Conversion of Atmospheric CO_2 to Solid Carbon: A Climate Change Mitigation Strategy

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Green House Effect of CO_2

- The ever-increasing energy needs of the industrialized world has continuously raised the concentration of carbon dioxide in the atmosphere
- CO_2 is the product of combustion of fossil fuels used in industry and transport and the production of oil and natural gas
- In 2020, we sent 40 billion metric tons of CO_2 into Earth's atmosphere, raising the concentration from about 315 ppm in 1957 to 415 ppm in 2021
- Excessive CO_2, the most common greenhouse gas, causes global warming, creating many undesirable effects on earth, including climate change and ocean acidification

C&E News: Carbon capture's steep climb, 99(26), 28-35, 2021.

Need of CO_2 Removal vs Reduction of CO_2 Addition to the Atmosphere

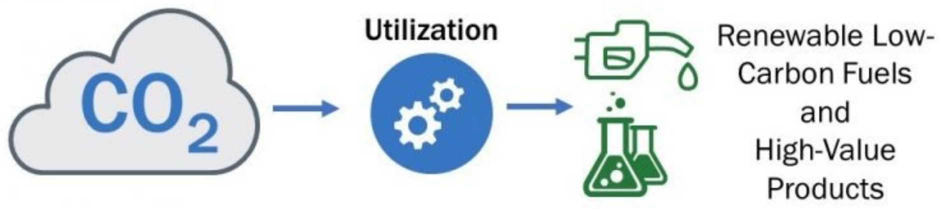
- Transition of power generation to solar and wind, and transportation shift to electric vehicles would reduce the further CO_2 addition into the atmosphere, nonetheless these will not be enough

- We will need gigaton-scale carbon removal in the coming decades to avoid the worst effects of climate change

- Carbon Capture and Sequestration (CCS) and Carbon Capture and Utilization (CCU) technologies are currently the focus of worldwide development efforts to enable the above

CO_2 Capture and Utilization (CCU)

- There is an urgent need for mitigation of the global warming effects, by capturing CO_2 from atmosphere



- Chemical and biological approaches can potentially lead to conversion of atmospheric CO_2 to valuable products, while contributing to climate change mitigation

- The global effort to find an innovative technology for conversion of CO_2 requires further technological advances offering high conversion efficiency, scalability, economic viability, and sustainability

Literature Survey of Approaches for CO_2 Conversion

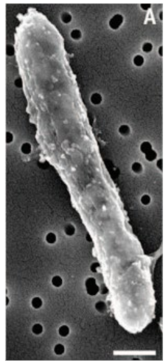
CO_2 conversion processes into value-added chemicals involve two possible approaches: chemical catalysis and bio-catalysis.

- Solid metallic catalysts have dominated chemical catalysis but suffer from low conversion efficiencies and are prone to deactivation by carbonaceous trace contaminants

  Also, industrial catalyst $Cu/ZnO/Al_2O_3$ and different variations widely tried for CO_2 hydrogenation to CH_3OH require extreme conditions of temperature (150–350 °C) and pressures (30 bar)

- Biocatalysts utilized in gas fermentation process operate under ambient temperatures and pressure and tolerate contaminants

  Acetogenic *Clostridium* organisms together with H_2 or CO as reductant, have been used as promising biocatalysts to produce biofuels and chemicals.



M. thermoacetica

CO_2 Conversion – Other Approaches

- Other alternative strategies focused on photo-catalytic or electro-catalytic reduction routes remain hinged on further technological advances

- Recently, Gallium (Ga)-based liquid metals (LM) have shown unique properties for catalysis, exhibiting a high reduction potential providing the overall driving force for the CO_2 reduction reaction

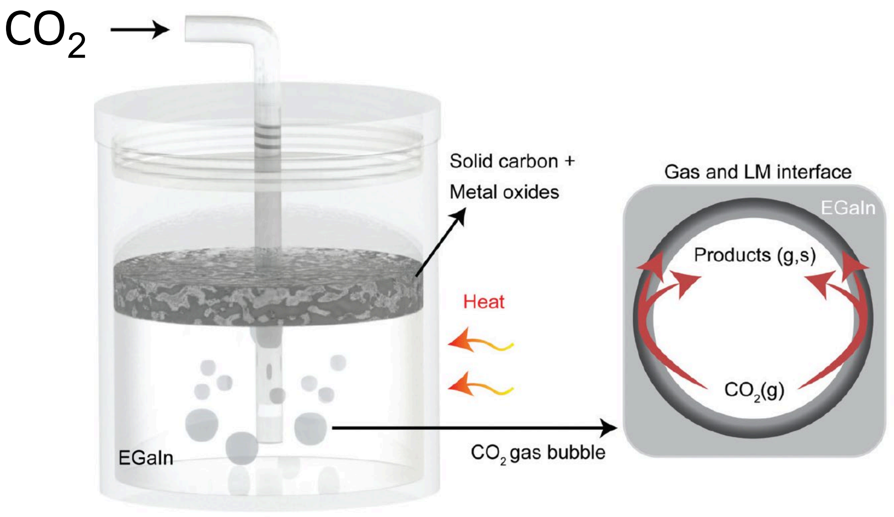
- Gallium (Ga) is a silvery-white liquid (much like mercury)

- Ga-based LMs can dissolve other metals to form a range of alloys and have been successfully used in CH_4 dehydrogenation producing H_2 and solid carbon

Zuraiqi et al., Liquid Metals in Catalysis for Energy Applications, *Joule* 4(11), 2290 – 2321, 2020.

CO_2 Reduction Process to Solid Carbon

- A new Australian process uses liquid metal alloy EGaIn heated to between 100-120°C
- EGaIn ensures that metal is in liquid phase even at room temperature
- CO2 gas is bubbled up to the surface of the heated liquid metal in a bubble column reactor to kickstart the chemical reaction

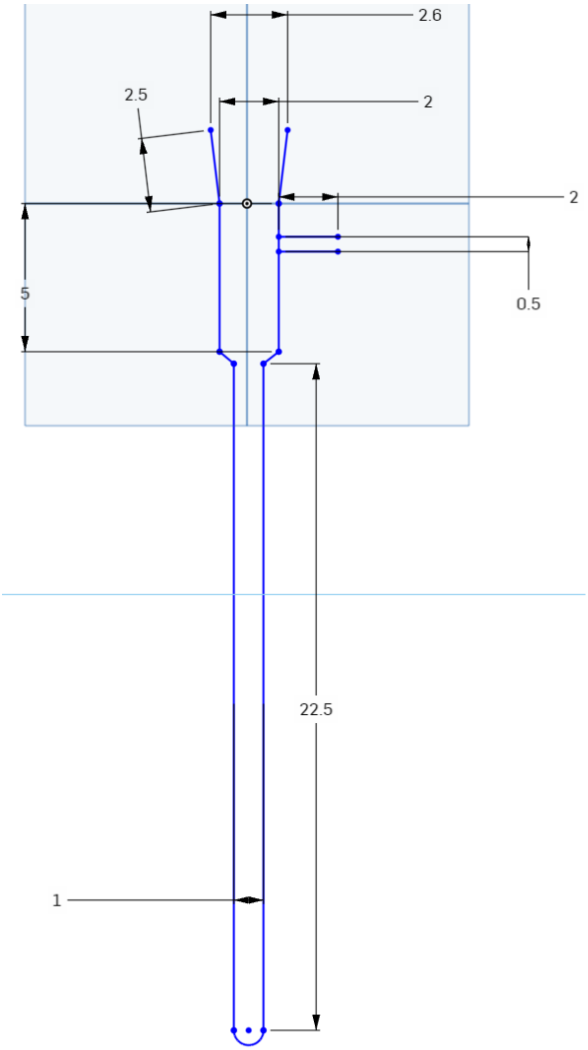


- The nonpolar nature of the liquid EGaIn interface allows the solid carbon flakes to exfoliate, keeping the active sites accessible

Zuraiqui et al., Direct conversion of CO_2 to solid carbon by Ga-based liquid metals, *Energy Environ. Sci.* 15, 595-600, 2022.

Materials Used in the Experiment

- Onshape (CAD Software) was used to design the glass bubble column reactor and it was fabricated from the Princeton University Glass Shop
- Glass Tube for CO_2 bubbling and Neoprene Stopper
- Gallium (99.99% Purity) and Indium (99.99% Purity) Metals
- 5 lb CO_2 Cylinder with CGA 320 Valve
- CO_2 Regulator with Bubble Counter and Check Valve
- CO_2 Proof Tubing 5/16 inch
- Ceramic Crucible Cup with Tongs
- Chemistry Lab Stand with Clamps
- Test Tubes – 30 mL with screw caps
- Glass Dropper with Bulb
- Heating Tape with Adjustable Thermostat
- Digital Weighing Scale
- Infrared Digital Thermometer



Design for Bubble Column Reactor

Reproducing 2022 Australian Research in a Simplified Experiment

- Designed a bubble column reactor with an exhaust port and an input CO_2 bubbling tube in a neoprene stopper so that it could be operated safely
- Used heating tape with a temperature controller and used infrared thermometer to monitor temperature
- Procured a 5 lb. CO_2 cylinder and a needle valve regulator from an aquarium supplier
- EGaIn (m.p. 15^{o}C) was formed by heating Ga (m.p. 30°C) with Indium (In) (m.p. 158^{o}C) in a ratio of 3:1 w/w at ~200^{o}C in a ceramic crucible
- The liquid metal alloy was maintained in the bubble column reactor at 100-150^{o}C and CO_2 was bubbled for 24 hours at a rate of about 200 bubbles per minute
- At the end of the experiment, carbon flakes appeared floating at the top of the liquid metal surface

Gallium, Indium metals and liquid EGaIn

Experimental Set Up for Liquid EGaIn-based CO_2 Reduction to Solid Carbon

Liquid Metal Bubble Column Reactor

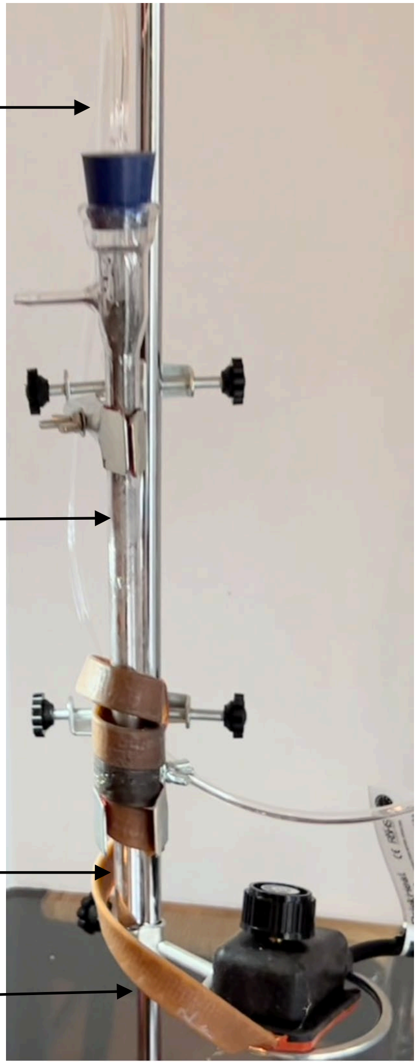
CO_2 Gas Cylinder

CO_2 bubbling tube

Bubble Column

Liquid EGaIn Alloy

Heating tape



Re-enacting Catalytic Reduction of CO_2 by EGaIn to Solid Carbon

CO_2 flow rate controlled via needle valve and bubble rate measurement
Temperature controlled via infrared measurement and a heating tape

Deposit of solid carbon on the side of the CO_2 bubbling tube and on the surface of bubble column

Summary: Instant Decarbonization of CO_2 to Solid Carbon

- The robust and highly selective method for the direct conversion of CO_2 to solid carbon uses EGaIn liquid metal (LM) alloy
- The "bubble column" method starts with heating liquid metal to about 100-150^{o}C
- CO_2 is bubbled into the liquid metal. As the bubbles move through the liquid metal, the gas molecule splits rapidly up to form flakes of solid carbon
- The process appears to have high conversion efficiency, scalability, economic viability, and sustainability

References

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Direct conversion of CO_2 to solid carbon by Ga-based liquid metals†

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The direct conversion of CO_2 to carbon is a highly providential route; however, conventional thermal and catalytic approaches are hindered by high energy demands and are limited by coking. Here, we report a robust and highly selective method for the direct conversion of CO_2 to solid carbon over EGaIn liquid metal (LM) alloy. We utilized the low-melting point of this alloy to facilitate the reduction of CO_2 at low temperatures, producing 319 μmol h^{-1} of carbon at 200 °C, and remarkably enabling CO_2 activation and carbon production even at room temperature, without the use of a supplementary reductant such as hydrogen. The deployed LM showed no signs of deactivation by coking and the generated carbon is shown to naturally accumulate at the top of the LM where it can be easily collected. *In situ* XPS measurements indicate an increase of 9.6% in the carbon–carbon bond content and an equivalent decrease in the Ga metal content, upon exposure of the LM to CO_2 for 30 mins at 200 °C and 1 bar. This led to the conclusion that solid carbon and gallium oxide are the final reaction products of this process. Density functional theory calculations shed further light on the adsorption and dissociation of CO_2 over Ga and EGaIn. The presented method creates a pathway to transforming CO_2 to perpetually stored solid carbon and can therefore set a trajectory for making a measurable impact on carbon intensive industries.

Broader context

The use of anthropogenic CO_2 as a building block for the synthesis of commodity chemicals is an integral element in establishing sustainable growth in the chemical industry and reducing emissions into the atmosphere. Designing materials that can provide a viable pathway for the utilization of CO_2 as feedstock remains challenging. Inspired by the demand for high activity, the need to replace conventional solid materials that are highly susceptible to coking, and the significance of overcoming high energy demands in CO_2 decomposition processes, a new method for the direct decomposition of CO_2 to solid carbon using liquid metals (LMs) is developed. The process presented here features LMs that are highly active, robust, and exceptionally resilient to coking. Continuous CO_2 conversions and excellent carbon product selectivity are demonstrated at mild temperatures without the use of an auxiliary reductant or source of energy. The outstanding performance of the deployed LMs is shown to enable the decomposition of CO_2 even at room temperature, laying the groundwork for the utilization of thermal conversion approaches and providing a pathway to fix CO_2 back to components of the chemical pool. Thus, nurturing the possibility of turning emission liability into products of economic value.

carbon. CO_2 is not only the most common greenhouse gas released into the environment but is also the most stable state of carbon.[1] Due to the high thermal stability of CO_2, its