

UCLA

UCLA Previously Published Works

Title

Solution and Active Site Speciation Drive Selectivity for Electrocatalytic Reactive Carbon Capture in Diethanolamine Over Ni-N-C Catalysts

Permalink

<https://escholarship.org/uc/item/4d72g19t>

Journal

ECS Meeting Abstracts, MA2026-01(58)

ISSN

2151-2043

Authors

Ross, Dominic

Han, Yulan

Jeong, Hui-Yun

et al.

Publication Date

2026-07-07

DOI

10.1149/ma2026-01582774mtgabs

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Solution and Active Site Speciation Drive Selectivity for Electrocatalytic Reactive Carbon Capture in Diethanolamine over Ni-N-C Catalysts

*R. Dominic Ross,^{1,2,‡} Yulan Han,^{3,‡} Hui-Yun Jeong,^{1,2} Jenna M. Ynzunza,⁴ Robert H. Lavroff,³ Avishek Banerjee,⁵
Aditya Prajapati,^{1, 2} Carlos G. Morales-Guio,⁵ Jesús M. Velázquez,⁴ Anastassia N. Alexandrova,^{3*} Christopher
Hahn^{1,2*}*

¹Materials Science Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

²Laboratory for Energy Applications for the Future (LEAF), Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

³Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA 90095, USA

⁴Department of Chemistry, University of California, Davis, Davis, CA 95616, USA

⁵Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, Los Angeles, CA 90095, USA

[‡]These authors contributed equally.

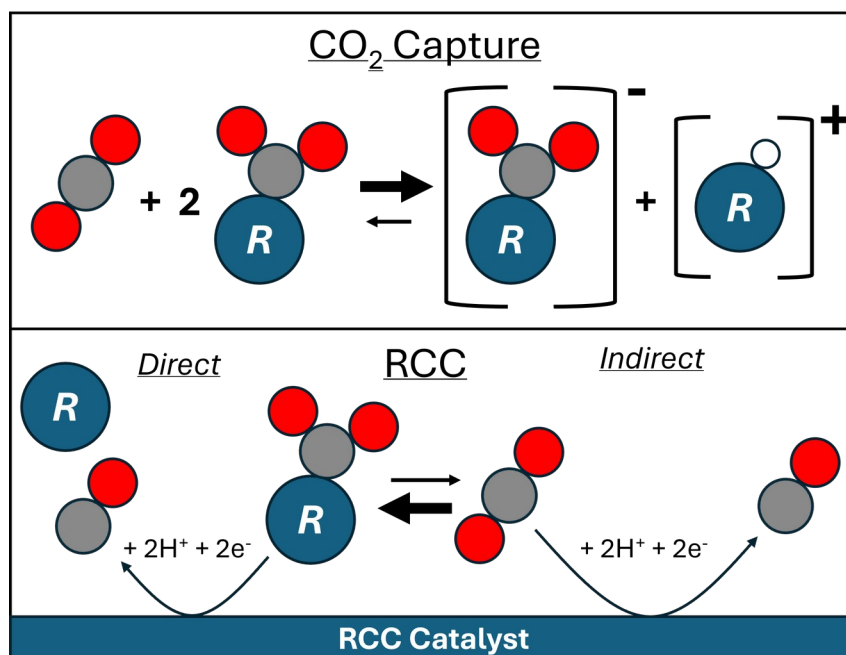
*Corresponding author emails: alexandrova@g.ucla.edu, hahn31@llnl.gov

Abstract

Direct conversion of captured forms of carbon, or reactive carbon capture (RCC), presents an opportunity to reduce the energy intensity and cost of direct CO₂ utilization from dilute sources. While amine-based sorbents effectively capture CO₂, their use for RCC presents numerous challenges with typical pure metal catalysts used for electrochemical CO₂ reduction (CO₂R). Here, using both theory and experiments, we find that Ni-N-C single atom catalysts are effective for RCC conversion to CO using a diethanolamine sorbent, in contrast to pure metal catalysts. Computational analysis reveals that the mechanism of converting captured CO₂ can proceed through direct reduction of the sorbent-CO₂ adduct or by C-N bond breaking facilitating CO₂ release and subsequent reduction. We find through varying sorbent concentration and partial pressure that the latter mechanism is most prevalent at potentials where RCC is most viable. At low overpotentials, we also find that the rate of CO production for RCC with Ni-N-C catalysts can exceed pure bicarbonate solutions at intermediate sorbent concentration under dilute (10-25%) streams of CO₂. The coordination environment of Ni sites and the solution speciation influence their RCC activity, with changes in protonation to coordinating N/C atoms resulting in changing the RCC mechanism and consequent activity. *In situ* X-ray absorption spectroscopy and computational analysis reveal restructuring under RCC conditions due to hydrogen co-adsorption with DEA that limits the stability of Ni-N-C catalysts. This work highlights the importance of carefully controlling the catalyst and solution environment to achieve active and stable RCC electrocatalysis.

Introduction

Processes powered by renewable electricity to capture and convert carbon dioxide (CO_2) from the atmosphere are urgently needed to mitigate the impacts of climate change. Benchmark sorbents for carbon capture are typically amines such as monoethanolamine (MEA) or diethanolamine (DEA), on account of their high affinity for CO_2 .¹ The capture of CO_2 by amines generates CO_2 -amine adducts (i.e. carbamates). For each negatively charged carbamate, an equivalent amount of the protonated amine is generated (**Scheme 1**). The highly thermodynamically stable carbamate also results in an energy-intensive regeneration step needed to achieve CO_2 -lean amine and pure CO_2 from the capture solution.^{2,3} Reactive carbon capture (RCC) integrates capture and conversion by directly reacting CO_2 in the capture media, subverting the need for successive capture, sorbent regeneration, and CO_2 conversion.⁴⁻⁶ This process presents the opportunity to reduce the cost and energy intensity of achieving carbon-neutral industrial processes⁶⁻⁸ by continuously valorizing CO_2 from industrial point sources (i.e. flue gas) such as cement production⁹ and power generation.¹⁰ The concentrations of CO_2 present in these streams are typically too dilute for efficient electrocatalytic conversion directly,¹¹ and often contain contaminants that poison typical catalysts for direct CO_2 electroreduction.¹²



Scheme 1. CO₂ capture process with amines (top, R = primary or secondary amine) and reactive carbon capture (RCC, bottom). RCC can proceed through the direct mechanism (left) where the CO₂-amine adduct (carbamate) binds to the catalyst surface and is reduced, or an indirect mechanism (right) where free CO₂ in equilibrium with the carbamate is released near the catalyst surface which can then bind to the surface and be reduced.

Pure metals that are typically exemplar electrochemical CO₂ reduction (CO₂R) catalysts exhibit negligible selectivity for RCC in amines, especially in the absence of an additional incoming CO₂ source.^{13–19} The primary causes are the promotion of HER by protonated amines,^{13,15,16} the capture of free CO₂ near the interface by lean amines,¹⁶ the difficulty in directly reducing thermodynamically stable carbamates,¹⁴ and the corrosion of metal surfaces.^{15,20} To achieve effective RCC with amines, some strategies to suppress HER by changing the catalyst microenvironment have been explored, such as the use of cationic (ammonium-based)

surfactants,¹⁷ larger alkali metal cations,^{18,21,22} non-aqueous solvents,^{23,24} molecular catalysts (in non-aqueous solvents),²⁵ and sterically hindered amines.^{24,26,27} However, no single approach has achieved both high rates of reaction and high selectivity for carbon based products using amines as a sorbent.

Metal-nitrogen doped carbon (M-N-C) single atom catalysts (SACs) have been utilized widely in CO₂ reduction, achieving nearly >90% selectivity for CO at high current density.^{28–31} This is largely due to effective suppression of HER by weakened H* adsorption on coordinated metal centers. Similarly, Ni-N-C SACs have been demonstrated to have some selectivity towards carbon-based products under RCC conditions.^{32–34} More broadly, SACs also have different active site structures (i.e. NiN_xC_{4-x}) depending on the exact synthesis conditions.^{35,36} The significant variability in active site ensembles complicates the analysis of these catalysts for RCC. While these catalysts are stable for CO₂R, their stability under RCC conditions remains largely unknown. Prior work on Ni-N-C catalysts for RCC has not thoroughly explored the relationship between CO₂ partial pressure and RCC activity, thus leaving the pathway through which Ni-N-C catalysts are able to produce carbon-based products unclear. At the same time, the performance of amine-based RCC systems is highly variable depending on the partial pressure of CO₂ in the capture solution.¹⁹ RCC is often demonstrated under CO₂ saturated conditions, which evaluates resiliency to operating in amines, but overlooks evaluating the prevalence of the “direct” RCC pathway, in which carbamates can be adsorbed to the catalyst surface and subsequently converted to carbon-based products (**Scheme 1**). A more thorough understanding of both speciation under different CO₂ feeds, as well as the dynamic speciation of catalyst active sites, is needed to develop generalizable insights for systematic RCC catalyst and sorbent co-design.

In this study, we demonstrate that Ni-N-C catalysts can partially suppress HER in diethanolamine (DEA), producing orders of magnitude higher CO selectivity than observed over pure metal catalysts and enhancing the rate for direct conversion of dilute streams of CO₂. Using theory, we evaluate different RCC pathways, and find that they are heavily influenced by the initial defect structure of the Ni-N-C catalyst and the applied potential. Importantly, applied potential influences the protonation environment on coordinating carbons around Ni sites, influencing the viability of RCC and the stability of Ni sites. By varying the CO₂ and DEA concentrations during experimental testing and using vapor-liquid equilibrium modeling, we find further evidence that free CO₂ (i.e. CO₂ not chemisorbed to an amine when it is reduced) is the primary driver of CO production over Ni-N-C catalysts, which is congruent with theory suggesting an indirect RCC pathway being dominant at the experimentally measured potentials. Through theoretical simulations and *in situ* experimental X-ray absorption spectroscopy measurements, we also find that evolving Ni site speciation during RCC plays a role in deactivation of the catalyst at highly negative potentials, providing previously unexplored insights into the role of catalyst dynamics during RCC in amines.

Results and Discussion

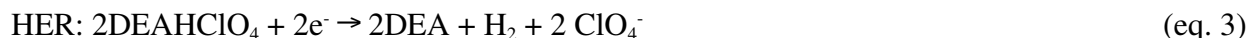
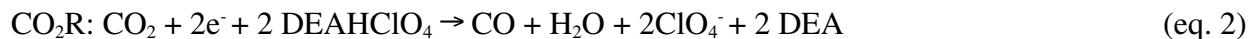
Evaluating Dependence of RCC Pathways on Ni-N-C Coordination

To model reaction pathways of RCC on Ni-N-C catalysts, we focused on four-coordinated Ni sites — representing the most stable configuration — and examined a series of NiN_xC_{4-x} environments (x = 0, 1, 2, 3, 4) (**Figures 1a, 1b** and **S1**), allowing for a systematic evaluation of how the local atomic environment influences catalytic behavior. To evaluate the relative importance of

each of these sites, we used experimental Ni K-edge extended X-ray absorption fine structure (EXAFS) measurements to obtain an ensemble coordination number of a representative Ni-N-C catalyst (**Figure 1c**, **Table S1** and **Table S2**). Probing the Ni K-edge EXAFS allows for obtaining an average number of nearest neighbors around Ni sites, with some sensitivity to the identity of the nearest neighbors based on different scattering. We found that the average coordination was $\text{NiN}_{3.3}\text{C}_{0.7}$, suggesting prevalent NiN_3C_1 and NiN_4 sites. Thus, we focus much of our detailed analysis on these two types of sites. Nonetheless, we still examined all possible sites theoretically, as minority sites can sometimes dominate catalytic activity. To consider the influence of proton transfer from amines to the catalyst, we assessed the thermodynamic stability of $\text{NiN}_x\text{C}_{4-x}$ catalyst surfaces under varying hydrogen coverages at reducing potential ($\text{pH} = \text{pKa}(\text{DEA}) = 8.9$). Our analysis reveals that hydrogen preferentially adsorbs on adjacent carbon sites rather than nitrogen sites (**Figure 1d** and **S2**), with the NiN_4 configuration having preference towards an unhydrogenated surface. As the potential becomes more negative, hydrogen coverage increases, and at sufficiently reducing conditions, the number of adsorbed hydrogen atoms approaches that of the surrounding C atoms.

To understand the likelihood of RCC proceeding on $\text{NiN}_x\text{C}_{4-x}$ to begin with, we also evaluated its thermodynamic viability against typical CO_2R and HER. We broadly define RCC as any adsorption of the carbamate to the catalyst surface, regardless of whether CO_2 is released or reduced while leaving the C-N bond intact. Furthermore, we also assume that kinetic limitations (i.e. lack of applied potential or heat) prevent carbamates in bulk solution from being a significant source of CO_2 . Even near the electrode surface, where the HER rapidly consumes protons and creates a locally alkaline environment, CO_2 liberation becomes further suppressed since

protonation - a prerequisite for decomposition - is disfavored. Nonetheless, when amine solutions are saturated with CO₂ there will be free CO₂ in equilibrium with DEA/carbamates, so we consider the thermodynamic competition between the following reactions:



We found that the calculated equilibrium potentials (**Figure S3**) followed the order HER (-0.53 V) < RCC (-0.78 V) < CO₂R (-1.11 V). This trend demonstrates that RCC is thermodynamically preferred to CO₂R. In other words, proceeding through a mechanism of reducing CO₂ facilitated by carbamate adsorption is thermodynamically preferable. However, HER facilitated by preferential adsorption of DEAH⁺ is competitive with RCC, consistent with past observations of low RCC selectivity. Going forward, we focused primarily on RCC and HER based on this analysis.

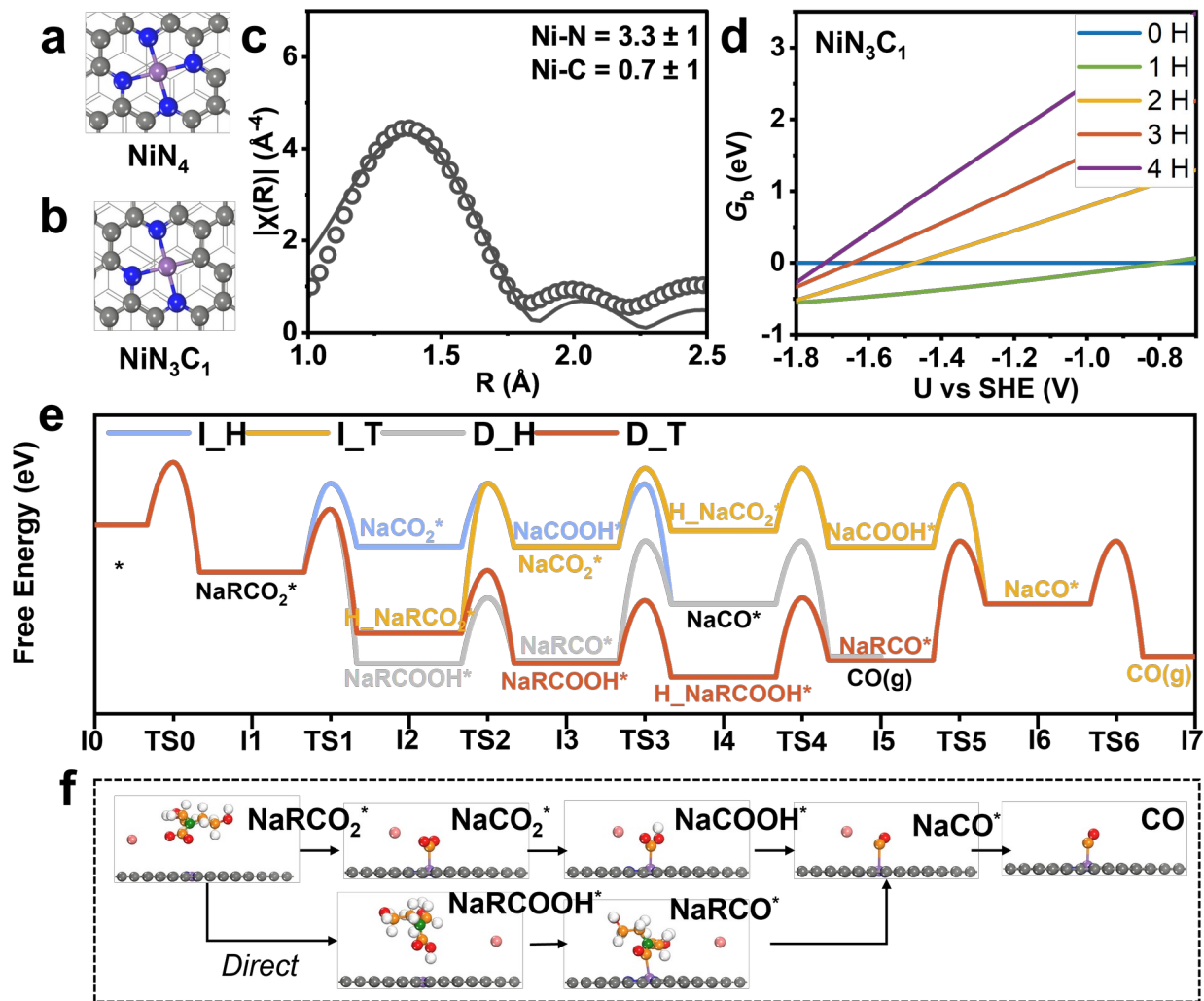


Figure 1. Optimized structures of a) NiN_4 and b) NiN_3C_1 obtained that are likely to make up the majority of Ni-N-C sites. Color code of atoms: Ni (purple), N (blue), C (gray), and H (white). c) Extended X-ray absorption fine structure (EXAFS) data (circles) and fitting (line) of as-synthesized Ni-N-C powder. d) Thermodynamic stability of NiN_3C_1 sites under varying hydrogen coverages. e) Reaction energy diagram on NiN_3C_1 at 0 H coverage and an applied potential of -1.2 V , illustrating four reaction pathways: I_H – Indirect CO_2 reduction with protons from the solvent (Heyrovsky-type); I_T – Indirect CO_2 reduction with a surface-adsorbed proton (Tafel-type); D_H – Direct CO_2 reduction with protons from the solvent (Heyrovsky-type); D_T – Direct CO_2 reduction with

surface-adsorbed H (Tafel-type). In all cases, R denotes the DEA (diethanolamine) group in the captured intermediate NaRCO_2 . Atom color code: Ni (purple), Na (pink), N of the catalyst (blue), N of DEA (green), C of the catalyst (gray), C of DEA (orange), and H (white). f) Corresponding structures for key intermediates along the RCC pathway with indirect pathway shown on top and the direct pathway shown on the bottom.

To understand the influence of the adsorbed hydrogen, we then investigated RCC reaction pathways on various Ni–N–C catalysts under different hydrogen coverages (**Figure 1e**) as a means of identifying the most likely mechanistic steps of RCC on Ni–N–C catalysts. The RCC mechanism can be classified into two main categories based on the sequence of C–N bond cleavage. The first category involves early C–N bond breaking immediately following NaRCO_2 adsorption, transitioning from RCO_2 to CO_2 , corresponding to *indirect CO_2 reduction*, where DEA serving as a shuttle of CO_2 to be released at the electrode. Note that the electrolyte cation, Na^+ , is included in the model, based on its electrostatic coordination to the negatively charged adduct; it assists the transport to the cathode. The second category involves later C–N bond breaking, occurring from RCO to CO corresponding to *direct RCC*, where CO_2 being reduced while on the adduct. These pathways are illustrated in **Scheme 1**. We also considered the origin of hydrogen involved in the hydrogenation steps. In a Heyrovsky-type mechanism, protons are donated directly from the solvent (DEAH^+), whereas in a Tafel-type mechanism, hydrogen is pre-adsorbed on the catalyst surface prior to the reaction. These two hydrogenation mechanisms, combined with the two C–N cleavage sequences, result in a total of four possible reaction pathways (**Figure 1e and 1f**). This classification provides a framework for rationalizing how the bond-breaking sequence and the hydrogen source diversify the RCC mechanism. To estimate reaction barriers, we employ the *energy span model*,³⁷

where reactivity is approximated by the largest energy difference between a transition state and an intermediate along the pathway — a process referred to as the rate-determining process (RDP).¹³ The calculated energy spans across different reaction pathways, catalysts, and hydrogen coverages are summarized in **Figure S2**.

By incorporating the Boltzmann distribution of hydrogen coverages and the corresponding energy span values, we determined the probability distribution of different reaction pathways for catalysts with each speciation (**Figures 2a, 2b and S4**). Our analysis reveals that as the potential becomes more negative, surfaces with higher hydrogen coverages contribute more prominently to the overall reaction for active sites that have direct carbon coordination (**Figure 2b and S4**). Furthermore, the dominant reaction pathway shifts from *I_H* to *D_H* (i.e. *indirect RCC* to *direct RCC* with protons coming from the DEAH⁺), while *D_T* (*direct RCC* with a pre-adsorbed proton) also contributes to reaction at intermediate potentials.

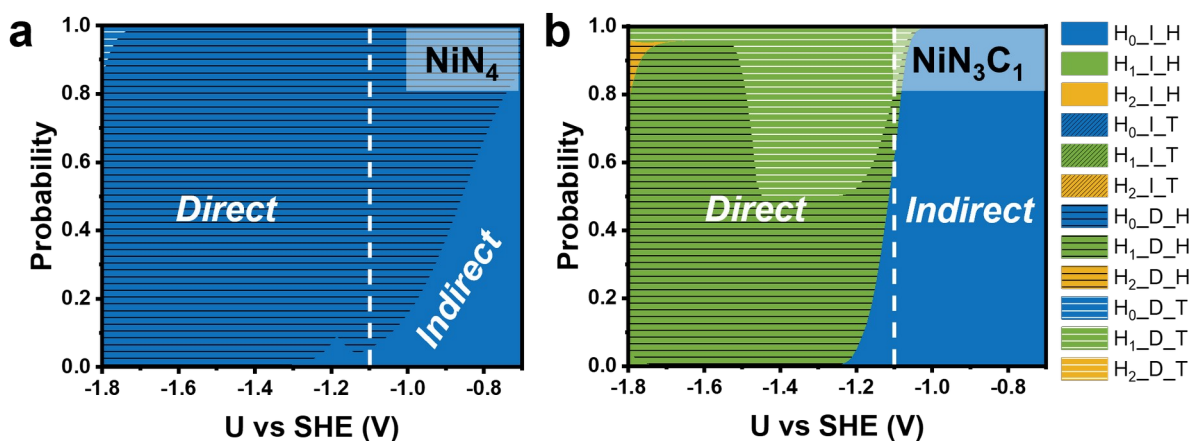


Figure 2. Probability distribution of different RCC pathways on a) NiN_4 and b) NiN_3C_1 with varying hydrogen coverages, highlighting their relative contributions to the reaction rate. $\text{H}_n\text{I}_\text{H}$ represents the *I_H* pathway on a surface with *n* adsorbed hydrogen atoms.

To rationalize the potential-dependent activity trends and locate the bottleneck of each reaction pathway, we further analyzed RDP for each pathway under different applied potentials (**Figure S5**). At lower overpotentials (-1.0 V), the I_H exhibits superior performance, with the rate-determining process primarily involving two key transitions: I1TS2 ($\text{RCO}_2^* \rightarrow \text{COOH}^*$) and I1TS1 ($\text{RCO}_2^* \rightarrow \text{CO}_2^*$). However, as the potential becomes more negative (-1.2 V), the energy span for I_H generally increases, shifting the rate-determining process predominantly to I1TS1. This shift occurs because the applied potential preferentially stabilizes RCO_2 rather than CO_2 . Simultaneously, D_H becomes more favorable, with its RDP transitioning from I2TS3 ($\text{RCOOH}^* \rightarrow \text{CO}^*$) and I3TS3 ($\text{RCO}^* \rightarrow \text{CO}^*$) to I2TS2 ($\text{RCOOH}^* \rightarrow \text{RCO}^*$), as the applied potential significantly enhances the binding energy of CO. Additionally, D_T demonstrates improved performance under more negative potentials, when it shares the same RDP as D_H. These findings provide a basis for tuning key steps to improve catalytic performance.

Next, we calculated the weighted energy spans for $\text{NiN}_x\text{C}_{4-x}$ under different applied potentials (**Figure 3a**). A lower weighted energy span corresponds to higher catalytic activity. Our results indicate that the activity follows the trend: $\text{NiN}_1\text{C}_3 \approx \text{NiN}_2\text{C}_2 > \text{NiN}_3\text{C}_1$, while NiN_4 and NiC_4 exhibit poor activity. As the potential decreases, the overall RCC activity increases, though the change in NiN_1C_3 remains relatively minor.

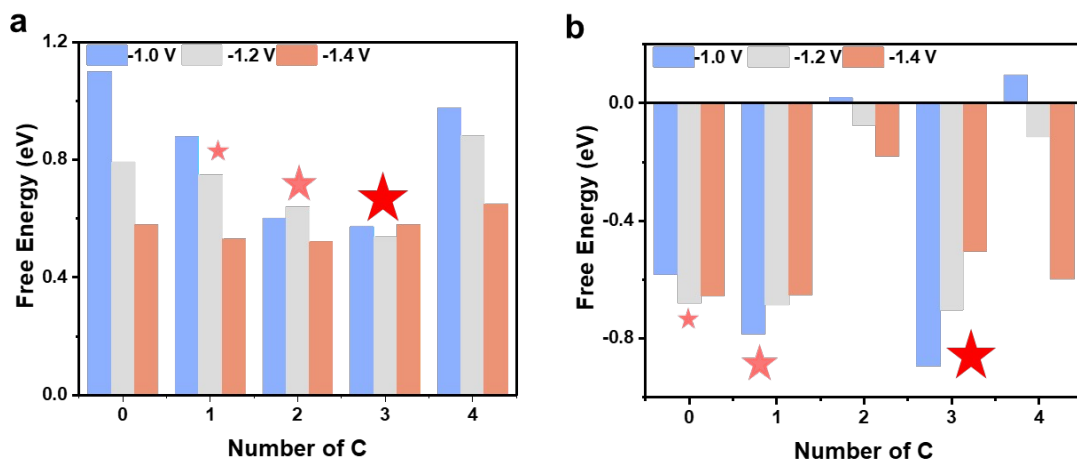


Figure 3. a) Calculated weighted energetic spans for RCC and b) the difference in weighted energetic spans between RCC and HER on $\text{NiN}_x\text{C}_{4-x}$ under varying applied voltages. The red stars highlight key data points indicating significant trends in the variations in energetic span.

To assess the viability of RCC in competition with HER, we calculated the energy span of HER on $\text{NiN}_x\text{C}_{4-x}$ catalysts under varying hydrogen coverages and applied potentials (**Figure S6**), followed by evaluation of the corresponding weighted energy spans (**Figure S7**). The difference between the weighted energy spans of RCC and HER was then used as a descriptor to quantify selectivity (**Figure 3b**). A more negative value indicates higher RCC selectivity. Our analysis reveals that NiN_2C_2 and NiC_4 exhibit poor selectivity, while the trend among the other catalysts follows $\text{NiN}_1\text{C}_3 > \text{NiN}_3\text{C}_1 > \text{NiN}_4$. Notably, out of these three most selective sites, selectivity decreases as the potential becomes more negative except for in the case of NiN_4 . Considering that the Ni–N–C sites are likely to have a nitrogen coordination number close to 4,³⁸ we expect NiN_1C_3 to be a minority compared to NiN_3C_1 , and yet could hypothetically dominate the RCC activity.

Experimental RCC Selectivity Dependence on Potential

To test our predictions about the behavior of Ni-N-C under RCC conditions, we first synthesized Ni-N-C according to a previously established procedure²⁸ with slight modifications, using a silica template to obtain a porous Ni-N-C catalyst (see Experimental Procedures for details). To evaluate the viability of RCC on Ni-SACs against previous examples of pure metals, we utilized a sealed rotating disk electrode (RDE) cell, as described elsewhere,^{15,39} to benchmark against pure metal catalysts measured in the same configuration. Initially, to prove successful synthesis of a high ratio of CO/H₂ from electroreduction, we conducted a CO₂R benchmark on the Ni-N-C on glassy carbon in 0.1 M NaHCO₃ (**Figure 4a**). As expected, there is a high selectivity for CO compared to H₂, with Faradaic efficiency (FE) at -12 mA cm⁻² exceeding 80%.

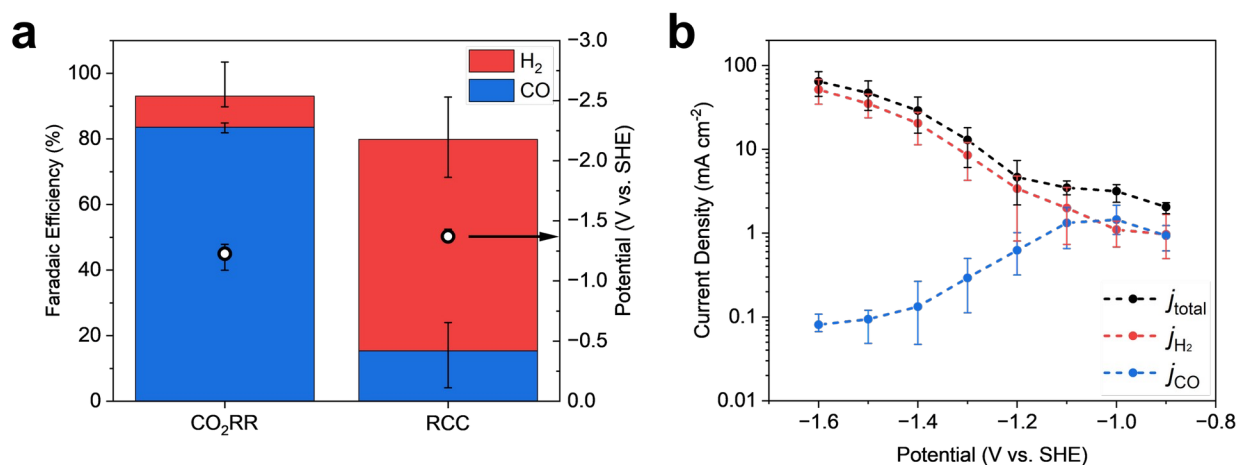


Figure 4. Kinetics of RCC with Ni-N-C catalyst measured in a sealed rotating disk electrode (RDE) cell under rotation at 800 rpm – error bars represent the minimum and maximum values over three parallel tests. a) Comparison of Faradaic efficiency (bars, left axis) and operating potential (dots, right axis) under constant current for conventional CO₂R (flowing CO₂ into 1 M NaHCO₃ solution) and RCC (flowing Ar into 0.5 M DEA/0.5 M NaClO₄ solution that was pre-purged with CO₂), and b) potential dependence of CO selectivity for RCC on Ni-N-C catalyst

under RCC conditions (flowing Ar into 0.5 M DEA/0.5 M NaClO₄ solution that was pre-purged with CO₂).

For a general evaluation of whether there would be detectable CO from RCC, we then measured the same dropcasted RDE in a solution of 0.5 M DEA and 0.5 M NaClO₄ that was pre-saturated with CO₂. During the measurement, the solution was purged with Ar. We observed an average of 15% FE for CO under these conditions (**Figure 4a**). Each parallel test represents an average over three samplings in a one-hour test in which the CO FE would decrease over the course of the measurement to as low as 1%. However, the observation of CO under RCC conditions at -12 mA cm⁻² was promising, as metal cylinders of Cu, Sn, Au, and Ag measured at an identical current density in the same cell showed <0.02% FE.¹⁵

After the initial demonstration of RCC on the Ni-N-C catalyst, we sought to understand how the performance varied across different applied potentials to correlate with our analysis of the mechanisms and energetics. We measured the activity and selectivity dependence of the Ni-N-C catalyst on the RDE while stepping from -0.9 V vs. SHE to -1.6 V vs. SHE (**Figure 4b**). Low overpotentials (-0.9 V, -1 V, -1.1 V vs. SHE) had moderate CO selectivity, with nearly 1:1 CO:H₂. At -1.2 V vs. SHE there is a noticeable drop in CO selectivity and increase in H₂ selectivity (**Figure 4b**). As the potential becomes more and more negative past -1.2 V vs. SHE, the total current density continuously increases and HER becomes dominant. At a potential of -1.6 V vs. SHE, the CO FE decreases to <1%. This shift in selectivity correlates with the increasing difference in the weighted energy spans of RCC and HER (**Figure 3b**), indicating a growing preference for HER. We also conducted vapor-liquid equilibrium (VLE) modeling (**Figure S8**) that indicates as CO₂ loading of the amine decreases, the availability of free CO₂ and carbamate will decrease in favor of DEA

(without bound CO_2). At more positive potentials, the moderate CO selectivity likely arises through thermodynamic preference for indirect RCC over HER in addition to a moderate availability of free/unbound CO_2 at the interface. At more negative potentials, higher current density will also drive a locally alkaline pH that will limit both free CO_2 and carbamates at the interface. Thus, RCC on Ni-N-C catalysts is limited to lower potentials by a combination of the intrinsic thermodynamics of RCC along with kinetic limitations imposed by the sorbent.

Experimental evidence also shows that in sequential or long-term testing, the partial pressures of CO_2 in the headspace also vary when purging with inert gas (**Figure S9**). Assuming the indirect pathway is dominant, this also leads to ambiguity of the intrinsic behavior of Ni-N-C catalysts under RCC conditions. The slightly more positive potential for RCC at the same current density (**Figure 4a**) is likely also accounted for by the decreasing CO_2 partial pressure causing an accompanying pH increase with decreased CO_2 loading (**Figure S9**). This decrease also accounts for the wider variability of RCC measurements compared to CO_2R . This motivates further systematic study with control over the concentration of the sorbent and the partial pressure of free CO_2 to decouple these contributions.

Sorbent and CO_2 Concentration Dependence on RCC Selectivity

To better understand the kinetic limitations on RCC as a result of solution speciation, we then utilized a two-compartment flow cell as a platform to evaluate the ideal conditions for RCC operation with Ni-SACs. The flow cell allowed high flux of captured CO_2 to the reactive interface, and use of an electrolyte reservoir separate from the cell allowed for quick swapping of electrolyte solutions that were pre-purged with CO_2 . In order to understand the role of free CO_2 ,

we varied partial pressures of CO₂ during the electrochemical tests (after fully saturating the solutions with CO₂ beforehand) . We conducted typical RCC measurements under pure Ar gas and pure CO₂ gas, as well as mixed 10% and 25% CO₂ gas streams that are relevant to CO₂ point sources such as flue gas. With each of these partial pressures of CO₂, we measured different concentrations of DEA. We maintained a 1:1 concentration of NaClO₄:DEA for all solutions, as Na⁺ plays a role in stabilizing surface intermediates, which may be particularly important for adsorption of carbamate. To interpret these results, we also used in-line pH monitoring (**Figure S10**) and the VLE models (**Figure S8**) to understand the evolving speciation under varied partial pressures of CO₂. We conducted each test at a constant potential of -1.1 V versus the standard hydrogen electrode (SHE). We used the SHE scale, rather than the reversible hydrogen electrode (RHE) scale due to the gradual increase in pH of tests under dilute CO₂ streams which leads to difficulty in setting a truly constant RHE potential.

For each CO₂ stream, increasing the concentration of DEA from 0.1 M to 0.5 M led to a higher j_{CO} (**Figure 5a**). The partial current density for HER increased with increasing sorbent concentration (**Figure 5b**) due to higher concentrations of the corresponding DEAH⁺ (**Figure S8**) as sorbent concentration was increased from 0.1 M to 1 M DEA. We also studied the effect of CO₂ partial pressure in the incoming gas stream, using different mixtures of Ar and CO₂. Each increase in CO₂ partial pressure led to an increase in j_{CO} at 0.1 M and 0.5 M concentrations of DEA (**Figure 5c**). HER activity, on the other hand, was relatively flat with 0.1 M NaHCO₃, 0.1 M DEA and 1 M DEA across different CO₂ partial pressures (**Figure 5d**). The HER activity does not strongly depend on the CO₂ partial pressure, likely since it does not significantly perturb the

concentrations of relevant HER proton donors (HCO_3^- and DEAH^+) in these systems as evidenced by the VLE models (**Figure S8**).

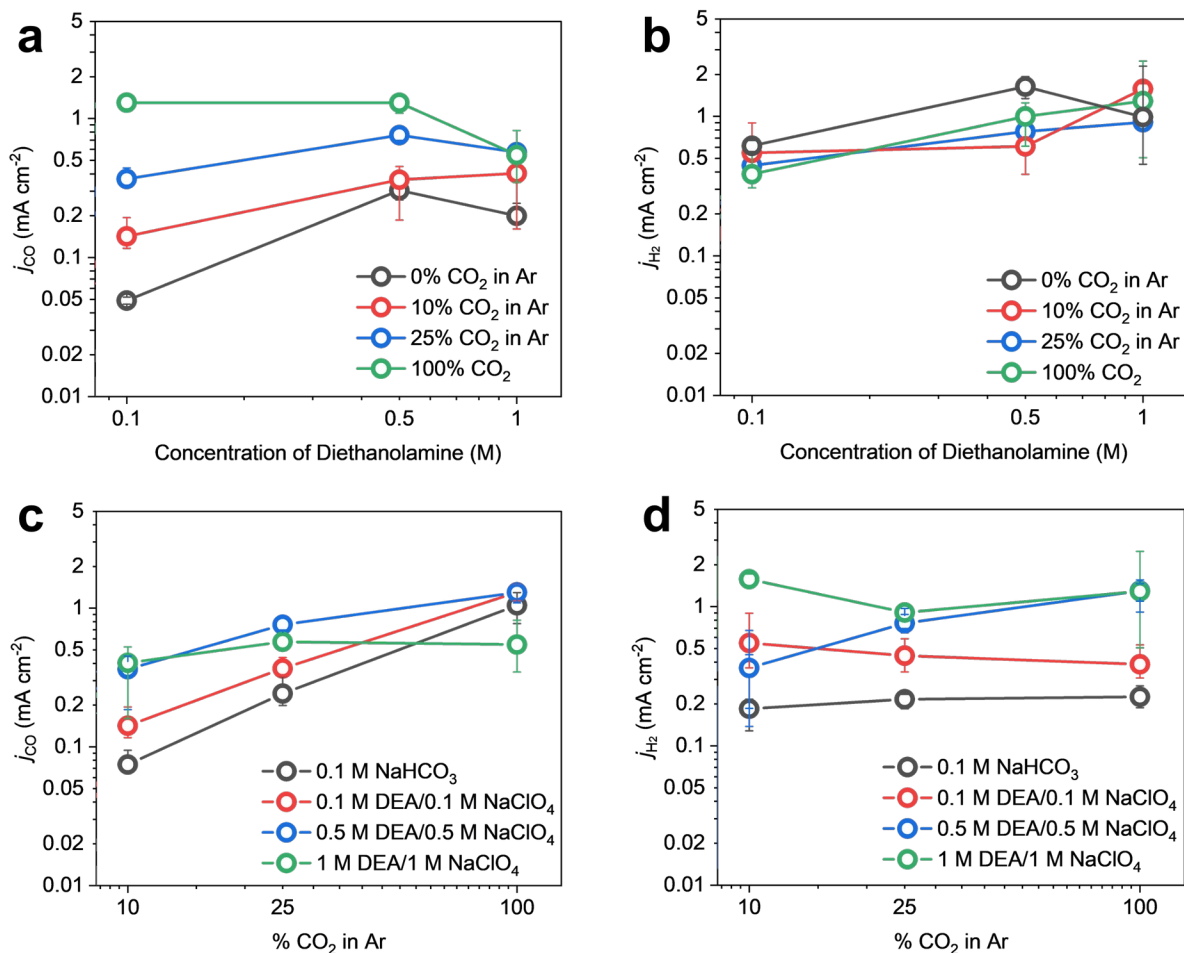


Figure 5. Evaluation of partial current density of CO at a constant potential of -1.1 V vs. SHE using Ni-N-C catalyst deposited on carbon paper and measured in a flow cell, varying a) j_{CO} and b) j_{H_2} while varying concentration of the diethanolamine sorbent (with 1:1 concentration of NaClO_4) and c) j_{CO} and d) j_{H_2} while varying partial pressure of the incoming CO₂ stream. Positive and negative error bars represent the maximum and minimum value, respectively, from at least two parallel tests.

While there are relatively small differences in starting pH (~7) between 0.5 M DEA and 1 M DEA (**Figures S10 and S11**), both indicate approximately 1:1 amine:CO₂ loading evidenced from the VLE modeling (**Figure S8**). At the saturation point, there is an increase in the amount of CO₂ in equilibrium with the capture solution. This explains the exponential activity increase between 0.1 M and 0.5 M DEA under 0% CO₂, since despite their increase in pH over time they also begin at the saturation point. With increased CO₂ partial pressure, there is a commensurate increase in j_{CO} . When the concentration of DEA is increased to 1 M, there are either diminishing returns or decreases in j_{CO} (**Figure 5a**). With 100% CO₂, there is also a noticeable drop in j_{CO} between 0.5 M and 1 M DEA (**Figure 5c**). Uniquely, the amount of free DEA is less than the carbamate or free CO₂. At lower concentrations, it is equal to or more than the carbamate and free CO₂ near the saturation point. The lack of available DEA may impede turnover of CO₂ to carbamate and subsequent adsorption and conversion of carbamates. Assuming CO₂ is unlikely to adsorb directly, this suggests that changes in the rate of CO production at different CO₂ partial pressures actually imply that the CO₂ mainly serves to maintain favorable concentrations of DEA, carbamates, and free CO₂ in solution to efficiently deliver carbamates to the interface. The observation of decreased activity from 0.5 M to 1 M DEA along with the exponential increase in activity from 0.1 M to 0.5 M DEA strongly supports the theoretically predicted dominance of the indirect RCC pathway at low overpotential (**Figure 2**). The FEs of Ni-N-C catalysts measured at -1.1 V vs. SHE under varied CO₂ partial pressures and DEA concentrations are summarized in **Figure S11**.

Notably, the results under Ar saturation have CO₂ concentrations that are less than 10% CO₂ in the headspace that generally decrease throughout each measurement and have consequent

changes j_{CO}/CO FE. These changes correlate with the drop in headspace CO_2 except for in the case of the 0.1 M NaHCO_3 electrolyte (**Figure S12**). NaHCO_3 has the lowest headspace CO_2 concentration (<1%) at the start of the test, and although there is a gradual decrease in headspace CO_2 , the apparent CO FE does not decrease.

While most tests were approximately one hour, we also conducted several longer tests with 1 M DEA to confirm consistency due to unaccounted charge (i.e. <100% total FE). We found that CO FE stayed consistent at ~40% under CO_2 -saturation (**Figure S13a**) due to consistent speciation, as evidenced by the unchanged pH (7.3) and consistent gas environment. Under Ar saturation, the CO FE slowly dropped due to a gradual decrease in headspace CO_2 (5% to 3%) and increase in pH (7.3 to 7.8). For both cases, the H_2 FE increased gradually over the course of two hours, with the total FE being ~60% upon the first GC injection and nearly 90% for the last several injections (**Figure S13b**). While the trends for j_{CO} track the CO FEs (**Figure S13c**), j_{H_2} is relatively consistent in both cases (**Figure S13d**). This leads us to believe that unaccounted charge mainly results from charging currents, which may be difficult to dissipate due to the combined porosity of the Ni-N-C catalyst and carbon paper substrate. The full results of the three >2 hour tests are shown in **Figure S14**.

In Situ Investigation of Ni-N-C Active Site Structures Under Operating Conditions

Although the changing concentrations of species near the interface drive decreases in CO selectivity at higher potentials/current densities, we also sought to understand the importance of catalyst active site evolution during RCC and the extent to which it led to decreases in selectivity. When going to potentials higher than -1.1 V vs. SHE, large drops in CO selectivity were

consistently observed (**Figure 6a**). After applying potentials where predominantly HER was observed, the selectivity could not be recovered by sweeping the potential back to potentials where the catalyst was previously CO selective. This suggests that there may be irreversible changes to the catalyst structure. To probe the structure around Ni sites (i.e. coordination within the carbon framework and adsorbates) as it evolved during immersion in DEA and under applied potential, we used *in situ* X-ray absorption spectroscopy (XAS). The *in situ* XAS cell mimicked the flow cell setup used for benchmarking, with an additional beveled opening in the backing plate near the cathode to allow incident X-rays through to the catalyst film (**Figure S15**).

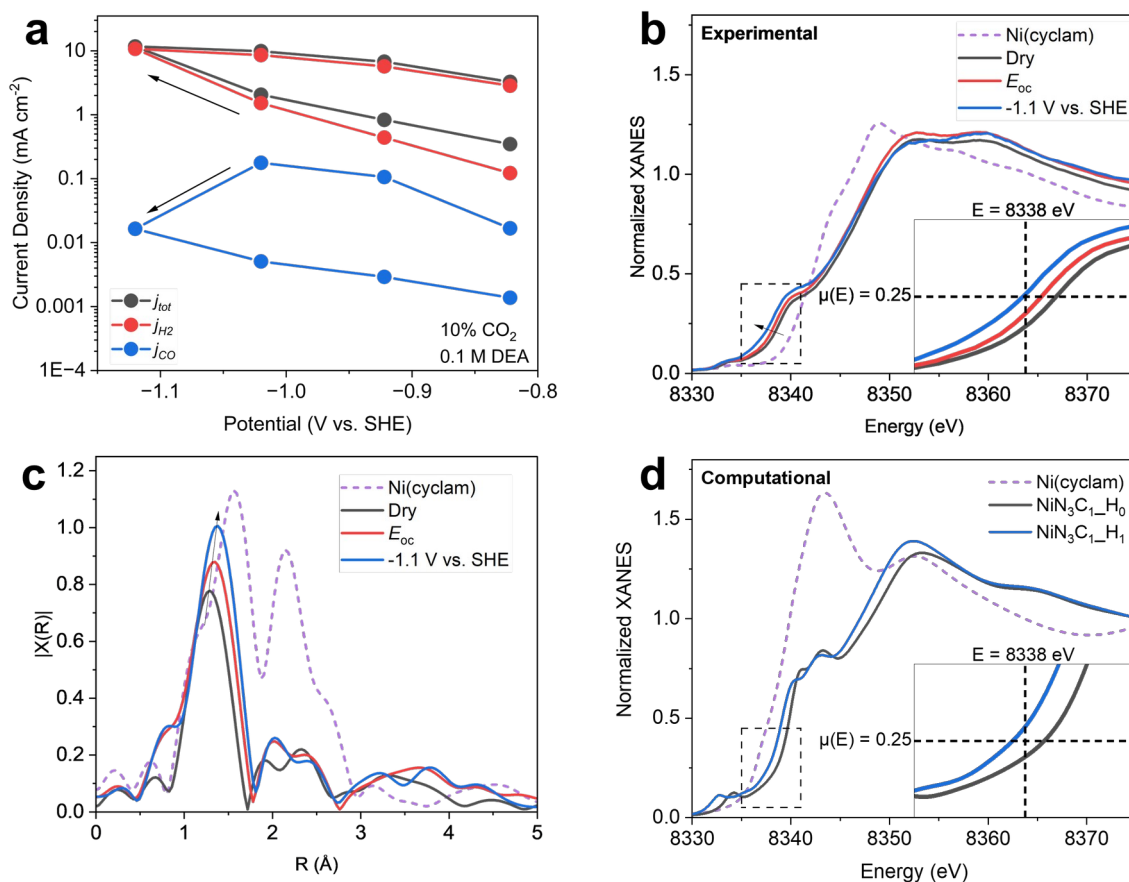


Figure 6. Evidence of the Ni-N-C catalyst restructuring assessment under RCC conditions. a) Constant potential measurements of Ni-N-C under RCC conditions (0.1 M DEA/0.1 M NaClO₄ with 10% CO₂ supply). b) Ni K-edge XANES of a dry Ni-N-C on carbon paper electrode compared to an electrode immersed at open circuit (E_{oc}) in CO₂-purged 1 M DEA/1 M NaClO₄ and an electrode in the same solution at -1.1 V vs. SHE, with c) corresponding k^2 -weighted EXAFS spectra, and d) simulated XANES spectra of NiN₃C₁ with (NiN₃C₁-H₁) and without (NiN₃C₁-H₀) adsorbed hydrogen on the coordinating carbon, with the simulated spectrum of four-fold coordinated Ni-N complex Ni(cyclam) shown for comparison.

The X-ray near edge structure (XANES) spectra shows a shift of the absorption edge of the Ni-N-C samples to lower energy upon immersion of the electrode into a CO₂-saturated 1 M DEA solution, and a subsequent shift to even lower energy under an applied potential of -1.1 V vs. SHE (**Figure 6b**). Notably, some previous studies of conventional CO₂R on Ni-N-C catalysts observe similar shifts in the absorption edge under CO₂R conditions,^{40–43} although typically CO₂ adsorption under open circuit conditions shows a positive shift in the adsorption edge. We hypothesize that under working conditions where indirect RCC is dominant, the primary adsorbate (free CO₂) interactions with the catalyst will be similar to conventional CO₂R, while under open circuit conditions interactions with the sorbent may be more prevalent. The extended X-ray absorption fine structure (EXAFS) of the Ni-N-C catalysts under the same conditions indicates a slight bond lengthening and increase in coordination in the first shell coordination of N/C around Ni (**Figure 6c**). Since the bond lengths and scattering factors of nitrogen and carbon atoms will be similar, this could indicate restructuring of the N/C coordination around the Ni or adsorption of the sorbent/CO₂. This observation also contrasts some other EXAFS measurements

of Ni-N-C catalysts measured *in situ* for CO₂R,^{40,42,43} which warrants further investigation to clarify whether these observations represent restructuring around the Ni within the graphitic carbon plane, or out of plane with the sorbent.

To better understand the coordination structure based on the experimental results, we simulated the XANES spectra for likely coordination structures of the Ni-N-C. We simulated the XANES spectra of NiN₃C₁ (**Figure 6d**) and NiN₁C₃ (**Figure S16**) under both dry conditions and working conditions at -1.2 V, where the active surface is characterized by the adsorption of a single hydrogen atom for NiN₃C₁. Our experimental results showed that under working conditions, the absorption edge shifts towards lower energy compared to the dry state, indicating a partially lower Ni oxidation state (**Figure 6b**). For the simulation of NiN₃C₁, we observed a similar absorption edge shift (~0.8 eV) to lower energy upon adsorption of a hydrogen on the coordinating carbon (**Figure 6d**). A similar trend is observed in NiN₁C₃ (**Figure S16**). The similarity in the absorption edge shift near $\mu(E) = 0.25$ between the experimental and simulated results suggest that protonation (at least partially) drives changes to the local structure of the catalyst active sites and further supports the prevalence of NiN₃C₁ sites in the synthesized catalyst. More complex features in the XANES, as well as the changes at open circuit, are likely explained by the effects of the primary adsorbates (*vide supra*). These results suggest that protonation changes the local structure of the Ni-N-C active sites under working conditions and thus, protonation at the active site is consequential for RCC activity.

To further investigate the impacts of protonation on NiN_xC_{4-x} catalysts and identify possible origins of restructuring, we used theoretical calculations to probe the nature of the restructuring under initial formation of the NiN_xC_{4-x} sites and under working RCC conditions. To assess the

thermodynamic stability of SACs, we calculated the relative formation energy of $\text{NiN}_x\text{C}_{4-x}$, as shown in **Figure 7a**. The results indicate that formation energy increases markedly with decreasing nitrogen coordination, suggesting that structures with higher nitrogen coordination are more thermodynamically stable, consistent with experimental observations of prevalent Ni- N_4 and Ni- N_3C_1 sites.

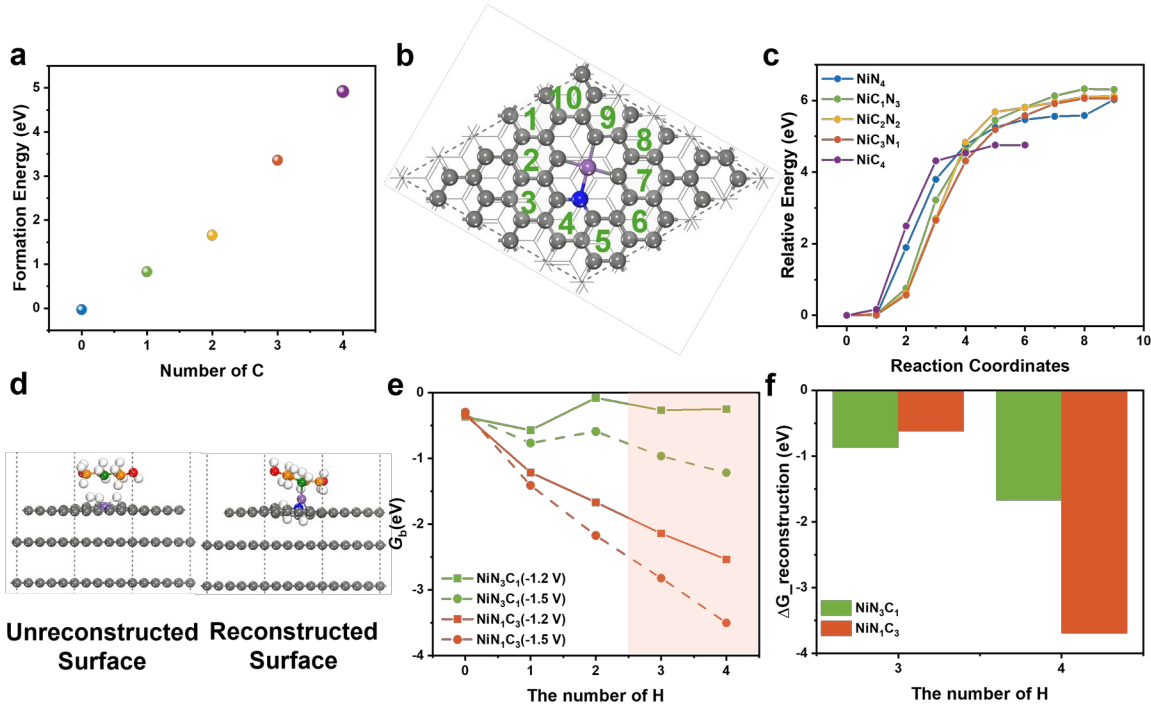


Figure 7. a) Formation energies of $\text{NiN}_x\text{C}_{4-x}$ structures. b) Ten potential Ni transfer sites. c) Energy profile along the reaction pathway for Ni diffusion from original site to an adjacent hollow site. d) Side view of the optimized DEA adsorption on $\text{NiN}_1\text{C}_3\text{H}_3$, comparing the unreconstructed and reconstructed structures. e) Gibbs free energy for co-adsorption of DEA and H on $\text{NiN}_x\text{C}_{4-x}$ surfaces under different applied potentials. The binding energy was computed as $G_b = G_{\text{total}(\text{NiN}_x\text{C}_{4-x} + \text{DEA} + \text{H})} - G_{\text{NiN}_x\text{C}_{4-x}} - G_{\text{DEA}} - G_{\text{H}}$, representing the overall stability of the DEA

+ H co-adsorbed states. f) Energy difference between the unreconstructed and reconstructed surfaces at -1.5 V.

To further assess dynamic stability of $\text{NiN}_x\text{C}_{4-x}$ catalysts, we analyzed the diffusion barrier of Ni atoms migrating from their original sites to adjacent hollow sites. We designed ten possible migration paths (**Figure 7b**) and identified the most thermodynamically stable final structures by comparing the relative energies between the initial and final states. These structures were then used to determine the Ni diffusion barrier. Our calculations reveal that, at least without the assistance of ligands from solution, such as the amine, the aggregation of dispersed Ni single atoms is unlikely to occur, as the diffusion barrier exceeds 4 eV for all catalysts. While ligand assistance likely will bring the barrier down, we can use these results to assess the relative stabilities of $\text{NiN}_x\text{C}_{4-x}$ sites. NiC_4 appears to be less stable compared to other catalysts (**Figure 7c**), but this structure is an insignificant fraction (*vide supra*). This likely rules out Ni plating as a source of the shift of the XANES absorption edge to the left.

Under operating conditions, metal sites may undergo chemical corrosion due to interactions with DEA that leads to Ni leaching. We examined two adsorption configurations of DEA: (1) Physisorption, where DEA interacts weakly with the surface, and (2) Chemisorption, where DEA forms a chemical bond with Ni, potentially leading to metal leaching (**Figure 6d**). To probe the driving force for surface restructuring, we evaluated the binding energies of DEA and H on NiN_3C_1 and NiN_1C_3 under different applied potentials. The red region in **Figure 7e** marks the potential range where the reconstructed surface becomes more stable. Our results show that as the potential becomes more negative, the increasing hydrogen coverage leads to more negative binding energies of DEA, suggesting a higher tendency for surface reconstruction and leaching. Comparing NiN_1C_3

and NiN_3C_1 , we find that NiN_3C_1 is more resistant to Ni leaching, as indicated by its less negative binding energy and smaller energy difference between the reconstructed and unreconstructed surfaces (**Figure 7f**). This trend suggests that, as the number of carbon atoms increases, the tendency for Ni leaching also increases, highlighting the importance of nitrogen coordination in stabilizing single-atom Ni sites. This is consistent with observations of deactivation at more negative potentials (**Figure 6a**) and Ni leaching into solution under more negative potentials and over extended periods of time, as evidenced by inductively coupled plasma mass spectrometry (ICP-MS) of the electrolyte after electrolysis (**Figure S17**). These structural changes likely decrease the number of active sites, therefore deactivating the catalyst. The HER activity at high overpotentials likely then at least partially originates from HER on the graphitic carbon support.

Considering catalytic activity, selectivity, and stability, we propose that NiN_3C_1 sites represent the dominant contribution to RCC performance. Therefore, to further verify the reliability of DFT in describing such systems with complex electronic structures and competing spin states,^{44–49} we performed a benchmark calculation using a quantum embedding approach that performs correlated electronic structure calculations on embedded fragments,^{50,51} including the $\text{NiN}_3\text{C}_1\text{H}_1$ active site and its graphitic surroundings. More details can be found in the supporting information. The DFT-computed spin states are consistent with results obtained from high-level wavefunction-based methods such as CASPT2 and CCSD(T), which supports the reliability of DFT for describing the ground state of this system and further validating the accuracy of our computational results.

Conclusions

This work brings attention to the need for co-design of catalysts, sorbents, and operating conditions to achieve optimal RCC activity. We found that by using a catalyst that can suppress HER, RCC is possible at low overpotentials. However, the source of CO₂ that is converted is still free CO₂ at operating potentials where RCC is kinetically viable. The CO₂ exists in equilibrium with the captured CO₂ or can be liberated from adsorbed carbamates.. We initially hypothesized this from computational analysis of RCC through both direct (carbamate reduction) and indirect (CO₂ release from carbamate followed by reduction of adsorbed CO₂) pathways. To demonstrate this, we experimentally studied different concentrations of CO₂ constantly fed into the system. Although there is not strong evidence for the direct electroreduction of carbamates on Ni-N-C catalysts, the presence of a sorbent (DEA) can nonetheless enhance the rate of CO production (compared to a solution only containing sodium bicarbonate) when a dilute CO₂ source is present. This enhancement is especially pronounced without an external source of CO₂, where bicarbonate solutions are ineffective as a CO₂ source to the catalyst, and results in a 19-fold enhancement (evidenced by the partial current density) in the rate of CO production in solutions of 0.5 M DEA. There is also a 3-fold enhancement in the rate at 10 and 25% concentrations of CO₂, which are most relevant for implementation of RCC from industrial sources. These rates are achievable at lower overpotentials than observed for Ag based catalysts, which have been observed to have significant RCC onset for CO at potentials more negative than -1.1 V vs. SHE in MEA. To enable enhancements from RCC, the potential must be such that the Ni-N-C sites do not restructure and the supply of carbamates/CO₂ near the interface is not depleted too rapidly. Our insights into the importance of the RCC microenvironment as well as the corresponding catalyst stability highlight

the importance of co-designing catalysts and sorbents, as well as tailoring concentrations of sorbent to the available stream of CO₂.

Experimental Section

Computational Methods. All plane-wave density functional theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP),^{52,53} employing the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) framework.⁵⁴ Projector-augmented-wave pseudopotentials (PAW) were employed with a plane-wave energy cutoff of 400 eV. The model systems were constructed using a p(5 × 5) unit cell with three atomic layers. The bottom two layers of the slab were fixed to mimic the bulk, while the top layer and all adsorbates were fully relaxed to represent the interfacial region. A vacuum space of 20 Å was added along the z-direction to eliminate interactions between periodic images. For solvation and surface charging calculations, all structures were symmetrized and the simulation cell was extended to 60 Å in the z-direction to accommodate the implicit solvation region. Geometry optimizations were considered converged when reaching a gradient smaller than 0.05 eV/Å, with a threshold of 1×10⁻⁵ eV for wave-function calculation. Γ -point (1 × 1 × 1) K-point mesh was used for all geometry optimizations. Gibbs free energies for adsorbates are obtained from the DFT energies with ZPE and entropy corrections determined from frequency calculations performed for all the considered structures using the Harmonic Oscillator approximation. The grand canonical free energy was evaluated by the grand canonical density functional theory (GCDFT) calculations, which is a surface charging technique. Details can be found in the supporting information and our previous article.^{15,55,56} Details of high-level embedding ab initio calculations are given in the SI.

Catalyst Synthesis. The catalyst synthesis was adapted from literature.²⁸ Briefly, amorphous silica nanoparticles (Thermo Scientific, 99.9%) were suspended in nanopure water, sonicated, and then heated at 1000 °C in a crucible for one hour. Then, nickel chloride hexahydrate was dissolved in 1-ethyl-3-methylimidazolium (EMIM-DCA) and added to the crucible with the annealed silica. The mixture was then placed back in a furnace and heated at 900-1000 °C for three hours. After cooling, the silica templates were etched away by etching three times with 2 M NaOH at 80 °C for three hours, and then a final etch with 1 M HCl in ethanol. The final product was collected by centrifugation.

Electrolyte Preparation. Electrolyte solutions for RCC were prepared by 1:1 molar amounts of sodium perchlorate (Sigma-Aldrich, $\geq 98.0\%$) and diethanolamine (Sigma-Aldrich, $\geq 99.0\%$). All solutions were treated by stirring with Chelex (Sigma-Aldrich, 50-100 mesh) for at least one hour prior to use. Electrolytes were purged with vigorous CO₂ bubbling for at least 15 minutes to achieve a stable pH/outlet flow rate of CO₂ from solution before use, then subsequently purged with the working gas.

Electrode Preparation. For RDE measurements, 20 μL of the catalyst suspension (10 mg/mL, 0.3 Nafion/catalyst mass ratio in ethanol) was dropcast onto a glassy carbon disk electrode (Pine Research Instrumentation, 5 mm diameter) and allowed to dry naturally in air. For flow cell measurements, pieces of AvCarb MGL370 (Fuel Cell Store) were cut into 4 cm x 4 cm squares and 200 μL of catalyst dispersion (6 mg/mL, 0.3 Nafion/catalyst mass ratio in ethanol) was dropcast onto the squares and allowed to dry naturally. Nafion was added from a corresponding amount of 5 wt% solution (Sigma-Aldrich).

Electrochemical Measurements. All electrochemical measurements were conducted on a VSP-300 potentiostat. RDE measurements were conducted in a sealed rotating cell, as described previously. Flow cell measurements were conducted in custom 3D printed flow cells (Formlabs, Clear v4 resin). The two-compartment cell was separated using an anion exchange membrane (Fumasep FAS-50, Fuel Cell Store). All measurements used a leakless Ag/AgCl electrode (Innovative Instruments Inc.) and typically used an iridium oxide on carbon paper anode (Dioxide Materials). The anolyte was either a 0.1 M or 1 M NaHCO_3 solution (to correspond to the same catholyte composition for CO_2R) or 1 M NaClO_4 (for RCC). The anolyte compartment was static and contained ~9 mL of electrolyte. For most tests, a pH probe (H1001, Hanna Instruments) was placed in-line in the catholyte flow loop by screwing into a 3D printed holder.

Gaseous products were detected with an on-line gas chromatogram (SRI 8610C MG#5) equipped with a 12 ft MolSieve 5A column (for H_2 separation), 6 ft HayeSep D column (for CO/CO_2 separation), flame ionization detector (FID) for CO/CO_2 quantification and a thermal conductivity detector (TCD) for H_2 quantification. RDE measurements were conducted at 800 rpm unless otherwise noted and flow cell measurements were conducted at a liquid flow rate of 40 mL/min with 75 mL of recirculating electrolyte unless otherwise noted.

X-ray Absorption Spectroscopy. X-ray absorption spectroscopy (XAS) measurements were conducted in fluorescence mode at beamline 4-1 of the Stanford Synchrotron Radiation Lightsource (SSRL). *In situ* XAS measurements were conducted in 3D printed flow cells similar to those used for performance benchmarking, except with a beveled opening on the front faceplate. The catalyst electrodes were sealed in on the front of the working chamber using Kapton tape. Data was processed using Larix/Larch or Athena. Fittings were processed in

Artemis To obtain an estimate of the amplitude reduction factor, S_0^2 , we fitted the measure spectra of Ni(cyclam), a molecular complex assumed to have a first shell Ni-N coordination of 4. By fixing the coordination number at a value of 4, we obtained $S_0^2 = 0.8 \pm 0.2$, so we carried forward a fixed value of $S_0^2 = 0.85$ for the fitting of the Ni-N-C EXAFS. For the Ni-N-C fitting we also fixed the Ni-N/C distance as 1.87 Å (from the optimized Ni-N₄ structure), the Ni-C coordination number to be the four minus the Ni-N coordination number, and guessed all other parameters.

ICP-MS. ICP-MS standards were prepared from nickel nitrate hexahydrate and prepared in a matrix of 0.5 M DEA/0.5 NaClO₄. Aliquots from the electrolyte were diluted 100-fold in a matrix of 0.5 M DEA/0.5 M NaClO₄.

Supporting Information Available: Additional computational details, additional data related to the flow cell testing of the Ni-N-C catalyst, VLE modeling of DEA, photo of assembled cell for XAS, and quantification of Ni leaching from flow cell testing.

Corresponding Authors

***Anastassia N. Alexandrova** – Department of Chemical and Biomolecular Engineering,
University of California, Los Angeles, Los Angeles, CA 90095, United States

Email: alexandrova@g.ucla.edu

***Christopher Hahn** – Materials Science Division, Lawrence Livermore National Laboratory,
7000 East Avenue, Livermore, CA 94550, United States

Email: hahn31@llnl.gov

Acknowledgements

This work was primarily supported as part of the Center for Closing the Carbon Cycle, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award Number DE-SC0023427. Work by R.D.R., H.J., A.P. and C.H. was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory (LLNL) under Contract DE-AC52-07NA27344. LLNL release number: LLNL-JRNL-2004640. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. The authors acknowledge the use of ChatGPT for minor language and grammar editing.

Competing Interests

The authors declare no competing interests.

References

- (1) El Hadri, N.; Quang, D. V.; Goetheer, E. L. V.; Abu Zahra, M. R. M. Aqueous Amine Solution Characterization for Post-Combustion CO₂ Capture Process. *Appl. Energy* **2017**, *185*, 1433–1449. <https://doi.org/10.1016/j.apenergy.2016.03.043>.
- (2) Rochelle, G. T. Amine Scrubbing for CO₂ Capture. *Science* **2009**, *325* (5948), 1652–1654. <https://doi.org/10.1126/science.1176731>.
- (3) Gao, W.; Liang, S.; Wang, R.; Jiang, Q.; Zhang, Y.; Zheng, Q.; Xie, B.; Ying Toe, C.; Zhu, X.; Wang, J.; Huang, L.; Gao, Y.; Wang, Z.; Jo, C.; Wang, Q.; Wang, L.; Liu, Y.; Louis, B.; Scott, J.; Roger, A.-C.; Amal, R.; He, H.; Park, S.-E. Industrial Carbon Dioxide Capture and Utilization: State of the Art and Future Challenges. *Chem. Soc. Rev.* **2020**, *49* (23), 8584–8686. <https://doi.org/10.1039/D0CS00025F>.
- (4) Dongare, S.; Zeeshan, M.; Aydogdu, A. S.; Dikki, R.; Kurtoğlu-Öztulum, S. F.; Coskun, O. K.; Muñoz, M.; Banerjee, A.; Gautam, M.; Ross, R. D.; Stanley, J. S.; Brower, R. S.; Muchharla, B.; Sacci, R. L.; Velázquez, J. M.; Kumar, B.; Yang, J. Y.; Hahn, C.; Keskin, S.; Morales-Guio, C. G.; Uzun, A.; Spurgeon, J. M.; Gurkan, B. Reactive Capture and

- Electrochemical Conversion of CO₂ with Ionic Liquids and Deep Eutectic Solvents. *Chem. Soc. Rev.* **2024**, 53 (17), 8563–8631. <https://doi.org/10.1039/D4CS00390J>.
- (5) Freyman, M. C.; Huang, Z.; Ravikumar, D.; Duoss, E. B.; Li, Y.; Baker, S. E.; Pang, S. H.; Schaidle, J. A. Reactive CO₂ Capture: A Path Forward for Process Integration in Carbon Management. *Joule* **2023**, 7 (4), 631–651. <https://doi.org/10.1016/j.joule.2023.03.013>.
 - (6) Langie, K.; Bak, G.; Lee, U.; Ki Lee, D.; Woo Lee, C.; Jeong Hwang, Y.; Hye Won, D. Advances in the Direct Electro-Conversion of Captured CO₂ into Valuable Products. *J. Mater. Chem. A* **2024**, 12 (18), 10597–10613. <https://doi.org/10.1039/D4TA01178C>.
 - (7) Li, M.; Irtem, E.; Iglesias Van Montfort, H.-P.; Abdinejad, M.; Burdyny, T. Energy Comparison of Sequential and Integrated CO₂ Capture and Electrochemical Conversion. *Nat. Commun.* **2022**, 13 (1), 5398. <https://doi.org/10.1038/s41467-022-33145-8>.
 - (8) Xia, Q.; Zhang, K.; Zheng, T.; An, L.; Xia, C.; Zhang, X. Integration of CO₂ Capture and Electrochemical Conversion: Focus Review. *ACS Energy Lett.* **2023**, 8 (6), 2840–2857. <https://doi.org/10.1021/acsenergylett.3c00738>.
 - (9) Kazemifar, F. A Review of Technologies for Carbon Capture, Sequestration, and Utilization: Cost, Capacity, and Technology Readiness. *Greenh. Gases Sci. Technol.* **2022**, 12 (1), 200–230. <https://doi.org/10.1002/ghg.2131>.
 - (10) Legrand, U.; Apfel, U.-P.; Boffito, D. C.; Tavares, J. R. The Effect of Flue Gas Contaminants on the CO₂ Electroreduction to Formic Acid. *J. CO₂ Util.* **2020**, 42, 101315. <https://doi.org/10.1016/j.jcou.2020.101315>.
 - (11) Gautam, M.; Hofsommer, D. T.; Uttarwar, S. S.; Theaker, N.; Paxton, W. F.; Grapperhaus, C. A.; Spurgeon, J. M. The Effect of Flue Gas Contaminants on Electrochemical Reduction of CO₂ to Methyl Formate in a Dual Methanol/Water Electrolysis System. *Chem Catal.* **2022**, 2 (9), 2364–2378. <https://doi.org/10.1016/j.checat.2022.08.001>.
 - (12) Ko, B. H.; Hasa, B.; Shin, H.; Jeng, E.; Overa, S.; Chen, W.; Jiao, F. The Impact of Nitrogen Oxides on Electrochemical Carbon Dioxide Reduction. *Nat. Commun.* **2020**, 11 (1), 5856. <https://doi.org/10.1038/s41467-020-19731-8>.
 - (13) Kowalski, R. M.; Banerjee, A.; Yue, C.; Gracia, S. G.; Cheng, D.; Morales-Guio, C. G.; Sautet, P. Electroreduction of Captured CO₂ on Silver Catalysts: Influence of the Capture Agent and Proton Source. *J. Am. Chem. Soc.* **2024**, 146, 20728–20741. <https://doi.org/10.1021/jacs.4c03915>.
 - (14) Shen, K.; Cheng, D.; Reyes-Lopez, E.; Jang, J.; Sautet, P.; Morales-Guio, C. G. On the Origin of Carbon Sources in the Electrochemical Upgrade of CO₂ from Carbon Capture Solutions. *Joule* **2023**, 7 (6), 1260–1276. <https://doi.org/10.1016/j.joule.2023.05.010>.
 - (15) Choi, J.; Chiu, S.; Banerjee, A.; Sacchi, R. L.; Veith, G. M.; Stieber, C.; Hahn, C.; Alexandrova, A. N.; Morales-Guio, C. G. Corrosion and Enhanced Hydrogen Evolution in Electrochemical Reduction of Ammonium Carbamate on Transition Metal Surfaces. *J. Phys. Chem. Lett.* **2024**, 15, 8007–8017. <https://doi.org/10.1021/acs.jpcclett.4c01638>.

- (16) Safipour, J.; Weber, A. Z.; Bell, A. T. Detrimental Effects of Monoethanolamine and Other Amine-Based Capture Agents on the Electrochemical Reduction of CO₂. *ACS Energy Lett.* **2023**, *8*, 5012–5017. <https://doi.org/10.1021/acsenenergylett.3c01953>.
- (17) Chen, L.; Li, F.; Zhang, Y.; Bentley, C. L.; Horne, M.; Bond, A. M.; Zhang, J. Electrochemical Reduction of Carbon Dioxide in a Monoethanolamine Capture Medium. *ChemSusChem* **2017**, *10* (20), 4109–4118. <https://doi.org/10.1002/cssc.201701075>.
- (18) Lee, G.; Li, Y. C.; Kim, J.-Y.; Peng, T.; Nam, D.-H.; Sedighian Rasouli, A.; Li, F.; Luo, M.; Ip, A. H.; Joo, Y.-C.; Sargent, E. H. Electrochemical Upgrade of CO₂ from Amine Capture Solution. *Nat. Energy* **2020**, *6* (1), 46–53. <https://doi.org/10.1038/s41560-020-00735-z>.
- (19) Leverick, G.; Bernhardt, E. M.; Ismail, A. I.; Law, J. H.; Arifutzzaman, A.; Aroua, M. K.; Gallant, B. M. Uncovering the Active Species in Amine-Mediated CO₂ Reduction to CO on Ag. *ACS Catal.* **2023**, *13* (18), 12322–12337. <https://doi.org/10.1021/acscatal.3c02500>.
- (20) Guan, Y.; Kümper, J.; Mürtz, S. D.; Kumari, S.; Hausoul, P. J. C.; Palkovits, R.; Sautet, P. Origin of Copper Dissolution under Electrocatalytic Reduction Conditions Involving Amines. *Chem. Sci.* **2024**, *15* (35), 14485–14496. <https://doi.org/10.1039/D4SC01944J>.
- (21) Chiu, S.; Alexandrova, A. N. Cation Effects on CO₂ Delivery to Cu Electrode in Reactive Capture of CO₂. *J. Phys. Chem. Lett.* **2025**, *16*, 6032–6039. <https://doi.org/10.1021/acs.jpcllett.5c01022>.
- (22) Khurram, A.; Yan, L.; Yin, Y.; Zhao, L.; Gallant, B. M. Promoting Amine-Activated Electrochemical CO₂ Conversion with Alkali Salts. *J. Phys. Chem. C* **2019**, *123* (30), 18222–18231. <https://doi.org/10.1021/acs.jpcc.9b04258>.
- (23) Pérez-Gallent, E.; Vankani, C.; Sánchez-Martínez, C.; Anastasopol, A.; Goetheer, E. Integrating CO₂ Capture with Electrochemical Conversion Using Amine-Based Capture Solvents as Electrolytes. *Ind. Eng. Chem. Res.* **2021**, *60* (11), 4269–4278. <https://doi.org/10.1021/acs.iecr.0c05848>.
- (24) Bruggeman, D. F.; Rothenberg, G.; Garcia, A. C. Investigating Proton Shuttling and Electrochemical Mechanisms of Amines in Integrated CO₂ Capture and Utilization. *Nat. Commun.* **2024**, *15* (1), 9207. <https://doi.org/10.1038/s41467-024-53543-4>.
- (25) Kumar Verma, P.; L. McCrory, C. C. The Influence of Exogenous Amines on the Electrochemical CO₂ Reduction Activity of a Cobalt–Pyridyldiimine Catalyst. *Chem. Commun.* **2024**, *60* (62), 8039–8042. <https://doi.org/10.1039/D4CC02709D>.
- (26) Choi, J.; Banerjee, A.; Ross, R. D.; Zhang, Z.; Chiu, S.; Sacchi, R. L.; Veith, G. M.; Hahn, C.; Alexandrova, A. N.; Morales-Guio, C. G. Amine Structure Governs Corrosion Rates of Copper Catalysts in Electrochemical Reactive Capture of CO₂. *J. Phys. Chem. C.* <https://doi.org/10.1021/acs.jpcc.5c03178>.
- (27) Li, P.; Mao, Y.; Shin, H.; Yang, Q.; Cheng, X.; Li, Y.; Li, K.; Yu, H.; Mulder, R.; Pang, W. K.; Jin, H.; Zhao, Y.; Zheng, Z.; Finch, E.; Hearn, K.; Jia, B.; Waterhouse, G. I. N.; Wang, Z.; Ma, T. Tandem Amine Scrubbing and CO₂ Electrolysis via Direct Piperazine Carbamate Reduction. *Nat. Energy* **2025**, 1–12. <https://doi.org/10.1038/s41560-025-01869-8>.
- (28) Jeong, H.-Y.; Balamurugan, M.; Choutipalli, V. S. K.; Jeong, E.; Subramanian, V.; Sim, U.; Nam, K. T. Achieving Highly Efficient CO₂ to CO Electroreduction Exceeding 300 mA

- Cm-2 with Single-Atom Nickel Electrocatalysts. *J. Mater. Chem. A* **2019**, 7 (17), 10651–10661. <https://doi.org/10.1039/C9TA02405K>.
- (29) Jiang, K.; Siahrostami, S.; Zheng, T.; Hu, Y.; Hwang, S.; Stavitski, E.; Peng, Y.; Dynes, J.; Gangisetty, M.; Su, D.; Attenkofer, K.; Wang, H. Isolated Ni Single Atoms in Graphene Nanosheets for High-Performance CO₂ Reduction. *Energy Environ. Sci.* **2018**, 11 (4), 893–903. <https://doi.org/10.1039/c7ee03245e>.
- (30) Möller, T.; Ju, W.; Bagger, A.; Wang, X.; Luo, F.; Thanh, T. N.; Sofia Varela, A.; Rossmeisl, J.; Strasser, P. Efficient CO₂ to CO Electrolysis on Solid Ni–N–C Catalysts at Industrial Current Densities. *Energy Environ. Sci.* **2019**, 12 (2), 640–647. <https://doi.org/10.1039/C8EE02662A>.
- (31) Liang, S.; Huang, L.; Gao, Y.; Wang, Q.; Liu, B. Electrochemical Reduction of CO₂ to CO over Transition Metal/N-Doped Carbon Catalysts: The Active Sites and Reaction Mechanism. *Adv. Sci.* **2021**, 8 (24), 2102886. <https://doi.org/10.1002/advs.202102886>.
- (32) Hyung Kim, J.; Jang, H.; Bak, G.; Choi, W.; Yun, H.; Lee, E.; Kim, D.; Kim, J.; Young Lee, S.; Jeong Hwang, Y. The Insensitive Cation Effect on a Single Atom Ni Catalyst Allows Selective Electrochemical Conversion of Captured CO₂ in Universal Media. *Energy Environ. Sci.* **2022**, 15 (10), 4301–4312. <https://doi.org/10.1039/D2EE01825J>.
- (33) Neves-Garcia, T.; Hasan, M.; Zhu, Q.; Li, J.; Jiang, Z.; Liang, Y.; Wang, H.; Rossi, L. M.; Warburton, R. E.; Baker, L. R. Integrated Carbon Dioxide Capture by Amines and Conversion to Methane on Single-Atom Nickel Catalysts. *J. Am. Chem. Soc.* **2024**, 146 (46), 31633–31646. <https://doi.org/10.1021/jacs.4c09744>.
- (34) Xiao, Y. C.; Sun, S. S.; Zhao, Y.; Miao, R. K.; Fan, M.; Lee, G.; Chen, Y.; Gabardo, C. M.; Yu, Y.; Qiu, C.; Guo, Z.; Wang, X.; Papangelakis, P.; Huang, J. E.; Li, F.; O'Brien, C. P.; Kim, J.; Han, K.; Corbett, P. J.; Howe, J. Y.; Sargent, E. H.; Sinton, D. Reactive Capture of CO₂ via Amino Acid. *Nat. Commun.* **2024**, 15 (1), 7849. <https://doi.org/10.1038/s41467-024-51908-3>.
- (35) Levell, Z.; Yu, S.; Wang, R.; Liu, Y. What Is the “Other” Site in M–N–C? *J. Am. Chem. Soc.* **2024**, 147, 603–609. <https://doi.org/10.1021/jacs.4c12479>.
- (36) Gong, Y.-N.; Jiao, L.; Qian, Y.; Pan, C.-Y.; Zheng, L.; Cai, X.; Liu, B.; Yu, S.-H.; Jiang, H.-L. Regulating the Coordination Environment of MOF-Templated Single-Atom Nickel Electrocatalysts for Boosting CO₂ Reduction. *Angew. Chem. Int. Ed.* **2020**, 59 (7), 2705–2709. <https://doi.org/10.1002/anie.201914977>.
- (37) Kozuch, S.; Shaik, S. How to Conceptualize Catalytic Cycles? The Energetic Span Model. *Acc. Chem. Res.* **2011**, 44 (2), 101–110. <https://doi.org/10.1021/ar1000956>.
- (38) Koshy, D. M.; Chen, S.; Lee, D. U.; Stevens, M. B.; Abdellah, A. M.; Dull, S. M.; Chen, G.; Nordlund, D.; Gallo, A.; Hahn, C.; Higgins, D. C.; Bao, Z.; Jaramillo, T. F. Understanding the Origin of Highly Selective CO₂ Electroreduction to CO on Ni,N-Doped Carbon Catalysts. *Angew. Chem. - Int. Ed.* **2020**, 59 (10), 4043–4050. <https://doi.org/10.1002/anie.201912857>.
- (39) Jang, J.; Rüscher, M.; Winzely, M.; Morales-Guio, C. G. Gastight Rotating Cylinder Electrode: Toward Decoupling Mass Transport and Intrinsic Kinetics in Electrocatalysis. *AIChE J.* **2022**, 68 (5), e17605. <https://doi.org/10.1002/aic.17605>.

- (40) Hursán, D.; Timoshenko, J.; Ortega, E.; Jeon, H. S.; Rüschler, M.; Herzog, A.; Rettenmaier, C.; Chee, S. W.; Martini, A.; Koshy, D.; Roldán Cuenya, B. Reversible Structural Evolution of Metal-Nitrogen-Doped Carbon Catalysts During CO₂ Electroreduction: An Operando X-Ray Absorption Spectroscopy Study. *Adv. Mater.* **2024**, *36* (4), 2307809. <https://doi.org/10.1002/adma.202307809>.
- (41) Martini, A.; Timoshenko, J.; Grosse, P.; Rettenmaier, C.; Hursán, D.; Deplano, G.; Jeon, H. S.; Bergmann, A.; Roldan Cuenya, B. Adsorbate Configurations in Ni Single-Atom Catalysts during CO_2 Electrocatalytic Reduction Unveiled by Operando XAS, XES, and Machine Learning. *Phys. Rev. Lett.* **2024**, *133* (22), 228001. <https://doi.org/10.1103/PhysRevLett.133.228001>.
- (42) Martini, A.; Hursán, D.; Timoshenko, J.; Rüschler, M.; Haase, F.; Rettenmaier, C.; Ortega, E.; Etxebarria, A.; Roldan Cuenya, B. Tracking the Evolution of Single-Atom Catalysts for the CO₂ Electrocatalytic Reduction Using Operando X-Ray Absorption Spectroscopy and Machine Learning. *J. Am. Chem. Soc.* **2023**, *145* (31), 17351–17366. <https://doi.org/10.1021/jacs.3c04826>.
- (43) Yang, H. B.; Hung, S.-F.; Liu, S.; Yuan, K.; Miao, S.; Zhang, L.; Huang, X.; Wang, H.-Y.; Cai, W.; Chen, R.; Gao, J.; Yang, X.; Chen, W.; Huang, Y.; Chen, H. M.; Li, C. M.; Zhang, T.; Liu, B. Atomically Dispersed Ni(I) as the Active Site for Electrochemical CO₂ Reduction. *Nat. Energy* **2018**, *3* (2), 140–147. <https://doi.org/10.1038/s41560-017-0078-8>.
- (44) Weser, O.; Freitag, L.; Guthier, K.; Alavi, A.; Li Manni, G. Chemical Insights into the Electronic Structure of Fe(II) Porphyrin Using FCIQMC, DMRG, and Generalized Active Spaces. *Int. J. Quantum Chem.* **2021**, *121* (3), e26454. <https://doi.org/10.1002/qua.26454>.
- (45) Abraham, V.; Mayhall, N. J. Selected Configuration Interaction in a Basis of Cluster State Tensor Products. *J. Chem. Theory Comput.* **2020**, *16* (10), 6098–6113. <https://doi.org/10.1021/acs.jctc.0c00141>.
- (46) Rask, A. E.; Zimmerman, P. M. The Many-Body Electronic Interactions of Fe(II)–Porphyrin. *J. Chem. Phys.* **2022**, *156* (9), 094110. <https://doi.org/10.1063/5.0079310>.
- (47) Vitale, E.; Li Manni, G.; Alavi, A.; Kats, D. FCIQMC-Tailored Distinguishable Cluster Approach: Open-Shell Systems. *J. Chem. Theory Comput.* **2022**, *18* (6), 3427–3437. <https://doi.org/10.1021/acs.jctc.2c00059>.
- (48) Zhou, C.; Gagliardi, L.; Truhlar, D. G. Multiconfiguration Pair-Density Functional Theory for Iron Porphyrin with CAS, RAS, and DMRG Active Spaces. *J. Phys. Chem. A* **2019**, *123* (15), 3389–3394. <https://doi.org/10.1021/acs.jpca.8b12479>.
- (49) Lei, J.; Zhu, T. Impact of Potential and Active-Site Environment on Single-Iron-Atom-Catalyzed Electrochemical CO₂ Reduction from Accurate Quantum Many-Body Simulations. *ACS Catal.* **2024**, *14* (6), 3933–3942. <https://doi.org/10.1021/acscatal.3c05999>.
- (50) Lavroff, R. H.; Kats, D.; Maschio, L.; Bogdanov, N. A.; Alavi, A.; Alexandrova, A. N.; Usvyat, D. Aperiodic Defects in Periodic Solids. arXiv November 25, 2024. <https://doi.org/10.48550/arXiv.2406.03373>.

- (51) Christlmaier, E. M. C.; Kats, D.; Alavi, A.; Usvyat, D. Full Configuration Interaction Quantum Monte Carlo Treatment of Fragments Embedded in a Periodic Mean Field. *J. Chem. Phys.* **2022**, *156* (15), 154107. <https://doi.org/10.1063/5.0084040>.
- (52) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B - Condens. Matter Mater. Phys.* **1996**, *54* (16), 11169–11186. <https://doi.org/10.1103/PhysRevB.54.11169>.
- (53) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6* (1), 15–50. [https://doi.org/10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0).
- (54) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- (55) Zhang, Z.; Gee, W.; Sautet, P.; Alexandrova, A. N. H and CO Co-Induced Roughening of Cu Surface in CO₂ Electroreduction Conditions. *J. Am. Chem. Soc.* **2024**, *146* (23), 16119–16127. <https://doi.org/10.1021/jacs.4c03515>.
- (56) Steinmann, S. N.; Michel, C.; Schwiedernoch, R.; Sautet, P. Impacts of Electrode Potentials and Solvents on the Electroreduction of CO₂: A Comparison of Theoretical Approaches. *Phys. Chem. Chem. Phys.* **2015**, *17* (21), 13949–13963. <https://doi.org/10.1039/C5CP00946D>.

For Table of Contents Only

