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# Direct air capture (DAC): molten carbonate direct transformation of airborne CO<sub>2</sub> to durable, useful carbon nanotubes and nano-onions†

Gad Licht,<sup>\*a</sup> Ethan Peltier,<sup>b</sup> Simon Gee<sup>b</sup> and Stuart Licht <sup>\*abc</sup>

This study introduces the concept and first demonstration of an effective molten carbonate chemistry for Direct Air Capture (DAC). Molten carbonate electrolysis is a high-temperature decarbonization process within Carbon Capture, Utilization and Storage (CCUS) that transforms chemistry transforming flue gas CO<sub>2</sub> into carbon nanotubes and carbon nano-onions. The key challenge for molten carbonate DAC is to split air's 0.04% CO<sub>2</sub> without heating the remaining 99.6%. This is accomplished by integrating a diffusive, insulating membrane over an electrolyte with a high affinity for CO<sub>2</sub>.

## Introduction

### Direct air capture technologies

Atmospheric Greenhouse gas removal is a necessary component to limit climate change.<sup>1,2</sup> Today's chemical Direct air capture decarbonization technologies<sup>2</sup> typically rely on active CO<sub>2</sub>-concentration, often using sorbents such as amine binding, or lime reactions, as described in the ESI.<sup>†3,4</sup> CO<sub>2</sub>-concentration is energy-intensive, produces rather than reduces CO<sub>2</sub>, and provides just the initial step in Carbon Capture and Storage (CCS) or Carbon Capture, Utilization, and Storage resulting in concentration, rather than storage. In contrast, this demonstration presents an efficient chemical DAC process that eliminates the need for active CO<sub>2</sub> concentration.

### C2CNT: transition metal nucleated electrolytic CCUS

We've developed a large-scale transition metal nucleated molten carbonate chemistry to electrolytically split CO<sub>2</sub> into carbon nanotubes (CNTs) and nano-onions (CNOs) and other Graphene NanoCarbon allotropes (GNCs) (ESI Section†). This

### Sustainability spotlight

The concept and first demonstration of an effective direct air capture molten carbonate chemistry is presented for removal of the greenhouse gas carbon dioxide to mitigate global warming which is an existential threat to the planet. Molten carbonate electrolysis is an CCUS high-temperature decarbonization chemistry transforming flue gas CO<sub>2</sub> to graphenes. Its direct air capture challenge is to split air's 0.04% CO<sub>2</sub> without heating the remaining 99.6% of the air, which is accomplished here by integration of a membrane over a high CO<sub>2</sub> affinity electrolyte.

C2CNT (CO<sub>2</sub> to Carbon Nano Technology) process is highly effective for flue gas decarbonization. Graphite, as a multi-layered graphene, demonstrates the long-term sequestration potential of structures built from graphene. The challenge for C2CNT as a DAC Technology is to efficiently split air's 0.04% CO<sub>2</sub> without heating the remaining 99.96% composition to the ~750 °C of the C2CNT electrolysis. This study presents the concept and first demonstration of an effective DAC molten carbonate chemistry.

CNTs possess the highest tensile strength ever recorded (93 900 MPa) and feature exceptional thermal conductivity, high charge storage, flexibility, and catalytic properties.<sup>5,6</sup> As described in the ESI,<sup>†</sup> they enhance structural materials such as cement and steel, and are used in a variety of applications including in medical and electrochemical fields, electronics, batteries, supercapacitors, sensing, plastics, textiles, hydrogen storage, and water treatment.

High-temperature molten carbonate electrolytic CO<sub>2</sub>-splitting into C and O<sub>2</sub> as a mitigation strategy was first introduced by our group in 2009–2010.<sup>7</sup> By 2015, it was demonstrated that this process could convert CO<sub>2</sub> into valuable, specialized graphene carbons, GNCs, through transition metal nucleated growth.<sup>8–10</sup> The type of useful GNCs, such as CNTs and CNOs produced depends on the electrochemical conditions (ESI†), which offers a promising climate change mitigation approach. The process follows a 4-electron redox reaction of carbonate:



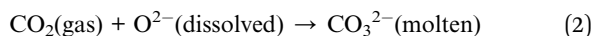
<sup>a</sup>Direct Air Capture LLC, A4 188 Triple Diamond Blvd, North Venice, FL 34275, USA.  
E-mail: slicht@gwu.edu

<sup>b</sup>Carbon Corp, 1035 26 St NE, Calgary, AB T2A 6K8, Canada

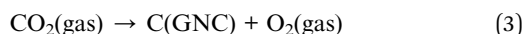
<sup>c</sup>Dept. of Chemistry, George Washington University, Washington DC 20052, USA

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The oxide reacts with CO<sub>2</sub> to regenerate carbonate:



These reactions combine to split CO<sub>2</sub> into carbon products and O<sub>2</sub>:



The CCUS molten carbonate electrolysis process for CNT and CNO production has evolved into a sophisticated technology. By adjusting the CO<sub>2</sub> electrolysis conditions, specific GNCs can be produced, including doped, thin, thick, long, magnetic, nano-bamboo, and helical CNTs, as well as nano-scaffold, graphene, nano-pearl, and nano-onion morphologies as described in the ESI.<sup>†9,10</sup>

We have explored alternative alkali carbonate mixtures and lower electrolysis temperatures, which can produce 3D-symmetry graphene scaffolds (ESI<sup>†</sup>). Electrolysis current densities ranging from 0.03–0.6 A cm<sup>-2</sup> affect GNC growth; higher densities favour the formation of helical CNTs (ESI<sup>†</sup>). Electrolysis requires a voltage range from 0.8–2 V. Using renewable energy sources can further reduce the CO<sub>2</sub> footprint (ESI<sup>†</sup>). High purity GNCs form directly on the cathode and are separated from the molten electrolyte through high-temperature filtration, as described in the ESI.<sup>†</sup>

C2CNT process modules are called the Genesis Device®, and large-scale CCUS Genesis modules transforming the 5% CO<sub>2</sub> flue gas from the Shepard Natural Gas Power Plant are operating in Calgary, Canada. Today, large-scale Genesis electrolysis uses cathodes over 10 000 cm<sup>2</sup>. The oxidation resistance of the CNTs produced is high, with a 97.1% TGA purity. SEM and TEM images of the CNT product are detailed in the ESI.<sup>†</sup> The units tested in this study are bench-top scale, using similar Muntz brass cathodes, 304SS anodes, and 99.5% purity Li<sub>2</sub>CO<sub>3</sub> electrolyte. These units are housed in a 12 × 12 × 15 cm carbon pot electrolyzer, which contains the molten electrolyte and serves as the electrolysis chamber, housed within a converted Caldera Paragon kiln. The CO<sub>2</sub>-concentration is measured with a CO2meter (<http://co2meter.com/>) sensor situated externally from the hot chamber connected *via* a 304SS tube which allows sufficient cooling to facilitate the room-temperature sensor performance.

C2CNT decarbonization is a unique process, unlike other CCS processes in that it directly (without pre-concentration) transforms CO<sub>2</sub> to high-purity, high-yield GNCs at ~750 °C. This decarbonization process, which eliminates the need for CO<sub>2</sub> concentration, as the electrolyte is a carbon sink that draws in CO<sub>2</sub> with a high affinity, applies to both C2CNT industrial CCUS (Carbon Capture, Utilization and Storage) and C2CNT DAC. However, the feed gas for industrial gas typically ranges from 5% CO<sub>2</sub> (natural gas power plant stack emissions) to over 30% CO<sub>2</sub> (cement plant emissions), and furthermore is generally hot coming off the industrial process. In contrast, DAC utilizes ambient temperature air containing a very low CO<sub>2</sub> concentration. Unlike C2CNT CCUS, DAC may require more energy to heat the entire air feed to >700 °C electrolysis

temperatures. Air contains 0.042% CO<sub>2</sub>, with the remaining >99.95% consisting of N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and Ar. While the latter are highly insoluble in molten carbonates, CO<sub>2</sub> dissolves reactively as shown in eqn (2). For effective DAC decarbonization, the C2CNT process energy should not be used to heat the 99.95% non-CO<sub>2</sub> components of air.

The first DAC technology is presented that simultaneously (1) directly (without preconcentration) removes CO<sub>2</sub> from the air, (2) transforms the CO<sub>2</sub> into a valuable product (such as CNTs) provides a strong incentive to remove this greenhouse gas, and (3) unlike previous regular C2CNT processes, insulates the feed air from the hot electrolysis chamber while still allowing CO<sub>2</sub> to diffuse into the electrolysis chamber.

### CO<sub>2</sub> diffusion through high temperature insulation

The known diffusion coefficient of CO<sub>2</sub> in air varies as:<sup>11</sup>

$$D_{\text{CO}_2}(T_K) = 2.7 \times 10^{-5} T_K^{1.59} / e^{(102.1/T_K)} \quad (4)$$

We recently characterized the rate of CO<sub>2</sub> diffusion at room temperature through a variety of high temperature porous insulations acting as membranes.<sup>11</sup> These diffusion results are now used to develop a new high temperature direct air capture, in which these membranes are placed between the feed air and a high-temperature molten electrolyte that removes CO<sub>2</sub> *via* electrolysis in the carbon pot. Insulation materials tend to be porous and low-density. The majority of high-temperature alumina or CaO/MgO silicate insulations we recently studied have densities ranging from 0.06–0.14 g cm<sup>-3</sup>, with a measured porosity, of  $\epsilon$  ranging from 0.89–0.96. Higher density-insulation (0.59 to 0.70 g cm<sup>-3</sup>) had a measured porosity of  $\epsilon = 0.45$ –0.67.<sup>11</sup> As expected, the manufacturer's thermal insulation values tend to vary linearly with thickness and, to a lesser extent, with density. For example, 1/4" insulation with densities of 0.10 and 0.13 g cm<sup>-3</sup> have respective *R*-values of 0.3 and 0.4, while 4× thicker insulation has *R*-values of 1.1 to 1.5. Alumina and CaO/MgO silicate insulations had similar *R*-values.

In that room temperature study, we determined that CO<sub>2</sub> readily diffuses through porous ceramic thermal insulators. The measured CO<sub>2</sub> diffusion coefficient for the silicate membranes was found to correlate with the measured open-channel porosity as follows:<sup>11</sup>

$$D_{\text{M-porous-CO}_2} = D_{\text{CO}_2} \cdot \epsilon(M)^{3/2} \quad (5)$$

These diffusion rates were further increased by approximately 50% with turbulent flow (either parallel or perpendicular flow) over the upper membrane surface.<sup>11</sup> These findings, combined with eqn (4) and (5), are now used to configure a DAC C2CNT process that enables the chemical permeation of CO<sub>2</sub> while insulating air's other components from the hot molten carbonate electrolysis.

## Experimental section

Electrolyses were conducted using a 750 °C Li<sub>2</sub>CO<sub>3</sub> (99.85%, Shanghai Seasongreen Chemical Co.) electrolyte, with or



without a  $\text{Li}_2\text{O}$  additive (99.5% Alfa Aesar), in a  $12 \times 12 \times 15$  cm tall 304SS pot and a Muntz brass cathode (Marmetal Industries). In these small-scale experiments, samples were collected from the cooled cathode, and acid-washed to remove electrolyte interspersed with the cooled product. In larger-scale experiments (ESI Section†) the molten electrolyte is directly extracted from the product using high temperature presses.

The Genesis DAC configuration was tested according to the lower left-illustration of Fig. 1 using the  $12 \times 12 \times 15$  cm tall 304SS pot. Air is fed into the upper chamber at a low flow rate, proportional to the applied constant electrolysis eqn (8). Higher flow rate conditions ( $\times 1.5$  and  $\times 2$  flow rate) conditions were also investigated.

Two aluminosilicate insulations were used as membranes in this configuration, a 1" (CeraBlanket 8254870040000) and a 1/4" (CeraBlanket 825680600200P2), with measured porosities of  $\epsilon = 0.93$  and  $\epsilon = 0.91$ , respectively.<sup>11</sup> Each was configured in the 3D open-bottom structure shown in the lower left of Fig. 1 with four  $20 \times 20$  cm walls and a top, providing a total membrane surface area of  $2000 \text{ cm}^2$ .

## Results and discussion

### A new C2CNT chemistry for DAC rather than CCUS

Fig. 1 compares Genesis CCUS to the new Genesis DAC decarbonization configuration.  $\text{CO}_2$  transfer between the ambient gas feed and the C2CNT electrolysis electrolyte interface is dominated by convection. The placement of the flue gas, exit,  $\text{CO}_2$ -sensor, and thermocouple placement are illustrated, as well as the external electrical connectors to the anode and cathode. A

matrix of GNCs, with interspersed electrolyte grows at the cathode and is periodically lifted to harvest the GNC product.

The Genesis DAC configuration in the bottom of Fig. 1 utilizes the recently characterized  $\text{CO}_2$  diffusion properties of open-channel porous thermal insulation, and reduces heat loss while sustaining  $\text{CO}_2$  transfer between an ambient air feed gas and the interior of the C2CNT electrolysis chamber, which acts as a carbon sink.  $\text{CO}_2$ -transport in the upper air feed chamber and in both the lower electrolysis chamber are dominated by convection. As illustrated at the bottom portion of Fig. 1, Genesis DAC positions a high-surface area porous insulation as a membrane creating a quiescent zone between the air feed and the electrolysis chamber. In this quiescent zone  $\text{CO}_2$  mass transport by diffusion, rather than by convection, dominates. By maintaining a high 3D surface area of this interfacial diffusion zone, sufficient  $\text{CO}_2$  enters the electrolysis chamber to replenish the  $\text{CO}_2$  consumed.

### Sustainable DAC rates and feed gas air flow

The membrane diffusion-limited sustainable  $\text{CO}_2$ -splitting current,  $\text{JM}_{\text{CO}_2}$ , is determined from  $D_{\text{M-porous-CO}_2}$ , eqns (4) and (5), and the volume  $V(T_K)$  of 1 mole of  $\text{CO}_2$  at temperature  $T_K$ .  $\text{JM}_{\text{CO}_2}$  has units of  $\text{mA cm}^{-2}$  when calculated from the  $\text{CO}_2$  transported per  $\text{cm}^2$  of the membrane, the membrane thickness  $l_M$  (cm), the  $\text{CO}_2$   $C_o = 0.042\%$  concentration in the air, and Faraday's constant  $F = 96485/\text{mole e}^-$ . For the  $n = 4e$   $\text{CO}_2$ -reduction is then:

$$\text{JM}_{\text{CO}_2}(T_K, \text{mA cm}^{-2} \text{ membrane}) = \frac{1000 \cdot 4F \cdot C_o D_{\text{M-CO}_2}(T_K) \cdot 1 \text{ cm}^2}{l_M \times V_{\text{ideal}}(T_K)}$$

where

$$V(T_K) = 22414 \text{ cm}^3 \text{ mole}^{-1} \times T_K/273.15 \text{ K} \quad (6)$$

These experiments are constant-current electrolyses at  $I_{\text{electrolysis}}$  (A) conducted for a time  $t_{\text{electrolysis}}$  (s). This charge passed is then converted to the max moles of  $\text{CO}_2$  at  $20^\circ\text{C}$ , which can be split by the  $n = 4$ -electron electrolysis,  $\text{mol}_{\text{max-CO}_2}$ :

$$\text{mol}_{\text{max-CO}_2} = (I_{\text{electrolysis}} (\text{amps})/4F) \cdot t_{\text{electrolysis}} (\text{s}) \quad (7)$$

This ideal conversion of  $\text{CO}_2$  will produce an equal number of maximum moles of carbon and oxygen, *i.e.*,  $\text{mol}_{\text{max-CO}_2} = \text{mol}_{\text{max-C}} = \text{mol}_{\text{max-O}_2}$ . From the respective molar masses, the maximum masses are calculated as  $m_{\text{max-CO}_2} = 44.01 \times \text{mol}_{\text{max-CO}_2}$ ;  $m_{\text{max-C}} = 12.01 \times \text{mol}_{\text{max-CO}_2}$ ;  $m_{\text{max-O}_2} = 32.00 \times \text{mol}_{\text{max-CO}_2}$ . Oxygen ( $\text{O}_2$ ) from the electrolysis evolves as a gas, and exits the electrolysis chamber.

The required  $20^\circ\text{C}$  airflow (LPM) per amp of electrolysis charge,  $f_A$ , is given by:

$$f_A (\text{LPM/A}) = \frac{C_o^{-1} \cdot 1 \text{ mol CO}_2 \cdot V_{\text{ideal}}(298.15 \text{ K}) (60 \text{ s min}^{-1})/4F}{(8)}$$

From eqn (8)  $f_A$  is 9 LPM air per A of  $\text{CO}_2$  splitting electrolysis.

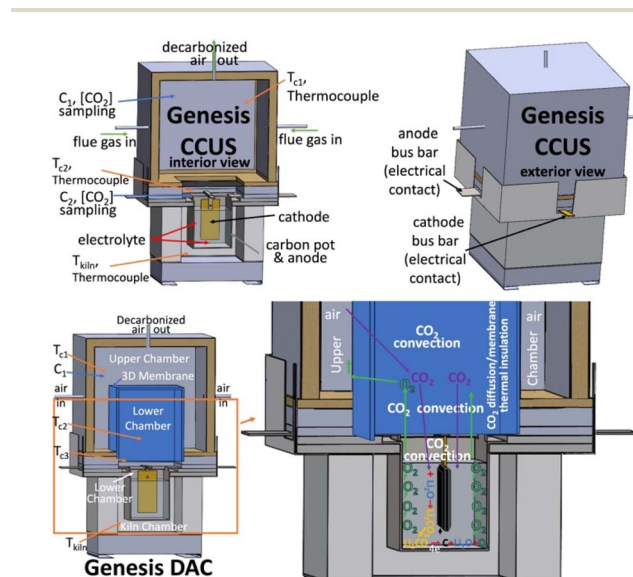


Fig. 1 Active component comparison of the new Genesis DAC for the decarbonization in air, compared to the Genesis CCUS for the decarbonization of flue gas. Both transform  $\text{CO}_2$  to GNCs, such as CNTs. (Top) Genesis CCUS interior (left) and exterior view (right) view for decarbonization of flue gas. (Bottom) Genesis DAC for direct air capture including a large 3D membrane separating the air feed and the electrolysis chamber, from an interior view (left) and viewing the decarbonization action (right).



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Fig. 3 A comparison of the DAC modelled  $\text{CO}_2$  diffusion limited currents and the experimentally measured DAC currents. Black data is measured with eqn (9) required airflow, and red and blue data with 2× higher flow.

measured at room temperature and extrapolated for use with the 750 °C electrolysis of the Genesis DAC configuration. Future studies will explore whether the membrane porosity exponent in eqn (5) ( $\epsilon(M)^{3/2}$ ) is itself a function of temperature, and the assumption of a linear temperature profile through the membrane's cross section. For example, the results suggest that the lower outer wall temperature of the membrane has a larger effect on the rate of  $\text{CO}_2$  diffusion.

### CNTs and CNOs products from $\text{CO}_2$ in the air

At 750 °C in  $\text{Li}_2\text{CO}_3$ , the  $\text{CO}_2$ -splitting electrolysis consistently produces high-purity CNTs as exemplified by the SEM images of the washed product in Fig. 4 panels A & B.

Under  $\text{CO}_2$ -limiting conditions, where insufficient air  $\text{CO}_2$  is fed into the DAC system, an oxide buildup occurs as described by eqn (1) oxide. In this case, we observe that the product tends to be high-purity carbon nano-onions (CNOs) as shown in Fig. 5, panels A through I. When excess  $\text{CO}_2$  is reintroduced to the DAC Genesis, CNT production resumes.

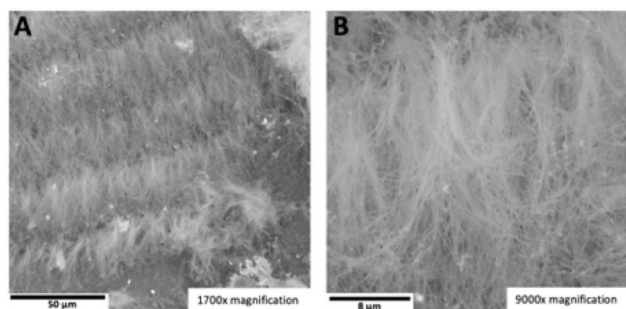


Fig. 4 DAC Genesis CNT products formed at  $\text{CO}_2$  sufficient conditions. 750 °C  $\text{Li}_2\text{CO}_3$  electrolyte electrolysis with a brass cathode and a stainless steel anode and case. SEM of the washed products: CNTs (A & B) 1700× and 9000× magnification.



Fig. 5 DAC Genesis CNO products formed at  $\text{CO}_2$  insufficient conditions. 750 °C  $\text{Li}_2\text{CO}_3$  electrolyte electrolysis with a brass cathode and a stainless steel anode and case. SEM of the washed products: CNOs sample 1 (A–F) magnification at 2000×, 2000×, 2050×, 5000×, 100 00×, 250 00×. CNOs sample 2 (G–I) 4100×, 10 000, and 250 00×.

As with CNTs,<sup>12</sup> and as seen in the upper left corner of Fig. 5 (panel A), the CNO growth begins with a thin layer of graphene (observed as removed from the cathode) from which a matrix of CNO growth occurs. Under conditions of insufficient  $\text{CO}_2$ , higher oxide concentration buildup in the electrolyte, this (i) reduces the solubility and prevalence of transition metal cations in the electrolyte, inhibiting CNT growth by transition metal nucleation, and (ii) induces  $\text{sp}^3$  defects in the  $\text{sp}^2$  graphene lattice. These  $\text{sp}^3$  sites favor the formation of spherical, rather than planar cylindrical, graphene growth.<sup>8,13</sup> Thus, an oxide-rich electrolytic environment promotes CNO over CNT growth.<sup>13</sup>

### Alternative graphene nanocarbon products from $\text{CO}_2$ in the air

We have studied the morphology and purity of the GNC products using  $\text{CO}_2$  from the air since 2015,<sup>8</sup> although previously without an effective means to separate heat losses between air and the molten electrolyte. In 2016, we demonstrated that using the  $^{13}\text{C}$  isotope resulted in the first pure  $^{13}\text{C}$  multiwalled carbon nanotube, and tracked the transformation of gas-phased  $\text{CO}_2$  into CNTs *via* electrolysis.<sup>14</sup> In 2021, we applied high current density ( $0.6 \text{ A cm}^{-2}$ ) and added oxides to the electrolyte, which induced  $\text{sp}^3$  defects and torsional effects transforming to  $\text{CO}_2$  to helical carbon nanotubes.<sup>15</sup> By controlling electrolysis conditions – including variations in current density, anode, cathode and electrolyte composition, and temperature – we can produce high purity morphologies with a range of properties, including thin-walled, magnetic, doped, nano-bamboo, nano-pearl, and nano-tree CNTs as detailed in the ESI.<sup>†10,12–24</sup>

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