

# The Holy Grail: Chemistry Enabling an Economically Viable CO<sub>2</sub> Capture, Utilization, and Storage Strategy

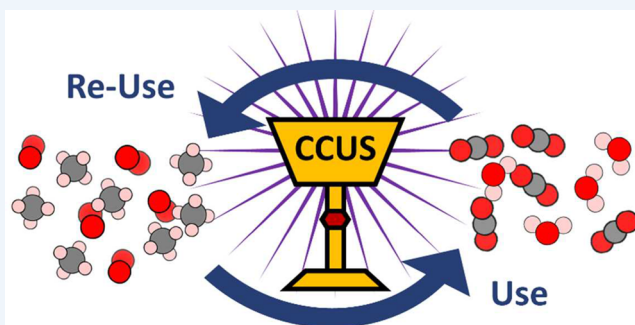
Published as part of the *Accounts of Chemical Research* special issue “*Holy Grails in Chemistry*”.

Thomas P. Senftle<sup>†</sup> and Emily A. Carter<sup>\*‡</sup> 

<sup>†</sup>Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544-5263, United States

<sup>‡</sup>School of Engineering and Applied Science, Princeton University, Princeton, New Jersey 08544-5263, United States

**ABSTRACT:** Technologies for reducing the concentration of CO<sub>2</sub> in our atmosphere are essential for mitigating the risks of climate change, and novel chemistry is required for such technologies to work at scale. Here, we highlight challenges that chemists must overcome to realize the Holy Grail of an economically viable strategy for CO<sub>2</sub> capture, utilization, and storage.



We are at the beginning of a new geological epoch: *Anthropocene*.<sup>1</sup> The consensus to declare *Anthropocene*—reached at the 35th International Geological Congress this year—marks yet another formal recognition of a long-suspected truth: humans are altering Earth’s climate on a geological scale. This is perhaps most evident in the concentration rise of atmospheric CO<sub>2</sub> from preindustrial levels near 280 to 400 ppm today, which in turn is correlated with rising global temperatures.<sup>2</sup> This is an unintended consequence of our progress as a human race, as we release ~36 Gt of CO<sub>2</sub> into the atmosphere each year to sustain our global economy. Without immediate action, this number is projected to reach ~50 Gt in the next 20 years, leading to concentrations of 500 ppm by the year 2050.<sup>2</sup> Cumulative CO<sub>2</sub> emissions must be limited to 1440 Gt between the years 2000 and 2050 for a 50% chance of restricting the global temperature rise to 2 °C above preindustrial levels.<sup>3</sup> The development and deployment of effective CO<sub>2</sub> capture, utilization, and storage (CCUS) strategies will be essential to reaching this goal as carbon-neutral energy technologies (e.g., solar, wind, hydro, geothermal, fusion, etc.) mature in the next century. Chemists will play a central role in this effort, as the development of CCUS will require the discovery, characterization, and optimization of novel molecules and materials with exceptional properties. In this commentary, we review the current state of the CCUS cycle (Figure 1), highlighting barriers that we must overcome to realize the Holy Grail of an economically viable CCUS strategy.

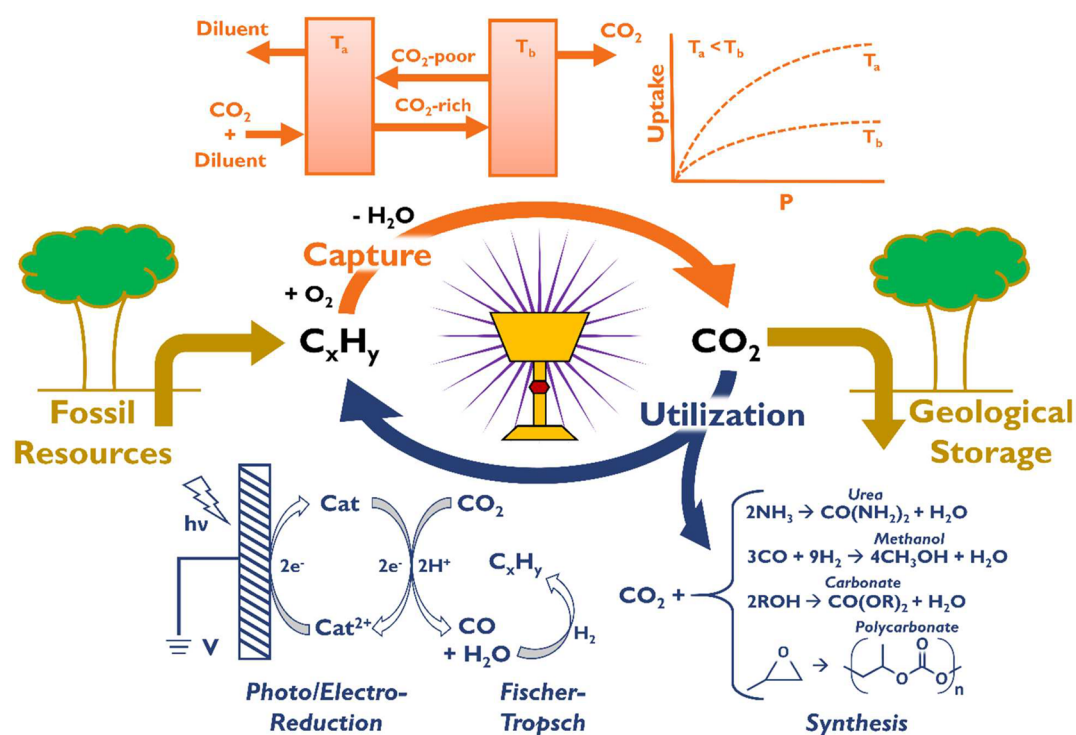
The most significant barrier to economically feasible CCUS is simply the sheer *scale* at which we must capture and process CO<sub>2</sub> generated from fossil resources. As pointed out in recent Perspectives,<sup>4,5</sup> the infrastructure alone required to transport CO<sub>2</sub> captured in the U.S. would be at least an order of

magnitude larger than the current infrastructure used to transport gasoline: the U.S. consumes ~0.5 Gt of gasoline per year and emits ~5.5 Gt of CO<sub>2</sub> per year. CCUS thus will be an expensive undertaking shaped by economic limitations, and as such economic incentives to capture CO<sub>2</sub> will be required. To achieve the Holy Grail, novel chemistries must allow profits derived from processing CO<sub>2</sub> feedstocks to outweigh the cost of capture, transportation, and conversion. Here, we focus on requirements for CO<sub>2</sub> capture from anthropogenic point sources (e.g., power plants reliant on fossil fuels, cement plants, etc.). Although direct capture from ambient air may play a role in reaching CO<sub>2</sub> reduction targets in the long term,<sup>6,7</sup> direct capture will not be sufficient to entirely offset point source emissions in the near term.<sup>8,9</sup> We also review target research areas for CO<sub>2</sub> utilization via catalysis and chemical synthesis, considering electro-, photo-, and thermochemical reduction. At present, technologies enabling capture are far closer to production than those enabling utilization. Because utilization as a fuel—the only practical strategy that scales—only delays the need for storage, the final fate of CO<sub>2</sub> must be geological sequestration.

Current capture research focuses on optimizing media for selective and reversible sorption of CO<sub>2</sub> via, for example, amine-based solutions, ionic liquids (ILs), or solid adsorbents. The most mature strategies employ aqueous alkanolamines, such as monoethanolamine (MEA), in combined absorption/desorption cycles.<sup>10</sup> In the absorption stage, CO<sub>2</sub>-rich flue gas contacts the aqueous amine and the basic amine group reacts exothermically with the acidic carbon atom of the CO<sub>2</sub>

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**Figure 1.** The Holy Grail: Chemistry enabling a closed CO<sub>2</sub> capture, utilization, and storage cycle with sample chemistries shown.

molecule. Strong exothermic interactions (typically  $\sim 75\text{--}100$  kJ mol<sup>-1</sup>), although advantageous during absorption, necessitate large energy input to regenerate the CO<sub>2</sub>-poor amine. High heat capacities of aqueous amines (e.g.,  $\sim 3.7$  kJ g<sup>-1</sup> K<sup>-1</sup> for 30% MEA solution at 25 °C) result in a prohibitive energy cost to achieve the necessary temperature swing for driving CO<sub>2</sub> desorption. Current benchmarks for this technology have an energy cost near 0.3 megawatt-hours per metric ton of captured CO<sub>2</sub>, which translates to  $\sim 35\%$  of a typical power plant's total output.<sup>10,11</sup> Thus, research efforts must aim to reduce the energy cost associated with sorbent regeneration (e.g., by combining active primary amines with less active tertiary amines to achieve balanced reactivity ideal for overall absorption/desorption). Other issues plaguing aqueous amines include high volatility and susceptibility to degradation under flue gas conditions, resulting in substantial loss of the sorbent.

Carbon capture utilizing ionic liquids (ILs) as the working sorbent has emerged as a possible alternative to aqueous alkanolamines.<sup>12</sup> Unlike the latter, ILs are noncorrosive, exhibit near-zero vapor pressures, and are robust against chemical degradation. More importantly, ILs are not aqueous and thus avoid high energy costs associated with heating a working fluid mostly comprised of water during the regeneration stage. Functionalization of ILs allows one to adjust their reactivity toward CO<sub>2</sub>, where the most successful ILs are functionalized with an amine moiety to yield increased uptake via a direct acid–base interaction.<sup>13</sup> The strength of the resulting C–N bond can be fine-tuned by subsequent functionalization with either electron withdrawing or donating groups. It is feasible to create “designer” ILs optimized for use at operating conditions characteristic of a particular power plant design, as recently demonstrated by Hong et al.<sup>14</sup> Fine-tuning approaches are a promising avenue for chemical research, though a more pressing question is whether ILs can efficiently be scaled for industrial operation. Numerous ILs with attractive properties

have been identified at the lab scale, yet these ILs are considerably more expensive ( $\sim \$1000$  per kg) than available amine-based solutions ( $\sim \$2$  per kg). Currently available ILs also interact strongly with water present in humid flue gas streams, which will impact overall CO<sub>2</sub> absorption capabilities.<sup>15</sup> As such, the IL–water interaction must be accounted for in both the molecular-level and process-level design of all IL-based capture schemes. At present, there is significant uncertainty in scale-up costs, related both to IL synthesis and operation, and as such research efforts must focus on demonstrating cost-effective pilot operations.

Capture based on the selective adsorption of CO<sub>2</sub> on solid-state media, such as amine-functionalized oxides, zeolites, and metal–organic frameworks (MOFs), are viable alternatives to liquid-based separation.<sup>16–18</sup> There are a number of advantages to employing solid-state separation media, including high uptake capacities, fast adsorption/desorption kinetics, and low heat capacities (incurring lower energy costs during regeneration). Porous silica supports can be functionalized with amine groups (e.g., through physical impregnation, covalent tethering, or polymerization) to achieve desirable acid–base reaction chemistry for CO<sub>2</sub> uptake. Design considerations include adsorption capacity, mass transfer limitations, and stability. In particular, stability in the presence of water, a well-known limitation for silica-based materials, is essential if cost-effective steam stripping is to be employed during the sorbent regeneration stage. Other solid-state approaches rely on physisorption in porous media to achieve high CO<sub>2</sub> adsorption capacities. Zeolites are naturally occurring porous materials in which the CO<sub>2</sub> physisorption mechanism can be tuned by altering charge-compensating cationic sites capable of interacting with CO<sub>2</sub>. These sites, however, also strongly interact with water, which can be detrimental to CO<sub>2</sub> uptake under humid flue gas conditions. Similar to zeolites, MOFs are materials that operate through the physical adsorption of CO<sub>2</sub> in pores

created by a metal–ligand framework. Pore sizes in MOFs are highly controllable, an ideal design characteristic for optimizing CO<sub>2</sub> adsorption capacities and kinetics. In addition to controlling porosity, maximizing the number of exposed metal sites is also beneficial for achieving optimal adsorption capacities, as metal sites can strongly interact with CO<sub>2</sub> by polarizing the quadrupole moment of the molecule.<sup>18</sup> The activity of both zeolites and MOFs can be enhanced via amine functionalization,<sup>19,20</sup> leading to intriguing hybrid materials. Other CO<sub>2</sub>-adsorbing materials are low-cost activated carbons with variable porosity, as well as metal oxides capable of chemisorbing CO<sub>2</sub> through acid–base interactions (e.g., CaO and MgO). Adsorption-based separations have greater potential than their absorption-based counterparts, because it is more straightforward to balance interactions at a solid–gas interface compared to a liquid–gas one. It is clear that CO<sub>2</sub> capture will inevitably require significant investment even with substantial design progress, and economic incentives again will be needed to achieve implementation at scale.

CO<sub>2</sub> utilization strategies, while in their nascent stages, offer the alluring possibility of turning CO<sub>2</sub> into valuable products, thus providing an economic incentive for CO<sub>2</sub> capture. Indeed, if the profit gained from such value-added products outweighs the cost of capture, then economics alone could provide the societal driving force for closing the carbon cycle. This is a lofty goal, far from realization, with research efforts still seeking to define many fundamental principles that will enable efficient, scalable CO<sub>2</sub> conversion. An enormous amount of research has focused on the electrochemical reduction of CO<sub>2</sub> in particular, which could be a viable strategy if powered by a carbon-neutral electricity source. The distribution of reduction products achieved in an electrochemical cell is dependent on both the nature of the employed electrode and the operating conditions.<sup>21</sup> Fe, Co, Ni, Pt, and Ag electrodes exhibit high current densities (reaction rates) but suffer from low efficiency due to competitive hydrogen evolution, in which protons from solution are reduced instead of CO<sub>2</sub>. Cu electrodes uniquely yield products that require multiple reduction steps, such as methane and ethane, and for this reason have been the subject of intense research efforts. Understanding the ability of Cu to selectively couple C–C bonds is essential for designing more efficient reduction schemes, as Cu itself requires prohibitively high overpotentials. It has also been established that the degree of oxidation on Sn and Cu electrodes can significantly alter overall selectivity, providing a research avenue for designing composite metal/metal-oxide electrode systems that simultaneously achieve high activity and selectivity.<sup>22,23</sup> An alternative approach is to employ an unreactive electrode in tandem with a homogeneous electrocatalyst to shuttle electrons to the reactants.<sup>24</sup> Such electrocatalysts typically reduce CO<sub>2</sub> to CO, which can then be mixed with H<sub>2</sub> and converted to fuels using well-known Fischer–Tropsch catalysts. Important classes of electrocatalysts feature metal center complexes with macrocyclic, bipyridine, or phosphine ligands, such as Ni(cyclam)<sup>2+</sup>, Re(bpy)(CO)<sub>3</sub>Cl, or Rh(dppe)<sub>2</sub>Cl, respectively. In addition to identifying catalysts that are inexpensive, active, selective, and robust, it remains a challenge to identify metal complexes that can facilitate the multielectron reductions essential for kinetically efficient CO<sub>2</sub> reduction.

The conversion of CO<sub>2</sub> into useful fuels via photocatalysts capable of harnessing energy from sunlight is another route for generating carbon-neutral fuels. Photocatalysts typically rely on the illumination of a semiconductor, where sufficiently

energetic photons can excite an electron from the valence band to the conduction band. Excited electrons reside in a high-energy state from which CO<sub>2</sub> reduction is thermodynamically feasible to a variety of products, such as CO, HCO<sub>2</sub>H, CH<sub>3</sub>OH, and CH<sub>4</sub>. Although some semiconductors (principally, TiO<sub>2</sub>) can directly reduce CO<sub>2</sub> at their surfaces, such schemes often require sacrificial electron donors and therefore are not catalytic. TiO<sub>2</sub> itself will not ever be an efficient photocatalyst, because its too-large band gap forbids all but a few percent of the solar spectrum to be absorbed. Just as with electrocatalysis, performance is enhanced by adding a cocatalyst that facilitates transfer of photoexcited electrons to reactants. This strategy has been demonstrated at GaP, CdTe, and CuInS<sub>2</sub> (photo)-electrodes, where lower overpotentials and enhanced faradaic efficiencies to produce methanol are achieved by adding an aromatic amine such as pyridine to the electrolyte. Our own work suggests that pyridine functionalizes the semiconductor surface, acting as an intermediary enabling hydride transfer to CO<sub>2</sub> to form HCOO<sup>−</sup>.<sup>25</sup> Others contend that this process occurs with the active pyridine-derived species residing in solution as opposed to on the semiconductor.<sup>26</sup> While the mechanistic role played by pyridine is still under debate, once understood it will establish guiding principles for designing other semiconductor/cocatalyst systems.

Even if fuel precursors such as methanol (converted to gasoline via the zeolite-based Mobil process<sup>27</sup>) are someday produced efficiently by (photo)electrocatalysis, technologies for separation of methanol and water—such as membranes that take advantage of a pervaporation strategy<sup>28</sup>—are energy intensive and require further development. CO<sub>2</sub> reduction driven by (photo)thermochemical processes (i.e., utilizing sunlight as heat) could eliminate energy-intensive liquid separations by producing gaseous instead of liquid products. One route could be two-step thermochemical cycles for splitting CO<sub>2</sub>.<sup>29,30</sup> In the first step, an inexpensive metal oxide is heated via concentrated sunlight to drive off oxygen. In the second step, the oxygen-deficient material is cooled, making it thermodynamically favorable to regenerate the oxide by reaction with CO<sub>2</sub>, yielding CO and O<sub>2</sub>. Analogous two-step cycles can be used to split water, generating H<sub>2</sub>, such that the CO and H<sub>2</sub> produced in both cycles can be combined to create syngas convertible to fuel via Fischer–Tropsch chemistry. All of these steps could benefit from innovations to reduce energy use and to increase efficiency.

Strategies utilizing CO<sub>2</sub> in fuel cells or as a precursor for the synthesis of industrially relevant chemicals and materials may also help close the carbon cycle.<sup>31</sup> Urea is readily synthesized from NH<sub>3</sub> and CO<sub>2</sub> feedstocks, a process that accounts for ~100 Mt yr<sup>−1</sup> of CO<sub>2</sub> utilization. Polymerization is also a viable strategy, as polycarbonates can be synthesized from CO<sub>2</sub> and propylene oxide over Zn-based catalysts. Carbonate fuel cells can harness CO<sub>2</sub> directly from flue gas, yielding a concentrated CO<sub>2</sub> stream for sequestration while at the same time generating energy by oxidizing H<sub>2</sub>.<sup>32</sup> Bioutilization schemes are emerging, where photosynthetic organisms transform CO<sub>2</sub> into energy-dense fuels or value-added chemicals; ultimately bioenergy followed by carbon capture and storage (BECCS), using geological storage discussed next to achieve not just zero but *negative* carbon emissions may be our ultimate savior. BECCS at scale, however, may be limited by the availability of land and water resources, where the risks associated with widespread land and water use must be carefully considered.<sup>33</sup>

Geological storage via mineralization by reaction with olivine or serpentine is promising,<sup>34</sup> although these minerals are extracted via mining operations with environmental drawbacks. Mineralization alternatively can be achieved by pumping CO<sub>2</sub> into geological formations replete with these minerals.<sup>35</sup> An encouraging study by Matter et al.<sup>36</sup> reported permanent disposal of CO<sub>2</sub> in the Iceland CarbFix storage site, where 95% of injected CO<sub>2</sub> was mineralized to carbonate after ~2 years (previous forecasts predicted hundreds, if not thousands, of years would be needed). Enhanced oil recovery (EOR), closely related to geological sequestration as CO<sub>2</sub> is pumped into depleted gas and oil fields, currently employs ~100 Mt of CO<sub>2</sub> per year;<sup>37</sup> altering EOR to maximally sequester CO<sub>2</sub>—rather than optimize its recovery and reuse—could be an important part of the answer.

The scientific community is just now beginning to understand fundamental reaction mechanisms, principles, and strategies for efficient CO<sub>2</sub> capture, utilization, and sequestration. While chemistry is central to many aspects of CCUS, ultimately it will take collaborations over many years among scientists and engineers covering chemistry, biology, physics, and geology to achieve this Holy Grail.

## AUTHOR INFORMATION

### Corresponding Author

\*eac@princeton.edu.

ORCID 

Emily A. Carter: 0000-0001-7330-7554

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