of sorbents containing chitosan. a) Cross-section view of HKUST-1@CS_{1:1}C cryogel bead. Reprinted with permission from [47]. Copyright 2023, American Chemical Society. b) ZIF-67/CS_{2:1} cryogel beads and surface morphology. Adapted from [46], Copyright 2023, with permission from Elsevier. c) Morphology of bleaching earth clay and d) chitosan-clay composite. Reprinted from [35], Copyright 2018, with permission from Elsevier. e) CuBTC on chitosan/PVA electrospun fibers prepared via deposition method. Reprinted from [48], Copyright 2020, with permission from Elsevier. f) EEG-GC18 cryogel. Reprinted from [44], Copyright 2024, with permission from Royal Society of Chemistry.

Table 2. Summary of chitosan-based adsorbents

Adsorbent	Adsorption Conditions	Adsorbent Structure	Adsorption measuring technique	CO ₂ adsorption capacity (mmol g ⁻¹)	Regeneration	CO ₂ /N ₂ Selectivity	Refs.
CS coated MCF-3	25°C, 1 atm, 100% CO ₂	Foam	Volumetric	0.98	-	-	[26]
	25°C, 1 atm, 50% CO ₂ in N ₂ , 60 mins	Foam	Gravimetric, 60 mins	0.34	TSA at 75°C, <15% drop in capacity over 4 cycles	-	
CS-(4-formyltriphenylamine)	25°C, 5 bar	Powder	Volumetric (Sievert)	0.85	-	-	[29]

PEI-CS	40°C, 1 bar	Cryogel Beads	Gravimetric–volumetric, fixed bed reactor (20% CO ₂)	Dry:~2.6 Humid: 4.3	TSA at 100°C in Argon steam	-	[30]
QCS/PVA	20°C, ambient P, 0.04% CO ₂	Cryogel	Fixed bed adsorption	0.18	Moisture swing	-	[31]
CS-TPPS	25°C, 5 bar	Powder	Volumetric (Sievert)	0.9	-	-	[32]
CS	25°C, 5 bar	Powder	Volumetric (Sievert)	0.05	-	-	
Furfuryl-imine-CS	22°C, 0.61 bar	Electrospun fibers	Volumetric	C: 0.438 CF ₂ : 0.978	-	-	[33]
CS/P(AMPSL-co-AAm)/SO ₃ Li	25°C, 1 bar	Cryogel	Volumetric	O-gel: 0.88 I-gel: 1.44 R-gel: 1.54	-	-	[34]
CS-bleaching earth clay	38°C, 1 bar, 25% CO ₂	Cryogel beads	Fixed bed reactor	7.84	TSA at 110°C with N ₂	-	[35]
CS ionogel in fumed silica	40°C, 1 bar	Inverse SILP	Volumetric	0.1-0.8	-	-	[36]
PIL-CS	25°C, 1 bar, 100% CO ₂	Aerogel beads	Gravimetric, 10 mins	0.7	He flow at ambient followed temperature increase to 120°C (TSA)	-	[37]
ZeY@CS	25°C, 1 bar	Powder	Volumetric	1.48	-	-	[38]
ZSM-5@CS	25°C, 1 bar	Powder	Volumetric	2.16	-	-	
ZX/CS	25°C, 1 bar	Cryogel beads	Gravimetric	4.23	VSA or TVSA at 150°C	10.4	[27]
LiCl-ZnCl ₂ /CS	0-25°C, 1 bar	Activated carbon	Volumetric	0°C: 7.9 25°C: 5.6	TVSA at 200°C	-	[39]
CS/KOH or NaOH	0-25°C, 1 bar	Activated carbon	Volumetric	KOH@0°C: 8.36 25°C: 5.43 NaOH@0°C: 7.38 25°C: 4.5	-	55.23	[40]
CS/GO	25°C, 1 bar	Cryogel	Volumetric, gravimetric	CS (pre-calcination): 0.4	TSA at 130°C	-	[41]

				CS-GO-% (pre-calcination): 0.60			
CS-GO	25°C, 1 bar	Cryogel	Volumetric/BET model	0.2579	-	-	[42]
CS-GO-Arginine	35°C, 1 bar	Cryogel	Gravimetric, 35 mins	5.48	TSA at 40- 100°C	-	[43]
Glycated CS/EEG	25°C, 1 bar	Cryogel	Gravimetric, volumetric	2.88	ESA at 165°C over 20 cycles	-	[44]
CS/ZIF-8	25°C, ~1.1 bar	Cryogel beads	Volumetric	Pre- calcination: 0.679 Calcined: 0.990	-	-	[45]
CS/ZIF-67	0-25°C, 1 bar	Cryogel bead	Volumetric	0°C: 1.21 25°C: 0.76 CS: ~0.1	TVSA at 100°C	-	[46]
CS/HKUST-1	0-25°C, 1 bar	Cryogel Beads	Volumetric	0°C: 2.68 25°C: 1.98 CS: 0.083	-	-	[47]
CS/PVA/CuBTC	25°C, 1 bar	Electrospun fibers	Volumetric	0.38	-	>14	[48]
CS/sod-ZMOF	25°C, 1 bar, 15% CO ₂ (PBR), 100% CO ₂ (TGA)	Powder	Packed bed reactor (PBR), gravimetric	PBR: 22.2 TGA: 0.57		-	[49]

2.2 Laser-induced Graphene

Laser-induced graphene (LIG) is the fabrication of graphene on a substrate surface using a laser (**Figure 4**). This method is much faster and environmentally friendly compared to traditional chemical and electrochemical processes as LIG can be made in minutes compared to hours or days, and large amounts of chemical reagents are not required. Since its discovery in 2014 using polyimide film, the use of different lasers and substrates have been explored for the optimal synthesis of graphene. In the case where a CO₂ laser with long wavelength of 10.6 µm is used, the conversion of polyimide to graphene is believed to be a result of photothermal effects where highly localized temperatures (>2,500°C) are generated by the laser irradiation [52]. Such high temperatures cleave C-O, C=O and N-C bonds, leaving behind aromatic units which rearrange themselves to form graphitic molecules.

In addition, the use of LIG has been explored for different applications, including thin and flexible heaters with customized patterns by applying electricity and Joule heating principles. For example, Bobinger et al. [53] used a self-developed computer numerical control (CNC) driven laser diode to create conductive patterns on 125 μm Kapton® HN polyimide films via photothermal ablation. By applying different power levels (0.2-1.4 W) to a 1 cm^2 LIG area, temperatures from approximately 50 to 200°C was achieved within a few minutes, which is sufficiently high for low temperature DAC. The temperature output in relation to the input power density was $131 \pm 5 \text{ }^\circ\text{C}\cdot\text{cm}^2/\text{W}$ and no changes in resistance were observed after 100 bending cycles, demonstrating their robustness. In another study, a CO_2 laser was used to evaluate the influence of the different laser parameters on the electrical resistance and quality (smoothness and substrate attachment) of LIG produced on 127 μm Kapton® film [54]. The main parameters were laser power, scanning speed, step interval/scanning pitch, and laser scanning mode (direction). It was found that three rounds of x-swing scanning mode with a coarse pitch (100 μm) produced the lowest average resistance and low degree of anisotropy in the resistance. Three patterned heaters were created using the ideal parameters. After 60 seconds, the single-faced rectangular heater reached over 70°C when 18V was applied, while the double-sided heater reached almost 90°C when 12V was applied.

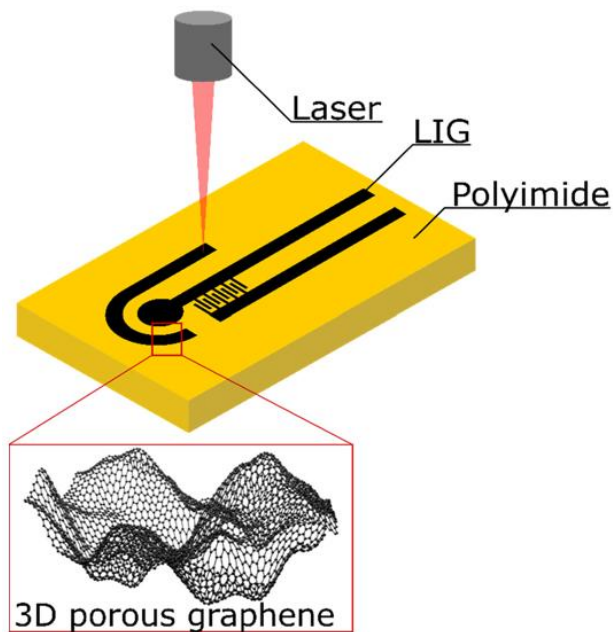


Figure 4. Schematic of the laser-scribing process of LIG on polyimide. Adapted under terms of the CC-BY license [55]. Copyright 2021 The Authors. Published by American Chemical Society.

2.3 Electric Swing Adsorption

In a temperature swing adsorption cycle there are three main steps. The first is the feed of a gaseous mixture containing CO₂ into the adsorption bed at ambient temperature. The second is the heating of the adsorbent bed to initiate desorption of CO₂ and bed regeneration, which may or may not be combined with the flow of purge gas to help remove the desorbed gas. Lastly, the cooling step uses purge gas to decrease the temperature of the bed before beginning a new cycle [56]. Whereas gas or steam is used in traditional TSA in the regeneration step to transfer heat to the sorbent, electrification of conductive materials is used in ESA (also known as electrothermal adsorption). Advantages of using ESA over TSA include providing direct heat to the sample with little to no extra heat used to heat ancillary parts, faster heating allowing for smaller systems, the heating rate of the sample can be independently controlled from the flow rate of the purge gas to enable optimization of each, and the heating rate is independent of the heat capacity of the heat source [56,57].

There are two general configurations of ESA: direct and indirect. Direct, the most popular to date, uses a (semi-) conductive sorbent which is connected to electrodes such that heating is generated internally. Indirect uses separate conductors to provide resistive heating to the chosen sorbent [58]. An example of indirect ESA is the Microlith developed by Precision Combustion, Inc. which consists of an inert but conductive metal mesh where zeolites are deposited [59]. It was developed for the removal of CO₂ and other gaseous contaminants from inside spacecrafts and submarines. A recent investigation filled biocarbon tubes with diatomaceous earth cylindrical pellets (**Figure 5d**), allowing a tube array to be connected to a power source [60]. After reaching equilibrium capacity for a feed containing 13.8% CO₂ with N₂, Joule heating of the tubes resulted in quick regeneration of ~4 min compared to ~16 min when only N₂ purge gas was used. In another case, 1 mm diameter NiCr wires were wrapped around the outside of an AC monolith [61]. While the wire reached 100°C in < 15s, the monolith reached a relatively homogeneous 50°C 80 s after the heating was stopped. Tlili et al. [62] also used AC in the form of an AC adsorbent layer fabricated with polydimethylsiloxane (PDMS) on metal rods to allow for direct heating.

Most CO₂ capture studies to date utilizing direct ESA have investigated the use of carbon-based sorbents due to their inherent electrical semi-conductivity. These sorbents may take different forms such as activated carbon fibers (ACF), activated carbon monoliths (ACM), or pellets. ACFs may feature faster adsorption rates and higher capacities than the more commonly found granular AC due

to their narrower pore size distribution. Moon et al. [63] investigated commercial pitch-based (aromatic hydrocarbon) ACFs and found it could adsorb up to 0.91 mmol of CO₂/g-ACF, which was twice the adsorbed amount of CH₄. Within 30 seconds of applying 30 V to the ACF, a temperature exceeding 200°C was reached. For CO₂ the regeneration efficiency was around 80% using both vacuum and ESA for desorption but there was found to be a limit in improvement of regeneration efficiency with the increase in desorption energy (increase voltage/current). ACFs have also been combined with phenolic resin to create carbonized and activated composites [64]. At 25°C the maximum adsorption capacity achieved was 2.91 mmol g⁻¹. When tested for ESA, they found that higher current levels always achieved higher desorption rates and shorter desorption time, while increasing the application time enhanced this effect. For a CO₂ feed concentration of 5.54% and 10.75%, the energy consumed for desorption was 216 J/mmol (4.9 GJ/t CO₂) and 132 J/mmol (3 GJ/tCO₂), respectively [65]. These results are comparable to the 3-4 GJ/tCO₂ needed for MEA to capture 13.3 wt% CO₂ [66]. Wang et al. [67] used polyacrylonitrile (PAN) fiber felt as a scaffold to create an AC aerogel-like sorbent. The structure could be controlled by first shaping the PAN felt, then covering it with phenolic resin and hexamethylenetetramine, followed by drying, carbonization and CO₂ activation. They tested a scroll-like configuration for ESA (**Figure 5b**), where the sorbent reached 287°C at equilibrium when 6 V was applied.

Carbon-based monoliths are a highly popular option for ESA. Luo et al. [68] compared AC in the form of a monolith, beads and fiber cloth and found that the monolith had the lowest pressure drop, highest electrical resistivity, and lowest cost. The beads had the largest throughput ratio and the most utilized bed length while the cloth had the largest adsorption capacity, fastest regeneration time and highest purity of gas obtained from desorption. While toluene was used for adsorption in this study, parallels can be drawn for other gases like CO₂. Using a stream of 4.51% of CO₂ with helium on a MAST© carbon monolith for ESA, Grande et al. [69] estimated a power consumption of 7.23 GJ/tCO₂ and a simulated recovery of 89.5% with 16.4% purity was obtained using a three-step cycle. Similar to previous reports [65], when CO₂ feed concentrations are higher the energy consumption is decreased, as demonstrated by the 5.64 GJ/tCO₂ energy used for 15% of CO₂ in N₂ by Zhao et al. [70] also using a MAST© monolith and an optimized four-step cycle. Another study focused on using a coated carbon monolith for improving indoor air quality using a four-step ESA swing with a temperature difference of only 20°C (30 to 50°C) which required 28.1 GJ/tCO₂ to recover waste gas with CO₂ concentration of 6732 ppm compared to the original 3000 ppm [71]. In the aforementioned

studies, the monoliths were fabricated via extrusion; however, the advancement of additive manufacturing has led to in-lab fabrication of 3D printed monoliths. One printed monolith consisting of 50:50 wt% AC powder and potassium silicate achieved rapid and homogenous heating to 150°C in less than 30 s using an 8 V potential [72].

Due to the lower capacity of AC materials at low partial pressures [56,73], others have investigated incorporating adsorbents with improved performance combined with carbonaceous compounds as the conductive element. The vast majority have explored the use of different zeolites since they are a well-known sorbent. An extruded monolith fabricated using AC (from phenolic resin) and 69 wt% zeolite NaUSY had a high CO₂ capacity of 1.75 mmol g⁻¹ at 0.1 bar and the electrical resistivity was increased [74]. Thus, the energy loss caused by the contact resistance between the copper electrode and monolith was reduced from 73% to 18% of the total resistance. Mendes et al. [75] explored 3D printed monoliths containing different combinations of zeolite 13X, AC, and graphite. At 0.15 bar and 30°C, the monoliths containing zeolite had the highest CO₂ capacities (Zeo-3D > Zeo-AC-3D > Zeo-G-3D), with a working capacity of 1.03 mmol g⁻¹ for Zeo-AC-3D. However, the graphite (Zeo-G-3D) had higher CO₂/N₂ selectivity and resulted in more efficient Joule heating by reaching 70°C in 22 s using 24 V while the AC hybrid sample (Zeo-AC-3D) only achieved 48°C after 96 s.

Sorbents in the form of hollow fibers which could be bundled have also been explored. PEI-impregnated (9 wt%) silicon carbide (SiC-PEI) fibres and fibres consisting of carbon nanotube (CNT) with dispersed zeolite particles (80 wt%) as seen in **Figure 5a**, had an estimated minimum energy requirement of 14.5 GJ/tCO₂ and 9.2 GJ/tCO₂, respectively, for a temperature cycle of 30 to 80°C [76]. By coating carbon fibers with mesoporous silica, cellulose acetate followed by PEI impregnation (**Figure 5c**), Lee et al. [77] created a wind driven DAC system utilizing ESA. At 100% CO₂ the sorbent coating (removed from fiber) had a capacity of 1.8 mmol g⁻¹ after 2 hours, while reaching 0.65 mmol g⁻¹ for the same time under 400 ppm (the sorbent coated carbon fiber was a bit lower at 0.44 mmol g⁻¹). A technoeconomic assessment revealed an estimated energy demand of 7.2 GJ/tCO₂ and \$160/tCO₂ removed if the system was powered with wind energy.

Mixing AC, zeolite 13X and carboxymethylcellulose (CMC) as a binder can be done to create extruded pellets [78]. Pellets containing 50%/50% AC/13X could reach 42°C in ~15 minutes but a ratio of 30%/70% did not increase in temperature when electrified due to their high resistivity. This

contrasts with results obtained by their group's previous results [79] when they developed a 3D printed monolith containing 30%/70% AC/13X.

The incorporation of MOFs in a 3D-printed monolith was explored by Kearns et al [80]. The printed monolith composed of 57 w/w% TIFSIX-Ni, 31 w/w% graphite and 7 w/w% bentonite clay and 5 w/w% ethyl cellulose (EC) could be heated to 70°C in 120 s by applying a 30 V potential. Rather than using graphite, the extracted 1-D derivatives including graphene and reduced graphene oxide (rGO) have also been used. Pristine graphene films and rGO aerogels were found to have high CO₂ capacities of 11.59 mmol g⁻¹ and 21.36 mmol g⁻¹, respectively, and could be fully regenerated using Joule heating at 0.3 A and 3 V [81]. In addition, a cryogel containing MgAl mixed metal oxide (MMO) nanoparticles and rGO could be heated electrically up to 400°C in N₂ atmosphere for a Joule heating efficiency of 33 °C W⁻¹ [82]. As with AC-based adsorbents, a decrease in resistivity was observed at increased temperatures [58], but these changes were fully reversible. As previously mentioned, Pal et al. [44] synthesized a GC and EEG cryogel where the graphene network enabled direct Joule heating of the adsorbent. By applying 1 A of current through the cryogel, the adsorbent temperature increased to 165°C for regeneration, maintaining 98.5% of the initial adsorption capacity after 20 cycles.

Few studies have not used a form of carbon as the conductive element for ESA. Jacobs et al. [83] 3D printed monoliths consisting of ion exchange resin (IER), silver coated glass flakes (AgFlake) with water, methyl cellulose and PEI as binders and rheological modifiers. 25 vol% of AgFlakes resulted in low enough resistivity (< 10 Ω m) for Joule heating regardless of sorbent expansion in different levels of humidity. The monolith could be heated up to an average temperature of 70°C in about 60 s by applying 3 A (~5 W), although there were observable hotspots possibly due to inhomogeneous dispersion of the AgFlakes.

To date, studies utilizing ESA have been heavily focused on direct ESA systems. **Table 3** provides a summary of the direct and indirect systems discussed. For indirect systems LIG has not yet been used for Joule heating in sorbent regeneration for CO₂ capture. There may be benefits to separating the sorbent and the joule heating systems within DAC including easier optimization of each component for its intended purpose, and allowing for more straightforward end-of-life processing when different materials are not mixed together.

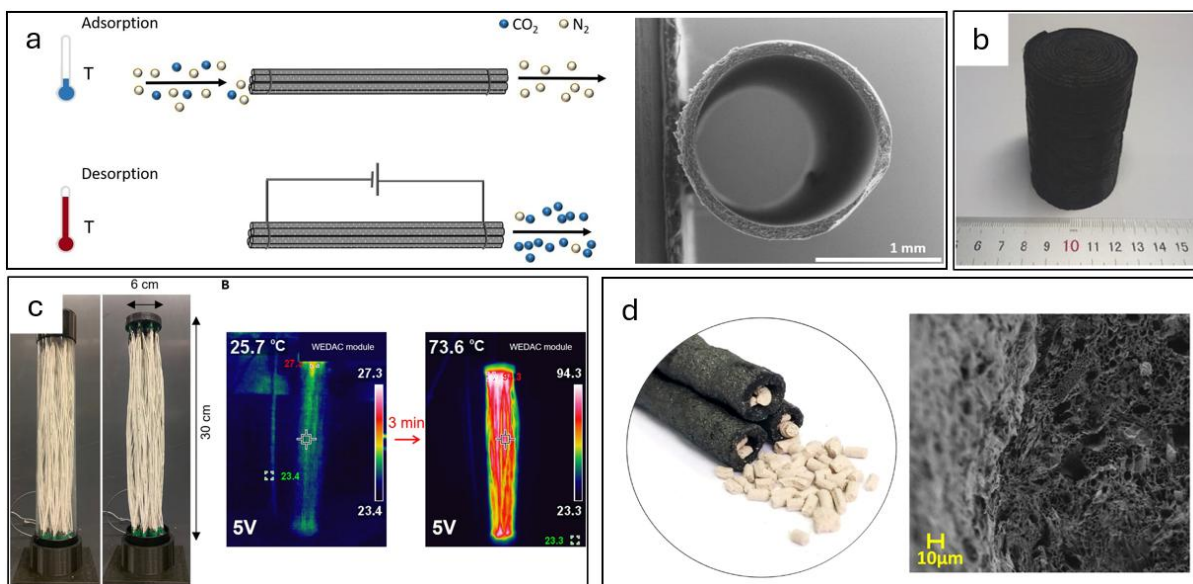


Figure 5. Sorbents used for ESA. a) ESA Schematic and SEM of CNT-zeolite hollow fibres. Adapted from [76], Copyright 2019, with permission from Elsevier. b) AC scroll-shaped monolith. Reprinted from [67], Copyright 2017, with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. c) DAC module with 120 sorbent-coated carbon fibres and thermal images of 5V being applied for 3 min. Reprinted from [77], Copyright 2023, with permission from Elsevier. d) Digital and SEM image of diatomaceous silica-filled biocarbon tubes. Adapted from [60], Copyright 2024, with permission from Elsevier.

Table 3. Summary of CO₂ capture studies utilizing ESA

Adsorbent	Adsorption Conditions	Adsorbent Structure	Adsorption measuring technique	CO ₂ adsorption capacity (mmol g ⁻¹)	Desorption Conditions	Regeneration	Resistance/ Resistivity	Refs.
Indirect ESA								
Biocarbon/diatomaceous earth	25°C, 1 bar, CO ₂ in N ₂	Pellets in an AC tube	Breakthrough, three & four step	4% CO ₂ : ≈0.08 7%: ≈0.15 10%: ≈0.19	50 mL/min N ₂ , 2-7 V DC, 185°C	0.45 MJ/kg sorbent, purity: ~45%	1.5-3.2 Ω (171°C-42°C)	[60]
AC/PDMS	25°C, 1 bar, 350 mL/min	Sorbent covered metal rods	Volumetric	≈2 (70 wt% AC)	-	-	-	[62]
	20°C, 1 bar, 10% CO ₂ in N ₂		Breakthrough, three-step	-	15-70 mL/min N ₂ , 15 A DC, 170°C	-	-	
Direct ESA								

Pitch-based ACFs	25°C, 1 bar	Fibers	Volumetric	0.91	-	-	-	[63]
	1 atm, 50% CO ₂ in N ₂		Packed bed/ Breakthrough		0.6-1 L/min, 5-30 V AC,	200°C in 30 s at 30V, >80% regen efficiency (VESA)	5-43 Ω (0- 50V)	
ACF/phenolic resin	25°C, ~1 bar	Molecular sieve monolith	Volumetric	25°C: 2.91 0°C: 4.5	-	-	-	[64]
	5.54% & 10.75% CO ₂ in N ₂		Breakthrough, three & four-step	5.54%: 0.53; 10.75%: 0.91	0.4-0.5 L/min N ₂ , constant 8 A DC	5.54%: 4.9 GJ/t (216 J/mmol), 10.75%: 3 GJ/t (132 J/mmol)	-	[65]
AC	1 bar	Scroll monolith	Volumetric	0°C: 5 25°C: 3.5	-	-	-	[67]
	25°C, 15% CO ₂ in N ₂		Breakthrough	1	150°C, 6 V, N ₂ flow	Purity: ~50%, regen efficiency: 92%	ρ: 0.38 Ωm	
AC monolith	24°C, 101 kPa, 4.51% CO ₂ in He	Extruded monolith	Breakthrough, three-step	≈3 (gravimetric, 26°C, 1 bar)	1.76 L/min, constant 12 V, electrification time: 45s, 150°C	7.23 GJ/t CO ₂ , purity: 16.4%, recovery: 89.5%	-	[69]
AC monolith	20°C, 1.03 bar, 15% CO ₂ in N ₂	Extruded monolith	Breakthrough, four-step	≈3.7 (volumetric, 20°C, 1 bar)	12A, electrification time: 80s, 600 ml/min N ₂ , 147°C (simulated)	5.64 GJ/t CO ₂ , purity: 52%, recovery: 76%	-	[70]
Coated AC monolith	30°C, 3000 ppm (0.3%) CO ₂ in air	Extruded monolith	Two-bed breakthrough, four-step	Max: 1.372 mmol/kg WC: 1.072 mmol/kg	6 & 30 L/min, 18 V, 50°C	28.1 GJ/tCO ₂ (57.8 kJ/m ³ air)	-	[71]
AC powder/potassium silicate	25°C, 30% CO ₂ in CH ₄	3D printed monolith	Breakthrough, four & five-step	0.60 (1.04 volumetric at 0.3 bar CO ₂ , 30°C)	100 NmL/min He for 15 s, constant 8 V, 150°C	8.7-22.1 GJ/tCO ₂ (15-55 s electrification @ 6 V) purity: 65%, Regen efficiency: 95%	25°C: 0.0181 Ωm, 100°C: 0.0156 Ωm	[72]
AC/NaUSY	20°C	Cylindrical bar	Volumetric	0.05 bar: 1.45 0.1 bar: 1.75			ρ: 0.0118 Ωm	[74]
		Monolith (model)	Breakthrough, four-step	2.01 g	600 ml/min N ₂ , 50 W	2.5 GJ/tCO ₂ , purity: 44%	-	
Zeolite 13X/bentonite/ AC or graphite	30-100°C, 0.15 bar	3D printed monolith	Volumetric	Zeo-AC: 1.03 Zeo-G: 0.94	-	171 J/g sorbent	Zeo-AC: 470 Ω Zeo-G: ~60 Ω	[75]
SiC-PEI	30°C, 15/100% CO ₂ in N ₂	Hollow fiber	Gravimetric, 60 min	100% CO ₂ : 0.2 (WC), 0.4 (MC); 15% CO ₂ : 0.09 (WC), 0.2 (MC)	80°C (WC)	14.5 GJ/tCO ₂	ρ: 0.00125 Ωm	[76]

CNT-zeolite				100% CO ₂ : 2.0 (WC), 4.8 (MC); 15% CO ₂ : 1.1 (WC), 2.3 (MC)		9.2 GJ/tCO ₂	ρ : 0.000303 Ω m	
CF/silica/cellulose acetate/10 wt% PEI	30°C, 0.04% CO ₂ in N ₂	Sorbent-coated fibers	Gravimetric, ~22 h	2h: 0.32 18h: 0.44 WC: 0.48 (coating only)	110°C 1 h	-	-	[77]
	0.04% CO ₂ in air, 50-200 sccm		Breakthrough, three-step	Dry: 0.40 Wet: 1.00 Prehydrated: 1.21	7 V, 1A DC, 110°C, 100 sccm Ar	7.2 GJ/tCO ₂ (full scale), regen efficiency: 95% in 10 min, purity: > 80%	-	
AC/zeolite 13X/CMC	30°C	Extruded pellets	Volumetric	50/50 AC/13X: 0.1 bar: $\approx$ 1.6 1 bar: $\approx$ 3.4		Selectivity 20/80 CO ₂ /N ₂ : 41.9	ρ : 0.25-0.57 Ω m (125°C-25°C)	[78]
	24°C, $\sim$ 1.3 bar, 23% CO ₂ in N ₂		Breakthrough, three-step	-	0.2 L/min N ₂ , <2800 s electrification, 18 V, 127°C	Regeneration in 1000 s	-	
TIFSIX-Ni/graphite/betonite/EC	25°C, air	3D printed monolith	Breakthrough	Dry: 0.86 Ambient humid: 0.69	2.1 A		315 Ω	[80]
Graphene	5% CO ₂ in N ₂	Film	Breakthrough, four-step	11.59	0.5 A, 3 V, $\sim$ 33°C Δ T	Regen efficiency: 100%	-	[81]
rGO	5% CO ₂ in N ₂	Aerogel	Breakthrough, four-step	21.36	0.5 A, 3 V, $\sim$ 38°C Δ T	Regen efficiency: 100%	-	
MgAl-MMO/rGO	300°C, 0.2-10 bar, 100% CO ₂	Cryogel	Gravimetric	1 bar: $\approx$ 0.75 8 bar: 2.3	400°C, $\approx$ 0.9 W·h	33 °C W ⁻¹	ρ : 0.07 Ω m	[82]
Glycated CS/EEG	25°C, 1 bar	Cryogel	Gravimetric, volumetric	2.88	165°C in $\sim$ 20 s, 1 A	Regen efficiency: $\sim$ 99.8%	-	
IER/Ag-coated glass flakes/methyl cellulose-PEI	9 vol% CO ₂ in N ₂	3D printed monolith	Gravimetric, 2 h	1.48 mmol g ⁻¹ dry IER	70°C in $\sim$ 60 s, 3 A, 1.5-1.8 V		ρ : < 10 Ω m	[83]
	25°C, 0.0004 bar		Volumetric	0.5 ($\sim$ 1 mmol g ⁻¹ dry IER)	-		-	

Chapter 3: Experimental

3.1 Materials

Low molecular weight (LMW) chitosan (75-85% deacetylation) and methanol ($\geq 99.9\%$) were purchased from Sigma-Aldrich. Copper hexafluorosilicate hydrate ($\text{CuF}_6\text{Si} \times \text{H}_2\text{O}$) was purchased from Oakwood Chemicals. Glacial acetic acid (99.7%) and pyrazine (98%) were purchased from Thermo Fisher Scientific. Polyimide (PI) Kapton® 5 mil film was used as a precursor for graphene synthesis.

3.2 Sorbent Preparation

3.2.1 SIFSIX-3-Cu

The preparation process outlined by Shekhah et al. [84] was followed. Briefly, 0.30 g of pyrazine was dissolved in 5.0 ml of methanol, then added to a 0.325 g of $\text{CuF}_6\text{Si} \times \text{H}_2\text{O}$ dissolved in 5.0 ml of methanol. The mixture was left overnight before the powder was collected via gravity filtration, washed with methanol, and dried under vacuum.

3.2.2 Chitosan Cryogel

Chitosan cryogels were prepared based on the findings of Cooney et al. [85] to achieve smaller, highly interconnected pores in the final cryogel. LMW chitosan was dissolved in 0.2 M aqueous acetic acid solution in DI water to make a 1 wt% sol by stirring and left to sit overnight. The chitosan sol (6 mL) was transferred into a petri dish mold and placed in a freezer for 1 hour before drying in a freeze dryer.

3.2.3 Chitosan/SIFSIX-3-Cu Cryogel

The preparation of MOF-chitosan composite is illustrated in **Figure 6**. The chitosan cryogel was used as a scaffold for in situ synthesis of SIFSIX-3-Cu similar to previous reports [51]. $\text{CuF}_6\text{Si} \times \text{H}_2\text{O}$ (0.325 g) was dissolved in 5 mL of methanol and slowly added to the chitosan cryogel. The cryogel was left to soak for 24 hours before removing excess liquid and freeze drying. Pyrazine (0.30 g) dissolved in 5 mL of methanol was then added to the Cu-doped cryogel for a 24-hour soaking before freeze drying to obtain the final chitosan/SIFSIX-3-Cu (CS/MOF) cryogel.

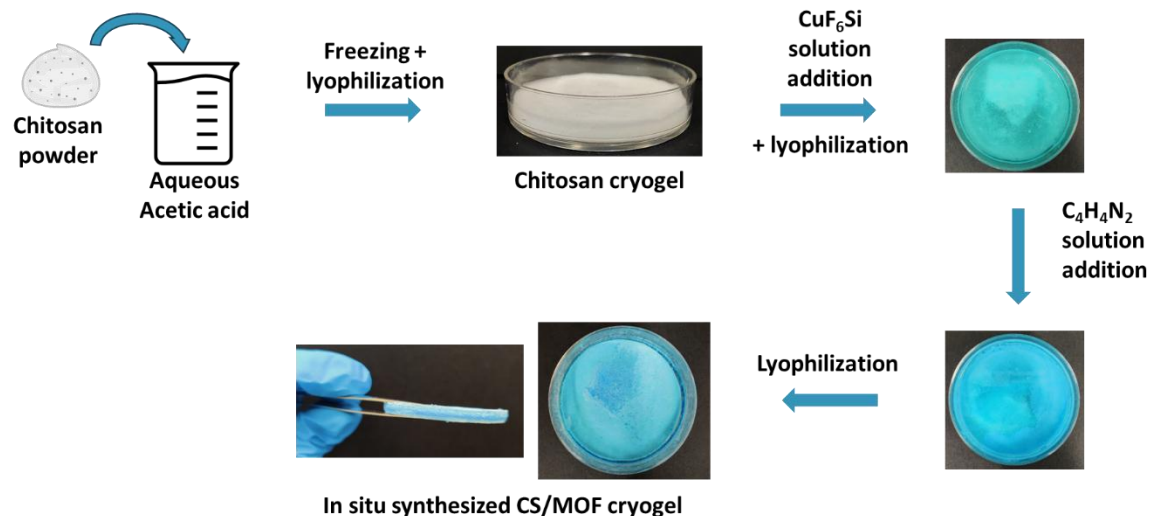


Figure 6. The process of fabricating CS/MOF cryogels. The chitosan cryogel is soaked in each MOF precursor solution for 24 hours. Freezing and lyophilization occur in between each step to obtain the final composite cryogel.

3.3 Laser-induced Graphene Preparation

Unmodified flexible PI film was used as a substrate for photothermal graphitization by a 30 W radio frequency laser tube type CO₂ laser (Thunder Bolt) with a wavelength of 10.6 μm . The range of lasing parameters which could produce LIG was first identified by exploring different laser parameters including speed (mm s^{-1}), laser power (%), and scan mode (x-swing or y-swing). In the swing scanning mode, lasing occurs as the laser arm moves back and forth in the specified direction (x or y) rather than only lasing as the arm moves forward (**Figure 7**). The scanning pitch or lasing interval was maintained at 0.1 mm. The preferred parameters were then narrowed down based on Joule heating capability and the quality of the sample, including uniformness, adherence to the PI film and bendability.

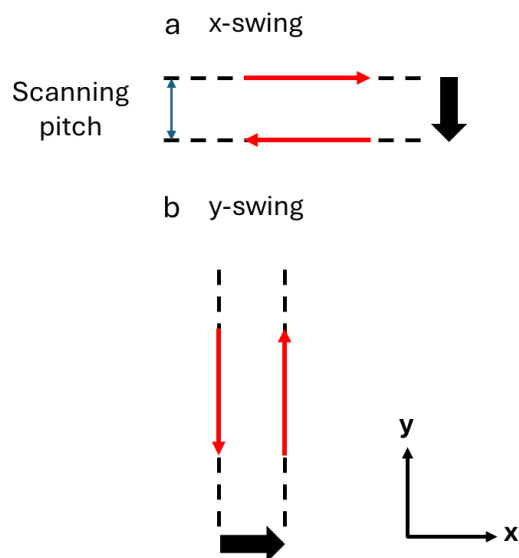


Figure 7. Schematic of x-swing and y-swing laser scanning modes and the scanning pitch.

3.4 Characterization

3.4.1 X-Ray Diffraction

X-ray diffraction (XRD) measurements were taken using a Bruker D8 Focus capable of Cu K α radiation ($\lambda = 1.54 \text{ \AA}$, 40 kV, 40 mA) to analyze sorbent crystallinity.

3.4.2 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was conducted using a Thermo Nexus 670 for the chitosan and CS/MOF cryogels and a Nicolet™ iN10 Infrared Microscope was used for pure MOF crystals to analyze molecular structures.

3.4.3 Scanning Electron Microscopy

To investigate the morphology of synthesized materials, scanning electron microscopic (SEM) images were taken using a Tescan VEGA TS-5130 from accelerating voltages between 10 to 30 kV. As required, samples were sputter coated with gold-palladium before analysis.

3.4.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was conducted using a TA Instruments Q500 to identify the degradation temperature of the adsorbents such that an appropriate regeneration temperature could be

identified. A TA Instruments Q550 was used for PI film and LIG degradation tests. All samples were placed under nitrogen gas and air from 20°C up to 1000°C at a ramp rate of 10.0°C/min.

3.4.5 Adsorption Testing

Gravimetric CO₂ adsorption tests were conducted using a TA Instruments Q600 on alumina pans at 1 bar. To prepare the sorbents for adsorption they were first subjected to nitrogen flow at 70-80°C for up to 12 hours to remove other gases and moisture. The temperature was then reduced to ambient (23°C) before switching the gas to pure CO₂ for up to 24 hours. The sample was then desorbed under nitrogen at 70-80°C for up to 12 hours. A flow rate of 100 mL/min of all gases was maintained throughout. Each cryogel type was tested multiple times, and the results of 2-3 samples were averaged. For PI film and LIG the same process was followed but the times were reduced to 2 hours for nitrogen purge and 12 hours for CO₂ adsorption. For cyclic adsorption tests, cryogels were exposed to 20 minutes of room temperature CO₂ followed by 40 minutes of nitrogen at the same desorption temperature. Nitrogen adsorption testing of SIFSIX-3-Cu and the two cryogels was conducted gravimetrically in the same manner as for CO₂.

3.4.6 Raman Spectroscopy

A Raman confocal microscope (WITec Alpha 300) at 532 nm was used to characterize the LIG directly on the PI substrate.

3.4.7 Resistivity

The resistivity of the LIG samples were measured at room temperature using the four-point probe method (Ossila T2001A). Each sample was measured at three different points and then averaged to account for spatial differences.

3.4.8 Joule Heating

The Joule heating capability of the LIG samples was tested by applying increasing voltage up to 23 V at a constant current (0.5 A) using a DC power supply (NaviTech NP3010H). For small samples, alligator clips were placed on either end of each sample and the temperature at the sample centre was measured using a thermocouple (THE-343). For larger customized graphene patterns, copper foils were placed on each end before attaching the alligator clips. Sorbents were placed directly on top of the LIG to be heated. Thermal images were taken using a HIKMICRO E01 thermal camera. The

thermal camera emissivity value ε was determined by placing LIG samples on a hot plate at 70°C and adjusting the emissivity such that the thermal image reading was aligned with the thermocouple that was in contact with the LIG.

Chapter 4: Sorbent Results and Discussion

4.1 Characterization

The FTIR results for SIFSIX-3-Cu, the chitosan cryogel and the CS/MOF cryogel are shown in **Figure 8a**. The spectra of the chitosan cryogel closely exhibits that of powdered chitosan [86,87], the broad absorption band from 3500-3000 cm^{-1} represents the N-H and O-H group vibrations, and hydrogen bonding on chitosan molecules. The peaks at 2937 and 2873 cm^{-1} represent C-H bond stretching symmetrically and asymmetrically, respectively [86]. The observed shift to lower wavenumbers of peaks 1641, 1547, 1414, and 1321 cm^{-1} from that of pure chitosan due to the acetic acid has been previously observed [86]. These peaks represent the stretching of C=O from amide I, N-H bending, CH_2 , and CH_3 symmetrical deformations, respectively. The small peak at 1381 cm^{-1} is attributed to C-N flexing of amide III due to residual N-acetyl groups [88]. For SIFSIX-3-Cu crystals the octahedral SiF_6 characteristic bands at 822 and 694 cm^{-1} can be observed [89], in addition to pyrazine aromatic C-H characteristic bands at 3105 and 3043 cm^{-1} and C-N characteristic bands at 1435, 1134 and 1076 cm^{-1} . For the CS/MOF cryogel we see matching MOF crystal peaks. The same is true for the XRD patterns (**Figure 8b**), although there is some shift in the peaks. The chitosan cryogel pattern indicates a mostly amorphous structure with weak peaks at 7.5° and 20° which is aligned with past reports [86,87].

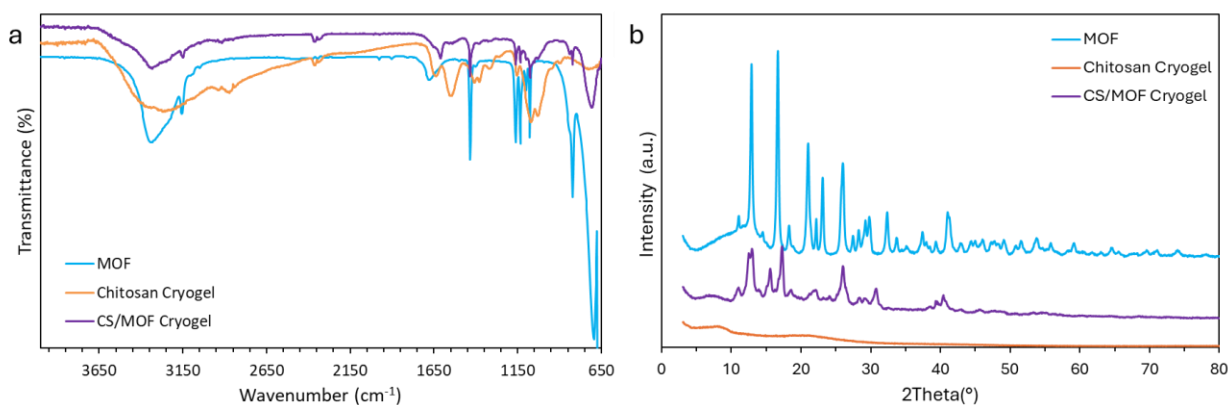


Figure 8. a) FTIR and b) XRD spectrum for SIFSIX-3-Cu, chitosan cryogel and CS/MOF cryogel.

SEM images were taken at varying voltages to assess the morphology of the SIFSIX-3-Cu crystals (**Figure 9a**) and the two cryogels. Due to the formation of ice crystals during freezing, a macroporous structure with smooth surfaces is observed for the pure chitosan cryogel (**Figure 9b**). Whereas for the

CS/MOF cryogel an evenly distribution of SIFSIX-3-Cu crystals can be observed on the surface of the chitosan cryogel (**Figure 9d**), indicating successful in situ synthesis of the SIFSIX-3-Cu MOFs in the cryogel structure. The pore structure of the CS/MOF (**Figure 9e**) also appears slightly denser than the original cryogel (**Figure 9c**), potentially due to capillary stress on the cryogel walls during soaking in the MOF precursor solutions.

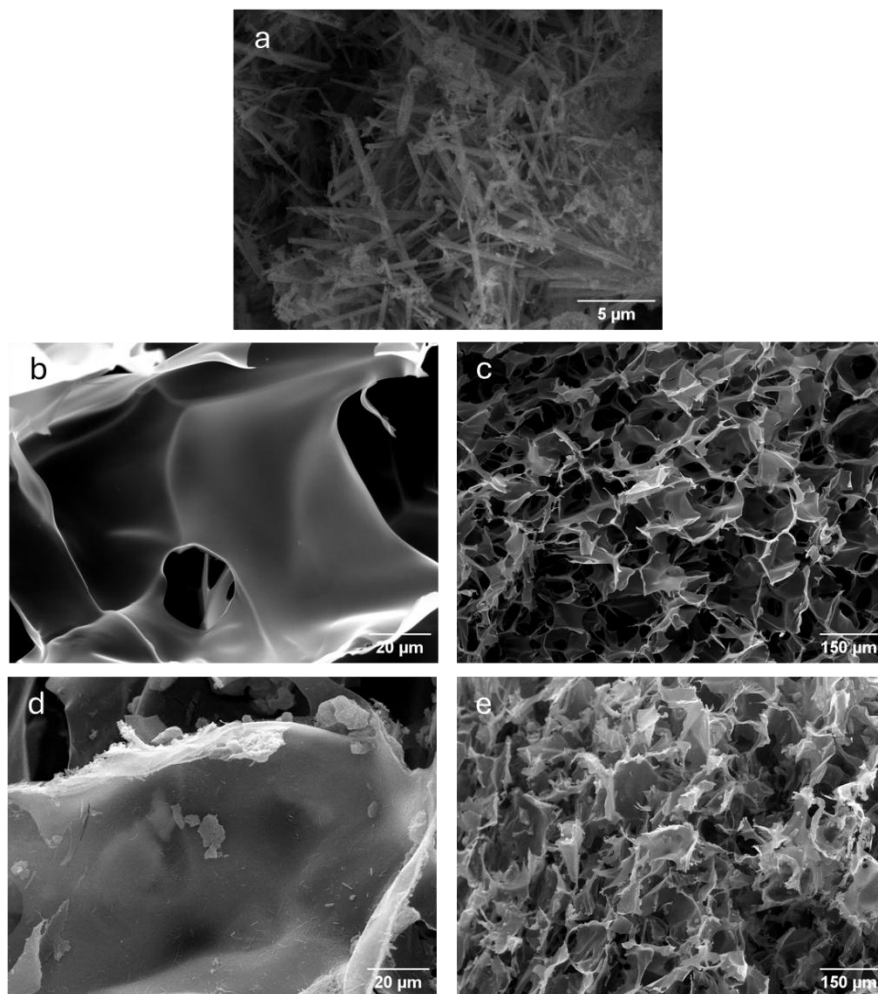


Figure 9. SEM images of synthesized sorbents. a) Pure SIFSIX-3-Cu crystals, b-c) pure chitosan cryogel cross section, d-e) CS/MOF cryogel cross section.

The degradation of the sorbents was evaluated under nitrogen (**Figure 10a**) and air (**Figure 10b**) to determine a suitable regeneration temperature. The pure SIFSIX-3-Cu crystals had similar results to previous reports [84], with about a 5% weight loss initially occurring due to guest molecule release followed by degradation of the MOF after 150°C under both nitrogen and air. The chitosan cryogel

observed a multi-stage weight reduction where more rapid and further degradation was observed under air compared to nitrogen. There was an initial reduction of almost 10% at 65°C from moisture and other guest molecule removal, followed by a more than 10% reduction from 100 to 200°C attributed to initial thermal depolymerization [47]. Lastly the final decomposition occurred after 250°C corresponding to the decomposition of deacetylated and acetylated groups on chitosan [47]. The CS/MOF cryogel degradation is comparable to the pure SIFSIX-3-Cu with a slightly higher weight drop under 150°C, indicating that the MOF crystals covering the surface of the chitosan cryogel dominate the composite behaviour. Under air, the composite cryogel experiences further weight loss after 350°C which is attributed to the breakdown of the chitosan component. Based on the observed thermal stability, a target regeneration temperature of 70-80°C was chosen to balance the speed of regeneration while maintaining the properties of the composite cryogel.

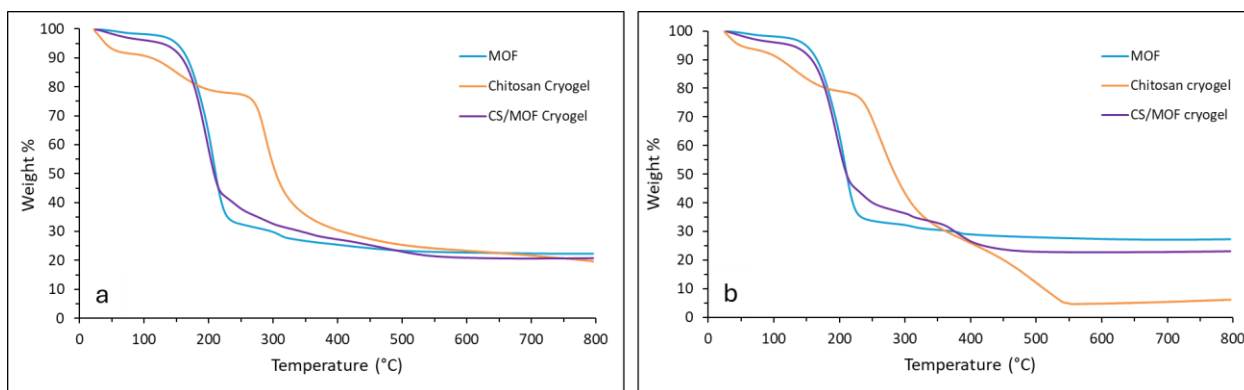


Figure 10. TGA curves under a) nitrogen and b) air flow

4.2 CO₂ Adsorption Performance

Figure 11 shows the CO₂ adsorption performance of the sorbents based on thermogravimetric measurements at ambient pressure and temperature (1 bar, 23°C). The pure MOF crystals demonstrate fast uptake kinetics and yields close to the 2.5 mmol g⁻¹ originally reported [84] within 5 minutes (**Figure 11b**). While the chitosan cryogel has much slower uptake due to the tortuous pathways that the gas molecules must travel to reach amine sites, it reaches 3.23 mmol g⁻¹ after 1 hour which is the highest capacity of the three sorbents tested. The composite cryogel curve initially follows the same rate of adsorption as the pure MOF indicating preferential uptake of CO₂ by exposed MOF crystals. Adsorption continues at a slower rate likely via amine interactions on the chitosan, reaching 1.58 mmol g⁻¹ after 1 hour. After 18 hours (1,080 minutes) the chitosan and

CS/MOF cryogel reach 10.38 mmol g⁻¹ and 2.92 mmol g⁻¹, respectively, surpassing the capacity of SIFSIX-3-Cu alone (**Figure 11a**). Notably, the chitosan cryogel is among the top performing chitosan-based sorbents previously reported. In some previous studies, chemical crosslinking strategies were used which improves the mechanical properties but utilizes amino groups in the process [90], resulting in reduced availability of NH₂ groups for interaction with CO₂. A similar amine group utilization is seen between SIFSIX-3-Cu and chitosan as indicated by the shift in the N-H peak from 1547 cm⁻¹ in the chitosan cryogel to 1608 cm⁻¹ in the CS/MOF cryogel FTIR spectra. This is supporting evidence for the adsorption performance of the CS/MOF cryogel being mostly limited to the MOF capacity. The desorption of the sorbents (**Figure 11c**) conducted at 72-77°C indicate that this temperature range is appropriate to induce the release of CO₂ while still being below the sorbent degradation temperature. Any variation in the desorption temperature was due to control limitations of the equipment. Four cycles consisting of 20 minutes of adsorption followed by 40 minutes of desorption on the CS/MOF cryogel and normalized to the capacity in the first cycle (**Figure 11d**), confirms its ability to be used multiple times with only a 12% decrease in CO₂ capacity. Nitrogen adsorption testing was also conducted over 24 hours (**Figure 11e**), after which 0.07 mmol g⁻¹ was adsorbed by the CS/MOF cryogel while the pure chitosan cryogel fluctuated between positive and negative nitrogen uptake with an average of 0.002 mmol g⁻¹. In both cases, little nitrogen is adsorbed relative to CO₂. For the CS/MOF cryogel the ratio of CO₂ to N₂ adsorbed after 18 hours was 42, while for the chitosan cryogel it was 3678, signifying good selectivity of CO₂.

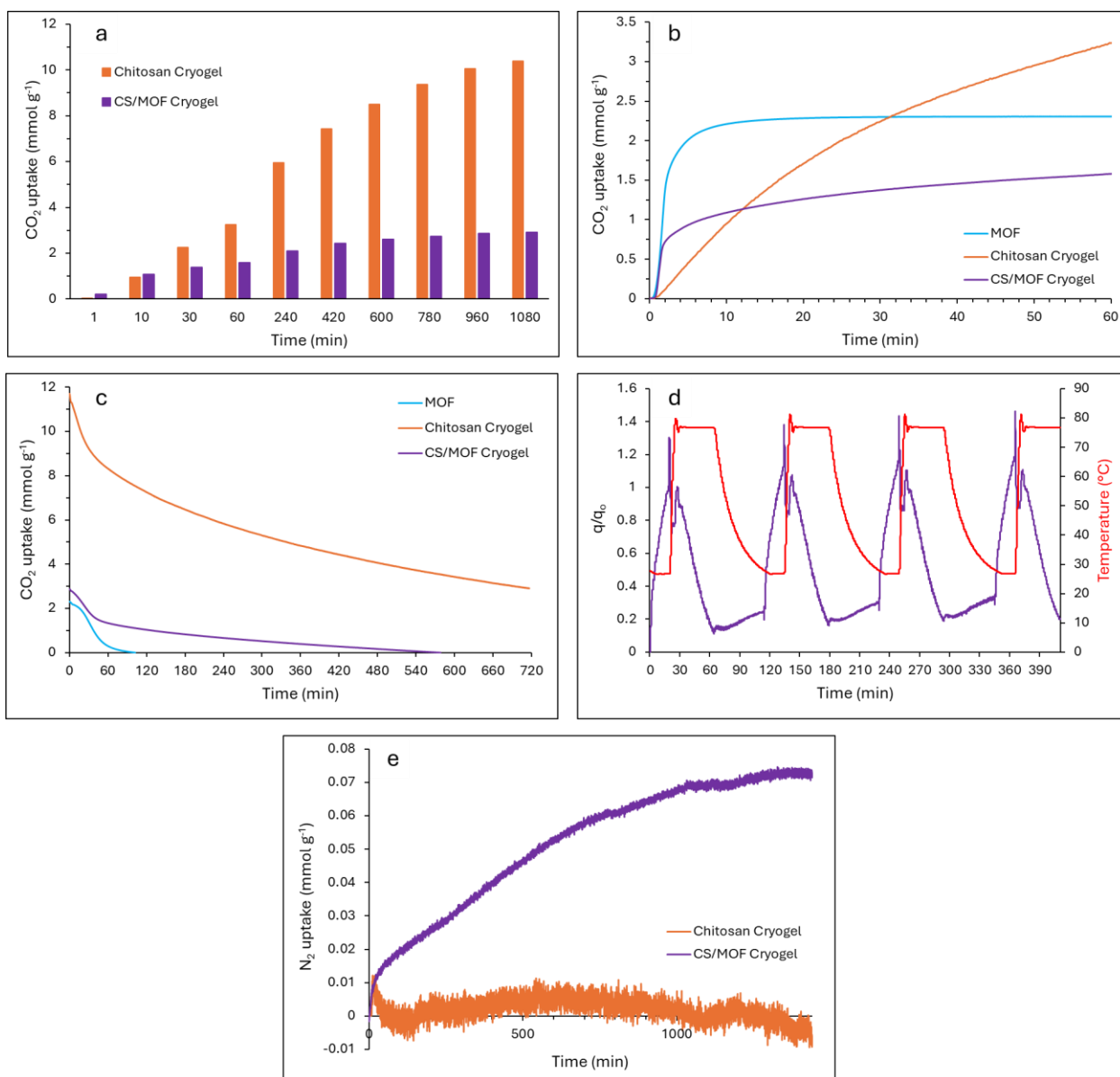


Figure 11. Adsorption curves. CO_2 adsorption (a) of the chitosan and CS/MOF cryogel after 18 hours and (b) of all the sorbents during the first hour. c) Desorption of all sorbents at a temperature of 70–80 $^{\circ}\text{C}$, after 24 hours of adsorption for the cryogels. Temperature variations were due to control limitations of the equipment. d) Four adsorption cycles of CS/MOF cryogel consisting of 20 minutes of adsorption followed by 40 minutes of desorption, normalized to the capacity adsorbed in the first cycle. e) Pure N_2 adsorption performance of the cryogels.

Chapter 5: Laser-induced Graphene Results and Discussion

After the adsorption process, sorbents undergo a desorption process to liberate the captured CO₂ for isolation and regenerate the sorbent for reuse. An electrothermal desorption method using thin and flexible laser-induced graphene (LIG) heaters is proposed here. By applying current through LIG synthesized on heat resistant and electrically insulative Kapton® film, the temperatures required for sorbent regeneration can be achieved via Joule heating.

5.1 Characterization

Synthesizing stable graphene on PI film through laser ablation required tuning various lasing parameters, including speed (mm s⁻¹), laser power (%), and scan mode (x-swing or y-swing), to produce optimum LIG for Joule heating. Rectangular samples of 20×3 mm and 35×3 mm were created for comparison. Samples were evaluated based on certain criteria including good adherence to the film and flexibility, as well as lack of PI film warpage. Generally, it was observed that shorter lasing distances resulted in improved graphene to film adherence; thus, for horizontal rectangular patterns y-swing scan mode produced overall higher quality LIG compared to x-swing and was selected for use. In addition, the Joule heating capability was evaluated by applying an increasing voltage at 0.5 A to observe the maximum achievable temperature. Temperatures generated by applying 15 V and 20 V on LIG samples created using 12% (3.6 W) and 13% (3.9 W) laser power at various lasing speeds is shown in **Figure 12a** and **Figure 12b**, respectively. For y-swing samples created using a power of 12% a temperature range from 20-120°C was observed for applied voltages of 15 V and 20 V, while for 13% power a range from 20 to 180°C was observed. Generally, higher temperatures were achieved in the 85 to 95 mm s⁻¹ lasing speed range. A wide range of LIG conductivities up to 2.4×10^6 S m⁻¹ were observed for these samples, which plays a major role in Joule heating. Based on these results, a power of 13% and speed of 95 mm s⁻¹ was chosen for further characterization and to create customized patterns for desorption, as it could reach a temperature of 118°C at 20 V. For the chosen laser parameters, a resistivity of $0.00589 \Omega\text{m} \pm 0.0031 \Omega\text{m}$ was measured, which is in line with ranges reported for good resistive heating [58].

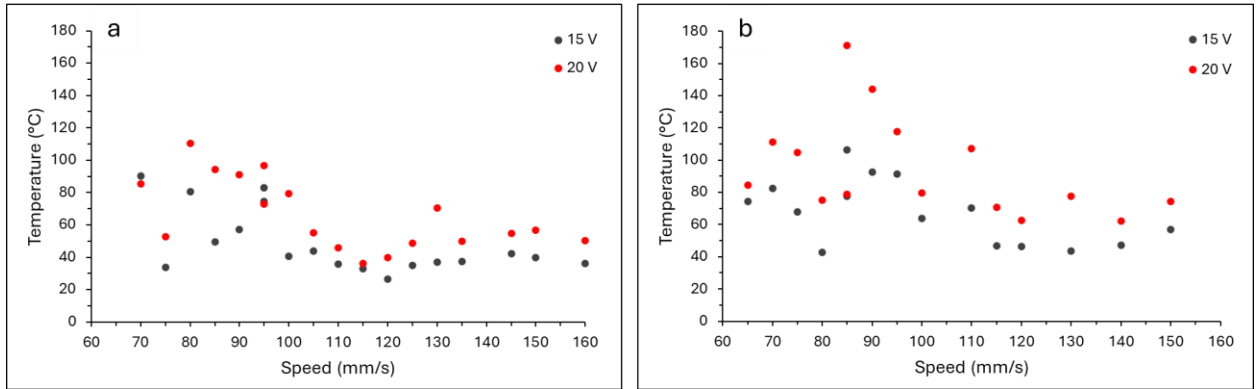


Figure 12. Joule heating temperatures generated by 20×3 mm LIG samples fabricated at various laser speeds at a) 12% power and b) 13% power.

As seen from both the top (**Figure 13a, b**) and side view (**Figure 13c**) SEM images of LIG, a 3D porous structure typical of laser-induced graphene has been achieved, which is in contrast to the 2D sheets synthesized during chemical or electrochemical methods. The range of macropores are derived from the escape of gases during the lasing process [91]. The thickness of the LIG layer is approximately 55 μm , which is 43% of the original thickness of the PI.

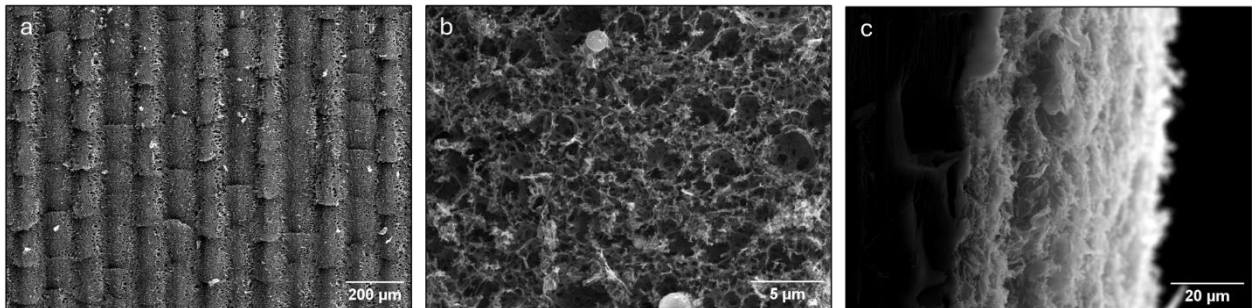


Figure 13. SEM images of a-b) LIG from the top view and c) from a cross-sectional view.

Raman spectroscopy was carried out on the LIG sample to confirm graphene formation (**Figure 14a**). Characteristic G and 2D peaks of graphitic material [92] were found at 1575 cm^{-1} , and 2673 cm^{-1} , respectively. The presence of the D band at 1345 cm^{-1} is indicative of defects in the graphene which can affect its Joule heating performance. The intensity ratio between the D and G bands (I_D/I_G), which was found to be 0.93, is indicative of the amount of graphene formation [52]. In addition, the 2D to G band ratio (I_{2D}/I_G) which is indicative of multilayers with smaller ratios [54] was 0.89 for the chosen laser parameters.

The degradation of pure PI film and LIG synthesized on PI was evaluated using TGA in both nitrogen and air (**Figure 14b**). Comparing the PI film before and after laser ablation, there is a decrease of roughly 15°C in the degradation onset temperature regardless of the gaseous environments used. However, for each material there is little to no difference in the degradation onset temperature when the gas is changed. The LIG is stable until approximately 550°C under both N₂ and air, after which there is a single stage weight reduction attributed to the breakdown of the PI [93,94]. This is well within the range required for low temperature regeneration for DAC. As the LIG on PI is paired with a cryogel sorbent as a system, gravimetric CO₂ adsorption testing was also conducted on pure PI film and on the LIG to determine if there would be additional impact. From **Figure 14c** it can be seen that for the PI film CO₂ adsorption is slightly higher than for the LIG, peaking at 0.14 mmol g⁻¹ compared to 0.12 mmol g⁻¹. While this is low compared to the cryogels, it can still contribute to the overall capture of the whole system.

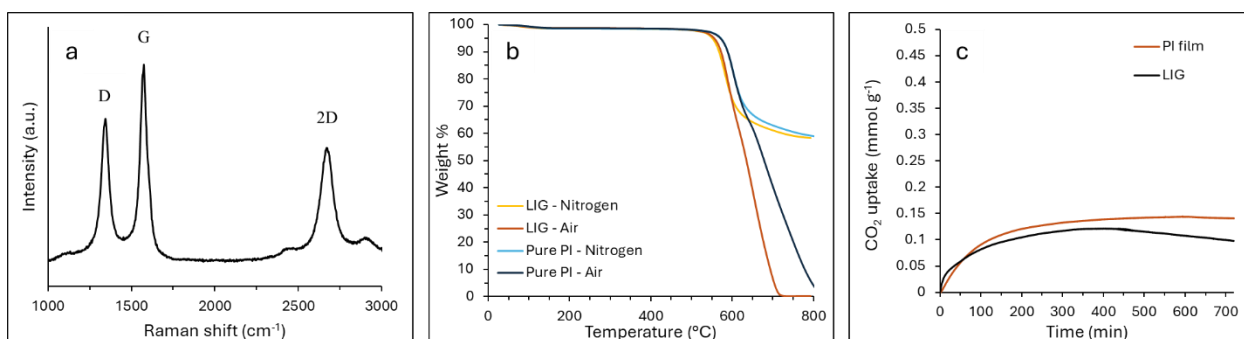


Figure 14. a) Raman spectra for LIG. b) TGA curve of pure PI film and LIG under nitrogen and air flow. c) CO₂ adsorption of pure PI film and LIG on PI.

5.2 Joule Heating Performance

A 70×60 mm customized striped grid pattern (**Figure 15a**) was fabricated for further Joule heating tests conducted at room temperature that could be applied to the cryogels. The pattern consisted of 9 rows which were 61.34×3 mm and equally spaced 3.5 mm apart. The rows were enclosed on each side by 4.33×60 mm sections. Each row in the pattern was fabricated before moving onto the next row. As seen in **Figure 16a**, the rate of the temperature rise varies based on the applied voltage with higher voltages having higher rates. When 23 V is applied, the approximate heating rate was found to be 9°C/s to reach 90% of the maximum temperature while the LIG cooled at a pace of 2.9°C/s from

the time the voltage supply was turned off to within 10% of the lowest temperature during cooling. However, 23 V reached over 120°C which would be close to the degradation temperature of chitosan and SIFSIX-3-Cu. Thus, for the regenerative heating of the cryogels 15 V was chosen as it produced a safe range of 70-80°C.

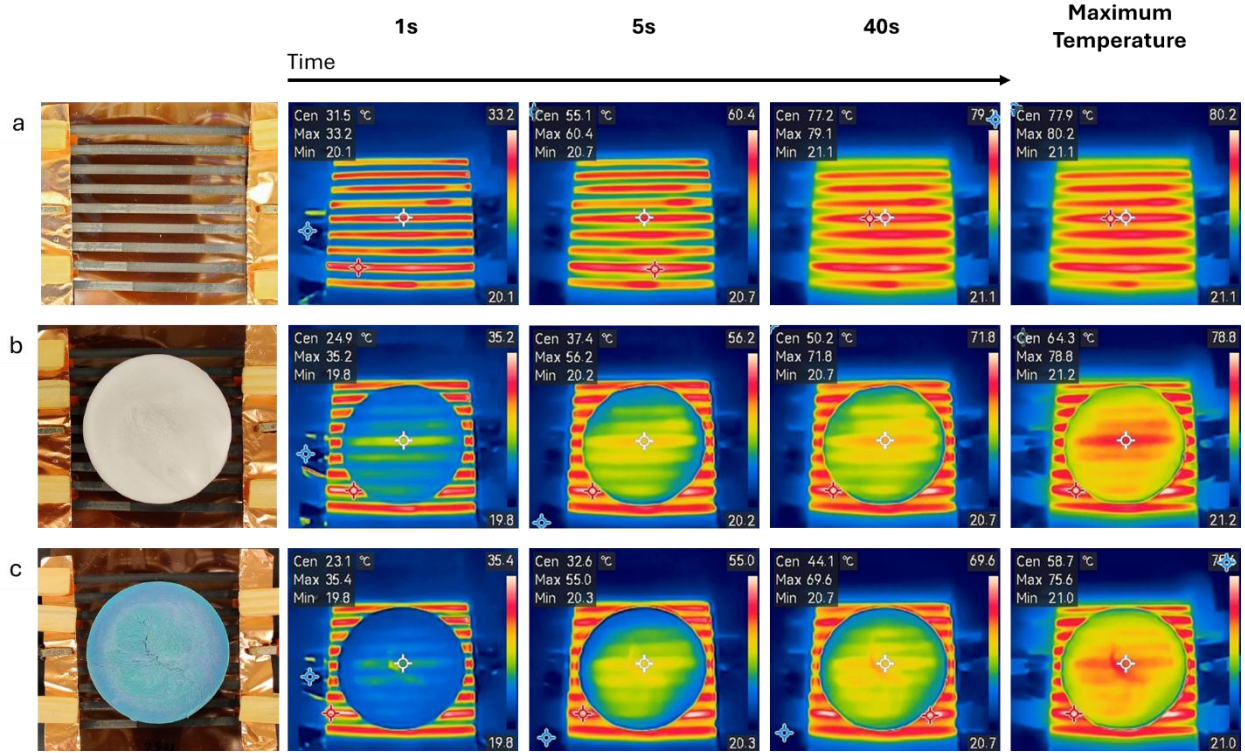


Figure 15. Digital images of the Joule heating setup and thermal images taken after 1s, 5s, and 40s after 15 V is applied, followed by the maximum centre temperature achieved during the test. Samples are of a) the 70×60 mm LIG grid, b) the chitosan cryogel on LIG, and c) the CS/MOF cryogel on LIG.

The chitosan and CS/MOF cryogels were placed directly on top of the LIG grid and the thermal images taken at 1 s, 5 s, and 40 s, after heating began show that the heat transfers through the cryogels (**Figure 15b, c**). The maximum temperature reached in the centre of the chitosan cryogel was 64.3°C and 58.7°C for the CS/MOF cryogel, which is less than the surface of the LIG but sufficient for CO₂ desorption. As these tests were conducted in open air, it's expected that that temperatures would be higher if placed inside an enclosure [72] due to the absence of convective cooling and possible thermal insulative properties of the enclosure walls. The heating and cooling rate of the cryogels is

also slower (**Figure 16b**). To reach 90% of its maximum temperature, LIG requires 18 seconds while the chitosan cryogel takes 48 seconds and the CS/MOF cryogel takes 66 seconds. For cooling, 39 seconds is needed for LIG alone, 63 seconds for the chitosan cryogel, and 69 seconds for the CS/MOF cryogel. In a real application, the cooling could be sped up by forced convection, however this would need to be balanced with the desired purity of the CO₂ effluent. Lastly, it was confirmed that the LIG grid could be used over multiple cycles and still generate the target desorption temperature range when 15 V was applied (**Figure 16c**). The rapid heating and cooling rates demonstrated are suitable for the short adsorption cycles tested on the cryogels (**Figure 11d**).

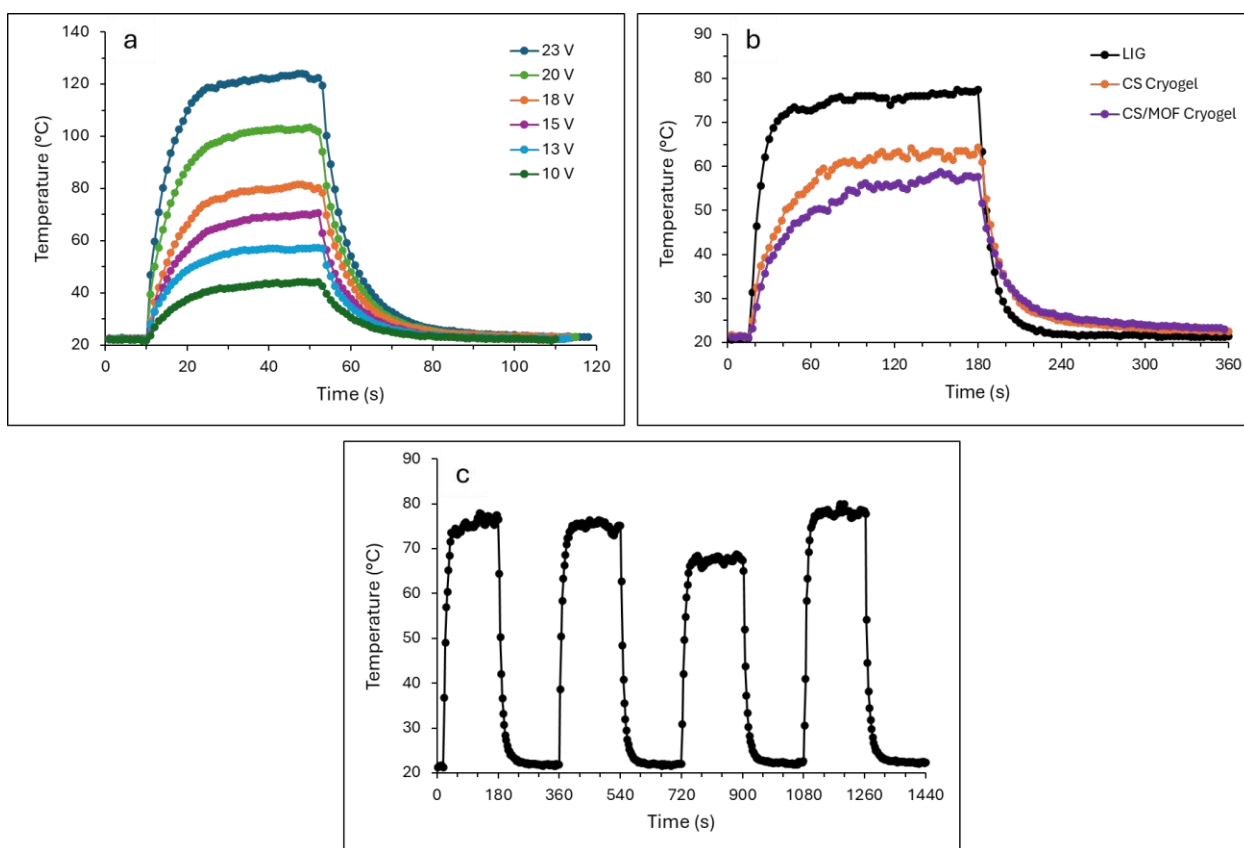


Figure 16. Thermal curves. a) LIG from 10 V to 23 V. b) Each cryogel placed on top of the LIG heater at 15 V. c) LIG with 15 V applied over 4 cycles. Data was extracted from IR camera images.

To improve the surface contact between the LIG grid and the cryogels and thereby enhancing the heat conduction as well as the handling of the materials for application, the synthesis of cryogels directly on LIG was explored. A custom mold was created to sit on the LIG grid and chitosan sol was poured

into the mold, frozen and lyophilized. The resulting cryogel attached to the LIG can be seen in **Figure 17** twisted, bent, upside down, rolled up, and heated via the LIG. This process allows for cryogels of custom thickness and shape to be synthesized with excellent contact to the LIG, without compromising the LIG's capability as a Joule heater. As seen in the IR image, the surface temperature of the outside of the rolled up LIG was 71.8 C while the inside surface temperature of the rolled up cryogel measured via thermocouple probe was 71.6°C. Hence, there is flexibility in the fabrication of the components of this DAC system. Either they can be fabricated separately and paired together after, or they can be fabricated as a single continuous piece.

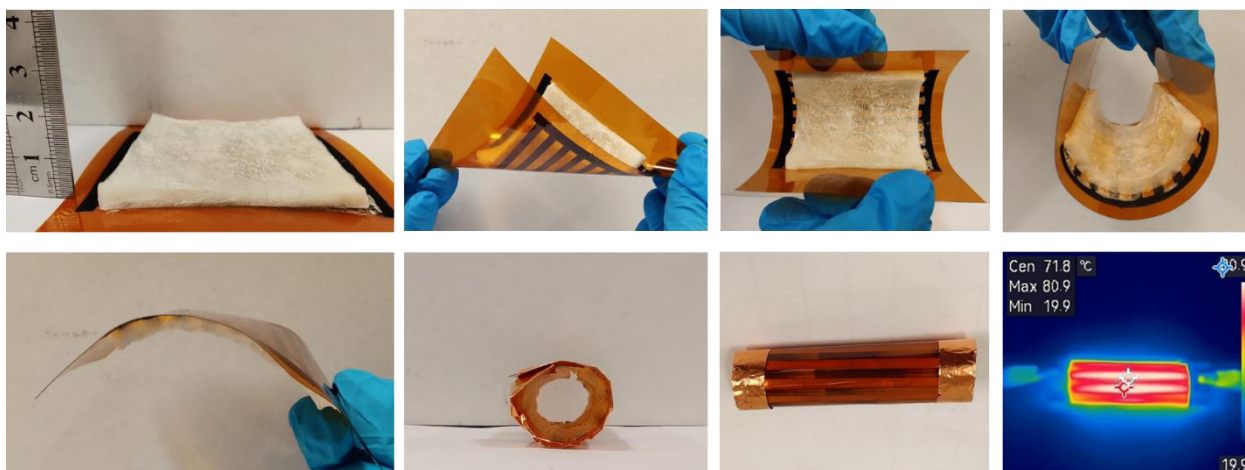


Figure 17. Chitosan cryogel synthesized directly on LIG grids. The cryogel adheres to the surface, can have customized thickness, be twisted, bent, and rolled up. The LIG maintains its heating capability.

Chapter 6: Conclusions and Future Work

6.1 Conclusions

In this work, the use of sustainable materials to create a low temperature DAC system based on ESA principles was demonstrated. Chitosan/SIFSIX-3-Cu hierarchically porous composite cryogels were synthesized and its desorption temperature range of 70-80°C was identified, balancing adsorbent degradation with the rate of desorption. The MOF crystals allow for rapid uptake and removal of gas while the chitosan fills a multipurpose role of providing a sustainable framework for MOF synthesis, in addition to further CO₂ removal. The composite cryogel demonstrated a promising CO₂ capacity of 2.82 mmol g⁻¹ after 18 hours, a high CO₂ to N₂ uptake ratio of 42, and the ability to be used over multiple cycles while maintaining 88% of its capacity.

For electrothermal regeneration of the adsorbent, laser-scribed flexible graphene heaters on PI film with rapid heating and cooling capability offers a facile, fast, and easily applicable option. The laser parameters were used to tailor the porous graphene characteristics such as resistivity and temperature generation, resulting in an optimum laser power of 3.9 W and speed of 95 mm s⁻¹ being selected. Customized LIG grids were fabricated and could generate the desired desorption temperature range over several cycles by applying 15 V at 0.5 A. The LIG grid was able to heat through the composite cryogel in 66 seconds and cooled in 69 seconds, allowing for fast turnaround between adsorption and desorption cycles, if desired. Lastly, these engineered layers could be synthesized as a continuous solitary piece to make the system more handleable without detracting from the LIG heating capability. The proof of concept of this DAC system has provided electrifying results thus far, however, further work can be done to improve and better understand its performance.

6.2 Future Work

To improve the feasibility of the DAC system presented for real world application, further study is required. Future work can focus on evaluating and improving the long-term stability of chitosan cryogel structures without sacrificing amine groups. One possibility is the use of higher molecular weights of chitosan to compare the structure, mechanical properties and capture performance. The degree of deacetylation of chitosan and source of chitosan may also have an influence on the CO₂ capture capacity and other properties. The use of fungal-based chitosan for example could reduce the overall environmental footprint of the system compared to marine-based chitosan [95] but the

presence of β -glucan may have unintended impacts. In addition, the presence of moisture has been known to reduce the CO₂ capacity of sorbents. Thus, to better understand real-world performance investigating the effects of humidity on the CO₂ adsorption capability and stability of chitosan, in addition to using lower CO₂ concentrations more representative of real world applications should be conducted.

In terms of the influence of MOFs, evaluating the long-term structural impact of the presence of in situ MOF crystals would be valuable. The ability to increase MOF loading within the cryogel structure could be investigated to improve adsorption capacity of the composite cryogel. Additionally, other MOFs with low GWPs, higher CO₂ capacity, and excellent stability in the presence of humidity could be investigated for synthesis with chitosan.

Lastly, further testing can be conducted on the LIG. The resistivity of carbonaceous materials are known to decrease during heating; thus, understanding this change and how it will influence the power supplied and the energy consumption of the desorption process is important [72]. Breakthrough adsorption testing would also allow the efficiency of the LIG heater to be determined, making it valuable for comparison with other ESA and DAC systems.

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Author: Nisrine Hammi, Mickaele Bonneau, Abdelkrim El Kadib, et al

Publication: Applied Materials

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Publication: Materials Today Sustainability

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Electrical swing adsorption on functionalized hollow fibers

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Publication: Chemical Engineering Journal

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Shape-Customizable Macro-/Microporous Carbon Monoliths for Structure-to-Functionality CO₂ Adsorption and Novel Electrical Regeneration

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Publication: Advanced Materials Technologies

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Won Hee Lee,Xin Zhang,Sayan Banerjee,Christopher W. Jones,Matthew J. Realff,Ryan P. Lively

Publication: Joule

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Electroactive tube arrays of diatomaceous silica-filled biocarbon for CO₂ separation through electric swing adsorption

Author: María E. Araoz, Rossana E. Madrid, Adolfo M. Avila

Publication: Sustainable Materials and Technologies

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Appendix A

Thermal Images

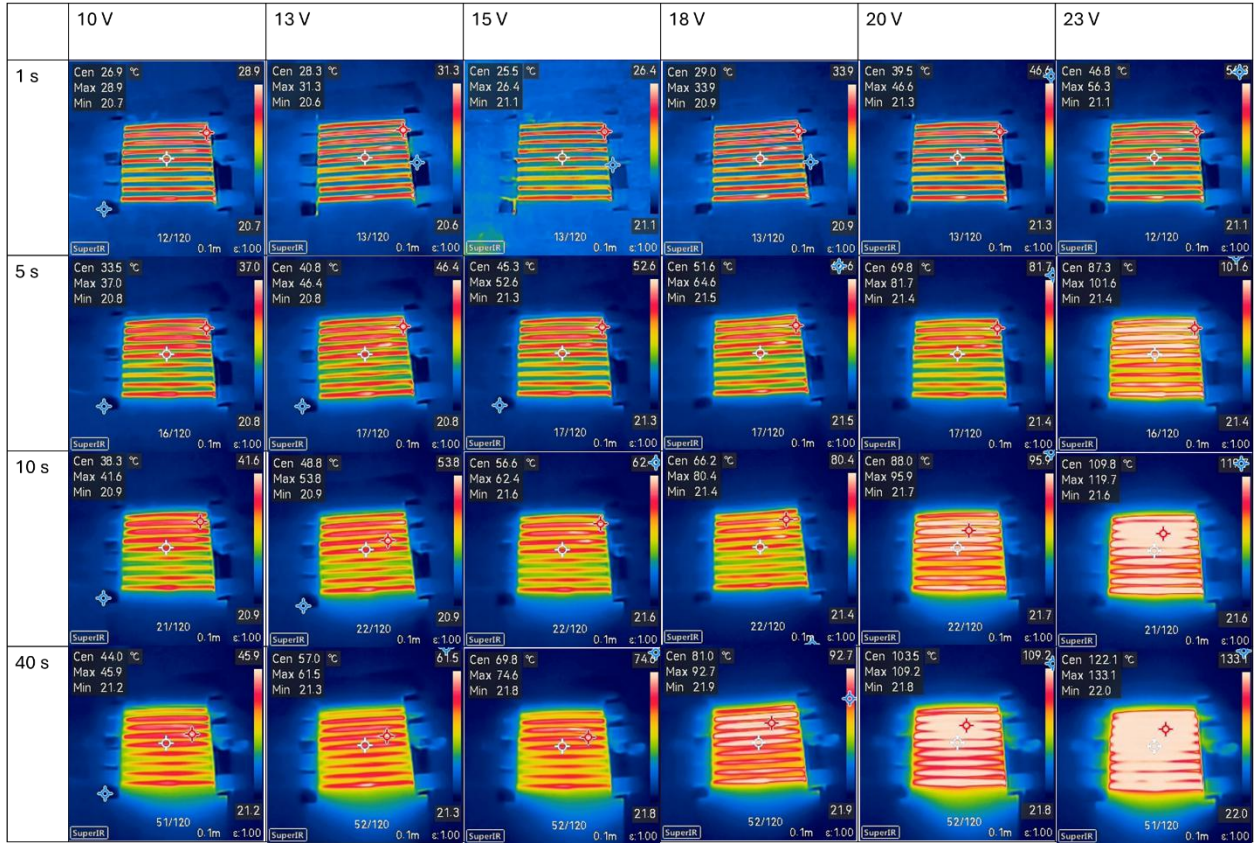


Figure A1. Thermal images of LIG taken 1s, 5s, 10s, and 40s after heating began at different voltages.