

Investigating Proton Shuttling and Electrochemical Mechanisms of Amines in Integrated CO₂ Capture and Utilization

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In this work, the authors demonstrate a fundamental issue that relates to the electrochemical capture and conversion (CCU) process in which amines and CO₂ react to form carbamate and ammonium for capturing CO₂ and subsequent in situ reduction of carbamate-released CO₂ at cathodes. They explore how amine steric structure and electrode property impact on CO₂ CCU. Two kinds of amine-containing molecules MEA and AMP with different steric hindrance are used as models to explore the effects of relevant ammonium and carbamate species on CO₂ reduction reaction on Cu and Pb electrode, respectively. By combining electrochemical CV, in situ FTIR spectroscopy and bulk CO₂ electrolysis methods, they found the MEA-H⁺ with lower steric hindrance (compared to AMP-H⁺) was uniformly arranged on the Cu electrode surface after applying a negative potential, which prevented the carbamate-released CO₂ attacking the electrode surface. On the contrary, the interaction between the MEA-H⁺ or AMP-H⁺ and Pb electrode is negligible, both of them all could transfer the CO₂ to the Pb electrode surfaces. I think the fundamental study is interesting and good, however, the following concerns should be addressed.

As shown in Figure 4 and 5, on both Cu and Pb electrodes, the MEA-CO₂ or AMP-CO₂ leads to poor CO₂ reduction currents compared with the dissolved CO₂ in the absence of amines owing to much lower surface CO₂ concentrations. Besides, the total FE of CO₂ reduction products is much less than 100% after adding MEA or AMP into the electrolyte, so what are the remaining products or where does the residual electricity go? It seems to be an energy-consuming process. If the addition of MEA or AMP does not promote the activity and selectivity of a desired product of CO₂ reduction, what is the practical and eye-catching significance of this work? How does the steric structure of amines affect the penetration of trace water molecules which are involved in the reacting with CO₂? Please refer to a previous report regarding this issue (doi.org/10.1073/pnas.1900761111). As for the impact of electrode materials, the authors may need consider the different potentials of zero charge for Cu and Pb electrodes which could lead to different adsorption behaviors at a given applied potential. Last but not least, the authors may also need to present a convincing guideline for the design of amines or other organic additives that favor improved electrochemical CO₂ CCU.

Reviewer #2

(Remarks to the Author)

The article examines the interplay between cathode materials and amines in CO₂ electroreduction within carbon capture and utilization (CCU) systems. It contrasts the performance of Cu and Pb cathodes with MEA and AMP amines, highlighting how amine structure and cathode interactions affect CO₂ reduction. Overall, it is an interesting work in understanding the interface interactions for directly converting capture solutions into fuels. My comments are given below:

1. The introduction section needs improvements. There are several statements are not well supported and a complete literature review is also needed. For example, why a synergistic coupling (i.e. direct process) between the two processes can improve the energy efficiency of the system leading to reduced cost of the products? A cascade system may allow for separate optimization of two processes hence leading to efficiency increase. An efficiency increase does not always lead to cost reduction. Please elaborate more to support this statement. The same concern goes for the statement: However, the process is still in its early stages of development as we know little about its governing parameters and rate-limiting factors,

so a rational design of such processes is not yet possible. This is not true as a lot of literature discusses electrochemical pathways for CO₂ capture and good understanding which enables rationale design is possible (recent literature for example: 10.1038/s44286-023-00003-3;10.1038/s41929-021-00699-7). More accurate descriptions are required.

2. Figure 1 lacks information on presenting the benefits of the direct processes.

3. The authors mentioned that an organic solvent is used to study the carbamates reduction mechanism. However, when MEA is usually used in an aqueous solution, is the reduction mechanism will be different? Or do the conclusions of this work still hold in a more practical situation?

4. On the Pb surface, why do we see a peak at -2.25 V for free CO₂? It is not straightforward to discuss the binding of atoms by only cyclic voltammetry data. I suggest re-organizing the results and discussions section to better support the statements.

5. Figure 4b, the $\delta_{as(NH_3)}$ at 1638 1/cm is not visible (or very weak) from the figure.

6. Can you comment on the bulk electrolysis data in Table 1 on why we do not see C₂+ products dominate as we usually find in an aqueous system?

7. Overall, the benefits of the direct process in this study are not well discussed as claimed in the abstract. Also, the product separation can be a challenge in the direct process. Especially in this study, the major product is the Formic acid, if the solution needs to be recycled for further capture process, the separation of liquid product is not straightforward, please elaborate on this point too.

Reviewer #3

(Remarks to the Author)

This manuscript by Garcia and coworkers addresses important questions of broad interest in the field of reactive capture of CO₂. Specifically the manuscript looks at the reactivity of Cu electrode with MEA -captured CO₂.

This topic is of general and broad interest at the present time and could be published in Nature Communications.

Main text

- To bring a broader appeal to the manuscript the authors could include a few more big picture citations in the introduction, or a couple citations to areas that are just a little outside of the scope (I define the scope as Cu mediated reduction of CO₂). Big picture references include recent perspective articles by Gallant (iScience), Xiang (Nature Catal), Berben (ACS Catalysis); Prakash (Acc ChemRes 2019)

- In the area of the mechanistic insights associated with amine-captured CO₂ and carbamate reactivity. There have been a couple very nice papers on this recently. By Morales Guio in Joule, by Gallant in ACS catalysis.

The manuscript is very detailed and contains a lot of work and a lot of material. This could be difficult to interpret and read for the non-specialist reader.

This work uses sulfolane as a solvent – and I see that this is important as a way to isolate the role of carbamate without interference from carbonate ions. It's a clever study. However, the behavior of these systems doesn't seem to model aqueous amine chemistry. It is known that a Cu electrode in aqueous amine solution dissolves so that the solution turns the blue color of Cu²⁺. IS the same observations made here? Can the authors make a direct link between these results – and generalize the observations to the behavior of Cu (or Pb) in aqueous amines?)

SI

- The use of sulfolane as a very polar but non-reactive solvent to isolate the behavior of the carbamate is a very creative and interesting aspect of this paper. It is certainly a good idea in terms of isolating the reactivity of the carbamate, even though it has the disadvantage of studying the carbamate under conditions that are less relevant to most carbon capture and conversion situations.

- another related comment about the sulfolane. I first noticed the use of this in the SI. Maybe the authors want to make it a little more clear in the main text about the strategy of using sulfolane.

- Section 4.2. I am not sure that 15 min is enough time to have the CO₂ react with the amine. In aqueous solution the reaction of the CO₂ with the amine takes 1 – 2 h. pH is a useful tool to measure completion in aqueous solution but I'm not sure if that is true in sulfolane. Can the authors provide additional CV's after the CO₂ has been sparging for 30 or 60 min or until it can be shown that changes stop?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed most of my concerns except the following issue. I think it should be resolved further before its potential acceptance.

The total FE of CO₂ reduction products is still far less than 100% after adding MEA or AMP into the electrolyte. The authors postulate that part of Faradaic current is used for a reduction or degradation of the solvent, thus leading to a decrease of FE. Nevertheless, it should be noted that GC and HPLC used for quantifying known components are not effective to detect or quantify unknown components. Therefore, it is recommended that the authors employ nuclear magnetic resonance spectroscopy for further detection and analysis of liquid products.

Reviewer #2

(Remarks to the Author)

My concerns are well addressed in the revised manuscript, and I am supporting the acceptance of the work.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have tried to apply NMR measurements to address my remaining concern. Due to the complication of the spectral results or the technical limit, I may accept their argument although it is not completely satisfying.

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Re: **Manuscript ID: NCOMMS-23-59441A**

“Unravelling Mechanisms and Proton Shuttling of Amines in Integrated Electrochemical CO₂ Capture and Utilization”.

We thank the reviewers for their constructive comments and for their compliments on our work. We have now revised the manuscript, addressing all the reviewers' comments. Changes in the revised version are **highlighted in yellow**. Below is a point-by-point response (in black) to the Reviewers' comments (in *blue italics*):

Reviewer comments 1:

1.As shown in Figure 4 and 5, on both Cu and Pb electrodes, the MEA-CO₂ or AMP-CO₂ leads to poor CO₂ reduction currents compared with the dissolved CO₂ in the absence of amines owing to much lower surface CO₂ concentrations. Besides, the total FE of CO₂ reduction products is much less than 100% after adding MEA or AMP into the electrolyte, so what are the remaining products or where does the residual electricity go?

We have now done new experiments and literature review to identify the remaining FE% obtained for amines-CO₂ (Figure 5). Figure S7 has been replaced and new chromatograms (Figure S8 and S9) related to the electrolysis experiments of the pure solvent and/or solvent-amine (without CO₂) have been added. Unfortunately the question of product formation remains somewhat open. Much more work, using different analysis would be needed to obtain full clarity.

We now discuss the results for the interested reader in the SI (page 20), and refer to this discussion on p.7 in the manuscript.

In the manuscript:

The remaining FE in Figure 5 suggests that not all of the electrons added to the electrochemical reduction of amine-CO₂ resulted into identifiable products, particularly with MEA as the CO₂ captor on Cu electrodes, in which electrolysis of pure sulfolane and sulfolane-amine (in absence of CO₂) showed a small current density (Figure S7), suggesting a reduction or degradation of the solvent is taking place (Table S7, Figure S7), though no product was detected by either GC and HPLC (Table S7, Figures S8 and S9). However, in situ FTIR analysis of the pure solvent and solvent-amine for both Cu and Pb electrodes characteristic bands at 3250–2750 cm⁻¹, assigned to C–H stretching of butane or tetrahydrothiophene which corresponds to sulfolane decomposition (cf. Figure S4 and S5). This suggests that solvent degradation, particularly prevalent on copper-based systems (Figure S4), is responsible for the FE losses observed in Figure 5. In the SI (Figures S7–S9), we discuss the possible reactions which may take place involving solvent degradation.

In the supporting information:

To understand the remaining FE% in Figure 5 for MEA-CO₂ and AMP-CO₂ on both Cu and Pb electrodes, we also performed electrolysis of the pure electrolyte (TEACl in sulfolane) and 1.0 M MEA or 1.0 M AMP in the electrolyte in the absence of CO₂, to investigate possible products from solvent reduction and or degradation (Figure S7). The HPLC and GC chromatograms of the corresponding measurements are shown in Figure S8 and S9, respectively.

In the case of the Cu electrode, we notice the current densities for MEA-CO₂ and AMP-CO₂ (Figure 3A) and (Figure S7A) are higher than the currents for free CO₂, however after 30 minutes of electrolysis, the current density for AMP-CO₂ has slightly decreased while the one corresponding to free CO₂ has increased. MEA-CO₂ remains at higher current density during the entire electrolysis measurement. In contrast, on the Pb electrode (Figure 3B), the current density for free CO₂ is higher than the currents obtained for MEA-CO₂ and AMP-CO₂; only at -2.5 V vs. Ag/AgCl the current densities of free-CO₂ and MEA-CO₂ are similar. Electrolysis measurements performed at -2.5 V vs. Ag/AgCl (Figure S7B) show that at fixed potential, MEA-CO₂ gives a higher current density, followed by free CO₂ and AMP-CO₂.

Noticeable all case, current density was obtained in the blank experiments (electrolysis of the amines without captured CO₂) which are shown in the SI (Table S7 and Figure S7C, D). The small currents resulting from the electrolysis measurements suggest that a reduction reaction and or a reductive degradation of the solvent are taking place. During the measurements, we therefore collected samples before and after electrolysis and analyzed them by HPLC and GC in order to quantify small organic molecules like 2-oxazolidone, N-(2-hydroxyethyl)-ethylenediamine, N,N'-di(hydroxyethyl)urea, 1-(2-hydroxyethyl)-2-imidazolidinone based on compounds that are detected in literature decomposition studies of amines. Unfortunately, the chromatograms only revealed peaks related the solvent and supporting electrolyte and minor impurities in the starting mixture that do not seem to increase over electrolysis time. An isolation from the (large amount) of organic supporting electrolyte and solvent and analysis method for the (low concentration) undesired byproduct / decomposition products (which also have a large variation in polarity) must be developed in order to investigate the products to obtain a more clear view on the missing FE. The mass and electron balance during

degradation cannot be completed with the current understanding of the breakdown chemicals in major amine-based solvents using our current HPLC and GC methods.

Previous literature on batteries have showed that the degradation of sulfolane primarily manifests through the cleavage of S=O bonds, leading to ring-opening reactions within the sulfolane molecule and eventually to the formation of SO₂. Despite the lack of discernible evidence in repeated GC and HPLC chromatograms for the pathways of sulfolane degradation, the in situ FTIR spectra (Figure S4A, C and E and Figure S5C) of the blank electrolyte (sat. TEACl in sulfolane) and 1.0 M MEA and 1.0 M AMP in the electrolyte (in absence of CO₂) show characteristic bands at 3250–2750 cm⁻¹, assigned to C–H stretching suggesting solvent degradation towards butane¹, or tetrahydrothiophene² which corresponds to known byproducts of reductive electrochemical sulfolane decomposition.

This suggests that solvent degradation, particularly prevalent on copper-based systems (Figure S4), might be responsible for the FE losses observed in Figure 5. Other investigations have highlighted the high reactivity of MEA's primary amine with SO₂, leading to the formation of R-NH₂-SO₂ adducts. Therefore, we propose that MEA can more readily engage in reactions with sulfolane's electrochemically reduced R-SO₂ species, owing to reduced steric hindrance, thereby generating intermediates that are more likely to attract and capture electrons. These observations support our hypothesis that the use of inner-sphere electrodes, such as those based on copper, may not be advisable when employing organic solvents or CO₂, given their propensity to enhance interactions with organic molecules through strong –C and –H bonds.

2. It seems to be an energy-consuming process. If the addition of MEA or AMP does not promote the activity and selectivity of a desired product of CO₂ reduction, what is the practical and eye-catching significance of this work?

Our work contributes to understanding the role and mechanism of amines in direct electrocatalytic CO₂ reduction in carbon capture and utilisation. Instead of employing the amine just as a capturing agent, we show that the way that amines interact with the electrode surface play a role in the reaction mechanisms for CO₂ and proton reduction reactions. Our findings concerning the electrode-amine interaction open new possibilities for developing electrochemical and chemical absorption setups for efficient carbon capture and utilization. By understanding the complex interactions involved in amine-based CO₂ reduction, our study motivates other researchers to design amines that can serve as templates that influence the composition of the final CO₂ reduction products. This is now explained and emphasised in the revised version (page 7 and 8) and abstract.

Our results contribute to understanding the role and mechanism of amines in direct electrocatalytic CO₂ reduction in carbon capture and utilization. We demonstrate that amines play an active part in surface mechanisms.

Unraveling the complex mechanisms of amine-based CO₂ reduction could encourage the development of template amines that dictate the product composition in CO₂ reduction outcomes.

Abstract:

This study reveals the detailed mechanistic synergies at the interface of the cathode and CO₂ sorption in a fully integrated carbon capture and utilization (CCU) system. We explore how amines absorb CO₂, forming ammonium and carbamate, and how these affect CO₂ electroreduction. Our analysis demonstrates that electron transfer mechanisms, carbamate bond strengths, and local proton concentrations critically influence the reduction process. On Cu electrodes, structural changes in amine-CO₂ complexes impede CO₂ reduction due to surface blockage by ammonium species. In contrast, on Pb electrodes, the absence of strong surface interactions allows proton-shuttling by ammonium, enhancing proton incorporation into hydrocarbon products, especially with sterically unhindered amines. Using in situ spectroscopic techniques, we dissect the complex molecular interactions essential for effective amine-based CO₂ electroreduction, providing insights into CCU technology optimization and promoting advances in selective CO₂ conversion.

3. How does the steric structure of amines affect the penetration of trace water molecules which are involved in the reacting with CO₂? Please refer to a previous report regarding this issue (doi.org/10.1073/pnas.190076111).

We have now explained this issue in the revised manuscript as follows (page 7).

The steric structure of amines, exemplified by the α-methyl groups in AMP, creates hindrance that affects the penetration and solvation of trace water molecules. These structural differences lead to stronger hydrogen bonding of water with the AMP nitrogen atom compared to MEA. Consequently, the reactivity with CO₂ is influenced, with a temperature-dependent shift in AMP's favor that facilitates carbamate formation. Essentially, the methyl groups in AMP modulate the hydrogen bond network, impacting both solvation dynamics and interaction with CO₂ in the presence of trace water

4. As for the impact of electrode materials, the authors may need consider the different potentials of zero charge for Cu and Pb electrodes which could lead to different adsorption behaviors at a given applied potential.

We have now explained this issue in the revised manuscript as follows (page 3).

The variance in onset potentials is attributable to the different potentials of zero charge (PZC), which dictates the adsorption preference for anions when the applied potential is higher than the zero-charge potential, and vice versa for cations. For Cu and Pb, PZC is +90 mV and -620 mV vs. NHE, respectively. The higher potential of zero charge of Cu suggests its enhanced ability to attract cations at less negative potentials compared to Pb. Consequently, this affects the electrochemical reaction kinetics and dictates the location of the reduction wave on the electrode surface. As a result, cationic species, such as protons and MEA/AMP-H⁺, preferentially accumulate at Cu, influencing the electrocatalytic activity and surface processes.

5. Last but not least, the authors may also need to present a convincing guideline for the design of amines or other organic additives that favor improved electrochemical CO₂ CCU.

We thank the reviewer for this suggestion. A guideline for the design of amines (and other organic additives that can improve electrochemical CO₂ CCU) has been included in the supporting information, which is referred to from the main manuscript Section S10. Guidelines for Developing a Single-Cell CCU system are now included on page 7

“10. Guidelines for Developing a Single-Cell CCU system.

More investigation into the different designs and materials is needed before scaling up a direct CCU system for industrial usage. Our goal is to provide researchers with some recommendations on necessary research topics and considerations while developing a single-cell CCU system. Strategies to probe these questions are needed, but the problems are complex: a small change in one solution parameter affects the entire system of complex equilibria.

- The amines must be compatible with electrodes used and electrochemically stable. The (CO₂-captured) amines need to be stable against parasitic reduction or (oxidation in a non-divided cell) during the voltage window of interest in order to be used in electrochemical systems.
- Knowing the active species clearly is crucial to knowing how CO₂ is reduced to its ultimate products. This will make it easier to understand and design amines with product selectivity in mind.
- Commercially available amines were created with specific purposes in mind, such as reduced energy needs for thermal desorption and controlled capacity swings. Further research is necessary to determine the specific requirements that may apply to amines used in electrochemical processes.
 - Aiming for low CO₂ absorption (i.e. in direct air capturing systems with low CO₂ concentration) to match the rate of electrochemical CO₂ conversion may be beneficial.
 - Weak amine-CO₂ interaction might be beneficial to ease CO₂ release at the electrode surface
 - Amines having additional proton shuttling capacity, such as additional -OH or -NH₂ groups, may produce more proton-containing or C₂ products.
 - Amines with multiple CO₂ binding spots might increase the formation of C₂ products.
 - The concentration of the active species may have an effect on product distribution; this has to be further studied.

All species should dissolve in the solvent, including CO₂, supporting electrolyte, and (CO₂-captured) amines. Simple miscibility problems (e.g., nonpolar amines cannot be readily dissolved in aqueous media) and changes in physicochemical characteristics of solutions caused by CO₂

- Absorption, leading to viscosity increases, precipitation, and gelation, can be detrimental to the electrochemical system
- Before choosing a solvent, one needs look at how the solvent interacts with the electrode, CO₂, and (CO₂-captured) amines. It is necessary to consider the H-bonding characteristics of water molecules in aqueous solvents and ammonium fragments in aprotic organic solvents.
- The avoidance of parasitic proton consumption from the amine or solvent is crucial for nonaqueous electrolytes. It is critical to ensure that there is proton flow from the counter electrode compartment. A shortage of protons might have long-term consequences for the reaction.
- The electrocatalyst must be compatible and stable with the amine and solvent systems, especially during long-term electrolysis.
- Because of the distinct features of each cathode material, product distribution varies by the combination of electrode material, amine, and solvent. This must be investigated prior to further optimization of the system.
- We believe that aligning CO₂ capture and electrochemical conversion rates would have a positive impact on the system.
- A disadvantage of a fully integrated system is that the different amounts of liquid and dissolved molecules make it difficult to separate the reaction mixture from the products. This must be further researched before the technology may be commercially viable. Science can explore biphasic solvent systems in which products are separated from

the bulk using amines and solvents with physicochemical properties that differ from those of the products being generated.”

Reviewer comments 2:

1. The introduction section needs improvements. There are several statements are not well supported and a complete literature review is also needed. For example, why a synergistic coupling (i.e. direct process) between the two processes can improve the energy efficiency of the system leading to reduced cost of the products? A cascade system may allow for separate optimization of two processes hence leading to efficiency increase. An efficiency increase does not always lead to cost reduction. Please elaborate more to support this statement.

We revised our introduction by providing a detailed comparison and outlining the advantages and drawbacks of both direct and indirect amine-based CCU systems. We have enhanced Figure 1 with an energy diagram, derived from Sullivan et al.’s work, to illustrate the energy savings offered by the direct system and the benefits of a single-unit process.

CCU processes comprise three important steps: CO₂ separation from the gas mixture, its release and capture material regeneration, and electrochemical conversion (Figure 1B). Electrochemical methods are gaining favor over traditional temperature or pressure modulation for their energy efficiency. These methods usually function as separate units, providing flexibility but requiring multiple systems.

Recent advancements suggest that integrating the capture and conversion processes can enhance energy efficiency and reduce costs (Figure 1C and 1D). For example, using captured CO₂ directly in electrolysis circumvents the energy-intensive desorption step, leading to cost savings on CO₂ compression and equipment. Energy analyses indicate potential energy savings of up to 44% for integrated systems over traditional ones.

The integration processes, however, introduces complex physicochemical and engineering considerations, necessitating a reevaluation of existing knowledge and exploration of new scientific frontiers. One of the key aspects of this integrated approach is the pH-dependent behavior of CO₂ capture using aqueous amines, which significantly influences both the capture efficiency and the subsequent electrochemical conversion process. For instance, studies by Morales-Guio et al and Gallant et al have delved into the pH dependence on the interaction between amines and CO₂, which leads to the formation of species like carbamates and bicarbonates, whose equilibrium is highly sensitive to the solution pH. The pH can influence the competitive adsorption of different species at the electrode interface, affecting electron transfer to the desired carbamate active species and ultimately the efficiency of CO₂ reduction. Their results suggest that the molecular design of amines, including their pKa, provides a means to tailor the capture-conversion process by affecting the initial reaction rate with CO₂, the strength of bonding with CO₂, and the pH of the solution. Amines with different pKa values can be used to optimize the capture solution pH to balance the demands for efficient CO₂ capture and favorable conditions for electrochemical conversion.

A considerable pH drop during capture can also promote the hydrolysis of the carbamate to bicarbonate, making it difficult to determine the involvement of the carbamate in aqueous conditions. Depending on the electrolyte medium, electrochemically reactive capture can produce a variety of products frequently with high selectivity, including CO, formic acid, and solid alkali carbonates.

These findings are vital for refining integrated CCU systems and enhancing their efficiency and selectivity for various products such as CO, formic acid, and solid alkali carbonates.

The application of carbamates for direct electrochemical CO₂ reduction is an emerging field of research, yet many of its critical parameters, such as amine type, solvent system, and electrocatalyst selection, along with rate-limiting factors like reactant concentration and reactor conditions, remain to be fully elucidated. This current gap in understanding hinders the systematic design of optimized direct capture-electrolysis reactors, underscoring the need for comprehensive investigations at this formative stage.

2. The same concern goes for the statement: However, the process is still in its early stages of development as we know little about its governing parameters and rate-limiting factors, so a rational design of such processes is not yet possible. This is not true as a lot of literature discusses electrochemical pathways for CO₂ capture and good understanding which enables rationale design is possible (recent literature for example: 10.1038/s44286-023-00003-3;10.1038/s41929-021-00699-7). More accurate descriptions are required.

Our intention was to indicate the use of carbamates as the exclusive source of CO₂. The statement has been revised for clarity, and the references suggested by the reviewer are now cited therein (page 1), as described above.

2. *Figure 1 lacks information on presenting the benefits of the direct processes.*

We have now added an energy diagram to Figure 1 to highlight energy benefits of the direct system and clarify the advantage of a single-unit only system.

3. *The authors mentioned that an organic solvent is used to study the carbamates reduction mechanism. However, when MEA is usually used in an aqueous solution, is the reduction mechanism will be different? Or do the conclusions of this work still hold in a more practical situation?*

The mechanism would be different in aqueous media. We have now clarified these issues on page 2:

Organic solvent sulfolane was used to solubilize amine and carbamate/ammonium ($R-COO^-/-H^+$) species, thus preventing the formation of insoluble carbonate ions (CO_3^{2-}) and bicarbonate, which water promotes. This approach avoids the complexities introduced by water acting as a proton shuttle and allows us to focus on the role of carbamate species as the sole CO_2 donor.

and on page 7:

As we expected, our findings with sulfolane solvent differ from those reported in aqueous solutions on Ag electrode. While we found an amine dependence, the studies in aqueous solvent show a weak amine-dependence although the proton shuttling effect of the formed ammonium species is clear. The most obvious explanation for such difference is the prevention of bicarbonate formation, which is favored in presence of water, however the significance of (pH dependent) H-bonds through water should not be overlooked.

4. *On the Pb surface, why do we see a peak at -2.25 V for free CO_2 ? It is not straightforward to discuss the binding of atoms by only cyclic voltammetry data. I suggest re-organizing the results and discussions section to better support the statements.*

We have now explained these results on page 3:

Conversely, on the Pb electrode (Figure 3B), which is more inert due to weaker binding of C and H atoms, the free CO_2 reduction takes place at -1.98 vs. Ag/AgCl. A pronounced peak at -2.25 V vs. Ag/AgCl aligns with the diffusion-limited behavior of CO_2 , in agreement with previous literature. This observation confirms that Pb surface follows the outer-sphere electron transfer pathway instead of surface substrate absorption.

5. *Figure 4b, the $\delta_{as(NH_3)}$ at 1638 $1/cm$ is not visible (or very weak) from the figure.*

We have revised the text on page 4.

“visible as a shoulder at 1638 cm^{-1} .”

6. *Can you comment on the bulk electrolysis data in Table 1 on why we do not see C_2+ products dominate as we usually find in an aqueous system?*

We have now explained these results on page 6.

These results contrast to previous literature for CO_2RR in aqueous solvent, where a high amount of C_{2+} hydrocarbons is produced. The mechanism to C_2 products can either follow a C_1 pathway, where *COH is the key intermediate, leading to both methane and C_2 products, or it can follow a C_2 pathway in which C-C coupling occurs via dimerization of two adsorbed *CO leading to the formation of only C_{2+} products. Our results suggest that dimerization follows the C_2 pathway because methane was not identified as a product under any of our experimental conditions (Table 1). However, the FE of C_{2+} is very low because a certain concentration of protons must be available for the hydrogenation of *CO intermediate to C_{2+} hydrocarbons. Similar results were obtained previously by our group on a Cu electrode in acetonitrile solvent in the presence of different concentrations of water. Ethylene, for instance, was detected only when the concentration of water

was higher than 500 mM. Additionally, the solubility of CO, the key intermediate, is lower in organic solvent than in aqueous medium, hindering accessibility of such species to the electrode surface.

7. Overall, the benefits of the direct process in this study are not well discussed as claimed in the abstract. Also, the product separation can be a challenge in the direct process. Especially in this study, the major product is the Formic acid, if the solution needs to be recycled for further capture process, the separation of liquid product is not straightforward, please elaborate on this point too.

We revised the abstract and introduction to better highlight the direct process's advantages, such as operational simplicity and energy efficiency, with a new energy diagram in Figure 1 for clarity. The revised version also addresses the separation of the products from the electrolyte (SI-Guidelines session).

Regarding the comments of reviewer 3:

1. To bring a broader appeal to the manuscript the authors could include a few more big picture citations in the introduction, or a couple citations to areas that are just a little outside of the scope (I define the scope as Cu mediated reduction of CO₂). Big picture references include recent perspective articles by Gallant (iScience), Xiang (Nat Catal), Berben (ACS Catal); Prakash (Acc ChemRes 2019).

We have updated the introduction in line with the reviewer's feedback to provide a comprehensive overview and have incorporated the additional references as recommended. (See response to question 1 – Reviewer 2)

2. In the area of the mechanistic insights associated with amine-captured CO₂ and carbamate reactivity. There have been a couple very nice papers on this recently. By Morales Guio in Joule, by Gallant in ACS Catal.

We appreciate the reviewer's comments and we have highlighted these papers in the introduction (page 1).

For instance, studies by Morales-Guio et al, and Gallant et al have delved into the pH dependence on the interaction between amines and CO₂, which leads to the formation of species like carbamates and bicarbonates, whose equilibrium is highly sensitive to the solution pH. The pH can influence the competitive adsorption of different species at the electrode interface, affecting electron transfer to the desired carbamate active species and ultimately the efficiency of CO₂ reduction. Their results suggest that the molecular design of amines, including their pK_a, provides a means to tailor the capture-conversion process by affecting the initial reaction rate with CO₂, the strength of bonding with CO₂, and the pH of the solution. Amines with different pK_a values can be used to optimize the capture solution pH to balance the demands for efficient CO₂ capture and favorable conditions for electrochemical conversion

3. The manuscript is very detailed and contains a lot of work and a lot of material. This could be difficult to interpret and read for the non-specialist reader.

We have modified parts of our discussion to make it more concise. We also added some discussion points in the SI. Some of our schemes in Figure 4 and 5, we prefer to keep in the text, indeed to help non-experts to better visualize our discussion.

4. This work uses sulfolane as a solvent – and I see that this is important as a way to isolate the role of carbamate without interference from carbonate ions. It's a clever study. However, the behavior of these systems doesn't seem to model aqueous amine chemistry. It is known that a Cu electrode in aqueous amine solution dissolves so that the solution turns the blue color of Cu²⁺. Are the same observations made here?

We have now clarified this by adding the following comments to the SI (session 6.1) and Figure S15.

The importance in working in a two-compartment cell is to avoid products generated at the cathode to be oxidized at the anode. Additionally, the oxidative environment (anodic /counter electrode compartment)—where ion leaching may occur—and the reductive environment (Cathodic / working electrode compartment)—where CO₂ reduction occurs—are separated by a membrane. As a result, there is little probability that Cu²⁺ will be present in our working electrode compartment, in case traces of water are also present in the solution. To examine the color shift of the solvent and presence of Cu²⁺, we also conducted the electrolysis of the amine using a Cu wire in a glass (see-through) H-Cell, as shown in Figure S15. No color change was observed during these experiments.

5. Can the authors make a direct link between these results – and generalize the observations to the behavior of Cu (or Pb) in aqueous amines?)

Because of the mechanism in water would differ from the mechanism in sulfolane solvent, we prefer to not make such link in the discussion of our work.

However for comprehension, while our study focuses on the electrocatalytic behavior in sulfolane solvent, where the reaction mechanisms may differ from those in aqueous solutions, there are fundamental insights that can be considered relevant across both media. In aqueous amines, the presence of nitrogen-containing compounds has been demonstrated to enhance the catalytic reduction of CO₂ on Cu and Pb electrodes due to disruption of CO₂ linearity or stabilization of reaction intermediates. These effects bear similarity to those observed in our sulfolane system. However, we observe that in sulfolane, the electrode surface tends to be covered with protonated species derived from the solvent, which differs from the aqueous condition where protonated amines are prevalent. The proton shuttling in our aprotic solvent system is facilitated by ammonium species, contrasting with the aqueous mechanisms involving water. While Pb electrodes benefit from this environment, Cu electrodes do not exhibit the same level of enhancement. Therefore, while direct comparisons are limited, the findings provide valuable contributions to the broader understanding of CO₂ reduction mechanisms on metal electrodes in different solvent environments.

For further context, we also refer the Reviewer to our response to question 3 by Reviewer 2, which addresses related aspects.

6. The use of sulfolane as a very polar but non-reactive solvent to isolate the behavior of the carbamate is a very creative and interesting aspect of this paper. It is certainly a good idea in terms of isolating the reactivity of the carbamate, even though it has the disadvantage of studying the carbamate under conditions that are less relevant to most carbon capture and conversion situations.

Thank you for your comment. We have clarified the advantage of using Sulfolane as a solvent. (page 2 and SI 1.3 session).

In the manuscript:

Organic solvent sulfolane was used to solubilize amine and carbamate/ammonium (R-COO⁻/-H⁺) species, thus preventing the formation of insoluble carbonate ions (CO₃²⁻) and bicarbonate, which are promoted by the presence of water. This approach avoids the complexities introduced by water acting as a proton shuttle and allows us to focus on the role of carbamate species as the sole CO₂ donor.

In the SI:

Sulfolane is a solvent that is used in a gas treatment process called the Sulfinol process. A Sulfinol[®] solution is a mixture of diisopropanolamine (30-45%) or methyl diethanolamine, sulfolane (40-60%), and water (5-15%).⁴² Because of this, we believe that organic solvents, such as sulfolane, might be a practical solution for CCU.

7. Another related comment about the sulfolane. I first noticed the use of this in the SI. Maybe the authors want to make it a little more clear in the main text about the strategy of using sulfolane.

We have now expanded the explanation in the SI and added a short explanation in the main text as suggested (Similar to the above answer).

8. Section 4.2. I am not sure that 15 min is enough time to have the CO₂ react with the amine. In aqueous solution the reaction of the CO₂ with the amine takes 1 – 2 h. pH is a useful tool to measure completion in aqueous solution but I'm not sure if that is true in sulfolane. Can the authors provide additional CV's after the CO₂ has been sparging for 30 or 60 min or until it can be shown that changes stop?

We have run additional experiments following the reviewer's suggestion, the results and experimental details are included in the revised supporting information (4.2 session and Figure S14A).

To assure that 15 minutes purging with CO₂ was sufficient, we performed CVs with a longer CO₂ purging period (Figure S12A, B). A slightly larger current density is seen when the amines are purged with CO₂ longer than 15 minutes. However, we found these experiments unsatisfactory when determining whether 15 minutes of CO₂ purging is sufficient due to the considerable overlap with free CO₂. Therefore, we performed ATR-FT-IR (ReactIR 15, Mettler-Toledo, 1400003) using a Silicon (Mettler-Toledo, 14472000) probe to track the formation of the carbamates ($N\text{-COO}^-$, ν_{as} , 1561 cm⁻² and 1579 cm⁻² for MEA and AMP respectively, Table S1). The probe is accessorized with a temperature probe to track the solvent's temperature because the CO₂-amine adduct production is an exothermic process. After around 9 minutes (Figure S12C, D), the band's intensity stabilized, suggesting that the amines were completely converted to carbamates. Moreover, the solvent temperature did not rise any higher beyond this point, suggesting that the reaction had reached complete conversion since no additional heat was released. Therefore, we conclude that 15 minutes is sufficient for full amine to carbamate conversion.

We trust that we have revised the manuscript as requested. We would be more than willing to make further changes if so required.

Manuscript ID: NCOMMS-23-59441B

“Unravelling Mechanisms and Proton Shuttling of Amines in Integrated Electrochemical CO₂ Capture and Utilization”.

We thank Reviewer for their valuable comment and we have done a new series of experiments, addressing the reviewer's 1 comment. Changes in the revised version are **highlighted in yellow**. Below is a point-by-point response (in black) to the Reviewers' comments (in *blue italics*):

Reviewer 1

The authors have addressed most of my concerns except the following issue. I think it should be resolved further before its potential acceptance.

The total FE of CO₂ reduction products is still far less than 100% after adding MEA or AMP into the electrolyte. The authors postulate that part of Faradaic current is used for a reduction or degradation of the solvent, thus leading to a decrease of FE. Nevertheless, it should be noted that GC and HPLC used for quantifying known components are not effective to detect or quantify unknown components. Therefore, it is recommended that the authors employ nuclear magnetic resonance spectroscopy for further detection and analysis of liquid products.

Response: We thank the Reviewer for his positive comment about our work and for the valuable feedback. We have now conducted additional experiments using ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy and the results and discussion are presented in Figure S16-S17 (page 26) and on page 7 in the manuscript.

Page 7 (manuscript)

Additionally, we performed ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy. Our results depicted in Figure S16 suggest that solvent decomposition indeed plays a role in the reduced FE observed in the absence of CO₂ (Figure 5). The presence of CO₂ shifts the system toward CO₂ reduction products like formic acid, thereby improving the FE. However, the overlapping NMR signals preclude the identification of all degradation products (Figure S17).

Page 26 (SI)

To study possible solvent degradation, and explain the remaining Faradaic efficiency, showed in Figure 5 (especially in the presence of amines), we ran ¹H and ¹³C nuclear magnetic resonance (NMR) experiments. The results are showed in Figure S16, while reference spectra are showed in Figure S17.

We first used ¹H NMR to detect degradation products in the electrolyte containing TEACl and Sulfolane (Figure S16A-B). However, the undeuterated solvent caused a large background peak between 1.5–4 ppm, making difficult the identification of products. Despite these challenges, minor peaks were observed in the NMR spectra, with a clearer one at 5.2 ppm, on both Pb and Cu electrodes, indicating possible decomposition of sulfolane or TEA⁺. However, due to the presence of overlapping peaks from the solvent, definitive identification of these degradation products was challenging. To overcome these limitations, we attempted to use ¹³C NMR, which typically offers more isolated peaks. However, due to the lower sensitivity of ¹³C NMR and the relatively small concentrations of degradation products, the results were inconclusive, and we did not include them.

We further investigated the electrolysis of MEA and AMP, in N₂ degassed and Amine-CO₂ solution (Figure S16C-J) to understand their roles in the system. The addition of MEA led to additional peaks in the ¹H NMR spectra, but as with the blank experiments, overlapping regions prevented the identification of new products. The results with AMP presented even more challenges, including phase separation during the NMR measurements, leading to peak broadening and further complicating the analysis. However, in the presence of CO₂ (amine-CO₂), a significant new peak appeared at 8.7 ppm on both Pb and Cu electrodes. We attribute this to the

formation of formic acid from the reduction of CO₂. Note that its intensity is smaller on Cu electrodes, in agreement with our results showed in Figure 5.

Interestingly, the absence of the previously observed peak at 5.2 ppm in these experiments supports the hypothesis that solvent decomposition significantly contributes to the missing FE in the absence of CO₂.

Reviewer 2

My concerns are well addressed in the revised manuscript, and I am supporting the acceptance of the work.

Response: Thank you very much for your positive feedback and for supporting the acceptance of our manuscript. We are glad that our revisions have satisfactorily addressed your concerns. Your insights and comments have been invaluable in improving our work.

We trust that the revisions meet the requested changes.