Perspective

Electrochemical reduction of CO$_2$ in the captured state using aqueous or nonaqueous amines

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SUMMARY

CO$_2$ 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$_2$ 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$_2$ 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$_2$ from flue gas (~12-14% CO$_2$ concentration) at ~40°C. Once the capture solution is saturated with CO$_2$, it is regenerated to produce a pure CO$_2$ stream along with lean amine for subsequent CO$_2$ uptake. Regeneration is typically achieved by a thermal-swing process at ~120°C in a desorber unit, with heating provided by steam redirected from the power plant turbines (Rochelle, 2009). At 2-4 GJ/ton CO$_2$—approximately 88-176 kJ/mol$_{CO_2}$—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 capitally intensive (Bui et al., 2018).

Separately, researchers have been investigating methodologies to electrocatalytically upgrade post-separation CO$_2$ 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$_2$ and H$_2$O using renewable electricity avoids these fossil emissions and may help incentivize broader adoption of carbon capture technologies (Jordaan and Wang, 2021). Electrochemical CO$_2$ conversion also has high energy requirements of ~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 (~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$_2$ management pipeline is, therefore, a priority.

In this context, recent years have seen growing interest in "reactive capture" concepts in which CO$_2$ absorption and chemical conversion, for example, CO$_2$ hydrogenation, are integrated (Bhattacharya et al.,

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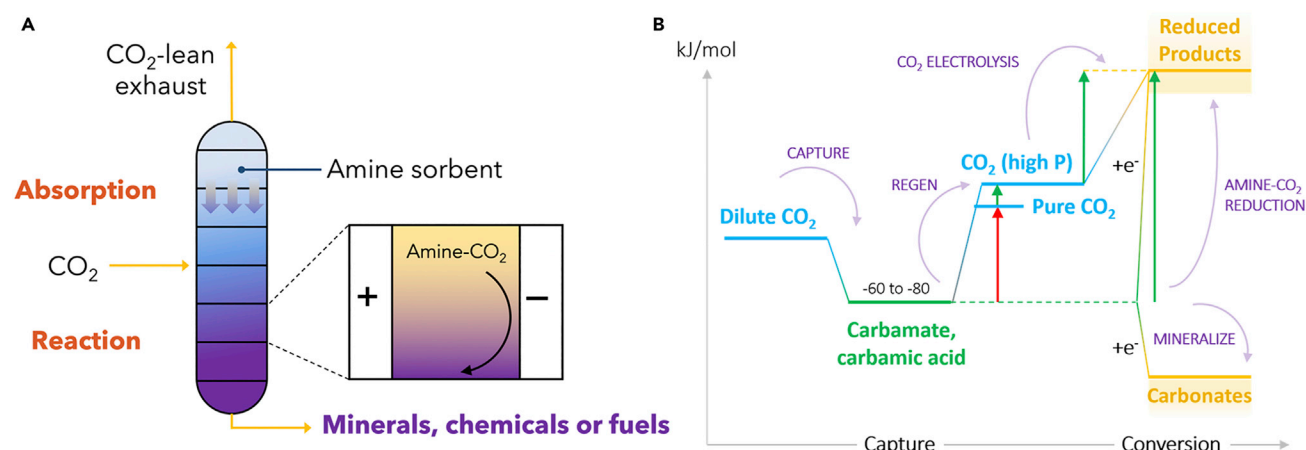
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Figure 1. Schematic and free energy landscape of integrated CO$_2$ capture and electrochemical conversion

(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$_{CO2}$). "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 "+e$^−$" 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).

2020a; Gutiérrez-Sánchez et al., 2022; Heldebrant et al., 2022; Kothandaraman et al., 2016, 2021; Liu et al., 2017; Mandal, 2020). 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
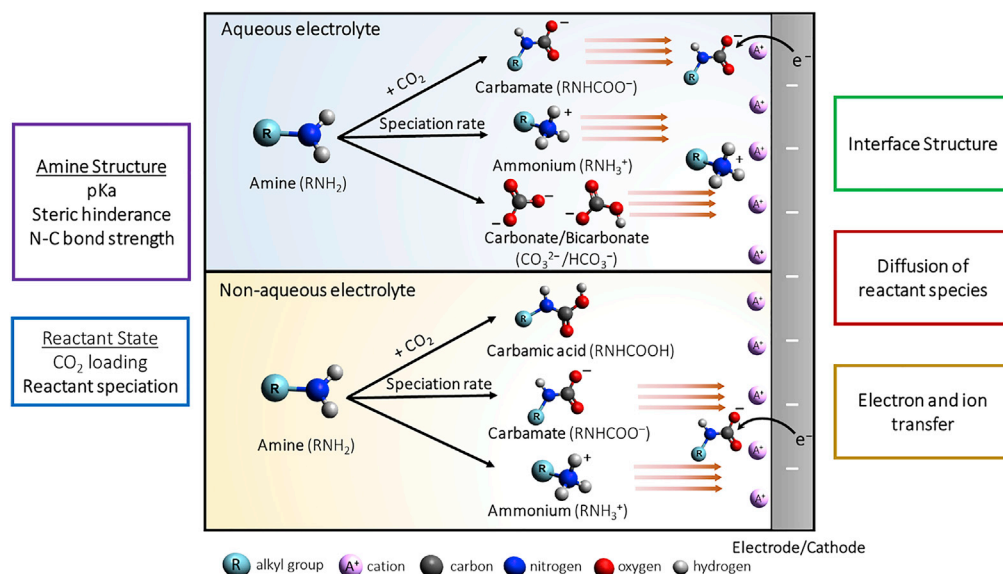
Figure 2. Parameters governing integrated CO_2 capture-electrochemical conversion
Multiple key factors are shown in call-out boxes, any of which can be rate-limiting, and have direct impacts on reactant-state and product formation. A^+ = monovalent alkali or organic cation; alkaline earth (A^{2+}) cations may also be utilized but are omitted for simplicity.

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.

EXEMPLAR 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_2O (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., $EEA-COO^-Li^+$). Given the availability of
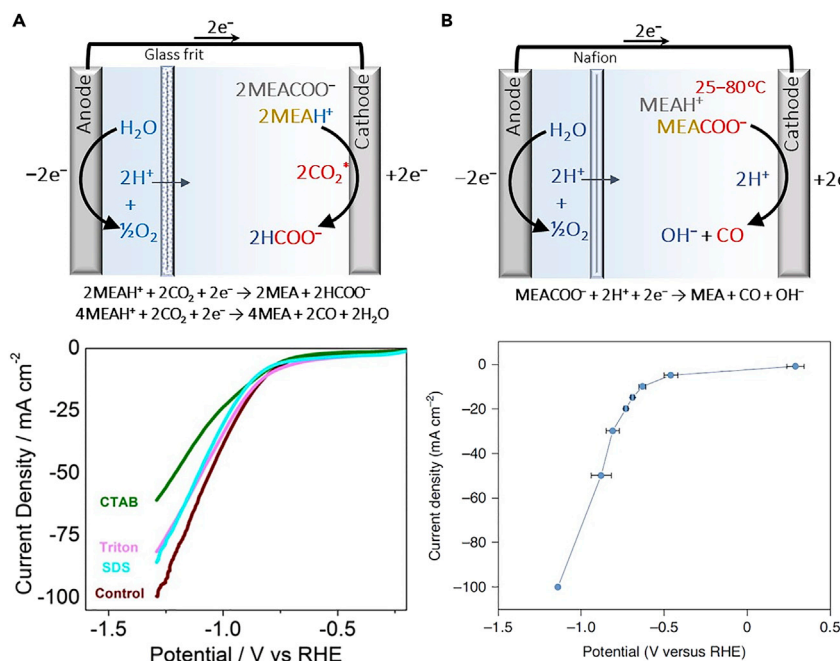
Figure 3. Electrochemical CO₂ reduction with amines in aqueous solution

(A) Schematic (top) and linear sweep voltammogram (bottom) of electrochemical CO_2 reduction in aqueous media with MEA (30%), using an In electrode with 0.1 wt% surfactant at 22°C (Chen et al., 2017). The asterisk denotes a surface-adsorbed state. Cetyltrimethylammonium bromide (CTAB), SDS and 4-octylphenol polyethoxylate (Triton X-100)) refer to surfactants. Reprinted with permission from Ref (Chen et al., 2017). Copyright (2017), John Wiley and Sons.

(B) Schematic (top) and averaged current density (bottom) resulting from potentiostatic polarizations in aqueous CO_2 capture solutions of 30 wt% MEA and 2 M KCl at an Ag electrode. Results were obtained at 60°C in a flow cell (Lee et al., 2021). Reprinted with permission from Ref (Lee et al., 2021). Copyright (2021), Springer Nature. Both schematics omit explicit labeling of product RNH_2, as indicated in the noted reactions, for clarity of viewing. Gray species are non-participating.

Li⁺, solid Li_2CO_3 was the main discharge product, along with co-produced carbon. Isotopic labeling confirmed that the produced solid carbonates originated selectively from CO_2.

Subsequent efforts further examined amine-CO_2 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 CO_2 in acetonitrile with TBAPF₆ salt, and found that reductive activity was observed only in the presence of CO_2 (Figure 4B) (Bhattacharya et al., 2020b). Under bulk electrolysis conditions, formate ($HCOO^-$) was the only product, with neither CO nor H_2 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 H_2O) 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 CO_2 reduction using CO_2 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 CO_2 and not amine-CO_2 directly.

In aqueous media, electrochemical cleavage of the amine-CO_2 bond has only recently been reported. Lee et al. observed only H_2 evolution occurring in MEA/water in the presence of CO_2. 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
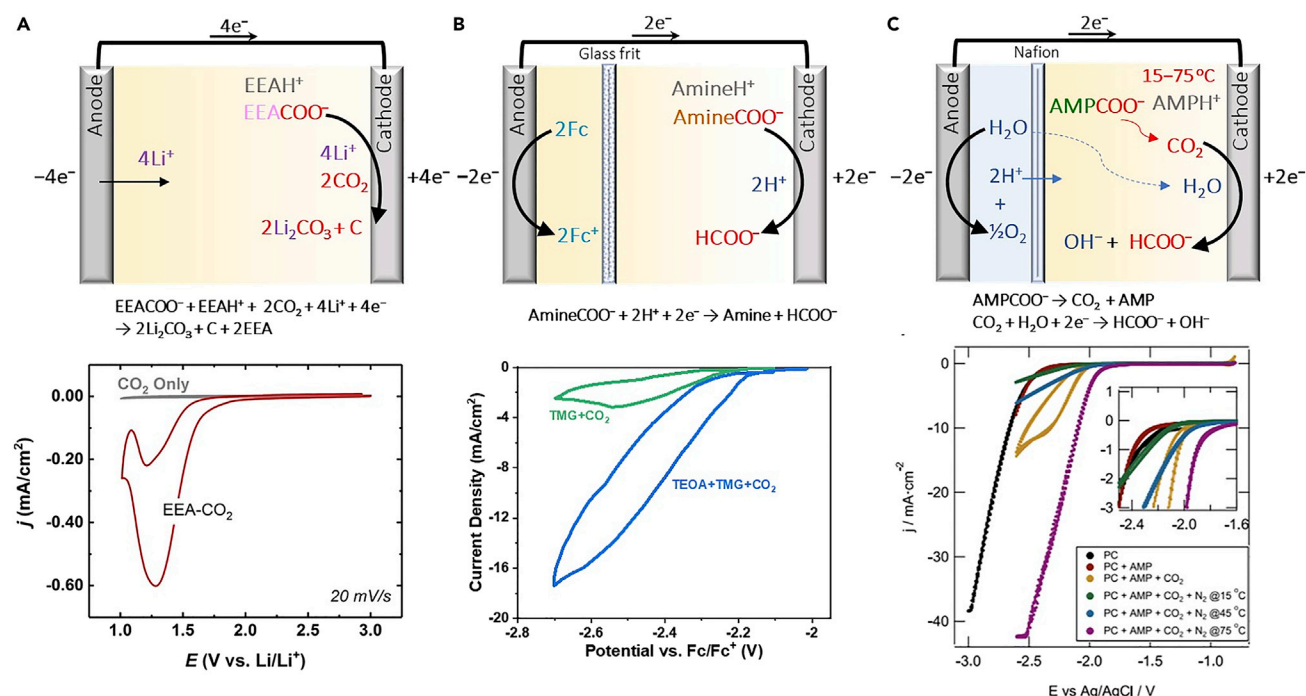
Figure 4. Electrochemical CO$_2$ reduction with amines in nonaqueous solution

(A) Schematic (top) and cyclic voltammograms (CV, bottom) on carbon with 0.1 M EEA-CO$_2$ and 0.3 M LiClO$_4$/DMSO (Khurram et al., 2018).

(B) Schematic (top) and CVs (bottom) using glassy carbon with 0.1 M amine-CO$_2$, 0.1 M 1,1,3,3-tetramethylgunaidine (TMG) in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) 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-CO$_2$ 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 RNH$_2$ for clarity. Gray species are non-participating.

included 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 CO$_2$ to the electrode. Additional studies have further examined amine-CO$_2$ reduction in aqueous electrolytes using Cu, Ag, and Au (Hossain et al., 2021), and reported up to 58% FE to CO at ~20 mA/cm^2 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-CO$_2$ 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 (CO$_2$ capture process) at present than about what occurs dynamically during electrochemical operation.

In the absence of sorbents, CO$_2$ 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
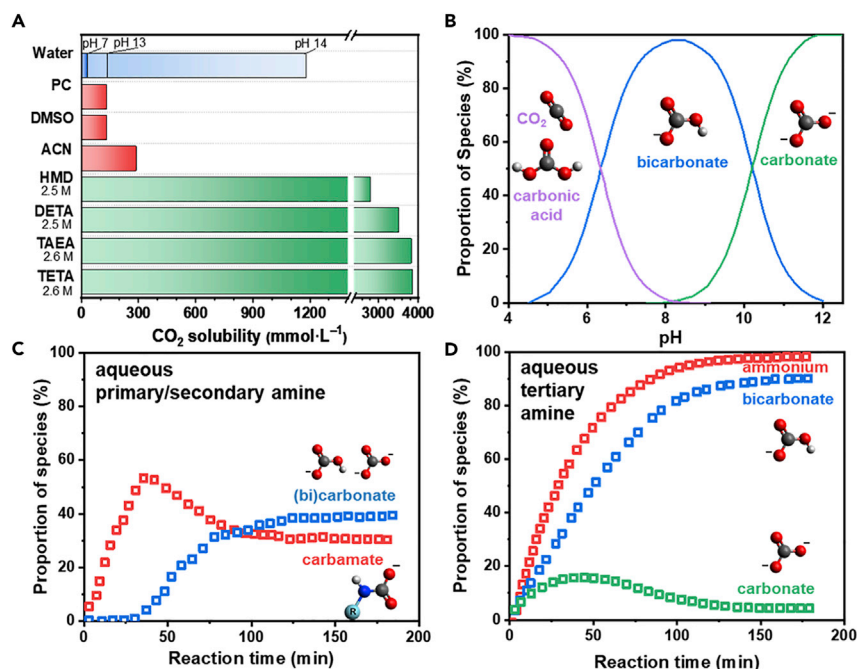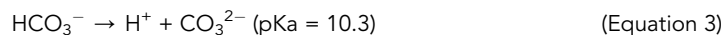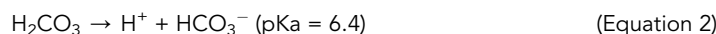
Figure 5. CO₂ absorption capacity and reactant speciation in aqueous electrolyte
(A) CO₂ absorption capacity in water (Hansen, 2007; Yoo et al., 2013), organic solvents (PC, DMSO, ACN (acetonitrile)) (Gennaro et al., 1990; Hansen, 2007), and aqueous amines (HMD (hexamethylenediamine), DETA (diethylenetriamine), TAEA (tris (2-aminoethyl) amine), TETA (triethylenetetramine)) (Singh et al., 2011).
(B) pH-dependent CO₂ equilibria in aqueous media. Reactant state speciation of (C) primary/secondary amines and (D) tertiary amines in aqueous media as a function of time, as determined from *operando* NMR measurements. Adapted with permission from (Kortunov et al., 2015a). Copyright (2015), American Chemical Society.

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:

$$H_2O + CO_2 \rightarrow H_2CO_3 \qquad \text{(Equation 1)}$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \ (pKa = 6.4) \qquad \text{(Equation 2)}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \ (pKa = 10.3) \qquad \text{(Equation 3)}$$

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
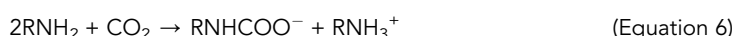
Amines are categorized as primary, secondary, or tertiary depending on the number of N−C bonds (1, 2, or 3, respectively) and, inversely, the number of N−H bonds (2, 1, or 0); cyclic amines are a sub-category and may be either secondary or tertiary. When a primary or secondary amine captures CO_2, the 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):

$$RNH_2 + CO_2 \leftrightarrow RNH_2^+COO^- \ \text{(primary amine)} \qquad \text{(Equation 4)}$$

$$RNH + CO_2 \leftrightarrow RNH^+COO^- \text{ (secondary amine)} \qquad \text{(Equation 5)}$$

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 (RNH_3^+), and corresponding to a maximum loading of 0.5 CO_2/amine. Depending on amine pKa, RNH_3^+ can also be formed by direct reaction with protons from carbonic acid, bicarbonate, or water. This pathway for RNH_3^+ formation lowers the attainable CO_2 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:

$$2RNH_2 + CO_2 \rightarrow RNHCOO^- + RNH_3^+ \qquad \text{(Equation 6)}$$

Carbamate hydrolysis:

$$RNHCOO^- + H_2O \rightarrow HCO_3^- + RNH_2 \qquad \text{(Equation 7)}$$

Hydrolysis more readily proceeds with low-pKa amines given their poor tendency to stably bind CO_2. Additionally, base-catalyzed amine regeneration from RNH_3^+ can occur if strong Bronsted bases such as KOH are used. These reactions can result in CO_2 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 CO_2 hydration reaction (Figure 5D):

$$CO_2 + R_1R_2R_3N + H_2O \rightarrow R_1R_2R_3NH^+ + HCO_3^- \qquad \text{(Equation 8)}$$
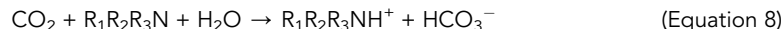
This pathway allows for higher CO_2 loadings to be achieved than with primary or secondary amines, that is, one CO_2/amine instead of 0.5. A similar outcome occurs with sterically hindered amines in which N–C bonds are destabilized, resulting in CO_2 loadings in excess of 0.5, for example, 0.5-0.8 (Bernhardsen and Knuutila, 2017).

The rate at which a capture solution achieves equilibrium upon CO_2 introduction, as well as the equilibrium speciation, is sensitive to a number of factors including amine structure, pKa, temperature and pressure, and CO_2 flow rates (Kortunov et al., 2015a; 2015c; 2015b). Primary and secondary amines with sufficiently high pKa ($\sim$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 CO_2 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 CO_2 reduction reactions (Chen et al., 2012) and has also been suggested to serve as the electroactive source of CO_2 upon reduction compared to physically dissolved CO_2 (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 CO_2 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 CO_2 absorption enthalpies for commercial amines range between -60 and -80 kJ/mol$_{CO_2}$ to balance demands for sufficient CO_2 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-CO_2 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 CO_2(g) and regeneration of the lean amine. Temperature also affects the solubility of CO_2, and thus the pH of the capture solution and the proportion of ionic species (Hamborg 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 CO_2 solubility, for example, $\sim$130 mM in DMSO and $\sim$300 mM in acetonitrile and tetrahydrofuran (Figure 5A), compared to water at near-neutral pH. These higher solubilities may benefit CO_2 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 CO_2. However, unlike in aqueous media, some nonaqueous solvents can stabilize the uncharged carbamic acid upon CO_2 uptake (Kortunov et al., 2015a). The competitive speciation reactions (written for primary amines) are:

$$2RNH_2 + CO_2 \rightarrow RNHCOO^- + RNH_3^+ \tag{Equation 9}$$

$$2RNH_2 + 2CO_2 \rightarrow 2RNHCOOH \tag{Equation 10}$$
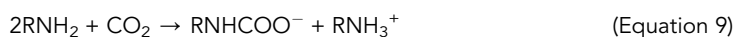
Carbamic acid corresponds to one amine/CO_2 versus 0.5 amine/CO_2 and is favored by solvents capable of strong hydrogen bonding. Examples include S=O and C=O functional groups in DMSO or 1-methyl-2-pyrrolidinone, respectively, which donate to the carboxylic acid proton (Kortunov et al., 2015c). In nonaqueous 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 CO_2 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 pyrrolidone (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 progress, 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 CO_2 uptake (Cantu et al., 2017; Heldebrant et al., 2017; Malhotra et al., 2019). Such advanced sorbent design strategies, translated from the CO_2 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 CO_2 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 CO_2-derived product oxidation. Depending on pKa, amine protons can be reduced directly to evolve H_2. 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 CO_2 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 $LiClO_4$ 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-CO_2 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 CO_2 introduction in nonaqueous solvents prohibit the use of amines at concentrations commensurate with aqueous media.

In aqueous media, CO_2 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 CO_2 capture, forced convection assists uptake of CO_2 and amine regeneration. Although forced convection is relevant in electrochemical systems for
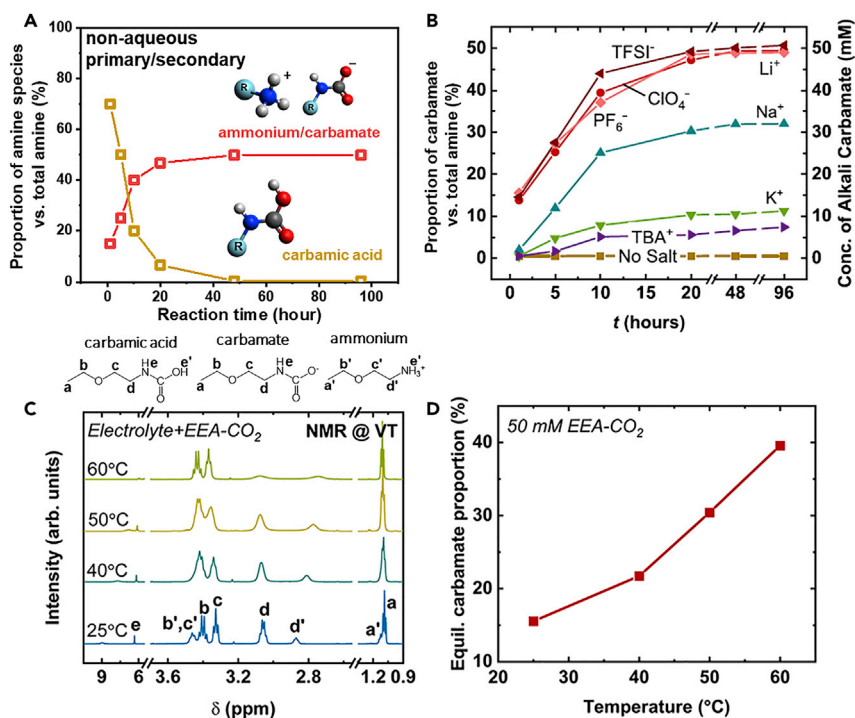
Figure 6. Reactant speciation in nonaqueous electrolytes

(A) Dynamic speciation of primary/secondary amines in nonaqueous media, as determined from ^{1}H NMR after introducing alkali salt to a solution of carbamic acid.

(B) Proportion of carbamate in the presence of alkali or tetrabutyl ammonium (TBA$^+$) cations under the same experimental conditions. The anion of Na$^+$, K$^+$, and TBA$^+$ is ClO$_4^-$.

(C) Variable temperature (VT) ^{1}H NMR spectra of 0.05 M EEA-CO$_2$ in DMSO-d_6, 24 h after 0.3 M LiClO$_4$ was introduced to the solution.

(D) Equilibrium proportion of carbamates from (C). A is adapted and B, C, and D are reproduced with permission from Ref (Khurram et al., 2019, 2020). Copyright (2019, 2020), American Chemical Society.

CO$_2$ 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, CO$_2$, 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 CO$_2$, the diffusion coefficient in water at ambient pressure is 1.9×10^{-5} cm^2/s, whereas diffusion in an organic solvent is faster, for example, 6.9 (0.2 MPa) and 6.7 (0.5 MPa) $\times 10^{-5}$ cm^2/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 D$_2$O of 8.8×10^{-6} cm^2/s before the introduction of CO$_2$, which is notably lower than the diffusivity of CO$_2$ owing to the larger molecule size. After CO$_2$ bubbling, MEA/MEAH$^+$ (indistinguishable in NMR) and MEACOO$^-$ showed modestly lower self-diffusion coefficients of 8.4 and 6.8×10^{-6} cm^2/s, respectively. With the addition of 0.3 M LiClO$_4$, the diffusion coefficients were largely unchanged.

In organic solvents, diffusivity is further hindered upon CO$_2$ uptake, for example, 6.7×10^{-6} cm^2/s for 0.1 M EEA in DMSO-d_6 before CO$_2$ addition vs. 3.6×10^{-6} cm^2/s for the carbamic acid. The diffusivities decreased notably with LiClO$_4$ 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
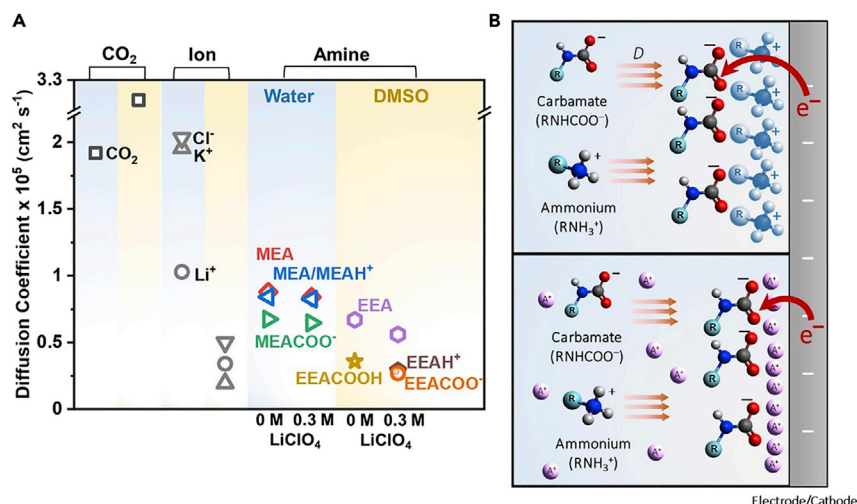
Figure 7. Transport and electrode-electrolyte interface considerations

(A) Diffusion coefficients of CO_2 (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 $LiClO_4$ D_2O or DMSO-d_6 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.

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 H_2 (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 CO_2 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 CO_2 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

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-CO_2 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

CO_2-loaded amines can participate in electrochemical reduction reactions to generate gas, liquid, and solid-phase products derived from CO_2. 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 CO_2 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 CO_2-loaded and CO_2-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 CO_2 (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 alkali/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/cm^2) 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 ($\sim$100 mA/cm^2). 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 CO_2 electrolysis, as with CO_2 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.

REFERENCES

Abdinejad, M., Mirza, Z., Zhang, X.a., and Kraatz, H.B. (2020). Enhanced electrocatalytic activity of primary amines for CO_2 reduction using copper electrodes in aqueous solution. ACS Sustain. Chem. Eng. 8, 1715–1720. https://doi.org/10.1021/acssuschemeng.9b06837.

Ahmad, N., Wang, X., Sun, P., Chen, Y., Rehman, F., Xu, J., and Xu, X. (2021). Electrochemical CO_2 reduction to CO facilitated by MDEA-based deep eutectic solvent in aqueous solution. Renew. Energy 177, 23–33. https://doi.org/10.1016/j.renene.2021.05.106.

Azizi, S. (2019). Evaluation of mass transfer resistance across the interface for CO_2–propylene carbonate system: experimental and mathematical modeling. Chem. Eng. Res. Des. 149, 34–44. https://doi.org/10.1016/j.cherd.2019.07.005.

Bernhardsen, I.M., and Knuutila, H.K. (2017). A review of potential amine solvents for CO_2 absorption process: absorption capacity, cyclic capacity and pKa. Int. J. Greenh. Gas Control 61, 27–48. https://doi.org/10.1016/j.ijggc.2017.03.021.

Bhattacharya, M., Sebghati, S., Vanderlinden, R.T., and Saouma, C.T. (2020a). Toward combined carbon capture and recycling: addition of an amine alters product selectivity from CO to formic acid in manganese catalyzed reduction of CO_2. J. Am. Chem. Soc. 142, 17589–17597. https://doi.org/10.1021/jacs.0c07763.

Bhattacharya, M., Sebghati, S., Vercella, Y.M., and Saouma, C.T. (2020b). Electrochemical reduction of carbamates and carbamic acids: implications for combined carbon capture and electrochemical CO_2 recycling. J. Electrochem. Soc. 167, 086507. https://doi.org/10.1149/1945-7111/ab8ed0.

Birdja, Y.Y., Pérez-Gallent, E., Figueiredo, M.C., Göttle, A.J., Calle-Vallejo, F., and Koper, M.T.M. (2019). Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels. Nat. Energy 4, 732–745. https://doi.org/10.1038/s41560-019-0450-y.

Boot-Handford, M.E., Abanades, J.C., Anthony, E.J., Blunt, M.J., Brandani, S., Mac Dowell, N., Fernández, J.R., Ferrari, M.C., Gross, R., Hallett, J.P., et al. (2014). Carbon capture and storage update. Energy Environ. Sci. 7, 130–189. https://doi.org/10.1039/c3ee42350f.

Böttinger, W., Maiwald, M., and Hasse, H. (2008). Online NMR spectroscopic study of species distribution in MEA–H_2O–CO_2 and DEA–H_2O–CO_2. Fluid Phase Equilib. 263, 131–143. https://doi.org/10.1016/j.fluid.2007.09.017.

Bui, M., Adjiman, C.S., Bardow, A., Anthony, E.J., Boston, A., Brown, S., Fennell, P.S., Fuss, S., Galindo, A., Hackett, L.A., et al. (2018). Carbon capture and storage (CCS): the way forward. Energy Environ. Sci. 11, 1062–1176. https://doi.org/10.1039/c7ee02342a.

Cantu, D.C., Malhotra, D., Koech, P.K., Heldebrant, D.J., Zheng, R., Freeman, C.J., Rousseau, R., and Glezakou, V.A. (2017). Integrated solvent design for CO_2 capture and viscosity tuning. Energy Proc. 114, 726–734. https://doi.org/10.1016/j.egypro.2017.03.1215.

Chakraborty, A.K., Bischoff, K.B., Astarita, G., and Damewood, J.R. (1988). Molecular orbital approach to substituent effects in amine-CO_2 interactions. J. Am. Chem. Soc. 110, 6947–6954. https://doi.org/10.1021/ja00229a003.

Chen, Y., Li, C.W., and Kanan, M.W. (2012). Aqueous CO_2 reduction at very low overpotential on oxide-derived au nanoparticles. J. Am. Chem. Soc. 134, 19969–19972. https://doi.org/10.1021/ja309317u.

Chen, L., Li, F., Zhang, Y., Bentley, C.L., Horne, M., Bond, A.M., and Zhang, J. (2017). Electrochemical reduction of carbon dioxide in a monoethanolamine capture medium. ChemSusChem 10, 4109–4118. https://doi.org/10.1002/cssc.201701075.

Chen, J., Zheng, Y., Melli, A., Spada, L., Lu, T., Feng, G., Gou, Q., Barone, V., and Puzzarini, C. (2020). Theory meets experiment for elucidating the structure and stability of non-covalent complexes: water-amine interaction as a proof of concept. Phys. Chem. Chem. Phys. 22, 5024–5032. https://doi.org/10.1039/c9cp06768j.

Choi, B.K., Kim, S.M., Lee, J.S., Park, Y.C., Chun, D.H., Shin, H.Y., Sung, H.J., Min, B.M., and Moon, J.H. (2020). Effect of blending ratio and temperature on CO_2 solubility in blended aqueous solution of monoethanolamine and 2-amino-2-methyl-propanol: experimental and modeling study using the electrolyte nonrandom two-liquid model. ACS Omega 5, 28738–28748. https://doi.org/10.1021/acsomega.0c04046.

Cussler, E.L. (1997). Diffusion: Mass Transfer in Fluid Systems, 2nd ed. (Cambridge University Press).

Dunwell, M., Lu, Q., Heyes, J.M., Rosen, J., Chen, J.G., Yan, Y., Jiao, F., and Xu, B. (2017). The central role of bicarbonate in the electrochemical reduction of carbon dioxide on gold. J. Am. Chem. Soc. 139, 3774–3783. https://doi.org/10.1021/jacs.6b13287.

Ebrahiminejadhasanabadi, M., Nelson, W.M., Naidoo, P., Mohammadi, A.H., and Ramjugernath, D. (2021). Investigation of mixed MEA-based solvents featuring ionic liquids and NMP for CO_2 capture: experimental measurement of CO_2 solubility and thermophysical properties. J. Chem. Eng. Data 66, 899–914. https://doi.org/10.1021/acs.jced.0c00618.

Gadikota, G. (2020). Multiphase carbon mineralization for the reactive separation of CO_2 and directed synthesis of H_2. Nat. Rev. Chem 4, 78–89. https://doi.org/10.1038/s41570-019-0158-3.

GCCSI (2020). Global Status of CCS 2020 (Glob. CCS Inst.).

Gennaro, A., Isse, A.A., and Vianello, E. (1990). Solubility and electrochemical determination of CO_2 in some dipolar aprotic solvents. J. Electroanal. Chem. 289, 203–215. https://doi.org/10.1016/0022-0728(90)87217-8.

Gurkan, B., Su, X., Klemm, A., Kim, Y., Mallikarjun Sharada, S., Rodriguez-Katakura, A., and Kron, K.J. (2021). Perspective and challenges in electrochemical approaches for reactive CO_2 separations. iScience 24, 103422. https://doi.org/10.1016/j.isci.2021.103422.

Gutiérrez-Sánchez, O., Bohlen, B., Daems, N., Bulut, M., Pant, D., and Breugelmans, T. (2022). A state-of-the-art update on integrated CO_2 capture and electrochemical conversion systems. ChemElectroChem 9, e202101540. https://doi.org/10.1002/celc.202101540.

Haas, R., Murat, M., Weiss, M., Janek, J., Natan, A., and Schröder, D. (2021). Understanding the transport of atmospheric gases in liquid electrolytes for lithium–air batteries. J. Electrochem. Soc. 168, 070504. https://doi.org/10.1149/1945-7111/ac0d66.

Hamborg, E.S., and Versteeg, G.F. (2009). Dissociation constants and thermodynamic properties of amines and alkanolamines from (293 to 353) K. J. Chem. Eng. Data 54, 1318–1328. https://doi.org/10.1021/je800897v.

Hansen, C.M. (2007). Hansen Solubility Parameters - a Users Handbook, 2nd edition (CRC Press).

Heldebrant, D.J., Koech, P.K., Glezakou, V.A., Rousseau, R., Malhotra, D., and Cantu, D.C.

(2017). Water-lean solvents for post-combustion CO_2 capture: fundamentals, uncertainties, opportunities, and outlook. Chem. Rev. *117*, 9594–9624. https://doi.org/10.1021/acs.chemrev.6b00768.

Heldebrant, D.J., Kothandaraman, J., Dowell, N.M., and Brickett, L. (2022). Next steps for solvent-based CO_2 capture; integration of capture, conversion, and mineralisation. Chem. Sci. *13*, 6445–6456. https://doi.org/10.1039/d2sc00220e.

Hossain, M.N., Ahmad, S., da Silva, I.S., and Kraatz, H.-B. (2021). Electrochemical reduction of CO_2 at coinage metal nanodendrites in aqueous ethanolamine. Chem. Eur. J. *27*, 1346–1355. https://doi.org/10.1002/chem.202003039.

Hwang, G.S., Stowe, H.M., Paek, E., and Manogaran, D. (2015). Reaction mechanisms of aqueous monoethanolamine with carbon dioxide: a combined quantum chemical and molecular dynamics study. Phys. Chem. Chem. Phys. *17*, 831–839. https://doi.org/10.1039/c4cp04518a.

IEA (2020). Energy Technology Perspectives 2020 (IEA).

Jordaan, S.M., and Wang, C. (2021). Electrocatalytic conversion of carbon dioxide for the Paris goals. Nat. Catal. *4*, 915–920. https://doi.org/10.1038/s41929-021-00704-z.

Joung, I.S., and Cheatham, T.E., 3rd (2009). Molecular dynamics simulations of the dynamic and energetic properties of alkali and halide ions using water-model-specific ion parameters. J. Phys. Chem. B *113*, 13279–13290. https://doi.org/10.1021/jp902584c.

Karlsson, H.K., Drabo, P., and Svensson, H. (2019). Precipitating non-aqueous amine systems for absorption of carbon dioxide using 2-amino-2-methyl-1-propanol. Int. J. Greenh. Gas Control *88*, 460–468. https://doi.org/10.1016/j.ijggc.2019.07.001.

Khurram, A., Yan, L., Yin, Y., Zhao, L., and Gallant, B.M. (2019). Promoting amine-activated electrochemical CO_2 conversion with alkali Salts. J. Phys. Chem. C *123*, 18222–18231. https://doi.org/10.1021/acs.jpcc.9b04258.

Khurram, A., He, M., and Gallant, B.M. (2018). Tailoring the discharge reaction in Li–CO_2 batteries through incorporation of CO_2 capture chemistry. Joule *2*, 2649–2666. https://doi.org/10.1016/j.joule.2018.09.002.

Khurram, A., Gao, H., and Gallant, B.M. (2020). Effects of temperature on amine-mediated CO_2 capture and conversion in Li cells. J. Phys. Chem. C *124*, 18877–18885. https://doi.org/10.1021/acs.jpcc.0c04803.

Kim, I., and Svendsen, H.F. (2007). Heat of absorption of carbon dioxide (CO_2) in monoethanolamine (MEA) and 2-(aminoethyl) ethanolamine (AEEA) solutions. Ind. Eng. Chem. Res. *46*, 5803–5809. https://doi.org/10.1021/ie0616489.

Kortunov, P.V., Siskin, M., Baugh, L.S., and Calabro, D.C. (2015a). *In situ* nuclear magnetic resonance mechanistic studies of carbon dioxide reactions with liquid amines in aqueous systems: new insights on carbon capture reaction

pathways. Energy Fuel. *29*, 5919–5939. https://doi.org/10.1021/acs.energyfuels.5b00850.

Kortunov, P.V., Siskin, M., Baugh, L.S., and Calabro, D.C. (2015b). *In situ* nuclear magnetic resonance mechanistic studies of carbon dioxide reactions with liquid amines in non-aqueous systems: evidence for the formation of carbamic acids and zwitterionic species. Energy Fuel. *29*, 5940–5966. https://doi.org/10.1021/acs.energyfuels.5b00985.

Kortunov, P.V., Baugh, L.S., Siskin, M., and Calabro, D.C. (2015c). *In situ* nuclear magnetic resonance mechanistic studies of carbon dioxide reactions with liquid amines in mixed base systems: the interplay of Lewis and Brønsted basicities. Energy Fuel. *29*, 5967–5989. https://doi.org/10.1021/acs.energyfuels.5b00988.

Kothandaraman, J., Goeppert, A., Czaun, M., Olah, G.A., and Surya Prakash, G.K. (2016). CO_2 capture by amines in aqueous media and its subsequent conversion to formate with reusable ruthenium and iron catalysts. Green Chem. *18*, 5831–5838. https://doi.org/10.1039/c6gc01165a.

Kothandaraman, J., Saavedra Lopez, J., Jiang, Y., Walter, E.D., Burton, S.D., Dagle, R.A., and Heldebrant, D.J. (2021). Integrated capture and conversion of CO_2 to methane using a water-lean , post-combustion CO_2 capture solvent. ChemSusChem *14*, 4812–4819. https://doi.org/10.1002/cssc.202101590.

Lee, G., Li, Y.C., Kim, J.Y., Peng, T., Nam, D.H., Sedighian Rasouli, A., Li, F., Luo, M., Ip, A.H., Joo, Y.C., and Sargent, E.H. (2021). Electrochemical upgrade of CO_2 from amine capture solution. Nat. Energy *6*, 46–53. https://doi.org/10.1038/s41560-020-00735-z.

Li, Y.C., Lee, G., Yuan, T., Wang, Y., Nam, D.H., Wang, Z., García de Arquer, F.P., Lum, Y., Dinh, C.T., Voznyy, O., and Sargent, E.H. (2019). CO_2 electroreduction from carbonate electrolyte. ACS Energy Lett. *4*, 1427–1431. https://doi.org/10.1021/acsenergylett.9b00975.

Liang, S., Altaf, N., Huang, L., Gao, Y., and Wang, Q. (2020). Electrolytic cell design for electrochemical CO_2 reduction. J. CO_2 Util. *35*, 90–105. https://doi.org/10.1016/j.jcou.2019.09.007.

Lin, Y.J., and Rochelle, G.T. (2016). Approaching a reversible stripping process for CO_2 capture. Chem. Eng. J. *283*, 1033–1043. https://doi.org/10.1016/j.cej.2015.08.086.

Liu, Q., Yang, X., Li, L., Miao, S., Li, Y., Li, Y., Wang, X., Huang, Y., and Zhang, T. (2017). Direct catalytic hydrogenation of CO_2 to formate over a Schiff-base-mediated gold nanocatalyst. Nat. Commun. *8*, 1407. https://doi.org/10.1038/s41467-017-01673-3.

Lobaccaro, P., Singh, M.R., Clark, E.L., Kwon, Y., Bell, A.T., and Ager, J.W. (2016). Effects of temperature and gas-liquid mass transfer on the operation of small electrochemical cells for the quantitative evaluation of CO_2 reduction electrocatalysts. Phys. Chem. Chem. Phys. *18*, 26777–26785. https://doi.org/10.1039/c6cp05287h.

De Luna, P., Hahn, C., Higgins, D., Jaffer, S.A., Jaramillo, T.F., and Sargent, E.H. (2019). What would it take for renewably powered electrosynthesis to displace petrochemical

processes? Science *364*, eaav3506. https://doi.org/10.1126/science.aav3506.

Malhotra, D., Cantu, D.C., Koech, P.K., Heldebrant, D.J., Karkamkar, A., Zheng, F., Bearden, M.D., Rousseau, R., and Glezakou, V.A. (2019). Directed hydrogen bond placement: low viscosity amine solvents for CO_2 capture. ACS Sustain. Chem. Eng. *7*, 7535–7542. https://doi.org/10.1021/acssuschemeng.8b05481.

Mandal, M. (2020). Integrated CO_2 capture and one-pot production of methanol. Dalt. Trans. *49*, 17140–17142. https://doi.org/10.1039/d0dt03667f.

Masiren, E.E., Harun, N., Ibrahim, W.H.W., and Adam, F. (2016). Effect of temperature on diffusivity of monoethanolamine (MEA) on absorption process for CO_2 capture. Int. J. Eng. Technol. Sci. *3*, 43–51. https://doi.org/10.15282/ijets.5.2016.1.6.1045.

McCann, N., Maeder, M., and Attalla, M. (2008). Simulation of enthalpy and capacity of CO_2 absorption by aqueous amine systems. Ind. Eng. Chem. Res. *47*, 2002–2009. https://doi.org/10.1021/ie070619a.

Mutty, C. (2019). Physiochemical Properties of Nonaqueous Amine-Containing Electrolytes (Massachusetts Institute of Technology).

Pérez-Gallent, E., Vankani, C., Sánchez-Martínez, C., Anastasopol, A., and Goetheer, E. (2021). Integrating CO_2 capture with electrochemical conversion using amine-based capture solvents as electrolytes. Ind. Eng. Chem. Res. *60*, 4269–4278. https://doi.org/10.1021/acs.iecr.0c05848.

Pfeiffer, O., Khurram, A., Olivetti, E.A., and Gallant, B.M. (2022). Life cycle assessment of CO_2 conversion and storage in metal–CO_2 electrochemical cells. J. Ind. Ecol. 1–22. https://doi.org/10.1111/jiec.13266.

Rabinowitz, J.A., and Kanan, M.W. (2020). The future of low-temperature carbon dioxide electrolysis depends on solving one basic problem. Nat. Commun. *11*, 5231. https://doi.org/10.1038/s41467-020-19135-8.

Rajan, V.K., and Muraleedharan, K. (2017). The pKa values of amine based solvents for CO_2 capture and its temperature dependence-An analysis by density functional theory. Int. J. Greenh. Gas Control *58*, 62–70. https://doi.org/10.1016/j.ijggc.2017.01.009.

Renfrew, S.E., Starr, D.E., and Strasser, P. (2020). Electrochemical approaches toward CO_2 capture and concentration. ACS Catal. *10*, 13058–13074. https://doi.org/10.1021/acscatal.0c03639.

Rheinhardt, J.H., Singh, P., Tarakeshwar, P., and Buttry, D.A. (2017). Electrochemical capture and release of carbon dioxide. ACS Energy Lett. *2*, 454–461. https://doi.org/10.1021/acsenergylett.6b00608.

Rochelle, G.T. (2009). Amine scrubbing for CO_2 capture. Science *325*, 1652–1654. https://doi.org/10.1126/science.1176731.

Ross, M.B., De Luna, P., Li, Y., Dinh, C.T., Kim, D., Yang, P., and Sargent, E.H. (2019). Designing materials for electrochemical carbon dioxide recycling. Nat. Catal. *2*, 648–658. https://doi.org/10.1038/s41929-019-0306-7.

Said, R.B., Kolle, J.M., Essalah, K., Tangour, B., and Sayari, A. (2020). A unified approach to CO_2-amine reaction mechanisms. ACS Omega 5, 26125–26133. https://doi.org/10.1021/acsomega.0c03727.

Semino, R., Zaldívar, G., Calvo, E.J., and Laria, D. (2014). Lithium solvation in dimethyl sulfoxide-acetonitrile mixtures. J. Chem. Phys. 141, 214509. https://doi.org/10.1063/1.4902837.

Shaughnessy, C.I., Sconyers, D.J., Lee, H.J., Subramaniam, B., Blakemore, J.D., and Leonard, K.C. (2020). Insights into pressure tunable reaction rates for electrochemical reduction of CO_2 in organic electrolytes. Green Chem. 22, 2434–2442. https://doi.org/10.1039/d0gc00013b.

Sheehan, S.W. (2021). Electrochemical methane production from CO_2 for orbital and interplanetary refueling. iScience 24, 102230. https://doi.org/10.1016/j.isci.2021.102230.

Shukla, S.K., and Mikkola, J.P. (2018). Intermolecular interactions upon carbon dioxide capture in deep-eutectic solvents. Phys. Chem. Chem. Phys. 20, 24591–24601. https://doi.org/10.1039/c8cp03724h.

Shukla, S.K., Khokarale, S.G., Bui, T.Q., and Mikkola, J.-P.T. (2019). Ionic liquids: potential materials for carbon dioxide capture and utilization. Front. Mater. 6, 42. https://doi.org/10.3389/fmats.2019.00042.

Singh, P., Brilman, D.W.F., and Groeneveld, M.J. (2011). Evaluation of CO_2 solubility in potential aqueous amine-based solvents at low CO_2 partial pressure. Int. J. Greenh. Gas Control 5, 61–68. https://doi.org/10.1016/j.ijggc.2010.06.009.

Smith, W.A., Burdyny, T., Vermaas, D.A., and Geerlings, H. (2019). Pathways to industrial-scale fuel out of thin air from CO_2 electrolysis. Joule 3, 1822–1834. https://doi.org/10.1016/j.joule.2019.07.009.

Snijder, E.D., te Riele, M.J.M., Versteeg, G.F., and van Swaaij, W.P.M. (1993). Diffusion coefficients of several aqueous alkanolamine solutions. J. Chem. Eng. Data 38, 475–480. https://doi.org/10.1021/je00011a037.

Sullivan, I., Goryachev, A., Digdaya, I.A., Li, X., Atwater, H.A., Vermaas, D.A., and Xiang, C. (2021). Coupling electrochemical CO_2 conversion with CO_2 capture. Nat. Catal. 4, 952–958. https://doi.org/10.1038/s41929-021-00699-7.

Tao, M., Gao, J., Zhang, P., Zhang, W., Liu, Q., He, Y., and Shi, Y. (2017). Biogas upgrading by capturing CO_2 in non-aqueous phase-changing diamine solutions. Energy Fuel. 31, 6298–6304. https://doi.org/10.1021/acs.energyfuels.7b00456.

Versteeg, G.F., and van Swaaij, W.P.M. (1988). On the kinetics between CO_2 and alkanolamines both in aqueous and non-aqueous solutions-I. Primary and secondary amines. Chem. Eng. Sci. 43, 573–585. https://doi.org/10.1016/0009-2509(88)87017-9.

Voskian, S., Brown, P., Halliday, C., Rajczykowski, K., and Hatton, T.A. (2020). Amine-based ionic liquid for CO_2 capture and electrochemical or thermal regeneration. ACS Sustain. Chem. Eng. 8, 8356–8361. https://doi.org/10.1021/acssuschemeng.0c02172.

Wang, Y., Song, L., Ma, K., Liu, C., Tang, S., Yan, Z., Yue, H., and Liang, B. (2021). An integrated Absorption−Mineralization process for CO_2 capture and sequestration: reaction mechanism, recycling stability, and energy evaluation. ACS Sustain. Chem. Eng. 9, 16577–16587. https://doi.org/10.1021/acssuschemeng.1c04731.

Wilcox, J. (2012). Carbon Capture (Springer).

Yamada, H. (2021). Amine-based capture of CO_2 for utilization and storage. Polym. J. 53, 93–102. https://doi.org/10.1038/s41428-020-00400-y.

Yoo, M., Han, S.J., and Wee, J.H. (2013). Carbon dioxide capture capacity of sodium hydroxide aqueous solution. J. Environ. Manage. 114, 512–519. https://doi.org/10.1016/j.jenvman.2012.10.061.

Yoon, B., and Hwang, G.S. (2020). Anomalous facile carbamate formation at high stripping temperatures from carbon dioxide reaction with 2-Amino-2-methyl-1-propanol in aqueous solution. ACS Sustain. Chem. Eng. 8, 18671–18677. https://doi.org/10.1021/acssuschemeng.0c07203.