Electrochemical reduction of CO\textsubscript{2} in the captured state using aqueous or nonaqueous amines

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**SUMMARY**

CO\textsubscript{2} capture and its electrochemical conversion have historically developed as two distinct technologies and scientific fields. Each process possesses unique energy penalties, inefficiencies, and costs, which accrue along the mitigation pathway from emissions to product. Recently, the concept of integrating CO\textsubscript{2} capture and electrochemical conversion, or “electrochemically reactive capture,” has aroused attention following early laboratory-scale proofs-of-concept. However, the integration of the two processes introduces new complexities at a basic science and engineering level, many of which have yet to be clearly defined. The key parameters to guide reaction, electrolyte, electrode, and system design would, therefore, benefit from delineation. To begin this effort, this perspective outlines several crucial physicochemical and electrochemical considerations, where we argue that the absence of basic knowledge leaves the field of designing metaphorically in the dark. The considerations make clear that there is ample need for fundamental science that can better inform design, following which the potential impacts of integration can be rigorously assessed beyond what is possible at present.

**INTRODUCTION**

To limit global temperature rise to well below 2°C, the International Energy Agency’s Sustainable Development Scenario estimates that installed CO\textsubscript{2} capture must scale from 40 MT/year in 2020 (GCCSI, 2020) to 10 Gt/year in 2070 (IEA, 2020). The most industrially mature capture process relies on solutions of aqueous amines, commonly 30 wt % monoethanolamine (MEA), which exothermically absorbs CO\textsubscript{2} from flue gas (12-14% CO\textsubscript{2} concentration) at \(\sim 40^\circ\text{C}\). Once the capture solution is saturated with CO\textsubscript{2}, it is regenerated to produce a pure CO\textsubscript{2} stream along with lean amine for subsequent CO\textsubscript{2} uptake. Regeneration is typically achieved by a thermal-swing process at \(\sim 120^\circ\text{C}\) in a desorber unit, with heating provided by steam redirected from the power plant turbines (Rochelle, 2009). At 2-4 GJ/ton CO\textsubscript{2}—approximately 88-176 kJ/mol CO\textsubscript{2}—for regeneration duty (Renfrew et al., 2020), this step is the most energy-intensive part of capture and leads to significant derating (up to 30%) of the plant’s power-generating capacity (Boot-Handford et al., 2014). After almost 100 years of development, temperature-swing methods with amines are reaching technical maturity, yet remain energetically and capital intensive (Bui et al., 2018).

Separately, researchers have been investigating methodologies to electrocatalytically upgrade post-separation CO\textsubscript{2} to products with market value (carbon capture and utilization, or CCU) (Birdja et al., 2019). Targeted products include chemicals (e.g., ethylene, carbon monoxide) (Luna et al., 2019; Ross et al., 2019) or fuels (Birdja et al., 2019; Sheehan, 2021) that currently rely on fossil-intensive production methods. Synthesizing these products from CO\textsubscript{2} and H\textsubscript{2}O using renewable electricity avoids these fossil emissions and may help incentivize broader adoption of carbon capture technologies (Jordaand and Wang, 2021). Electrochemical CO\textsubscript{2} conversion also has high energy requirements of \(\sim 400-700\) kJ/mol of product at the electrolyzer stage (Li et al., 2019; Smith et al., 2019). These requirements accrue alongside those of upstream capture, compression (\(\sim 10-15\) kJ/mol (Lin and Rochelle, 2016)), and post-conversion product separation energy. Finding ways to decrease energy demand, capital costs, and process complexity along the entire CO\textsubscript{2} management pipeline is, therefore, a priority.

In this context, recent years have seen growing interest in “reactive capture” concepts in which CO\textsubscript{2} absorption and chemical conversion, for example, CO\textsubscript{2} hydrogenation, are integrated (Bhattacharya et al., 2021).
In this scheme, the reactant is not CO$_2$(g) but rather an amine-CO$_2$ adduct such as a carbamate. A sub-category of reactive capture employs electrochemical, rather than chemical conversion (Sullivan et al., 2021), in which amine-CO$_2$ adducts are subjected to an electrochemically reducing (cathodic) current flow (Figure 1A). As a result, they may form reduction products (energetically uphill, Figure 1B) or, alternatively, can react with alkaline (Li$^+$, Na$^+$, Mg$^{2+}$, Ca$^{2+}$) ions to form solids such as carbonates (energetically downhill (Khurram et al., 2018; Wang et al., 2021)). In both pathways, the thermal regeneration step is avoided. Notably, for the electrolytic pathway, thermal energy requirements (red arrows) are fully replaced with a process driven by renewable electricity (green arrows), allowing better utilization of fossil sources for energy production; in both cases, the requirement for a co-located steam supply is removed (Figure 1B). As Figure 1B denotes thermodynamics, a second possible integration advantage is the potential to alter the kinetic barriers and selectivity of conversion (Ross et al., 2019), as CO$_2$ bound to an amine is electronically more similar to activated CO$_2$ than the highly stable, linear CO$_2$(g) (Sullivan et al., 2021). A third benefit may be cost savings resulting from simpler processes (Lee et al., 2021). We note that, because electrochemically reactive capture yields CO$_2$-derived products rather than CO$_2$(g), it is distinct from electrochemical or pH swing processes under development for separations (Gurkan et al., 2021; Renfrew et al., 2020; Rheinhardt et al., 2017).

Electrochemically reactive capture has so far been found capable of yielding a range of products depending on the electrolyte medium, such as carbon monoxide (CO) (Chen et al., 2017; Abdinejad et al., 2020; Hossain et al., 2021; Lee et al., 2021; Pérez-Gallent et al., 2021), formate (HCOO$^-$) (Chen et al., 2017; Bhattacharya et al., 2020b; Pérez-Gallent et al., 2021), and solid alkali carbonates (Khurram et al., 2018), often with high selectivity. Although prior studies have now demonstrated basic scientific feasibility, given the early stage of the field, influential parameters and rate-limiting factors have not yet been thoroughly studied, and rational design of such processes is not yet possible. Hence, this perspective aims to articulate critical considerations that arise when an amine sorbent is engineered to function simultaneously as a capture solution, electrolyte, and reactive medium. We define influential, and possibly rate-limiting parameters that require further characterization so that researchers can learn how to better manipulate and

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**Figure 1. Schematic and free energy landscape of integrated CO$_2$ capture and electrochemical conversion**

(A) Conceptual schematic of an integrated CO$_2$ capture and electrochemical conversion process.

(B) Free energy landscape of such a process using amines (typical sorption enthalpies of $-60$ to $-80$ kJ/mol CO$_2$). "Pure CO$_2$" represents separated CO$_2$ at 1 atm, with further compression to high pressure as shown. The minimum work to separate dilute CO$_2$(12-14% in flue gas) to pure CO$_2$ at 1 atm is on the order of 5-10 kJ/mol CO$_2$ depending on starting and ending purities (Wilcox, 2012). The minimum work of compression of pure CO$_2$ to $-150$ atm is 12 kJ/mol (Renfrew et al., 2020). Production of formally reduced products (chemicals, fuels) from either post-separation CO$_2$ or carbamates is energetically uphill (electrolytic cell). Electrochemically induced mineralization requires electron transfer to the carbamate to balance alkali cation transfer, producing solid (Li, Na, Mg, or Ca-based) carbonates, and is a downhill (galvanic) reaction electrochemically. As a rough (lower) estimate of scale, typical CO$_2$ mineralization enthalpies of magnesium carbonate and calcium carbonate with respect to CO$_2$ and their oxides (MgO, CaO) are $-180$ to $-240$ kJ/mol (Gadikota, 2020). For ease of representation, energy levels are not to scale, co-reactants (such as water, Mg$^{2+}$ or Ca$^{2+}$) and products (e.g., O$_2$ for electrolysis) are omitted, and "+$^-" does not imply stoichiometry given that multiple processes and products are allowed. "Reduced products" refers to chemical or fuel outputs such as CH$_4$, CH$_3$OH, or CO and is represented generically as a range. Red arrows denote thermal processes, while green arrows denote processes that can be electrified (B) is inspired in part by (Heldebrant et al., 2022).
improve integrated capture-conversion reactions. Throughout, we employ the terminology “reduction reaction” as defined with respect to an electrode process, regardless of whether the CO$_2$ is formally reduced (e.g., producing CO) or routed to a CO$_2$-derived product without a formal oxidation state change (e.g., a carbonate induced to form electrochemically), as long as the process is driven by cathodic current flow. As we discuss, many unique and non-obvious considerations arise with integrated processes that are distinct from those in either conventional CO$_2$ capture or electrochemical conversion alone. These include but are not limited to (Figure 2) specific physicochemical properties of amine sorbent-electrolytes; unique considerations for transport and interfacial processes in multi-ion reacting systems; and in the concerted impact of amine-CO$_2$ adduct, salt ions, and water/solvent on reaction pathways and products. Altogether, these factors define a research frontier characterized by its complexity but also versatility.

EXEMPLARY PROCESSES

We first briefly describe early exemplar systems that have employed amines in combined capture-electrochemical reduction scenarios (Figures 3 and 4). Chen et al. (Figure 3A) first examined CO$_2$ reduction on a series of metal catalysts (e.g., In, Pb, Ag) in CO$_2$-saturated 30% (w/w) aqueous MEA solution (Chen et al., 2017). The amine’s principal effect was described as its buffering ability to maintain the electrolyte pH at 8.6; along with electrode design and use of surfactant, the competitive hydrogen evolution reaction (HER) was suppressed, favoring moderate Faradaic efficiency (FE) of dissolved CO$_2$ toward CO (22.8%) and formate (54.5%). The authors rationalized that the HER proceeded primarily via the reduction of amine-bound protons, given the lower pKa and thus weaker proton binding of MEAH$^+$ (9.4) vs. HCO$_3$ or H$_2$O (10.3 and 15.7, respectively).

The first evidence for amine-CO$_2$ bond activity under electrochemical conditions was attained in the nonaqueous electrolyte. To avoid the competitive and often-obscuring HER, our group examined the cathodic reduction of CO$_2$ bound to 2-ethoxyethylamine (EEA) in dimethyl sulfoxide (DMSO) with Li$^+$ salt (Figure 4A) (Khurram et al., 2018). Li metal was used as the anode to provide a continuous source of alkali cations for reaction, and carbon was used as the cathode substrate. The use of nonaqueous solvent proved beneficial for enabling the fundamental electrochemistry of amine-CO$_2$ adducts to be studied. Although cells without EEA exhibited negligible activity for physisorbed CO$_2$ conversion, markedly improved activities were observed in the presence of the amine. As discussed later, the active species was identified to be an alkali cation-associated carbamate (i.e., EEA-COOLi$^+$). Given the availability of
Li⁺, solid Li₂CO₃ was the main discharge product, along with co-produced carbon. Isotopic labeling confirmed that the produced solid carbonates originated selectively from CO₂.

Subsequent efforts further examined amine-CO₂ reduction in nonaqueous media. Bhattacharya et al. reported cyclic voltammetry of amines such as aniline, morpholine, diethylamine (DEA), triethylamine (TEA), and triethanolamine (TEOA) bound to CO₂ in acetonitrile with TBAPF₆ salt, and found that reductive activity was observed only in the presence of CO₂ (Figure 4B) (Bhattacharya et al., 2020b). Under bulk electrolysis conditions, formate (HCOO⁻) was the only product, with neither CO nor H₂ detected. The authors concluded that carbamates can be directly reduced electrochemically; however, the lack of a bulk source of reactive ions (such as alkali metal or H₂O) in these experiments may limit the reaction to one involving irreversible consumption of amine or solvent to yield the protonated products. In a different approach, Perez-Gallent et al. attempted CO₂ reduction using CO₂ released thermally from an electrolyte solution of the sterically hindered, primary amine 2-amino-2-methyl-1-propanol (AMP) with tetraethylammonium chloride (TEACl) in propylene carbonate (PC) (Figure 4C). Under cyclic voltammetry (CV) conditions, the authors observed limited reduction activity at room temperature. However, as temperatures increased to 75°C, protons supplied from trace water, which permeated through the cell membrane from the anode compartment, led to increased activity. Chronopotentiometry measurements evidenced the production of formic acid (FE of ~45%), CO (~45%), and minor amounts of glycolic acid and oxalic acid. Notably, all products were proposed to derive from locally thermally regenerated CO₂ and not amine-CO₂ directly.

In aqueous media, electrochemical cleavage of the amine-CO₂ bond has only recently been reported. Lee et al. observed only H₂ evolution occurring in MEA/water in the presence of CO₂. However, CO formation, with up to 72% FE at 50 mA cm⁻² on Ag electrodes, was achieved when alkali cations (e.g., K⁺, Cs⁺) were...
Figure 4. Electrochemical CO₂ reduction with amines in nonaqueous solution
(A) Schematic (top) and cyclic voltammograms (CV, bottom) on carbon with 0.1 M EEA-CO₂ and 0.3 M LiClO₄/DMSO (Khurram et al., 2018).
(B) Schematic (top) and CVs (bottom) using glassy carbon with 0.1 M amine-CO₂, 0.1 M 1,1,3,3-tetramethylguanidine (TMG) in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile at 0.1 V s⁻¹ (Bhattacharya et al., 2020b).
(C) Schematic (top) and CV (bottom) using a Pb electrode with 1 M AMP-CO₂ in 0.7 M TEACl/PC (Pérez-Gallent et al., 2021). Reprinted with permission from (Pérez-Gallent et al., 2021). Copyright (2021), American Chemical Society. Schematics omit labeling of product RNH₂ for clarity. Gray species are non-participating.

include as a co-salt and temperatures were increased to 70°C (Figure 3B). As discussed later, this study evidences the significance of supporting electrolyte selection when amines are used to deliver CO₂ to the electrode. Additional studies have further examined amine-CO₂ reduction in aqueous electrolytes using Cu, Ag, and Au (Hossain et al., 2021), and reported up to 58% FE to CO at ~20 mA/cm² on Cu (Abdinejad et al., 2020), an atypically high FE for this catalyst.

Collectively, these studies indicate the viability of conducting electrochemical reduction on amine-CO₂ solutions to form various products. There is a lack of consensus about the amine’s role and whether direct N–C bond cleavage occurs—which may be highly system-dependent—as well as the role of temperature. We next describe considerations that influence the complex and sensitive reactant speciation unique to integrated capture-conversion, the illumination of which is likely to help answer these complex questions in further research.

PARAMETERS GOVERNING THE CAPTURE PROCESS AND RESULTING SOLUTION SPECIATION
Integration of amines and electrolyte constituents (solvent and salt) yields complex media in which sorption, speciation, transport, reaction, and electrochemical regeneration processes occur in a coupled manner (Figure 2). Hence, it is helpful to first examine these processes individually, noting that substantially more is understood about the reactant state (CO₂ capture process) at present than about what occurs dynamically during electrochemical operation.

In the absence of sorbents, CO₂ reduction in aqueous media is limited by low solubility (~34 mM) in neutral water (Figure 5A), which restricts current densities in common bulk electrolysis-type cells (Liang et al., 2020; Lobaccaro et al., 2016). This concentration increases at higher pH, for example, ~140 and ~1180 mM at pH
13 and 14, respectively (Yoo et al., 2013), although such conditions are not ideal for electrochemical conversion (Rabinowitz and Kanan, 2020). The speciation of physically dissolved CO$_2$ is subject to the well-known water equilibria (Figure 5B) dependent on pH:

\begin{align*}
\text{H}_2\text{O} + \text{CO}_2 & \rightarrow \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \rightarrow \text{H}^+ + \text{HCO}_3^- \quad \text{(pKa} = 6.4) \\
\text{HCO}_3^- & \rightarrow \text{H}^+ + \text{CO}_3^{2-} \quad \text{(pKa} = 10.3)
\end{align*}

Incorporation of amines amplifies CO$_2$ absorption capacity proportional to the amine concentration, for example, on the order of 2-4 M (Singh et al., 2011), which significantly boosts reactant availability at more moderate pH.

**Reactant speciation with aqueous amines: Carbamate versus (bi)carbonate**

Amines are categorized as primary, secondary, or tertiary depending on the number of N–C bonds (1, 2, or 3, respectively) and, inversely, the number of N–H bonds (2, 1, or 0); cyclic amines are a sub-category and may be either secondary or tertiary. When a primary or secondary amine captures CO$_2$, the nonbonding electron pair on the nitrogen atom and the acidic CO$_2$ act as a donor-acceptor pair, and an N–C bond is formed (Chakraborty et al., 1988; Hwang et al., 2015). Initially, a zwitterion (RNH$_2$COO$^-$ or RNH$^+$COO$^-$) also forms (Said et al., 2020; Yamada, 2021):

\begin{align*}
\text{RNH}_2 + \text{CO}_2 & \leftrightarrow \text{RNH}_2^+\text{COO}^- \quad \text{(primary amine)}
\end{align*}
RNH + CO₂ ⇌ RNH⁺COO⁻ (secondary amine)  \hspace{1cm} \text{(Equation 5)}

where R represents substituent groups. A proton is subsequently transferred to a second amine, forming a carbamate anion (RNHCOO⁻ for primary amine) and ammonium cation (RNH₃⁺), and corresponding to a maximum loading of 0.5 CO₂/amine. Depending on amine pKa, RNH₃⁺ can also be formed by direct reaction with protons from carbonic acid, bicarbonate, or water. This pathway for RNH₃⁺ formation lowers the attainable CO₂ loading owing to the blockage of the binding site by the proton, rendering the amine unable to participate in the above capture mechanism. The major possible reactions are listed later in discussion, using primary amine as the example (Figure 5C):

Carbamate formation:

\[ 2RNH₂ + CO₂ \rightarrow RNHCOO⁻ + RNH₃⁺ \] \hspace{1cm} \text{(Equation 6)}

Carbamate hydrolysis:

\[ RNHCOO⁻ + H₂O \rightarrow HCO₃⁻ + RNH₂ \] \hspace{1cm} \text{(Equation 7)}

Hydrolysis more readily proceeds with low-pKa amines given their poor tendency to stably bind CO₂. Additionally, base-catalyzed amine regeneration from RNH₃⁺ can occur if strong Bronsted bases such as KOH are used. These reactions can result in CO₂ loadings in excess of 0.5.

In contrast to primary or secondary amines, tertiary amines lack a labile proton and thus cannot stably form carbamate. Consequently, the amine acts as a base catalyst for the CO₂ hydration reaction (Figure 5D):

\[ CO₂ + R₁R₂R₃N+H₂O \rightarrow R₁R₂R₃NH⁺ + HCO₃⁻ \] \hspace{1cm} \text{(Equation 8)}

This pathway allows for higher CO₂ loadings to be achieved than with primary or secondary amines, that is, one CO₂/amine instead of 0.5. A similar outcome occurs with sterically hindered amines in which N–C bonds are destabilized, resulting in CO₂ loadings in excess of 0.5, for example, 0.5-0.8 (Bernhardsen and Knuutila, 2017).

The rate at which a capture solution achieves equilibrium upon CO₂ introduction, as well as the equilibrium speciation, is sensitive to a number of factors including amine structure, pKa, temperature and pressure, and CO₂ flow rates (Kortunov et al., 2015a; 2015c; 2015b). Primary and secondary amines with sufficiently high pKa (~7.0-9.5) initially favor carbamate at shorter timescales, but the solutions tend to undergo significant pH decreases during capture (e.g., from >10 to 7-8 depending on pKa and concentration), which drives hydrolysis to bicarbonate (Figure 5C). Consequently, bicarbonate can become the dominant species over time, as occurs for instance with MEA (pKa of 9.4). Tertiary amines, on the other hand, form purely bicarbonate, though may proceed through a carbonate intermediate at shorter timescales (Figure 5D). The wide versatility in speciation, pH sensitivity, and sluggish temporal evolution has important implications for subsequent conversion. Processes that attempt conversion immediately following CO₂ capture will be operating on non-equilibrium solution states with ill-defined speciation. Of note, bicarbonate, in addition to acting as a pH buffer, serves as a proton donor in CO₂ reduction reactions (Chen et al., 2012) and has also been suggested to serve as the electroactive source of CO₂ upon reduction compared to physically dissolved CO₂ (Dunwell et al., 2017). Hence, its presence (often predominance) in capture media cannot be overlooked.

Molecular design of the amine’s pKa provides a powerful handle to tailor numerous aspects of the capture-conversion process. A high pKa reflects high nucleophilicity, leading to a fast reaction rate and strong bonding with CO₂ for primary and secondary amines, along with good proton acceptor characteristics to form the stoichiometric ammonium cation (Bernhardsen and Knuutila, 2017). Longer alkyl R-groups generally correlate with higher pKa owing to their electron-donating nature, which modulates the nitrogen basicity. Additionally, secondary amines can achieve the highest pKa values compared to similar primary and tertiary amine structures (Kortunov et al., 2015a). Although stronger bonding drives the capture reactions (Equation 6) to the right (favoring higher loadings), it also necessitates a higher energy requirement.
for thermal regeneration, and presumably also for electrochemically driven N–C bond cleavage. Typical CO₂ absorption enthalpies for commercial amines range between −60 and −80 kJ/molCO₂ to balance demands for sufficient CO₂ capacity and capture rate (stronger N–C bonds) and regeneration energy and release rate (weaker N–C bonds) (Kim and Svendsen, 2007; McCann et al., 2008). The effect of N–C bond strength on electrochemical reactions, including optimal values, is not yet known.

Increasing the temperature at which capture occurs decreases the stability of both the amine-CO₂ species and bicarbonate (Kortunov et al., 2015a). Upon heating, bicarbonate converts to carbonate (for solutions of tertiary amines) or carbamate (for solutions of primary or secondary amines) (Yoon and Hwang, 2020), with eventual desorption as CO₂(g) and regeneration of the lean amine. Temperature also affects the solubility of CO₂, and thus the pH of the capture solution and the proportion of ionic species (Hamburg and Versteeg, 2009; Rajan and Muraleedharan, 2017). We note that speciations are also sensitive to partial pressure and amine concentration, which further complicate the above considerations; we refer to readers to discussions elsewhere (Böttinger et al., 2008; Choi et al., 2020). Overall, the amine speciation is far from straightforward and requires careful analysis for a given electrochemical system, especially if the elevated temperature is to be used to facilitate kinetics and/or transport.

Reactant speciation with nonaqueous amines: carbamate versus carbamic acid

Organic solvents show roughly an order of magnitude higher CO₂ solubility, for example, ~130 mM in DMSO and ~300 mM in acetonitrile and tetrahydrofuran (Figure 5A), compared to water at near-neutral pH. These higher solubilities may benefit CO₂ conversion kinetics. However, the lack of a proton source in aprotic solvents limits the reaction pathways to those producing solid carbonates (when alkali cations are used) and carbon (Khurram et al., 2018), or protic species formed by irreversible solvent consumption, unless water is explicitly added.

The speciation in strictly nonaqueous systems exhibits a richness that is distinct from aqueous systems and depends sensitively on electrolyte properties. In nonaqueous media, the absence of water suppresses the hydrolysis pathway of carbamate to bicarbonate (Equation 7). Not only does this suppression result in different speciation, it also renders tertiary amines (which form only bicarbonate via hydrolysis) fully unable to capture CO₂. However, unlike in aqueous media, some nonaqueous solvents can stabilize the uncharged carbamic acid upon CO₂ uptake (Kortunov et al., 2015a). The competitive speciation reactions (written for primary amines) are:

\[ 2RNH₂ + CO₂ → RNHCOO^− + RNH₃⁺ \]  \hspace{1cm} (Equation 9)

\[ 2RNH₂ + 2CO₂ → 2RNHCOOH \]  \hspace{1cm} (Equation 10)

Carbamic acid corresponds to one amine/CO₂ versus 0.5 amine/CO₂ and is favored by solvents capable of strong hydrogen bonding. Examples include S=O and C=O functional groups in DMSO or 1-methyl-2-pyrrolidinone, respectively, which donate to the carboxylic acid proton (Kortunov et al., 2015c). In nonaqueous media, speciation among carbamic acid and carbamate is similarly sensitive to temperature and pressure as in aqueous media, with higher temperatures and lower partial pressures of CO₂ favoring carbamate (Kortunov et al., 2015b). Solvents examined for nonaqueous capture range broadly, for example, dimethyl sulfoxide (Kortunov et al., 2015b), ethanol (Versteeg and van Swaaij, 1988), propylene carbonate (Karlsson et al., 2019), or n-methyl pyrrolidine (Ebrahiminejadhasanabadi et al., 2021). These solvents are not always relevant to electrochemical systems as discussed later.

Precipitation and significant increases in solution viscosity, leading to gel formation as capture progresses, have been observed in nonaqueous media and must be considered in solvent screening (Karlsson et al., 2019; Tao et al., 2017). Increased viscosity arises from the nature of amine N-H functionalities as strong hydrogen bond donors (Heldebrant et al., 2017). One effective strategy to mitigate viscosity is to design sorbents that promote intramolecular, rather than intermolecular, hydrogen bonding, or which alternatively form entirely non-charged species upon CO₂ uptake (Cantu et al., 2017; Heldebrant et al., 2017; Malhotra et al., 2019). Such advanced sorbent design strategies, translated from the CO₂ capture and reactive capture fields, hold great promise for adaption to electrochemically reactive capture.
SPECIAL CONSIDERATIONS FOR ELECTROCHEMICAL SYSTEMS

Simple screenings for the selection of amines

Amines that have been developed for CO₂ capture provide an initial starting point for the exploration of sorbents for electrochemically reactive capture. However, they are not necessarily optimized, and many may not even be suitable for electrochemical reactions. To be applied in electrochemical systems, both the lean amine and intermediate species must be stable against parasitic reduction or oxidation within the voltage window of interest. Oxidative stability against the electrochemical cell’s counter electrode is also important, as that electrode may reach high voltages to balance reduction reactions at the working electrode, necessitating proper fritting and possibly use of dual-compartment cells to avoid exposure of amines to such environments (Figures 3 and 4). Dual-compartment cells are also effective in mitigating undesired side reactions involving CO₂-derived product oxidation. Depending on pKa, amine protons can be reduced directly to evolve H₂. Although such processes may be tolerated (Chen et al., 2020) in aqueous media, avoidance of parasitic proton consumption from the amine or solvent is critical for nonaqueous electrolytes. The selection of amines is further constrained by simple miscibility considerations (e.g., nonpolar amines cannot be dissolved readily in aqueous media) and changes in physicochemical properties of solutions upon CO₂ uptake, such as viscosity increases, precipitation, and gelation as noted previously.

Electrolyte salt effects on reactant speciation

In nonaqueous media, amine/solvent combinations that form primarily uncharged carbamic acid require the addition of a supporting electrolyte salt to provide electrolyte conductivity. Salt selection has been found to substantially alter the speciation in solvents that otherwise favor carbamic acid formation. For example, in DMSO, the inclusion of Lewis acid-alkali cations (Li⁺, Na⁺, K⁺) in EEA solutions substantially increases the proportion of carbamate at the expense of carbamic acid in the solution. This phenomenon has been attributed, via NMR, to electrostatic interactions of the cation with –COO⁻ in the carbamate (Figure 6A) (Khurram et al., 2019). The proportion of alkali carbamate with respect to carbamic acid increased strongly with increasing cation Lewis acidity (Figure 6B). In addition, elevated temperature accelerated carbamate generation rates, for example, from 16% at room temperature to 40% at 60°C after 24 h with 0.3 M of LiClO₄ salt (Figures 6C and 6D) (Khurram et al., 2020).

In DMSO, carbamate was found to be the electrochemically active species given that little electrochemical activity was observed when solutions consisted of primarily carbamic acid (i.e., early timepoints in Figure 6B). Additionally, no protonated products, such as carboxylates (LiCOOH) were observed in the discharged solid phase, indicating negligible proton consumption from the solvent or amine. This can be rationalized by the fact that, although carbamic acid may be present in solution to minor degrees, a negatively polarized cathode will attract alkali cations, which in turn interact strongly with carbamates. Notably, salt addition to EEA-CO₂ in other solvents (tetraethylene glycol dimethyl ether (TEGDME), dimethoxyethane (DME), PC, tetrahydrofuran (THF), dimethylformamide (DMF)) exhibited either severe gelation or salt precipitation, rendering the solutions unusable for electrochemical reactions (Khurram et al., 2018). Changing the amine from EEA to diisopropylamine (DIPA) (Khurram et al., 2020), however, mitigated this issue even in viscous solvents (e.g., TEGDME), indicating that electrolyte constituents (amine, concentration, solvent, and salt selection) must be co-designed. At present, untenable increases in viscosity at higher amine concentrations (>0.1 M) upon CO₂ introduction in nonaqueous solvents prohibit the use of amines at concentrations commensurate with aqueous media.

In aqueous media, CO₂ uptake by amines produces carbamate, ammonium, and bicarbonate, converting the uncharged medium to a de facto electrolyte. The ionic conductivity of the resulting solutions may not be ideal owing to the bulkier nature of the amine-derived ions or non-optimized distribution and population of charge carriers, motivating further inclusion of a supporting electrolyte salt. Given that aqueous media generally favors carbamate, the salt-induced carbamic acid-carbamate interplay discussed above is less relevant. However, supporting salts may certainly influence the capture rate and resulting speciation, which has received little study so far.

Mass transport considerations

Within the absorber and stripper units in conventional CO₂ capture, forced convection assists uptake of CO₂ and amine regeneration. Although forced convection is relevant in electrochemical systems for...
CO₂ uptake (e.g., bubbling or flowing of the gas to achieve contacting with the amine electrolyte), electrochemical systems additionally require the migration of reactants to an electrified interface, which places further exacting requirements on mass and ion transport. The diffusion coefficients and mobilities of carbamic acid, carbamate, ammonium, bicarbonate, CO₂, and supporting salt cations and anions are all relevant to this process, yet have been little studied in amine-based electrolytes so far.

Given the relatively limited data, we highlight what is known about some of these species (Figure 7A). For CO₂, the diffusion coefficient in water at ambient pressure is $1.9 \times 10^{-5}$ cm²/s, whereas diffusion in an organic solvent is faster, for example, 6.9 (0.2 MPa) and 6.7 (0.5 MPa) $\times 10^{-5}$ cm²/s in acetonitrile and PC, respectively (Cussler, 1997; Azizi, 2019; Shaughnessy et al., 2020). To our knowledge, the diffusivity of carbamic acid/carbamate and ammonium cations has been less examined (Masiren et al., 2016; Snijder et al., 1993). Our measurements using diffusion ordered spectroscopy (DOSY) NMR under atmospheric pressure conditions indicated a self-diffusion coefficient of 0.1 M MEA in D₂O of 8.8 $\times 10^{-6}$ cm²/s before the introduction of CO₂, which is notably lower than the diffusivity of CO₂ owing to the larger molecule size. After CO₂ bubbling, MEA/MEA⁺ (indistinguishable in NMR) and MEACOO⁻ showed modestly lower self-diffusion coefficients of 8.4 and 6.8 $\times 10^{-6}$ cm²/s, respectively. With the addition of 0.3 M LiClO₄, the diffusion coefficients were largely unchanged.

In organic solvents, diffusivity is further hindered upon CO₂ uptake, for example, 6.7 $\times 10^{-6}$ cm²/s for 0.1 M EEA in DMSO-d₆ before CO₂ addition vs. 3.6 $\times 10^{-6}$ cm²/s for the carbamic acid. The diffusivities decreased notably with LiClO₄ salt addition (Figure 7A), indicating that supporting salt selection has significant implications not only for speciation but also for ion and reactant transport in the electrolyte. As expected, mutual interactions between carbamate, ammonium, and supporting salt cations and anions also
affect the ionic conductivity (Mutty, 2019). Future studies to quantify diffusivity and transference numbers of charged species in aqueous and nonaqueous media are needed.

Considerations for electron transfer: Surface adsorption and nitrogen-carbon bond strength

Given the multi-ionic nature of amine-based electrolytes, competition for adsorption occurs at a polarized electrode interface. Lee et al. have shown that in the absence of a supporting salt, ammonium cations adsorb at a negatively polarized electrode interface, blocking electron transfer to the carbamate and evolving only H2 (Figure 7B). Introduction of an alkali cation (e.g., K+ or Cs+) enabled preferential adsorption of these more compact ions, which helped to exclude blocking ammonium cations and facilitated electron transfer to the desired carbamate active species, yielding CO (Lee et al., 2021). The sterics and structure of the carbamate can be hypothesized to play an important role, as sterically hindered amines may prevent adequate surface interactions with the cathode, although detailed studies are needed. Meanwhile, structures that favor multiple amine-binding sites, such as diamines (Abdinejad et al., 2020), may help address orientational barriers of the carbamate when approaching the electrified interface. However, molecules with multiple amine sites need careful consideration because of their tendencies to undergo enhanced inter- and intramolecular hydrogen bonding (Shukla and Mikkloa, 2018), which can result in increased viscosity as well as hindered diffusivity.

Once carbamates are adsorbed at the electrified interface, the ability to facilitate N–C bond breakage will be governed by the amine structure (including pKa and sterics) as well as the degree of electronic hybridization with the electrode surface. In aqueous media, a multitude of electrocatalysts has been examined for amine-facilitated CO2 conversion (Chen et al., 2017; Pérez-Gallent et al., 2021; Lee et al., 2021), with design principles elucidated for tailoring interactions of key reduction intermediates to produce desired products (e.g., CO, ethylene) which high selectivity and partial current densities. However, the role of the electrocatalyst—and indeed whether it plays a conventionally electrocatalytic role when carbamate is the reactant—remains largely unexplored in integrated capture-conversion systems. Simplistically, the N–C bond should be sufficiently strong to capture CO2 and generate stable carbamate species, but weak enough to enable its cleavage under electron transfer at the cathode and/or upon activation by the electrocatalyst. Studies are, therefore, needed to obtain quantitative data about N–C bond strengths in relevant media as well as how electronic structure is modulated upon adsorption at a catalyst site. It is equally important to

Figure 7. Transport and electrode-electrolyte interface considerations

(A) Diffusion coefficients of CO2 (Cussler, 1997; Haas et al., 2021), ions (Joung and Cheatham, 2009; Semino et al., 2014), and amines in water (blue background) and DMSO (yellow background). The diffusion coefficients of amines with 0 and 0.3 M LiClO4 D2O or DMSO-d6 were measured using diffusion-ordered spectroscopy (DOSY) NMR. Note that MEA/MEAH+ signifies a mixture of lean amine and ammonium species.

(B) Electrical double layer of aqueous amine electrolyte without (top) and with (bottom) supporting salt cations. Blue shaded adsorbates (top) and pink spheres (bottom) at the electrode surface are ammonium species and alkali cations, respectively. (B) is adapted with permission from (Lee et al., 2021). Copyright (2021), Springer Nature.
understand how tailoring of N–C bond strength, which directly relates to the amine pKa, may influence proton transfer in aqueous media, which is necessary to form reduced products. Overall, quantification and parametrization of the amine-CO₂ electrochemical energetics must begin with better thermodynamic understanding, but will ultimately evolve to include unique kinetic and mass/ion transfer considerations. Relating these factors to product speciation represent one of the most open-ended and exciting aspects of the field.

OUTLOOK

CO₂-loaded amines can participate in electrochemical reduction reactions to generate gas, liquid, and solid-phase products derived from CO₂. Previous studies have mainly focused on product analysis and cell-level performance metrics. As discussed, such systems are highly complex, making it likely that early exemplar systems are far from optimized. Unlike with classical electrolyzers, the limiting factors and design tradeoffs of electrochemically reactive capture are still unclear, making it challenging to assess quantitative impacts.

At present, relatively more is understood about the post-capture, pre-electrochemistry speciation than any other aspect of the integrated process. There is a great opportunity to conduct basic physical chemistry research on the properties of sorbent-electrolytes to better understand all factors defining this reactant state. Speciation equilibration can occur over minutes to hours-long timescales in capture media depending on contacting method, solution volume, selected chemistries, and many other factors, which will impact the design of both absorber-reactors and their operation modes (i.e., continuous vs. batch). Accelerating the formation of carbamate, or learning how to run conversion predictably while under non-equilibrium conditions are interesting strategies to pursue if the slow sorption timescales prove cumbersome.

It is also noteworthy that amines for CO₂ capture, that is, those that are commercially available, were developed with certain functionality in mind, such as low energy requirements for thermal desorption and targeted capacity swings between CO₂-loaded and CO₂-lean states. Such considerations are not always directly relevant to electrochemical processes. Consequently, molecular design of amines or other next-generation sorbents that function optimally in an integrated capture-conversion context are of great interest. For example, amine-functionalized ionic liquids or deep-eutectic solvents are interesting potential candidates given their high degree of chemical and structural tunability (Ahmad et al., 2021; Shukla et al., 2019; Voskian et al., 2020).

Once the loaded capture solutions are perturbed from equilibrium by an electrochemical process, the picture becomes notably more complex. There are exciting opportunities to employ operando methodologies such as liquid NMR, surface-enhanced IR spectroscopy, online gas, and liquid chromatography, and others to confirm the complex speciations occurring under reaction conditions, which may occur both in the bulk liquid as well as at the electrode interface. Although prior studies found that the amine can be electrochemically regenerated to a degree to re-bind CO₂ (Khurram et al., 2018; Lee et al., 2021), the above-mentioned spectroscopy is also needed following longer-duration reactions to confirm the durability of the amines and identify any possible deactivation modes.

The field will continue to benefit greatly from the examination of model systems, which should proceed alongside more advanced engineering. Studies in nonaqueous media have played an important role in assessing the scientific feasibility of amine-facilitated conversion and may continue to provide fundamental insights into factors driving amine, solvent, and salt selection relevant to nonaqueous and aqueous systems alike. Ultimately, systems must move away from irreversible consumption of reactants, including scarce and costly metals such as Li. Cradle-to-grave processes that yield low-carbon sources of more earth-abundant alkalai/alkaline earth cations are needed before carbonate-producing systems can be deemed to have practical viability (Pfeiffer et al., 2022). Additionally, the rates of carbonate-forming reactions in nonaqueous media are much slower (<1 mA/cm²) to date than those systems producing gas or liquid products, which have benefitted so far by exploiting optimized electrolyzer designs in aqueous media and have much higher current densities (~100 mA/cm²). Given the significant need for basic science as well as the feasible demonstration of practical systems, we advocate for both approaches in the coming years. Recalling that CO₂ electrolysis, as with CO₂ capture, has benefitted from multi-decadal research to yield tremendous gains, electrochemically reactive capture appears poised to have an enriching road ahead if similar resources can be brought to bear on these much newer systems.
iScience Perspective

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AUTHOR CONTRIBUTIONS

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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