Tailoring the Discharge Reaction in Li-CO_2 Batteries through Incorporation of CO_2 Capture Chemistry

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SUMMARY

The search for viable end-uses of CO_2 has motivated considerable research into CO_2 utilization in energy storage devices such as alkali metal-based O_2 /CO_2 and -CO_2 batteries. However, efforts have been stymied by the low electrochemical activity of CO_2 in most organic media. In this work, we report a mediated CO_2 capture and conversion process, based on amine (e.g. 2-ethoxyethylamine (EEA)) chemisorption, which provides a new electrolyte system for facilitating the discharge reaction in Li-CO_2 batteries. Our results indicate that electrochemical reduction of CO_2-loaded amines proceeds at significantly higher discharge potentials (~2.9 V vs. Li/Li^+) compared to physically dissolved CO_2, which is inactive in the amine's absence. The discharge reaction forms solid-phase Li_2CO_3 as the primary discharge product and yields high discharge capacities (> 1000 mAh/g_c), highlighting the coupling of CO_2 capture chemistry to nonaqueous batteries as a promising approach for the design and manipulation of CO_2 conversion reactions.

KEYWORDS

Carbon dioxide, CO_2, CO_2 capture, CO_2 conversion, amine, Li-CO_2 battery, electrochemical reduction, ethoxyethylamine, Li_2CO_3

INTRODUCTION

Identifying viable technologies to mitigate carbon dioxide (CO_2) emissions and enable sustainable power generation represents one of the most pressing scientific and engineering challenges of our time.[1-2] Significant efforts have been expended to develop post-combustion carbon capture technologies, with the most industrially mature systems based on solutions of aqueous amines such as monoethanolamine (MEA).[3-4] However, a major challenge that currently limits the widespread implementation of capture technologies is the large energy requirement for thermal CO_2 regeneration, estimated to require up to 30% of the power plant generating capacity.[5] Even if this figure is expected to be lowered through continued research and development, the safety and reliability of long-term geological storage of compressed CO_2 remains unproven.[6]

This last point has motivated consideration of other end uses of post-combustion CO_2, in particular its conversion to fuels, chemicals, or otherwise benign storage phases, by chemical or electrochemical processes.[7-9] The latter is the focus of the current work. By many arguments, the ideal medium in which to conduct electrochemical CO_2 reduction is water, owing to the ability to couple electron and proton transfer to yield fuels (e.g. methane (CH_4)), chemicals (e.g. formic acid), or chemical feedstock (e.g. carbon monoxide (CO)).[10-11] However, aqueous conversion requires large energy inputs to attain selectivity towards the most desirable, highly reduced products. For example, achieving modest conversion to CH_4 requires exceedingly high overpotentials (> 1 V) when utilizing state-of-the-art metal catalysts such as Cu, with yields of only ~20% at -1 V vs. RHE.[12] The wide range of co-products formed alongside will necessitate additional complex and costly separation strategies. Meanwhile, even the simplest two-electron transfer product, CO, can only be formed with acceptable Faradaic efficiencies of ~40-50% at overpotentials of 0.5 – 1.0 V,[13-14] with parasitic H_2 evolution as the major co-product. Therefore, it is worthwhile to continue the search for possible end uses of CO_2 that help to address or avoid altogether the challenges associated with aqueous reduction.

Recently, researchers in the battery community have explored an alternative end-use for CO_2 that involves its incorporation into nonaqueous energy delivery and storage devices.[15-34] In such a scheme, CO_2 (post-capture and separation) is recycled into a gas cathode in a battery, e.g. one utilizing a lithium (Li) or sodium (Na)-based anode and organic electrolyte. CO_2 was initially proposed for use in gas cathodes as a "gas assist" additive to increase the capacity of Li- or Na-oxygen batteries, i.e. a so-called "O_2/CO_2" battery.[35-36] In these cases, O_2 is the electroactive species, and chemically reacts with CO_2 followed by subsequent chemical or electrochemical steps, typically resulting in the formation of alkali carbonate (e.g., $4Li + O_2 + 2CO_2 \rightarrow 2Li_2CO_3$).[37-38] As demonstrated more recently, CO_2 can also be used as the reactant in a standalone gas cathode.[15-19] The attraction of an alkali-CO_2 battery is the high theoretical energy density (1879 and 1136 Wh/kg, respectively, for Li-CO_2 or Na-CO_2, assuming the reaction ($4(Li, Na) + 3CO_2 \rightarrow 2(Li, Na)_2CO_3 + C$), compared to Li-ion batteries (~500 Wh/kg at the active materials level).[39] The first Li-CO_2 battery was proposed by Archer and co-workers[19] as a primary battery, and utilized an ionic liquid and moderate temperatures (60 – 100°C) to achieve reasonable discharge capacities of 2000 – 4000 mAh/g_c. Subsequently, a number of publications explored different electrolytes and cathode materials in an attempt to make the Li-CO_2 battery rechargeable.[15-17, 20, 23] Utilization of nanoscale carbons, such as graphene or carbon nanotubes combined with tetraethylene glycol dimethyl ether (TEGDME) electrolytes, were reported to facilitate discharge at moderate potentials (~2.7 V vs. Li/Li^+) and high capacities normalized to carbon (~ 8000 mAh/g),[15-16] and also enabled Li_2CO_3 to be nominally charged, albeit still at very high potentials (> 4 V vs. Li/Li^+).[16] Subsequently, a number of works have investigated the use of metal-based catalysts such as Ru[23] or Mo[18] to lower the charging voltage and promote full reversibility by facilitating re-combination of C and Li_2CO_3 back into CO_2. The choice of electrolyte in these combined works appears to be critical, as nearly all reports utilize TEGDME with either lithium

trifluoromethanesulfonate ($LiCF_3SO_3$)[23, 26] or lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)[15, 22] salts. Due to severe kinetic limitations however, direct CO_2 reduction, which entails reconfiguration of a stable CO_2 molecule to a reactive, CO_2 anion radical intermediate,[40] has been reported to have little to no activity in other solvents such as dimethyl ether (DME)[41] and dimethyl sulfoxide (DMSO),[32] although there is some disagreement in the literature.[24] Given the very early stages of this field, careful mechanistic studies of these electrochemical conversion reactions are still needed. Additionally, as described above, the set of viable solvents for direct CO_2 reduction in organic, room-temperature battery electrolytes remains exceedingly small to date, hindering further development.

In an attempt to address this latter challenge, in this work, we present a new concept to facilitate CO_2 discharge in a Li-CO_2 battery by avoiding the rate-limiting step in classical electrochemical CO_2 reduction, namely, direct electroreduction of physisorbed CO_2 to the CO_2^- radical. Specifically, we introduce an approach in which CO_2 is "pre-activated" by incorporation into an amine adduct, prior to reduction of the adduct at a carbon electrode. Generation of the adduct, which is spontaneous upon introduction of CO_2 to the electrolyte, involves formation of an N-C bond and reconfiguration of the linear, highly stable CO_2 to a bent –COO moiety in the bound state. Such a reaction scheme is well-known in the CO_2 capture community,[42-44] which typically employs aqueous amines to exergonically bind and separate CO_2 from flue gas streams. In CO_2 capture, the end-goal is to regenerate CO_2 to the gas phase for storage while returning the amine to its pre-capture state, where it can continue to react; this regeneration, which involves N-C bond cleavage, is usually accomplished using thermal or pressure-swing desorption.[45] In contrast, the purpose of this work was to investigate the use of the CO_2-loaded amine solution as an electroactive electrolyte to promote the activity of the discharge reaction. This is accomplished, as shown schematically in **Figure 1**, through a modified discharge mechanism that involves electrochemical cleavage of the N-C bond and amine regeneration for subsequent cycling **(Figure 1).** While one recent study[46] investigated direct electroreduction of amine-CO_2 adducts in aqueous electrolytes with metal catalysts, the adduct was reported to lack intrinsic activity, and instead mainly facilitated the hydrogen evolution during reduction of physisorbed CO_2. Switchable solvents, which chemically bind CO_2, have also been employed to chemically release CO_2 near an electrode for direct electroreduction.[47] However, to the best of our knowledge, intrinsic electroactivity of CO_2 adducts involving N-C bond cleavage has not been reported.

To investigate the viability of the proposed approach, we employed an alkyl amine, ethoxyethylamine (EEA), in a solvent (DMSO) in which CO_2 typically exhibits poor activity. EEA is a primary amine that has been previously employed for CO_2 capture in nonaqueous solvents.[48] We show that the formed EEA-CO_2 adduct is not only highly electroactive in the presence of Li^+ salts, but that the N-C bond is selectively cleaved upon electron transfer, ultimately facilitating conversion of CO_2 gas to Li_2CO_3 through reaction with the amine as an intermediary step. We find evidence that the amine can be regenerated during this process, opening new opportunities to

develop continuous conversion reactions with further development. Moreover, the reduction potentials of this reaction are as high as ~2.9 V vs. Li/Li^+, which is strongly competitive with direct CO_2 discharge voltages in Li-CO_2 batteries. This high voltage presents the possibility of either extracting energy from CO_2 reduction by Li in a primary battery; or, in the longer term, of enabling a higher-voltage rechargeable battery. In addition to "activating" CO_2 in previously nonviable solvents, inclusion of EEA - and the design of novel, nonaqueous amine-containing electrolytes - opens up a possible route to combine CO_2 capture and electrochemical conversion in a single device.

RESULTS AND DISCUSSION

Electrolyte Screening: Amine and Solvent Selection

Primary amines are most commonly used in aqueous CO_2 capture, where typical solutions contain ~30% amine by volume.[3] Consequently, CO_2-uptake reaction mechanisms and product speciation in water have been widely studied.[42-43] Under typical conditions, CO_2 uptake by primary or secondary amines is a termolecular reaction involving two amine molecules, resulting in formation of an ammonium carbamate salt ($2RNH_2 + CO_2 \rightarrow RNHCOO^- + RNH_3^+$).[44] Detailed spectroscopic investigations using nuclear magnetic resonance (NMR) have revealed a high sensitivity of the amine-CO_2 adduct speciation to both the amine chemistry and the solution conditions, including the amine structure (whether primary, secondary or tertiary), its pKa and related nucleophilicity towards CO_2, concentration, and CO_2 loading.[48] Relatively fewer studies have investigated amine-based capture in nonaqueous solutions such as alcohols[49-51] or battery-relevant solvents, such as DMSO,[52-53] dimethylformamide (DMF),[54] TEGDME,[55] and tetrahydrofuran (THF).[56] However, to the best of our knowledge, none have involved alkali-based electrolyte salts, which are required in a combined capture-electrochemical conversion process. Therefore, a significant aspect of the present study was the translation of aqueous amine capture chemistry to nonaqueous (aprotic) electrolytes, and characterization of the amine-CO_2 product speciation, which determines the reactant state for the subsequent discharge reaction.

For an amine candidate, a primary amine, 2-ethoxyethylamine (EEA), was selected. EEA was deemed attractive for a first study due to (a) its higher solubility in polar organic solvents[48] as compared to more commonly employed amines such as monoethanolamine (MEA), and (b) the chemical stability of the EEA backbone in the presence of Li metal. The latter point is in contrast to alkanolamines such as MEA, which were found to rapidly evolve hydrogen from the terminal -OH. The stability of EEA was confirmed by ^1H NMR measurements before and after exposure of EEA-CO_2/solvent solutions to stabilized Li, which yielded identical spectra (**Figure S1**).

To identify a viable electrolyte, a qualitative screening was performed by preparing dilutions of EEA in a range of solvents and then bubbling CO_2 into the solution vials. As has been widely described in the literature, CO_2 uptake by many amines results in unwanted precipitation

of ammonium carbamate salts[57] and/or dramatic increases in viscosity[58] under CO_2-rich conditions in both aqueous and nonaqueous solvents. The viscosity increase has been attributed to formation of a dense, intermolecular hydrogen-bonded network between neighboring CO_2-adducts, and/or between CO_2-loaded amines and solvent molecules.[59] In our screening, we considered a set of representative battery-relevant solvents including TEGDME, DMSO, THF, DME, DMF and PC. As shown in **Figure 2**, none of the investigated amine/solvent solutions exhibited observable changes upon introduction of CO_2, suggesting, at first pass, that they might all be potentially viable candidates as evidenced by their ability to stabilize EEA-CO_2 species in the solution phase, either as carbamic acid and/or ammonium carbamate (discussed further below). However, when 0.3 M $LiClO_4$, the electrolyte salt, was added to the above solutions, dramatically different outcomes were observed. In PC, DMF, DME, and THF, instant precipitation occurred upon salt addition, which is proposed to arise from the formation of Li carbamate and/or ammonium perchlorate salts, rather than ammonium carbamate. This hypothesis was rationalized by the lack of precipitation observed in the same solvents in the absence of $LiClO_4$, where ammonium carbamate is a likely product. In contrast, in TEGDME, $LiClO_4$ salt addition led to the formation of a highly viscous, gel-like substance, indicating the formation of extensive hydrogen-bonding networks, which rendered it unsuitable for use as an electrolyte. Such formation of a gel-like material upon CO_2 loading is a common occurrence in solvents with inherently high viscosities.[60] The sole exception was DMSO - a polar yet comparatively lower viscosity solvent - in which no changes were observed. This indicates DMSO's superior ability to solubilize EEA-CO_2 adducts due to solvent-specific chemical interactions, which are discussed later in the text. In the remainder of this study, 0.3 M $LiClO_4$ in DMSO was used as the electrolyte, with varying concentrations of EEA as noted.

Products of CO_2-Loaded EEA with $LiClO_4$ Salt

Given the apparently unique ability of DMSO to solubilize EEA-CO_2 adducts in the presence of Li^+ salts, a detailed investigation of the solution chemistry was next undertaken. The goal was to determine the product speciation upon CO_2 binding by EEA in the DMSO-based electrolyte, and thus the "reactant state" on which electrochemistry would subsequently be performed.

CO_2 uptake reactions by primary amines like EEA have been studied previously in aprotic media, including in DMSO, in the absence of additional salts.[52-54] In DMSO, ^{1}H NMR has shown that the formed adducts exist in a mixed state consisting of a combination of carbamic acid (1:1 ratio of CO_2 per amine) and/or ammonium carbamate (1:2 ratio of CO_2 per amine) **(Figure S2)**. To accurately determine the distribution of EEA-CO_2 adducts under the electrochemical conditions to be used in this study, the equilibrium product speciation upon CO_2 uptake by 50 mM EEA in DMSO-d_6 was examined at room temperature using ^{1}H NMR. As no significant difference between ^{1}H NMR spectra acquired for samples containing 50 mM and 100 mM was observed, we chose 50 mM as the amine concentration for NMR measurements to circumvent shimming problems common to concentrated samples and attain more well-resolved spectra.

Figure 3 shows the proton NMR spectra of lean EEA (bottom) and CO_2-loaded EEA (top) in DMSO-d_6. Upon introduction of CO_2, the ^{1}H NMR resonance of –N**H**$_2$ protons, initially observed at 1.3 ppm, disappeared and was replaced by two new peaks, a stronger peak at 6.6 ppm and a weaker and broad peak at 10.2 ppm. The triplet resonance at 6.6 ppm represents the –N**H**- protons of the carbamate and carbamic acid species, whereas the peak at 10.2 ppm corresponds to the –COO**H** protons of carbamic acid that may be in fast exchange with the –N**H**$_3^+$ protons of the ammonium cation. The relative quantities of carbamic acid and ammonium carbamate were found by comparing the integrated area ratio of the peak corresponding to –N**H**- at 6.6 ppm to that of –COO**H** ⇌ –N**H**$_3^+$ at 10.2 ppm – a peak area ratio of 1:1 or 1:3 corresponds to pure carbamic acid or pure carbamate, respectively.[48] In **Figure 3**, peak area ratio was found to be 1:1.01, indicating that carbamic acid is the dominant adduct state. This observation is consistent with previous reports of CO_2 uptake by EEA in DMSO-d_6 (solvent only) at low amine concentrations ($\leq$ 3 M).[52] The preferential stabilization of neutral carbamic acid over charged carbamate species is unique to highly polar solvents like DMSO, in which hydrogen bonding occurs between the sulfonyl group of DMSO and the carboxyl group[48] **(Figure S3)**.

Interestingly, addition of an electrolyte salt, 0.3 M $LiClO_4$, induced chemical changes that altered the equilibrium speciation over a timescale of approximately 24 hours. This evolution, and final state of adducts formed, were investigated by taking ^{1}H NMR spectra at multiple-hour intervals during this process (**Figure 4**). As shown in **Figure 4A**, one hour after salt addition, three new sets of peaks, centered roughly around 3.5 ppm, 2.87 ppm and 1.15 ppm, were evident in addition to the original carbamic acid features, indicating the formation of a new yet EEA-derived product. Owing to its proximity to the quartet methylene (CH_3C**H**$_2$$OCH_2$-) and the triplet methylene (CH_3CH_2OC**H**$_2$-) resonance, both of which appear slightly above 3.4 ppm for pure carbamic acid without salt, the new set of peaks at ~3.5 ppm was assigned to overlapping ^{1}H resonances of the two methylenes (CH_3C**H**$_2$$OC$**H**$_2$-) in the new product. Similarly, the newly emerged triplets at 2.87 and 1.15 ppm were reasoned to reflect the resonances of the N-methylene hydrogens and the terminal methyl hydrogens, respectively. The presence of a triplet for the N-methylene peak at 2.87 ppm, rather than a quartet, indicates that the N-methylene protons of the new product formed upon salt addition are coupled solely with neighboring methylene protons, and not with proton(s) attached to the adjacent nitrogen atom, which has been reported previously to occur with $–CH_2NH_3^+$ terminal groups.[61] Based on these observations, we conclude that the product responsible for the newly emerged spectral features in the presence of $LiClO_4$ is the ammonium cation ($CH_3CH_2OCH_2CH_2NH_3^+$). The enhanced presence of ammonium cation upon the addition of $LiClO_4$ can be explained by $LiClO_4$ driving a shift in equilibrium from predominantly carbamic acid towards greater carbamate formation **(Figure 4B)**. Note that the ^{1}H NMR spectrum of the carbamic acid (RNHCOOH) and the carbamate anion ($RNHCOO^-$) are largely identical and therefore cannot be distinguished from one another, and thus we rely on evidence based on shifts in the ammonium speciation. We hypothesize that in the presence of $LiClO_4$, the hydrogen bonding network in DMSO responsible for stabilizing the carbamic acid is disrupted. The Li cation - a strong Lewis acid – may preferentially stabilize the carbamate anion

over the neutral acid species, which results in the simultaneous formation of an accompanying ammonium cation via an intermolecular proton transfer and also necessitates the loss of a CO_2 molecule back to the gas phase **(Figure 4B).** This ammonium cation may then pair with the ClO_4^- anion. It is worth noting that a direct reaction between carbamic acid and lithium perchlorate to form perchloric acid and lithium carbamate ($RNHCOOH + LiClO_4 \rightarrow RNHCOOLi + HClO_4$) cannot occur spontaneously because it requires the formation of strong acid ($HClO_4$) from a weak acid (RNHCOOH), for which the Gibbs free energy change is positive.

Over time, the ^{1}H NMR spectrum of the electrolyte after salt addition undergoes additional evolution consistent with gradually increasing Li^+ carbamate formation **(Figure 4A**, spectra b-d**)**: (a) The integrated areas of the new set of peaks centered around 3.5, 2.87 and 1.15 ppm increase with time at the expense of the intensity of the original methylene and methyl features (the solvent residual peak at 2.5 ppm is used as an internal reference); (b) The integrated area of the –N**H**-C- proton resonance decreases with time, which indicates an overall decrease in CO_2 loading consistent with the conversion of carbamic acid (initially a 1:1 loading of CO_2 per amine) to carbamate (CO_2 loading of 1:2); (c) The integrated area ratio of the –N**H**- peak and the –COO**H** $\rightleftharpoons$ –N**H**$_3^+$ peak changes from 1:1.01 before $LiClO_4$ addition (indicating almost exclusively carbamic acid) to 1:1.10 after 1 hour, 1:1.21 after 9 hours, and 1:1.33 after 24 hours post-$LiClO_4$ addition, respectively. Quantitatively, these results reveal that after 24 hours, ~30% of the carbamic acid has been converted to carbamate, which we assign as the "active" species (see electrochemical results and associated discussion, below). We note that similar results were obtained when the salt was added prior to EEA-CO_2 adduct formation (**Figure S4)**. It is also worth noting that the –COO**H** $\rightleftharpoons$ –N**H**$_3^+$ resonance, the amide resonance (–N**H**-C-), and the N-methylene resonance shift slightly upfield with time. This may reflect either a concentration-dependent variation of the chemical shifts due to the participation of the aforementioned protons in intermolecular hydrogen bonding,[62-64] or, given the relatively long timescale (hours) of the spectral features' evolution, may be related to solution-phase aggregation of EEA-CO_2 adducts in the presence of a Li salt. We note that attempts to characterize the solution-active species using mass spectroscopy, which would have helped to elucidate possible strong intermolecular interactions including aggregation, was not possible because the high inlet temperatures required by the measurement resulted in loss of bound CO_2 to largely yield lean amine.

To support the interpretation of the solution-phase processes occurring upon salt addition, we performed two additional time-evolving ^{1}H NMR studies. First, to exclude possibility of parasitic chemical reactivity between the ClO_4^- anion and the amine as responsible for the observed new ^{1}H NMR features, similar measurements were conducted using a different anion, PF_6^- (**Figure S5A-S5B)**. Qualitatively similar spectral features, namely three newly emergent sets of peaks with comparable peak separation, were observed as in $LiClO_4$, indicating that the induced interactions were not unique to the ClO_4^- anion. Moreover, a comparison between the chemical shifts of the newly emerged peaks reveals that the new features are shifted further downfield for PF_6^- **(Figure**

S6), suggesting stronger electrostatic interactions that lead to deshielding of the EEA protons through induction at the $–NH_3^+$ moiety. By the logic of the above peak assignments, use of an alternate alkali metal cation, which would modulate the strength of ion pairing with the carbamic acid/carbamate, should give rise to a different proportion of ammonium cations but not dramatically alter their electronic structure. Indeed, upon conducting identical measurements with $NaClO_4$ **(Figure S5C-S5D**), nearly identical chemical shifts were observed as those when Li^+ was the cation **(Figure S6)**. However, the new features were noticeably weaker with Na^+ than with Li^+, suggesting that the cation size has some influence on the percentage conversion of carbamic acid to carbamate at equilibrium, with a smaller cation resulting in greater carbamate formation. The detailed role of the salt composition in inducing shifts in reactant-state equilibria is the subject of a future planned study.

Electrochemical Activity of CO_2-Loaded EEA in DMSO Electrolytes

Prior to conducting electrochemical measurements, the intrinsic redox activity of the EEA-CO_2 adduct was first screened under homogeneous conditions. To do so, the electrolyte containing the adduct was rapidly mixed with a chemical reductant, namely cobaltocene ($CoCp_2$), while monitoring the solution using UV-Visible spectroscopy. The reduction potential of the $CoCp_2$ / $CoCp_2^+$ couple occurs at approximately 2 V vs. Li/Li^+,[65] and therefore, any observed homogeneous reaction would indicate the ability of the EEA-CO_2 adduct to accept an electron at potentials higher than 2 V. As shown in **Figure 5A**, electrolyte containing lean EEA with $CoCp_2$ exhibited an absorbance around 526 nm, which is characteristic of $CoCp_2$. A similar absorbance peak was observed for physically dissolved CO_2 alongside $CoCp_2$, indicating that $CoCp_2$ could not reduce physically dissolved CO_2 **(Figure S7)**. Upon the addition of $CoCp_2$ to electrolyte containing CO_2-loaded EEA, however, the characteristic absorbance for $CoCp_2$ at 526 nm disappeared and was replaced by an absorbance around 409 nm, which indicates an oxidation of $CoCp_2$ to $CoCp_2^+$ upon exposure to the CO_2-loaded amine species. This color change was consistent with that observed upon direct electrochemical oxidation of $CoCp_2$ to $CoCp_2^+$ cation **(Figure 5B)**, and implies that a homogeneous electron transfer to the EEA-CO_2 adducts occurred. Gas chromatography measurements of gaseous samples extracted from the headspace of the solution vial containing EEA-CO_2 and $CoCp_2$ further indicated that no gas-phase products, specifically H_2, CO, or CH_4 were evolved under homogeneous reduction**.** This confirmed that the observed color changes in UV-Visible measurements arose from electron transfer from $CoCp_2$ to EEA-CO_2 and not from parasitic reactions with the electrolyte.

To examine the discharge behavior of the CO_2-loaded EEA in a Li-CO_2 battery, two-electrode Swagelok-type cells were constructed. The cells consisted of a pre-stabilized (soaked in PC electrolyte) Li foil anode, where the intentionally pre-formed solid electrolyte interphase (SEI) was grown as a protective film to block parasitic reactivity of Li with EEA-CO_2 and DMSO;[66] and a porous carbon cathode (Vulcan carbon (VC), XC72) coated onto a Celgard separator **(Figure S8)**. For simplicity, the electrolyte, containing 100 mM EEA/ 0.3 M $LiClO_4$ in DMSO, was purged

and loaded with CO_2 prior to its use in the cell. Upon assembly, the Li-CO_2 cells were subjected to an additional purge step with CO_2 (conducted inside an Ar-filled glovebox), pressurized to ~1.4 bar, and sealed for testing. All cells were rested for a minimum of 20 hours before discharge. The initial open circuit voltage for cells assembled using the aforementioned method typically ranged from 2.9 – 3.2 V vs Li/Li^+. It is interesting to note that during the resting period, the OCV routinely experienced an initial drop of approximately 0.2 - 0.3 V, after which it recovered to ~ 3 V vs. Li/Li^+ (**Figure S9**). We found that the OCV recovery to a value $\gtrsim$ 3 V vs. Li/Li^+ was crucial for normal functioning of the Li-CO_2 cell, and that cells that did not exhibit this voltage recovery yielded negligible capacity upon discharge. This observation not only provides evidence of a direct correspondence between the chemical and electrochemical thermodynamics, but also supports the assignment of the Li carbamate as the electroactive species, owing to its evolution over similar timescales as the OCV recovery.

Galvanostatic discharge measurements of Li - CO_2 cells were performed over a range of current densities from open circuit to a cutoff potential of 2 V vs. Li/Li^+ (**Figure 6**). As shown in **Figure 6A,** discharge at 10 mA/g_C of cells under argon only (containing DMSO electrolyte without EEA or CO_2), physically dissolved CO_2 in DMSO, or lean (unloaded) EEA in DMSO exhibited negligible capacity. We note that the negligible capacity of CO_2-only cells agrees with previous studies, which reported that CO_2 could not be directly electrochemically reduced in either DMSO or glyme-based (DME) electrolytes.[37] The absence of significant capacity of the lean EEA in DMSO indicates that no part of the alkyl ethoxy tail, nor the amino ($–NH_2$) terminal group, are electrochemically active in the examined potential range. In stark contrast, discharge of EEA-CO_2 cells, in which both the CO_2-loaded amine and physically dissolved CO_2 are present, yielded significant different behavior: a clear voltage plateau was observed at ~2.9 V vs. Li/Li^+. Moreover, discharge was sustained to relatively high capacities of ~2100 mAh/g_C at 10 mA/g_c. Increasing the discharge current to 30 and 50 mA/g_c resulted in a modest decrease in the discharge voltage and attainable capacity; e.g., ~1860 mAh/g_C was attained at 30 mA/g_c, as shown in **Figure 6B**. Further increases in current densities (e.g. 100 and 200 mA/g_c), however, caused a rapid decrease in discharge performance, e.g., 215 mAh/g_C and 34 mAh/g_C were attained at 100 and 200 mA/g_C, respectively (**Figure S10**). The decrease in capacity at high currents was found to arise at least in part from transport limitations. In separate measurements, linear sweep voltammetry measurements were conducted in a rotating-disk electrode setup as a function of rotation rate **(Figure S11)**, and indicated a significantly increased activity as well as dramatically positively shifted onset reduction potential (~ 0.4 V) under forced convective conditions (900 and 1600 RPM). This behavior is attributed at least in part to the viscosity of EEA, which limits the reaction at high rates. We note that the structure of the amine was not optimized in the present work; future efforts to optimize the structure of the amine, for instance by using shorter alkyl chains or cyclic amines,[67] are anticipated to enable improvements in rate capability. Tailoring the amine structure may also have corresponding benefits on the overall cell energy density of an ultimate device, by minimizing the weight of the electrolyte (capacities of **Figure 6B**, normalized instead to the weight

of the amine, are provided in **Table S1** for comparison). We note that, significantly, cells that did not contain physically-dissolved CO_2 also exhibited negligible capacity **(Figure S12)**, indicating that physically-dissolved CO_2 is also an essential participant in the discharge mechanism. Unfortunately, attempts to distinguish between the contributions of chemically-bound and physically-dissolved CO_2 using isotopic labeling were unsuccessful, owing to rapid interchange between physisorbed and chemisorbed CO_2, as revealed by ^{13}C NMR spectroscopy (**Figure S13**). We also note that similar findings regarding the activity of EEA-CO_2 were obtained from cyclic voltammetry measurements performed at 0.05 mV/s from 3.2 to 2 V vs. Li/Li^+ (**Figure S14)**. In particular, significant reduction currents were obtained only for CO_2-loaded EEA at a high onset reduction potential, ~2.95 V vs. Li/Li^+, in good agreement with the reduction potential under galvanostatic conditions.

To further confirm that the loaded amine could be implicated in the observed high discharge capacities, the effect of amine concentration was also studied under galvanostatic conditions at a fixed current density of 30 mA/g_c, as shown in **Figure 6C.** Specifically, a proposed mechanism involving direct reduction of the CO_2-loaded EEA implies that increasing the amount of EEA-CO_2 should lead to an increase in discharge capacity (in the absence of competing effects). Indeed, our results indicated that increasing the amine concentration from 50 mM to up to 115 mM resulted in the discharge capacity also increasing linearly, from ~1300 mAh/g_c to ~2000 mAh/g_c. The increase is not directly proportional to the amount of amine present, i.e., a doubling of the concentration from 50 to 100 mM resulted in a less-than-doubled discharge capacity (1320 and 1860 mAh/g_C, respectively), and is attributed to amine concentration-dependent product speciation mentioned earlier. In the region where amine concentration is positively correlated to discharge capacity, i.e. from 50 mM to 115 mM, the scaling of capacity with concentration provides strong evidence of the CO_2-loaded EEA's role in the observed discharge voltage and capacity. Increasing the EEA concentration beyond 115 mM, however, resulted in a rapid decrease in discharge capacity **(Figure 6C-6D)**, attributable to the noticeable increases in the solution viscosity under CO_2-rich conditions at higher EEA concentrations. As shown in **Figure 6C**, the discharge potential also displays a clear sensitivity to the EEA concentration. This voltage trend was found to depend most strongly and inversely on the charge transfer resistance, R_{CT}, as determined by electrochemical impedance spectroscopy (EIS) measurements of Li-CO_2 cells with varying EEA concentrations **(Figure S15).** Interestingly, the overall trend in voltage (and thus R_{CT}) is not perfectly monotonic. This finding indicates that there is a complex interplay between concentration/activity (influencing the thermodynamics), charge transfer resistance (influencing the kinetics), and reactant and ion transport that governs the behavior of these electrolytes, which merits future studies to elucidate in detail.

Discharge Product Characterization

Having established the electrochemical activity of the CO_2-loaded EEA in DMSO, we next turned to identifying the products formed, which are critical for revealing the discharge reaction

taking place. First, as shown in **Figure 7A**, X-ray diffraction measurements conducted on discharged gas diffusion layer (GDL) electrodes revealed at least partially crystalline Li_2CO_3 as the primary solid phase product. Discharged GDL electrodes, instead of VC-coated Celgard, were more suitable for XRD analysis because the characteristic XRD peaks for pristine GDL had minimal overlap with those for Li_2CO_3. SEM images of the discharged electrode supported the formation of a solid-phase product, which appeared as spherical formations with a characteristic size of ~ 500 nm, and which were homogeneously distributed throughout the electrode **(Figure 7B)**. The observed spherical-like structure of the discharge product is similar to the spherical shape of Li_2CO_3 observed in Li-O_2/CO_2 batteries.[25, 37] Upon further examination of the discharged electrode using attenuated total reflectance-IR (ATR-IR), several noticeable peaks were observed that were not present in the pristine electrode (**Figure 7C**). Specifically, the strong transmittance peaks at 1426 cm^{-1} and 863 cm^{-1} are characteristic of the antisymmetric stretch and out-of-plane bending mode of the CO_3^{2-} anion.[26, 68] Importantly, the lack of N-H and N-C stretches in the IR spectrum of the solid-phase discharge product, which typically appear between the ranges 3300-3500 cm^{-1} (not shown) and 1080-1360 cm^{-1} respectively, indicates that the amine or derived products were not incorporated in the solid phase; this was further confirmed by X-ray photoelectron spectroscopy (XPS) measurements **(Figure S16)** which also indicated a lack of nitrogen in the discharged phases. Taken together, these data provide strong evidence that electrochemical reduction of CO_2-loaded EEA proceeds through the selective cleavage of the N-C bond, as only CO_2-derived phases are found in the solid phase.

To rule out the possibility that the Li_2CO_3 could arise from decomposition of the amine, electrolyte, or carbon electrode, galvanostatic discharge measurements using isotopically labeled $^{13}CO_2$ (Cambridge Isotope Laboratories, 99%) were conducted in comparable Li-CO_2 cells with ^{12}C-containing Vulcan carbon electrodes and electrolyte. Upon termination of discharge, electrodes were extracted from Li-CO_2 cells and washed with DME prior to being treated with acid (2 M H_3PO_4), which selectively decomposes Li_2CO_3 to release CO_2. Once this process was completed, it was followed by an additional treatment of any potential remaining solids in the electrode with Fenton's reagent, which selectively oxidizes organic species such as Li carboxylates (HCO_2Li, CH_3CO_2Li) to similarly release CO_2.[66] The headspace of the reaction vessel was monitored using mass spectroscopy to distinguish between the release of $^{13}CO_2$ or $^{12}CO_2$. **Figure 7D** shows the amount of CO_2 evolved from this prescribed electrode treatment. The analysis reveals that 94% of the evolved CO_2 from the acid treatment originated from labeled $Li_2{}^{13}CO_3$, whereas only 6% of the evolved CO_2 came from $Li_2{}^{12}CO_3$, likely formed as a result of trace parasitic side reactions occurring in the cell. This provides strong evidence that the vast majority of the Li_2CO_3 formed on the discharged electrode can be attributed to amine-bound CO_2 reduction with physically dissolved $^{13}CO_2$ as co-reactant. Furthermore, the addition of Fenton's reagent to the discharged electrode did not evolve any $^{12}CO_2$ nor $^{13}CO_2$, indicating the absence of any unwanted Li carboxylates on the electrode. The absence of carboxylates provides further evidence that Li carbamate, which contains no protons around the –COO moiety, is the active species

compared to the carbamic acid (-COOH), which is also present in solution. Loss of labile protons to the solid phase through formation of carboxylates is undesired, as it hinders desired amine regeneration for re-binding of CO_2. Finally, the carbon electrode stability was also investigated by performing discharge measurements on a ^{13}C positive electrode. Upon repeating the above treatment, no $^{13}CO_2$ evolution was observed. This further indicates that the carbon electrode did not contribute to the solid phases observed in discharged cells.

Having determined that the solid phases contain Li_2CO_3 that is derived solely from CO_2, we next investigated gas- and liquid-phase products. For gas analysis, Swagelok-type cells were constructed with $LiFePO_4$ (LFP) counter electrodes and subjected to gas chromatography (GC) analysis at the end of discharge; however, no product gases, specifically CO or H_2 **(Figure S17)**, were observed. We note that the LFP counter electrode was used to eliminate the possibility of H_2 evolution from a parasitic chemical reaction between Li metal and CO_2-loaded EEA or lean EEA. To gain insight into the state of the amine after discharge, galvanostatic discharge measurements were performed using a glass electrolysis-type cell containing a gas diffusion layer (GDL) working electrode, a PC-stabilized Li counter electrode, and electrolyte containing both CO_2-loaded EEA and physically dissolved CO_2, consistent with conditions in Swagelok cells. The glass cell setup employs a higher electrolyte volume (> 1 mL vs. 100 μL in Swagelok cells), making it easier to extract significant quantities of electrolyte for spectroscopic characterization in the post-reduction state. The cell was discharged at 5.65 $\mu A/cm^2$ to a fixed capacity of ~1 mAh (approximately one-third of the total expected capacity), and electrolyte samples were drawn before and after discharge for ^1H NMR analysis **(Figure S18A)**. ^1H NMR measurements of the electrolyte after discharge revealed that the amine backbone ($R=CH_3CH_2OCH_2CH_2$-) remained intact. Consistent with the proposed electrochemical reduction of EEA-CO_2 adducts, the peak areas of protons corresponding to $RNHCOOH/RNHCOO^-$ decreased during discharge as a result of the consumption of $RNHCOO^-$. Additionally, the ^1H resonances of the protons associated with the ammonium cation ($-NH_3^+$) disappeared, and new features corresponding to lean EEA appeared. The broad peak at ~3.5 ppm was confirmed to correspond to a labile proton, as adding a few drops of D_2O suppressed it entirely **(Figure S18B)**. We therefore attribute this emergent peak to the -N**H**$_2$ resonance of the regenerated amine in a modified chemical environment after reduction, as reflected by its downfield shift from the original position (δ=1.3 ppm, **Figure 4A**). We further note that even though the experimental results lend evidence to amine regeneration, the finite capacity observed to date suggests that the amine gradually becomes deactivated, possibly by reaction with Li at the anode to form a lithium amide. The fate of the capture molecule upon extended reduction, and strategies to increase the turnover, will be the focus of future work.

It is interesting to note that no ammonium cations, and consequently no carbamate anions, were detected in the electrolyte after discharge, even though the discharge reaction was stopped prematurely (the absence of ammonium cations directly implies an absence of the accompanying carbamate anions, which are difficult to determine directly due to the identical ^1H NMR spectral features for RNHCOOH and $RNHCOO^-$). This may occur due to the vastly different rates of the

chemical, $LiClO_4$-driven carbamic acid-to-carbamate conversion step and the subsequent electron transfer step, with the former being rate-limiting (timescale of several hours, **Figure 4A**). Under such a scenario, the rate at which ammonium cations and carbamate anions are consumed greatly exceeds the rate at which they are produced. Therefore, in accordance with our observations, they could not accumulate in the electrolyte for detection via NMR.

Finally, to determine the feasibility of using EEA in a rechargeable Li-CO_2 battery, Li-CO_2 cells discharged to a limited capacity of 1000 mAh/g_c were subsequently charged, yielding a stable charging potential > 4 V vs. Li/Li^+ **(Figure S19A)**. E*x situ* FTIR analysis of the charged electrode revealed complete oxidation of Li_2CO_3, as indicated by the lack of characteristic Li_2CO_3 peaks **(Figure S19B)**. This was further confirmed by SEM images of the charged electrode **(Figure S19C)**, which indicated an absence of the spherical Li_2CO_3 particles observed in **Figure 7B**. The cycling performance of the Li- CO_2 cell was also investigated by subjecting the cell to continuous discharge-charge cycles at a fixed rate of 30 mA/g_c to two different cutoff capacities, Q_{max} (500 mAh/g_c and 1000 mAh/g_c). As shown in **Figure S20**, the Li-CO_2 cell demonstrates stable cycling performance for up to ten cycles with Q_{max}= 500 mAh, and up to six cycles for Q_{max}= 1000 mAh/g_c, after which significant decreases in both the voltage and discharge capacity are observed. To understand the origin of this deterioration in cycling performance, oxidative decomposition potentials of both the lean EEA (no CO_2), which is present to some extent in discharged cells, as well as that of CO_2-loaded EEA (both in DMSO electrolyte at 100 mM concentration) was measured and compared with the charging behavior of the previously-discharged Li-CO_2 cell containing Li_2CO_3 **(Figure S21)**. As shown in **Figure S21**, the charging potential for Li_2CO_3 decomposition was in excess of 4.25 V vs. Li/Li^+ (red trace), and overlapped with the oxidative potentials of both the lean EEA and the EEA-CO_2-containing electrolyte. This makes parasitic electrolyte decomposition inevitable alongside Li_2CO_3 oxidation, and therefore adversely impacts the cyclability of the cell. These findings indicate that the amine, while potentially oxidatively unstable at high charging voltages, is highly effective on discharge in activating discharge pathways that are not otherwise accessible. Moreover, significantly, it appears to retain its activity as a discharge promoter over multiple cycles. Future work will investigate subsequent charging and cycling behavior in greater mechanistic detail.

Proposed Discharge Reaction

Our measurements indicate that a Li^+-associated carbamate, $RNHCOO^-Li^+$, is a reactant during discharge. Moreover, they also reveal that both bound CO_2 and physisorbed CO_2 are necessary to observe discharge activity. The formation of predominantly Li_2CO_3 as the solid product indicates that analogous, although not identical, reactions may be occurring between more conventional Li-CO_2 batteries and EEA-CO_2 batteries. The following reactions have been proposed elsewhere for direct CO_2 reduction in Li-containing environments:[19]

$$2CO_2 + 2Li \rightarrow Li_2CO_3 + CO, \quad E^0 = 2.49 \text{ V vs. } Li/Li^+ \quad (1)$$
$$3CO_2 + 4Li \rightarrow 2Li_2CO_3 + C, \quad E^0 = 2.80 \text{ V vs. } Li/Li^+ \quad (2)$$

and involve formation of either CO or C as a co-product to Li_2CO_3. Likewise, discharge reactions in EEA-CO_2 cells, in order to ensure mass balance, must involve formation of an additional product derived from CO_2 other than Li_2CO_3. We unambiguously rule out (1), because there is no evidence of CO formation from gas chromatography analysis as noted earlier. In the absence of obvious CO formation, we propose that carbon is the likely secondary product alongside Li_2CO_3 in Li-CO_2 cells. Attaining evidence for carbon formation in (2) has so far been challenging, because the discharge reactions themselves occur on carbon electrodes. Discharge experiments on carbon-free electrodes such as Ni foam, and Au-sputtered Ni foam have been attempted, but appear to modify the discharge reaction in ways that are not yet fully understood, as lower reduction potentials (by several hundred mV) are observed **(Figure S22)**. The surface-dependence of amine-CO_2 reduction is the study of a planned future study.

According to the discussion above, we propose the following reaction occurring upon reduction of EEA-CO_2, which is fully consistent with our experimental results:

$$RNHCOO^- + RNH_3^+ + 2CO_2 + 4Li^+ + 4e^- \rightarrow 2Li_2CO_3 + C + 2RNH_2 \quad (3)$$

Based on this reaction, the amount of Li_2CO_3 formed, as determined from mass spectroscopy **(Figure 7D)**, is higher by approximately five times than what is expected for a single amine turnover. Note that an alternative reaction is also possible, involving two EEA-CO_2 adducts and one physically dissolved CO_2 molecule ($2RNHCOO^- + 2RNH_3^+ + CO_2 + 4Li^+ + 4e^- \rightarrow 2Li_2CO_3 + C + 4RNH_2$), which would yield the number of amine turnover to be twice that observed for (3) (~ 9.42, see Supplemental Information for calculations). Given the complexity of this system, including the fact that the reaction does not occur at standard state and the lack of available thermochemical data for EEA species, defining a thermodynamic potential from reported thermodynamic properties of the reactants and products was unfortunately not possible at this stage. We do note that, interestingly, the discharge potentials observed, ~2.9 V vs. Li/Li^+, are higher than those corresponding to direct CO_2 reduction (Reactions (1) and (2)), which can arise from the fact that different reactants and products are implicated in the reaction mechanism than those previously studied, i.e. consumption of carbamate (rather than CO_2) and conversion to lean amine. Future spectroscopic and modeling efforts will investigate the activity of various electrolyte constituents including lean and loaded EEA, which may aide in providing a more accurate estimate of expected thermodynamic reduction potentials. Overall, the results show that incorporation of otherwise unreactive CO_2 into an adduct imparts emergent electrochemical activity that, if properly tuned, can give rise to highly selective reaction pathways and products in Li-CO_2 batteries.

Conclusion

In summary, we have presented a new strategy to facilitate the discharge reaction in Li-CO_2 batteries by "preactivating" CO_2 through adduct formation. To do so, aqueous CO_2 capture chemistry based on an alkyl amine, EEA, was translated to nonaqueous electrolytes, specifically DMSO, an electrolyte solvent that otherwise was found to exhibit negligible discharge capacity for CO_2 reduction on carbon electrodes. The resulting –COO moiety, containing CO_2 in a modified environment, is intrinsically electroactive in the absence of electrocatalysts, with reduction leading to detachment and subsequent conversion to CO_2-only derived products. We find that the Li^+-containing salt is implicated in the formation of an active species, and enables crucial shifts in speciation that permit discharge at high potentials (2.9 V vs Li/Li^+) with high selectivity. As this particular amine-electrolyte combination was not extensively optimized in this initial proof-of-concept study, these findings reveal the potential for developing alternative CO_2 reactive pathways through synthesis of novel electrolytes. Such an approach can be useful for enabling CO_2 conversion pathways in a broader range of media, which may help in identifying improved, stable electrolytes and/or catalysts for both the discharge and charge reactions in Li-CO_2 batteries; and for learning new strategies to tailor and manipulate CO_2-relevant reactions with improved selectivity. Future challenges will include developing systems with higher amine turnover to approach near-continuous operation or long cycle life, and to increase the capacity attainable at higher powers. Given the large number of capture chemistries currently under development, it is likely that a wide parameter space can be explored in the search for other potential capture-conversion electrolytes that facilitate optimal – neither too strong nor too weak – N-C bond formation and enable subsequent electrochemical transformations.

EXPERIMENTAL PROCEDURES

See Supplemental Information for details regarding experimental procedures.

SUPPLEMENTAL INFORMATION

Supplemental Information including experimental procedures, twenty-two figures, an amine turnover calculation, and a table comparing discharge capacity metrics can be found online with this article.

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AUTHOR CONTRIBUTIONS

A.K. and B.M.G. conceived of and designed the experiments, and A.K. conducted the measurements and performed the data analysis. A.K. and B.M.G. co-wrote the manuscript. M.H. performed Raman measurements and assisted in ^{1}H NMR analysis for reaction mechanism determination.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Figure 1: (A) Schematic of a combined capture-and-conversion Li-CO_2 cell with amine regeneration. (B) Discharge reaction scheme showing the target reduction pathway via selective cleavage of the N-C bond.

Figure 2. Photographs of (top row) solvent samples containing 0.1 M CO_2-loaded EEA species, and (bottom row) the same solutions upon introduction of 0.3 M $LiClO_4$.

Figure 3. ^1H NMR spectra of 50 mM EEA (bottom) and CO_2-loaded EEA (top) in DMSO-d_6.

Figure 4: (A) Time-dependent ^1H NMR spectra of a solution containing 50 mM CO_2-bound EEA in DMSO-d_6 before the addition of 0.3 M $LiClO_4$ (a), and 1 hour (b), 9 hours (c), and 24 hours (d) after the addition of 0.3 M $LiClO_4$. (B) Reaction scheme showing conversion of carbamic acid to carbamate and a free CO_2 upon Li^+-salt addition in DMSO.

Figure 5. (A) UV-Visible spectra of 0.3 M $LiClO_4$/DMSO containing $CoCp_2$ and EEA in the presence and absence of CO_2. The spectra of $CoCp_2$ and $CoCp_2^+$ are provided as reference. (B) Photograph showing color changes upon addition of $CoCp_2$ to the electrolyte containing either lean EEA (right) or CO_2-loaded EEA (center). A solution containing $CoCp_2$ and the electrolyte, not shown, yielded a color identical to the one observed for $CoCp_2$ with lean EEA.

Figure 6. *(*A): Discharge profiles of Li-CO_2 cells at 10 mA/g_c under Ar only, CO_2 only (physically dissolved, no EEA), lean (unloaded, no CO_2) EEA in DMSO, and loaded EEA-CO_2 in DMSO. (B) Discharge profiles for cells containing 100 mM EEA-CO_2 at varying current densities. (C) and (D) Concentration effect of EEA-CO_2 on discharge potential and capacities for Li-CO_2 cells discharged at 30 mA/g_c.

Figure 7. (A) X-ray diffraction of a GDL electrode discharged at 5.65 μA/cm^2. The XRD spectrum of crystalline Li_2CO_3, acquired from the International Center for Diffraction Data (ICDD) database (Ref. code: 00-001-0996) is provided as a reference. (B) SEM images of a discharged Vulcan carbon cathode at 30 mA/g_c. The inset shows an SEM image of a pristine electrode. (C) ATR-IR (transmittance) spectra of a pristine electrode, and an electrode discharged at 30 mA/g_c. (D) Ex-situ mass spectrometer analysis measuring moles of CO_2 evolved after discharged electrode treatment with H_3PO_4 and Fenton's reagent.[69] The discharged Li-CO_2 cell contained $^{13}CO_2$ and a ^{12}C cathode.