

Enhanced Electrocatalytic Activity of Primary Amines for CO₂ Reduction Using Copper Electrodes in Aqueous Solution

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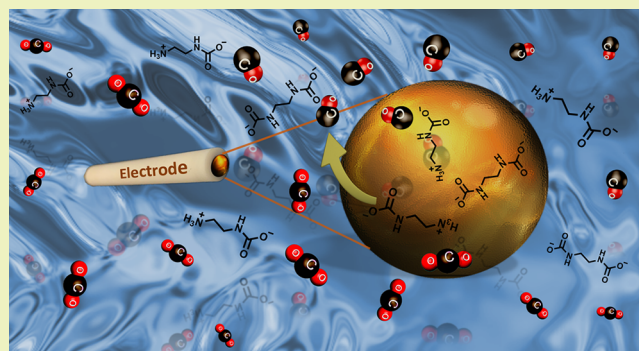
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Supporting Information

ABSTRACT: Carbon dioxide (CO₂) is an environmentally harmful “greenhouse gas” that is present in abundant quantities in the Earth’s atmosphere. Due to the stability of its structure, it is notoriously regarded as an inert molecule that will only react under harsh conditions such as high temperature or pressure. Electrochemical reduction of CO₂ to value-added materials is a sustainable and potentially profitable way to curb greenhouse gas emissions; however, the challenge of amassing a sizable CO₂ concentration in the active medium persists. Here, we find that various amines, already known to be effective absorbents for CO₂ through the formation of carbamates, can be used directly as substrates for selectively reducing CO₂ to carbon monoxide (CO) at room temperature and ambient pressure. Several primary amines were evaluated using glassy carbon and copper working electrodes for systematic comparison. Here, we demonstrated that use of copper electrodes dramatically enhances current density (up to −18.4 mA/cm² at −0.76 V vs RHE) compared to glassy carbon electrodes (−0.63 mA/cm²) using ethylenediamine (EDA) as the catalyst. Moreover, the faradic efficiency was significantly increased from 2.3% to 58%. This concrete finding shows potential to enhance amine catalytic activity for efficient CO₂ reduction. This research has introduced a potentially more sustainable and green method for carbon capture and reduction systems.

KEYWORDS: CO₂ conversion, CO₂ capture, Electroreduction of CO₂, CO₂ utilization, Green chemistry, CO₂RR and Copper



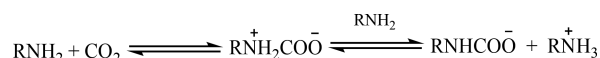
■ INTRODUCTION

Carbon dioxide (CO₂) is the main greenhouse gas responsible for climate change.¹ The strong correlation between elevated anthropogenic CO₂ emissions and meteorologic aberrations has encouraged researchers and governments to develop new carbon capture and storage (CCS) strategies to reduce atmospheric CO₂ concentrations.² The capture of CO₂ using amine complexes is well studied and has been applied industrially for the past seven decades,³ but attention has since shifted to approaches that can convert CO₂ to value-added materials through different techniques like CO₂ reduction reactions (CO₂RR).^{4–8} Current industrially implemented CCS strategies involve aqueous solutions of primary or secondary amines such as monoethanolamine (MEA) and diethanolamine (DEA), which can selectively separate and capture CO₂ from a mixture of gases and subsequently release it at high temperatures as a pure, concentrated stream that can be stored by various means.^{9–11}

The reversible mechanism by which primary and secondary amino groups first react with CO₂ to form zwitterions, followed by reaction with another mole of amine to yield a carbamate salt, was first proposed by Caplow (Scheme 1).^{12,13} Further work by Hwang et al. has shown water can interact

with the carbamate to regenerate the amine via protonation/deprotonation steps.¹⁴

Scheme 1. Carbamate Formation Using Primary and Secondary Amines



Although widely implemented, there are several challenges associated with CCS. These include the high cost of the capturing process (around 50–150 USD per ton of CO₂),^{3,15} release of corrosive products from the degradation products of amine solutions, and the risk of potential leakage from underground stores of CO₂.^{16,17} As such, strategies that can capture and convert CO₂ into reusable, value-added synthons such as methanol,¹⁸ carbon monoxide, and formate ions^{19–21} have proven to be more attractive in recent years.^{7,22} Of the various approaches taken for CO₂ capture, electrochemical

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methods offer a greener alternative to the harsh conditions and reagents typically associated with industrial use of amine-based CO₂ absorbents.^{7,23,24}

A number of researchers have performed electrochemical reduction of CO₂ using various metal electrodes;^{23,25–29} copper (Cu) has been shown to be the most effective at producing hydrocarbons.^{24,27,30–34} It has also been shown that copper itself can reduce CO₂ to different products such as CO and formic acid.^{34,35}

Herein, in this project, the electrocatalytic activities of common, commercially available amine compounds including monoethanolamine (MEA) (1), ethylenediamine (EDA) (2), and decylamine (DCA) (3) (Figure 1) were studied using

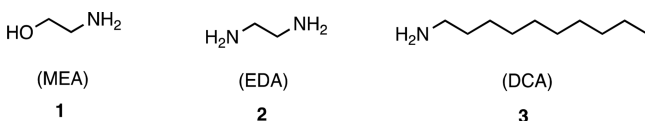


Figure 1. Molecular structures of MEA (1), EDA (2), and DCA (3).

both glassy carbon electrodes (GCEs) and Cu electrodes for a systematic comparison. These compounds, whose carbon capture ability has already been proven,^{12–14,36} are shown to also possess notable potential for application in CO₂ valuation and have demonstrated to reduce CO₂ to CO.

RESULTS AND DISCUSSION

A small volume (1 mL) of each compound (1–3) was purged with CO₂ in a scintillation vial at room temperature to obtain carbamate salts in either viscous form (in the case of compound 1, shown in Figure S1) or as a white solid (in the case of compounds 2 and 3). The resulting carbamate salts of compounds 1–3 were characterized using nuclear magnetic resonance (NMR) and Fourier-transform infrared spectroscopy (FTIR).

The ¹³C NMR spectroscopy, which is one of the most sensitive methods to detect inorganic carbon species in solutions,¹⁵ was used to identify the presence of the carbamate peak around 164 ppm in EDA-CO₂. This peak was absent in the spectrum of the starting material (Figure S2) and is consistent with literature values.³⁷ In the case of MEA, the small carbonyl peak (Figure S4) was further confirmed using labeled carbon dioxide (¹³CO₂), as indicated by a sharp peak at 164 ppm (Figure S5).

To differentiate the formation of the desired carbamate product from the possible formation of carbonate byproducts due to the presence of moisture during the purging process, a ¹³C NMR control experiment was performed with DCA using J. Young NMR valve tubes (Figure 2b). The ¹³C NMR results of DCA-¹³CO₂ in CDCl₃ under sealed and moisture-free conditions (Figure 2b) were compared with dissolved ¹³CO₂ in water and CDCl₃ (Figure 2c). This comparison clearly differentiates the carbamate peak at 164 ppm from the carbonate peak at 161 ppm, confirming that the small amount of environmental moisture present in our experiments was negligible and that the desired carbamate was the major product of the reaction.

The formation of the carbamate from compounds 1–3 was further confirmed by FTIR (Figures S3, S6, and S8), in which the presence of the single N–H stretch at ~3300 cm^{–1} suggests the formation of a secondary amine. Moreover, the

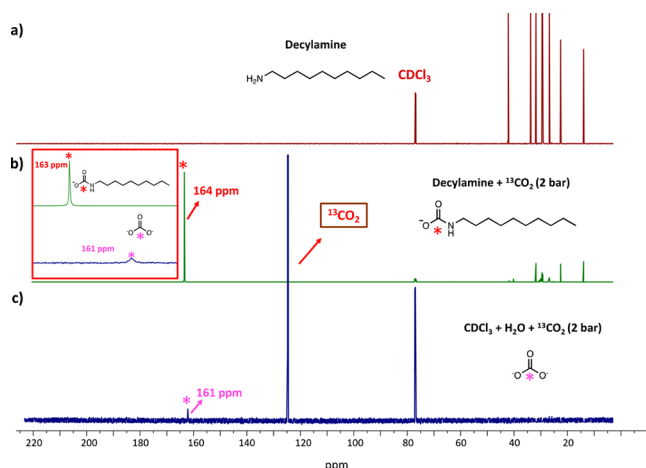


Figure 2. ¹³C NMR spectra of neat DCA (a), DCA-¹³CO₂ (b), and H₂O-¹³CO₂ (c) in CDCl₃.

characteristic carbamate peaks at ~1630 and ~1550 cm^{–1} further support its formation.

A two-compartment electrochemical H-cell was used for CO₂ electrolysis (Figure S10). The cathodic compartment contained either GCE or Cu as the working electrode and was placed in close proximity to the Ag/AgCl reference electrode. The anodic compartment included platinum (Pt) as the counter electrode which was separated from the cathodic compartment by a Nafion exchange membrane. The common measure of evaluating electrochemical performance is through cyclic voltammetry (CV) and controlled potential electrolysis.³⁸ Experiments were performed in the presence and absence of CO₂ using bare GCE and Cu working electrodes as well as with carbamate compounds to uncover the role of both electrodes and amino groups in the reduction of the carbamate.

Figure 3a and b compares the CV of carbamate compounds 1–3 (0.1 mM) using GCE as the working electrode and 0.1 M NaClO₄ as the electrolyte in water. Although an increase in the

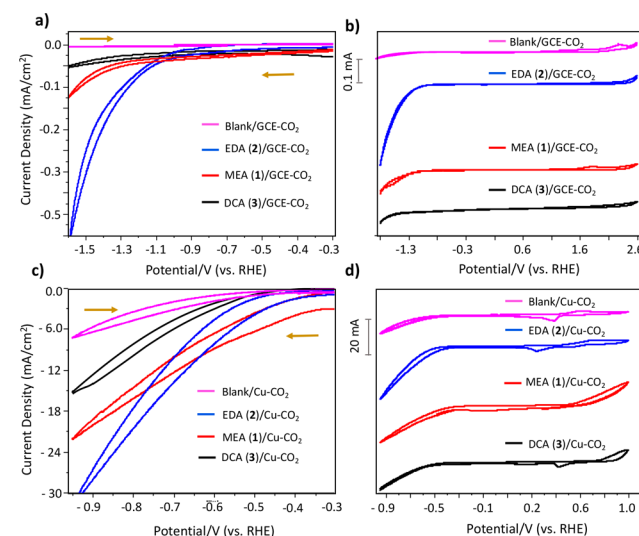


Figure 3. Cyclic voltammogram of (a) and (b) compounds 1–3 (0.1 mM) under CO₂ with GCE and (c) and (d) compounds 1–3 (0.1 mM) under CO₂ with Cu electrode in 0.1 M NaClO₄ solution. Conditions: scan rate, 100 mVs^{–1}; working electrode, glassy carbon/copper; reference electrode, Ag/AgCl; counter electrode, platinum.

cathodic current was observed upon addition of CO₂ to each analyte, the significant increase in current density with EDA-CO₂ (2) far outpaces that of MEA-CO₂ (1) and DCA-CO₂ (3) at approximately −1.0 V vs RHE. This increase in the cathodic current was significantly enhanced when the Cu working electrode was used (Figure 3c and d). A single reduction peak (Cu^{II}/Cu^I) at 0.43 V vs RHE in the cathodic potential scan and at 0.6 V vs RHE in the return anodic potential scan was observed.^{39,40} The peak pair is attributed to the anodic and cathodic peaks of the Cu (0) to Cu(II) oxidation.⁴¹

Next, electrochemical CO₂ reduction in a 0.1 M NaClO₄ aqueous solution was performed under controlled electrode potentials using chronoamperometry (Figure 4). The electro-

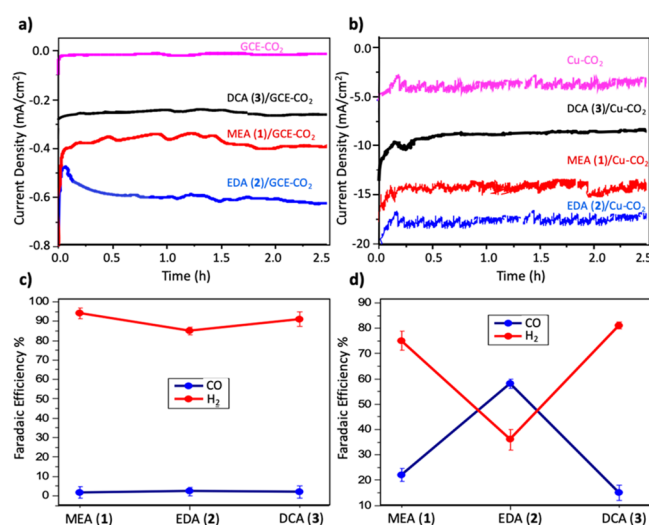


Figure 4. Representative chronoamperograms of electroreduction of CO₂ catalyzed by compounds 1–3 for 2.5 h at −0.78 V vs RHE using (a) glassy carbon electrode and (b) copper electrode as working electrodes under CO₂. Faradaic efficiency of compounds 1–3 using (c) glassy carbon electrode and (d) copper electrode at −0.78 V vs RHE in 0.1 M NaClO₄ solution. Conditions: working electrode, glassy carbon/copper; reference electrode, Ag/AgCl; counter electrode, platinum.

lyte was saturated with CO₂ (pH 6.9) and stirred at a rate of 600 rpm under sealed conditions during electrolysis. The effect of the applied potential on product selectivity and efficiency was studied for all three compounds 1–3. Electrolysis of 1–3 was performed for 2.5 h at −0.78 V vs RHE using GCE (Figure 4a) and Cu (Figure 4b) electrodes. The liquid and gas phases were analyzed using gas chromatography–mass spectrometry (GC-MS) and gas chromatography (GC) to identify the reduced products. CO and H₂ were observed as the main products for both electrodes, and no products were detected in the liquid phase for either cases.

As shown in Figure 4a and b, the current density was systematically higher using the Cu electrode compared to GCE. Using GCE, the highest catalytic efficiency was achieved with EDA (2) with a current density of −0.63 mA/cm² and Faradaic efficiency (FE) of 2.3% at −0.78 V vs RHE (Figure 4c). At the same potential, remarkable enhancement in current density (−18.4 mA/cm²) and a FE of 58% was achieved using the Cu electrode.

Turn over frequency (TOFs) and turn over numbers (TONs) were calculated using the whole catalyst concen-

tration in the solution, an approach that underestimates the activity of the catalyst.^{7,42} As expected, no reduction products were observed using the GCE in the absence of the catalysts, but with the Cu electrode, a small amount of CO was observed at −4.7 mA/cm² with a FE of 1.1% (Table 1). This trend is in

Table 1. Product Analysis of Constant Potential Electrolysis for CO₂ Reduction

Compound	Current density (mA/cm ²)	[CO] (ppm)	[H ₂] (ppm)	FE% (CO)	FE% (H ₂)	TON	TOF (h ^{−1})
GCE-CO ₂	−0.03	—	—	—	—	—	—
1 GCE-CO ₂	−0.42	67	449	1.7	94	19	7.6
2 GCE-CO ₂	−0.63	73	334	2.3	85	20	8.2
3 GCE-CO ₂	−0.28	38	215	1.8	91	13	5.2
Cu-CO ₂	−4.7	1	520	1.1	84	0.3	0.2
1 Cu-CO ₂	−14.8	729	334	22	75	151	60
2 Cu-CO ₂	−18.4	891	178	58	36	252	100
3 Cu-CO ₂	−9.7	401	228	19	77	138	55

agreement with the work of Hori's group, who similarly reported CO formation at −5 mA/cm² and a FE of 1.3%.⁴³ These values are lower than the FE of CO (33%) observed by Noda's group.⁴⁴ The FE of compounds 1, 2, and 3 using GCE are 1.7%, 2.3%, and 1.8%, while those using the Cu electrode were 22%, 58%, and 19%, respectively. Compound 2 was seen to be the most effective in terms of CO₂ to CO conversion. Using GCE, molecule 2 had a FE of 2.3% with a current density of −0.63 mA/cm² and TON of 20, whereas use of the Cu electrode saw a significant increase in catalytic efficiency (FE 58%) with a current density of −18.4 mA/cm² and TON of 252 at −0.78 V vs RHE. These values are higher than those reported in previous research with up to 1.7% FE with reducing CO₂ to CO using Cu electrodes²⁴ but similar to another work that reported a FE of 45% using copper foam.⁴⁵

All the catalysts (1–3) exhibited higher current density and catalytic efficiency on the Cu electrode as it itself acts as a catalyst for converting CO₂ to CO,^{25,46–49} unlike the glassy carbon electrode which serves solely as the working electrode. Moreover, protonation of amino groups under aqueous conditions gives rise to −NH₃⁺ groups. The strong interaction between these −NH₃⁺ groups, which act as Lewis acids, with CO₂, which acts as a Lewis base, result in its enhanced solubility.⁴⁷ Therefore, the two active −NH₃⁺ sites in the structure of EDA make it possible for improved catalytic performance to be achieved.

Theoretically, when primary or secondary monoamines are used, half a mole of CO₂ is absorbed per mole of amine to form carbamate.⁵⁰ Therefore, since EDA had the highest catalytic efficiency due to the two viable capture sites unique to its structure, here a mass balance study was performed to further investigate the kinetics of CO₂ uptake by EDA. A small volume (2 mL) of neat EDA was purged with CO₂, and the mass was recorded every 10 s, for a total of 80 s. As shown in Figure 5, the uptake of CO₂ per mole of EDA slowly increased over time, plateauing at 60 s. Further addition of CO₂ did not significantly affect the mass of the gel-like material, and the bubbling was stopped at 80s.

Although EDA is a primary diamine and the molar uptake of CO₂ is expected to be higher than 0.5 mol, only ~0.33 mol of CO₂ was absorbed per mole of EDA (Table S1). We propose that cooperative hydrogen bonding and ionic interactions drive

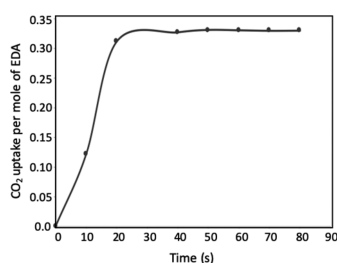


Figure 5. Molar uptake of CO₂ by neat EDA at room temperature.

the self-assembly of zwitterionic carbamate species, trapping and immobilizing the unreacted EDA molecules (Figure S11).

In this project, the main reduced product was CO; however, other possible hydrocarbon products may have been missed due to low concentrations under detection limit. Previously, amines and pyridine-based media similar in composition to ionic liquids have been used as electrolytes for the reduction of CO₂ since they are able to bind and reduce CO₂ via a Lewis base adduct,⁵¹ with high FE and low overpotentials.⁵² On the other hand, the mechanism of CO₂RR on Cu and other metal complexes is not well understood. Several parameters such as pH or the nature of the electrolyte can have a substantial effect on the reaction outcome. Work by Koper et al. on CO₂ reduction mechanisms using Cu has led to a proposed mechanism whereby negatively charged intermediates (CO₂•[−]) play a crucial role in the formation of C1 products.⁵³

CONCLUSION

In conclusion, we have devised a system where electroreduction of CO₂ to CO can be performed using easily accessible primary amino compounds with remarkable activity, durability, and selectivity in aqueous solutions. We have discovered that the catalytic efficiency of the amine functional group is significantly improved in the presence of a copper working electrode with a FE of 58%, compared to GCE with a FE of 2.3% in a sealed and closed system. Moreover, we have shown that EDA (**2**) is compatible with both electrodes and has the best electrocatalytic performance at −0.78 V vs RHE on a Cu electrode owing to its dual capturing sites which makes it more efficient compared to compounds **1** and **3**. Therefore, the superior performance of EDA over that of industrially prominent MEA makes it deserving of reconsideration as a molecular catalyst for CO₂ capture and electrochemical reduction applications, which could lead to a widespread reconsideration of different molecular catalysts evaluated previously in a homogeneous condition.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.9b06837>.

Reagents and chemicals, material characterizations, electrochemical measurements, 11 figures, and one table (PDF)

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Notes

The authors declare no competing financial interest.

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