

Electrode–Electrolyte Engineering and In Situ Spectroscopy for Urea Electrosynthesis from Carbon Dioxide and Nitrate Co-Reduction

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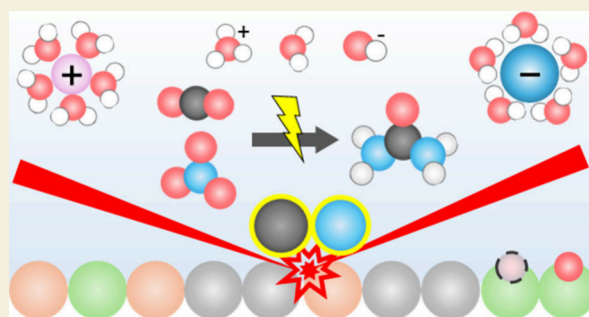
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ABSTRACT: The biogeochemical cycles of carbon and nitrogen are globally disturbed due to the intensive use of fossil fuels and fertilizers, which is reflected by the accumulation of carbon dioxide in the atmosphere and nitrate in water streams. The co-electroreduction of carbon dioxide and nitrate is a promising low-carbon alternative for urea synthesis that would help to reestablish both carbon and nitrogen cycles. This Perspective highlights the importance of rational catalyst and electrolyte engineering to enable electrochemical urea synthesis. Although the field has gained significant attention over the past few years, fundamental research under well-defined conditions remains underexplored. We highlight the importance of investigating structure-sensitivity and electrolyte effects on electrochemical C–N coupling through complementary in situ spectroscopy and online techniques. Model studies, including in situ surface-sensitive investigations, will be crucial to understand the molecular mechanisms and thus to rationally design more efficient systems for urea electrosynthesis, paving the way for their scalable and industrial applications.

KEYWORDS: electrochemistry, electrocatalysis, urea synthesis, C–N coupling, in situ spectroscopy, electrode–electrolyte engineering, nitrogen cycle



1. INTRODUCTION

Urea is one of the most widely used organonitrogen compounds in agriculture due to its high nitrogen content, with an estimated annual production of around 200 million tons.¹ Nevertheless, the energy-intensive Bosch–Meiser process currently used for urea production makes this industry a significant source of carbon dioxide (CO₂) emissions.² This method combines ammonia, produced via the Haber–Bosch process, with CO₂ to form urea under a high pressure and temperature.^{1,3} Besides that, both carbon and nitrogen cycles are globally disturbed by the intensive use of fossil fuels and fertilizers, as reflected by the accumulation of CO₂ in the atmosphere and nitrate (NO₃[−]) ions in water streams.⁴ Therefore, electrochemical urea synthesis from the co-reduction of CO₂ and NO₃[−] is a promising sustainable alternative to address these critical challenges when powered by renewable energy.^{2,5} To ensure charge balance, this process must be coupled with an oxidation reaction at the anode, such as biomass or water oxidation.⁶ This approach not only mitigates CO₂ emissions but also reduces the harmful concentration of NO₃[−] in water streams, helping to restore both carbon and nitrogen cycles.^{4,7} Figure 1 schematically shows both traditional (Bosch–Meiser process) and alternative sustainable (electrochemical) routes for urea synthesis.

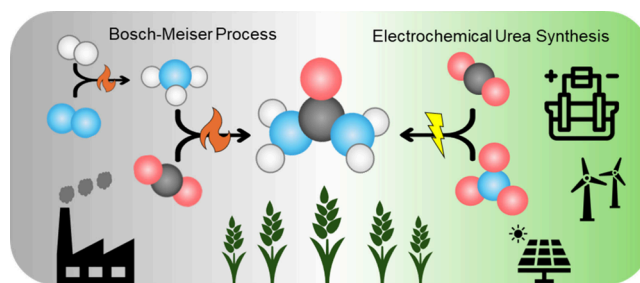


Figure 1. Scheme comparing the traditional Bosch–Meiser process with the alternative electrochemical co-reduction of CO₂ and nitrate to produce urea.

Despite the promising potential of electrochemical urea synthesis from CO₂ and NO₃[−], its practical application has

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significant obstacles to be addressed, primarily due to the myriad of byproducts and competing possible reaction pathways coming from both reduction processes.^{2,7,8} This challenge underscores the need for highly efficient and selective electrocatalysts to drive reactions toward the desired intermediates and products. Addressing these challenges relies heavily on active site and electrolyte engineering,^{9–11} which are crucial for enhancing catalytic performance, allowing us to favor the desired reaction pathways and therefore improving the selectivity needed for urea production.

To successfully synthesize urea from the reduction of CO₂ and NO₃[−], we need to electrochemically generate the correct precursor species capable of coupling to form a C–N bond. Understanding how the interaction between catalytic active sites and electrolyte species tunes the simultaneous formation of these precursors is crucial for efficient urea synthesis. Gathering evidence on the roles of both catalyst structure and electrolyte species in these electrocatalytic processes demands precise control of experimental conditions along with the application of electrochemical methods and in situ spectroscopic techniques.^{10,12–14}

Many recent reviews have explored the mechanistic aspects of the co-reduction of CO₂ and NO₃[−] for urea synthesis, emphasizing catalyst properties that are required to promote key steps in C–N coupling.^{1–3,5,7,15–19} In this Perspective, we considered the proposed mechanisms in the literature to put forward a discussion of how the current knowledge of the structure sensitivity and electrolyte effects in the individual reduction reactions can guide future studies in urea synthesis. By exploiting this fundamental understanding, along with the use of coupled in situ and online techniques, we aim to stimulate the rational design of electrode–electrolyte interfaces to promote the C–N bond formation and favor urea synthesis.

Herein, we propose a systematic approach to assess the different roles of both electrocatalytically active sites and electrolyte species in the co-reduction of CO₂ and NO₃[−]. First, we describe some of the mechanisms reported in the literature for the urea synthesis from CO₂ and NO₃[−] reduction in terms of the identity of the C–N coupling species. Given that these C and N precursors must be generated simultaneously, we explore how current insights into catalyst structure sensitivity and electrolyte effects in both CO₂ and NO₃[−] reduction can be applied to optimize urea synthesis. To accurately assign these roles, we recommend using coupled experimental techniques, such as electrochemical methods and in situ spectroscopies, to monitor the reaction progress in real time. Finally, we highlight some key opportunities in catalyst and electrolyte advancements that should be considered for the rational design of electrocatalytic systems for urea electrosynthesis.

2. MECHANISTIC ASPECTS OF C–N COUPLING FOR UREA ELECTROSYNTHESIS

The specific carbon and nitrogen species responsible for C–N coupling for electrochemical urea production are a topic of debate in the literature, as they can vary depending on the role of the electrocatalytically active sites for both reduction reactions. We can classify the proposed C–N coupling steps into two different types: adsorbate + adsorbate (Figures 2a–c), and adsorbate + dissolved species (Figures 2d–f). Both types of mechanisms demand a detailed understanding of how active sites and mass transport aspects influence the likelihood of C–N coupling, which is crucial for improving key parameters, such as selectivity and activity toward urea.

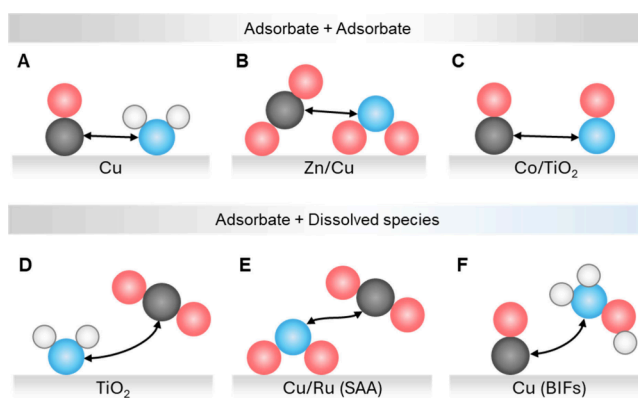


Figure 2. Scheme of six different proposed steps for the coupling of C–N species: (a) coupling of *CO and *NH₂ on a Cu gas diffusion electrode,²⁰ (b) coupling of *CO₂ and *NO₂ on a bimetallic Cu/Zn electrode,²² (c) coupling of *CO and *NO on a Co-supported TiO₂ catalyst,²³ (d) capture of molecular CO₂ with *NH₂ on a TiO₂ electrode,²⁴ (e) capture of molecular CO₂ via *NO₂ on a Cu single atom alloyed (SAA) with Ru,²⁵ and (f) nucleophilic attack of hydroxylamine to adsorbed CO on Cu sites in boron imidazolate frameworks (BIFs).²⁷ Black, blue, red, and white spheres represent carbon, nitrogen, oxygen, and hydrogen atoms, respectively.

The simultaneous formation of two distinct adsorbed species for successful C–N coupling suggests that the catalyst must have two different active sites close enough to each other to facilitate the bond formation.^{2,7} In their pioneering investigations, Shibata et al.²⁰ studied the activity of copper gas diffusion electrodes for urea electrosynthesis, in which they attributed the C–N coupling step to the previous formation of CO and NH₂ precursors (Figure 2a). They propose that urea is formed from the previous reduction of CO₂ to CO and NO₂[−] to NH₂, which would react (CO + 2NH₂) and form urea ((NH₂)₂CO). In the same direction, Meng et al.²¹ propose that *CO and *NH₂ are the C–N coupling species when investigating the activity of core–shell Cu–Zn nanowires. Based on in situ spectroscopic and theoretical calculations, they proposed that after the independent reduction of CO₂ and NO₃[−], *CO and *NH₂ couple to form *CONH₂, which subsequently reacts with *NH₂ species to produce urea. Luo et al.²² explored the combination of Zn and Cu active sites that promotes the *CO₂ + *NO₂ (Figure 2b) coupling and *CO₂NH hydrogenation, respectively. Tu et al.²³ reported the occurrence of the C–N coupling step through *CO and *NO species on single-atom Co-decorated TiO₂, showing that alkali cations stabilize both adsorbates and boost the catalyst activity for this process. For these proposed C–N coupling steps, it is essential to promote either the reduction of CO₂ to *CO (Figures 2a and c), CO₂ adsorption (Figure 2b), or the reduction of NO₃[−] to *NH₂, *NO₂, or *NO (Figures 2a–c, respectively). Forming those species requires an understanding of the roles that distinct active sites and electrolyte species play in promoting the simultaneous adsorption processes.

Alternatively, the C–N coupling step can occur via adsorbed and dissolved species (Figure 2d–f). In these cases, we must selectively form the adsorbate, namely, *NH₂, *NO₂, or *CO, which captures a specific dissolved species: CO₂ (Figures 2d and e) or hydroxylamine (NH₂OH) generated from NO₃[−] reduction (Figure 2f). This type of mechanism requires active site selectivity toward the desired adsorbate and optimized mass transport of dissolved species through migration, diffusion, and convection processes that can be influenced by

electrolyte species. Huang et al.²⁴ employed TiO_2 electrocatalysts and attributed the enhanced urea synthesis to the role of $^*\text{NH}_2$ species in capturing CO_2 and activating its reduction to $^*\text{NH}_2\text{CO}$ (Figure 2d). By employing a Cu single atom alloyed (SAA) with Ru, Wang et al.²⁵ found that the C–N coupling step occurs via the reaction of adsorbed $^*\text{NO}_2$ with molecular CO_2 at $\text{Cu}_1\text{–Ru}$ sites, forming a $^*\text{CO}_2\text{NO}_2$ intermediate that would be further reduced and hydrogenated to form urea (Figure 2e). In the same direction, Cai et al.²⁶ propose that $^*\text{NO}_2$ and dissolved CO_2 are the C–N coupling species for urea production on iron-doped InOOH nanosheets through theoretical calculations that also indicated that the introduced iron could reduce the thermodynamic free energy of $^*\text{CO}_2\text{NH}_2$ protonation. Gerke et al.²⁷ employed Cu single active sites for electrochemical urea production; in this case, Cu sites were inside boron imidazolate frameworks (BIFs). They found that the C–N coupling step occurs via a reaction between adsorbed $^*\text{CO}$ and dissolved NH_2OH (Figure 2f). Once formed, NH_2OH can be easily over-reduced to NH_3 ,²⁸ and the simultaneous production of $^*\text{CO}$ would allow the nucleophilic attack required to perform C–N coupling. To minimize ammonia formation, it is important to ensure that the production of NH_2OH from NO_3RR occurs with optimized kinetics to promptly react with adsorbed $^*\text{CO}$. This interaction would enable the nucleophilic addition–elimination reaction necessary for urea formation.²⁹

According to the Sabatier principle, the activity of a catalyst is maximized when the interaction between the catalytic surface and the reaction intermediates is neither too strong (hindering its desorption) nor too weak (insufficient activation).⁹ This leads to volcano plots; the understanding of the key descriptors allows us to approach the top of the volcano, as has been shown for different electrocatalytic reactions, such as oxygen electroreduction.³⁰ Applying this principle for the CO_2 reduction reaction (CO_2RR), the correlation of the catalyst bond strength with $^*\text{CO}$ and $^*\text{H}$ adsorbates dictates whether it will be selective toward CO , H_2 , formic acid or hydrocarbons.^{10,31} For the electrochemical reduction of NO_3^- (NO_3RR), we can correlate the atomic nitrogen–metal and oxygen–metal bond strengths with electrocatalytic selectivity.³² Theoretical studies suggest that strong adsorption energies for both N (ΔE_{N}) and O (ΔE_{O}) favor N_2 formation, whereas moderate ΔE_{N} and ΔE_{O} are necessary for selective ammonia production.³³

To shed light on how theoretical studies can deepen our understanding of mechanisms for urea synthesis, we highlight some works that employ computational studies to suggest key descriptors for urea synthesis. Density functional theory (DFT) calculations are a powerful technique for investigating the electronic structure, adsorption energies, and reaction kinetics at the electrode–electrolyte interface.^{34,35} Thus, they provide crucial insights into the mechanisms of C–N coupling in electrochemical urea synthesis. By modeling the interactions between active sites and intermediates, DFT can help us to identify favorable binding configurations and catalytic pathways for the simultaneous reduction of CO_2 and NO_3^- as well as elucidate the role of electrolyte components in stabilizing the key adsorbates.

Wan et al.³⁶ theoretically analyzed the thermodynamic and kinetic aspects of key steps that enable C–N coupling during the co-reduction of CO and NO using DFT calculations. They investigated how the binding strengths of $^*\text{CO}$, $^*\text{NO}$ and $^*\text{H}$ on various metals correlate with activity toward urea synthesis,

identifying Cu as the optimal metal that effectively binds $^*\text{CO}$ and $^*\text{NO}$ while avoiding $^*\text{H}$. They proposed a mechanism for urea formation on Cu, in which NO is preferentially reduced at a lower overpotential than CO , the first C–N coupling step would occur via $^*\text{N}$ and $^*\text{CO}$, and the second one would happen through the reaction between $^*\text{CONH}$ and $^*\text{N}$. Using DFT to evaluate the possible mechanisms for urea synthesis on Zn, Long et al.³⁷ found that the first C–N coupling occurs via $^*\text{CO}$ and $^*\text{NOH}$ and the second one occurs through $^*\text{CONH}$ and $^*\text{N}$. These theoretical investigations provide valuable mechanistic insights into the roles of different active phases in promoting key steps for urea synthesis, guiding us for the development of more efficient catalytic systems.

It is essential to identify which are the key adsorbates and reactions that must happen for urea synthesis to finely tune both geometric and electronic effects and optimize the electrocatalytic activity. To date, most reported strategies rely on mixing different metals and/or oxides, resulting in changes in electronic bands of a given active site.^{2,3,7,8,15} Nevertheless, there is a limited experimental understanding of how the geometry of the active site influences its activity in electrochemical C–N coupling. Most studies concentrate on polycrystalline substrates, which feature numerous potential active sites and unknown facet distributions,³⁸ hindering our ability to accurately assign structural roles to the catalytic activity. Thus, it is crucial to evaluate the structural sensitivity for urea electrosynthesis through model studies on well-defined catalysts with a regular and known distribution of active sites such as single crystalline electrodes. This approach enables us to isolate and analyze specific electrocatalytic responses associated with different facets.

3. STRUCTURE SENSITIVITY OF CO_2 AND NO_3^- REDUCTION ON CU-BASED CATALYSTS

Understanding the role of active site geometry in forming the correct precursors from CO_2RR and NO_3RR is essential to rationally design improved electrocatalysts for urea electrosynthesis. For metals with a face-centered cubic (fcc) lattice (Au, Ag, Cu, Pt, Pd, and Ir), we can obtain three different basal planes depending on the crystallographic orientation.^{9,39} They are classified by Miller indexes (111), (100), and (110), in which each metal has 9, 6, or 4 neighboring atoms, i.e., coordination numbers, respectively.

As discussed in the previous section, Wan et al.,³⁶ by evaluating the binding energy of $^*\text{CO}$, $^*\text{NO}$, and $^*\text{H}$ with various transition metals, found that only Cu exhibits the optimal properties for simultaneously forming key precursors for C–N coupling while avoiding the competing HER. Additionally, copper is one of the most studied catalysts at a fundamental level for NO_3RR and CO_2RR due to the high overlap between the π^* orbitals of NO_3^- and CO_2 and the occupied d band of Cu that favors the desired charge transfers.^{40,41} These favorable electronic properties of Cu for NO_3RR and CO_2RR motivated our discussion on its structure sensitivity in both reactions and how it correlates with the properties required for C–N coupling. Most studies in the literature that evaluate the structure sensitivity of Cu usually compare the selectivity of the basal planes Cu(100) and Cu(111) for CO_2RR ^{42,43} and NO_3RR .⁴⁴ This consolidated literature motivated us to put these foundations in context with the desired catalytic properties for urea synthesis. We encourage the review of studies on single crystals toward both CO_2RR ^{45,46} and NO_3RR ^{47,48} for other promising

catalysts, enabling the community to focus efforts on the most effective catalyst design strategies for electrochemical C–N coupling.

Comparing the activity of Cu(100) and Cu(111) for CO₂RR, multiple studies suggest that Cu(100) favors C₂₊ products formation, while methane is the main product formed on Cu(111).^{10,42,43,49,50} Schouten et al.⁴² used online electrochemical mass spectrometry on Cu(100) and Cu(111) during CO₂RR. Their results demonstrate that Cu(100) favors C–C coupling leading to ethylene formation via a pH-independent route through the formation of a *OCCO[−] intermediate (Figure 3a). In contrast, on Cu(111), CH₄ is formed through a

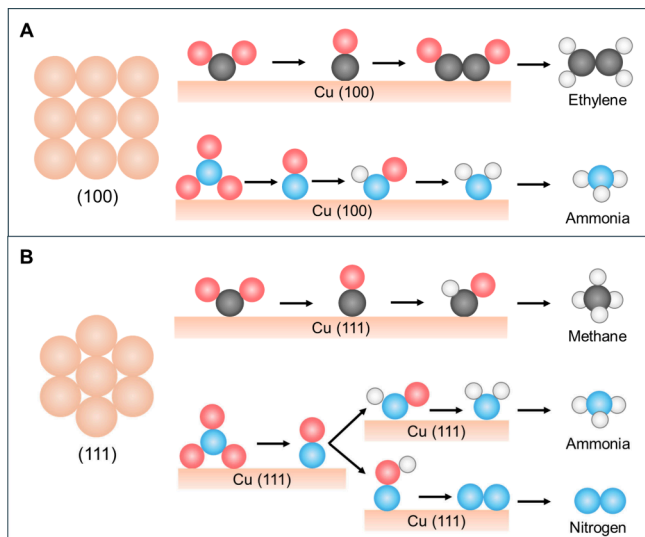


Figure 3. Illustration of the top view of (a) Cu(100) and (b) Cu(111) facets with the respective proposed mechanisms for nitrate and carbon dioxide reduction. Black, blue, red, and white spheres represent carbon, nitrogen, oxygen, and hydrogen atoms, respectively.

proton transfer via the *CHO intermediate (Figure 3b). In this same direction, Pérez-Gallent et al.⁵¹ used in situ Fourier transform infrared (FTIR) spectroscopy to detect the formation of *OCCO only on Cu(100) and not on Cu(111). Considering these results, we would need to avoid a high Cu(100) surface ratio to minimize C–C bond formation and favor C–N coupling. Contrary to the previous studies, Scholten et al.⁵² showed that both Cu(100) and Cu(111) surfaces favor the hydrogen evolution reaction (HER) over CO₂RR. They discuss that surface defects and steps formed during the pretreatment yield the formation of methane at the expense of H₂. From this point of view, combining terrace sites, which provide *H for hydrogenation processes, with step sites, which form the desired CO₂RR intermediates, would be an alternative for C–N coupling.

Moving to the structure sensitivity of Cu for the formation of nitrogen adsorbates, Pérez-Gallent et al.⁴⁴ studied the pH-dependent activity of NO₃RR on Cu(100) and Cu(111). They showed that at pH 1, ammonium (NH₄⁺) is formed through *NO, which is produced at a lower overpotential on Cu(111), while at pH 13 the formation of NH₂OH is faster at Cu(100). To form NH₂OH from *NO, the hydrogenation of *NO via the N atom to form *NHO is required, followed by two proton-coupled electron transfers (Figure 3a and b).²⁹ If *NO is hydrogenated through the O atom, we favor the formation of N₂, which is more likely to happen on the Cu(111) surface

(Figure 3b).⁵³ Considering this observation, if we assume that NH₂OH is needed to form urea, according to the mechanism proposed by Gerke et al.²⁷ (Figure 2f), a higher ratio of Cu(100) facet distribution would improve the selectivity for urea production on Cu-based catalysts.

From the theoretical point of view, Calle-Vallejo⁵⁴ compared computationally the roles of both identity and structure of the metal electrodes in *CO and *NO hydrogenation steps. He showed that *COH is more favorably formed on the Cu(100) (Figure 3a) basal plane, while Cu(111) favors the formation of *CHO (Figure 3b). For *NO hydrogenation, both *NHO and *NOH can be formed on Cu(111) (Figure 3b), while mainly *NHO is formed on Cu(100) (Figure 3a), which is in agreement with what was experimentally found by Pérez-Gallent et al.⁵⁵ The formation of *NOH would favor N–N coupling, while the NO hydrogenation through the N atom would favor the production of *NH₂ adsorbates, which is crucial for urea synthesis for two different proposed C–N coupling steps (Figures 2a and d).^{20,24}

Wu et al.⁵⁶ recently reported a computational study that evaluated mechanistic aspects of electrochemical C–N coupling on Cu single-crystalline surfaces. Their results revealed that *CO–NH and *NH–CO–NH are the key intermediates, and increasing the Cu(100) surface ratio would promote the catalyst efficiency for urea formation. Considering this theoretical indication of structural dependence in urea synthesis on Cu, it is compelling to explore this finding experimentally to validate and further understand the role of surface structure in catalyst performance. Therefore, we encourage fundamental studies of single-crystalline electrodes to assign the role of the different basal planes in forming the desired precursors for more efficient and selective urea electrosynthesis.

4. ELECTROLYTE EFFECTS ON CO₂ AND NO₃[−] REDUCTION

Electrochemical reduction reactions occur through electron transfer from the electrode to electrolyte species within the electric double layer (EDL), a nanometric region at the electrode–electrolyte interface.¹⁴ In this region, the electrolyte composition affects the availability of reactants, stability and reactivity of adsorbates, the electric field within the Stern layer, mass transport, etc.^{57,58} The comprehension of the dynamics of electrolyte species within the EDL under electrochemical CO₂RR and NO₃RR is crucial to enable the formation of the desired precursor species for optimized urea synthesis. In this section, we discuss the effect of electrolyte pH, cations, and anion species on the individual reduction reactions of CO₂ and NO₃[−], highlighting how these factors can be leveraged for efficient urea synthesis.

The electrolyte pH controls the availability of protons for proton-coupled electron transfer (PCET) reactions, impacting key steps of CO₂RR, NO₃RR, and the competing HER. Additionally, pH determines the acid–base equilibria of key carbon and nitrogen species, such as CO₂, bicarbonate, carbonate, ammonia, and hydroxylamine (Figure 4a).^{59,60} Although promoting reduction reactions under acidic conditions is challenging due to the prevalence of HER as a competing reaction, optimizing the pH is essential to promote specific PCET steps required for efficient urea synthesis from CO₂RR and NO₃RR. Furthermore, the occurrence of reduction reactions increases local,^{61,62} and potentially bulk,⁶³ electrolyte pH through the consumption of protons,

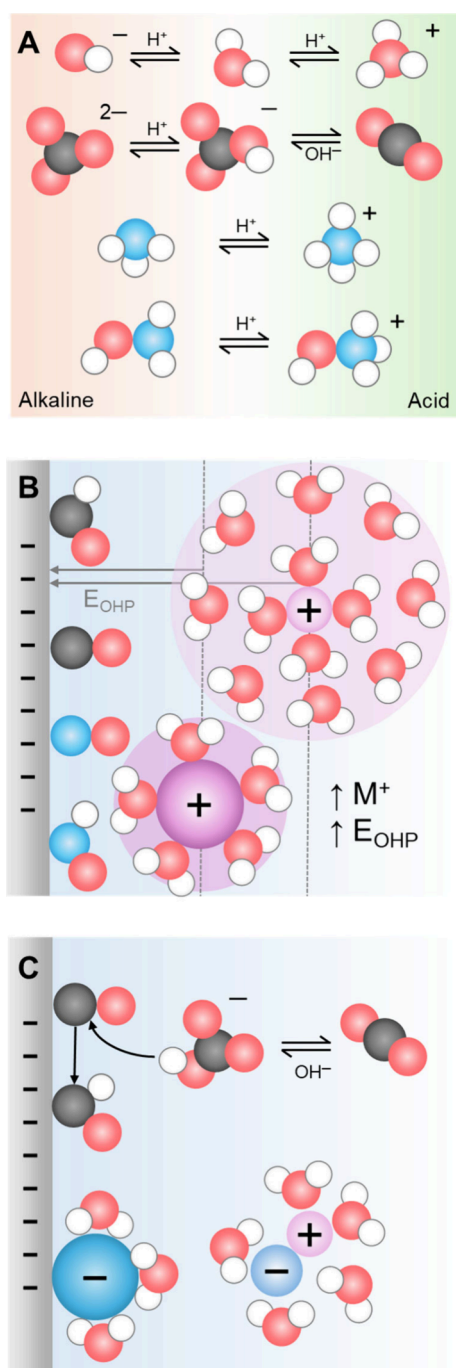


Figure 4. Illustrations of electrolyte effects. (a) Impact of pH in the acid–base equilibria of key species: water, CO₂, ammonia, and hydroxylamine. (b) Effect of the size of alkali cations (shades of purple) on the length of the OHP and consequent stabilization of C and N adsorbates. (c) Effect of buffering anions and the size of halides (shades of blue). Black, blue, red, and white spheres represent carbon, nitrogen, oxygen, and hydrogen atoms, respectively.

which can hinder following PCET steps. Therefore, it is important to employ experimental approaches that allow us to maintain optimal mass transport and effective buffering conditions to optimize the electrolyte pH for urea synthesis.

Several studies have investigated the effects of cations on CO₂RR^{11,57,58,64–71} and NO₃RR.^{72–75} There are different phenomena through which cations can either promote or hinder electrochemical reactions. The smaller the cation, the

thicker its solvation sphere (Figure 4b), meaning that it requires a higher number of water molecules for electric field stabilization. Cations alter the electric field within the Stern layer depending on how they accumulate at the outer Helmholtz plane (OHP). Larger cations with smaller hydration shells result in a thinner EDL, intensifying the electric field, which can enhance both CO₂RR and NO₃RR by stabilizing adsorbates with dipole moments.⁷⁶ Thus, a higher interfacial electric field would stabilize the *CO, *NHO, *CHO, and *NO that can be formed on the catalyst surface (Figure 4b).^{65,76}

Studying the effect of alkali cations on NO₃RR, Wen et al.⁷³ demonstrate that Cu's Faradaic efficiency toward ammonia follows the trend Li⁺ < Cs⁺ < Na⁺ < K⁺, as potassium accelerates the proton transport from the bulk into the EDL, facilitating PCET reactions. For the competing HER, the presence of hydrated cations at the OHP promotes the Volmer step at low overpotentials by stabilizing its transition state,⁵⁸ which could either enhance HER activity or promote PCET steps for CO₂RR and NO₃RR. For urea electrosynthesis, we must know which are the desired precursors for C–N coupling, as well as the key PCET steps to improve the cation-mediated co-reduction of CO₂ and NO₃[−].

The effect of anions on the CO₂RR and NO₃RR usually relies on their adsorption properties and buffer capacities, both illustrated in Figure 4c. Larger halides, and higher specific adsorptions, lead to lower catalytic activity of CO₂RR⁷⁷ and NO₃RR (at lower overpotential).^{75,78} At higher overpotential, Katsounaros et al.⁷⁵ reported an opposite trend for NO₃RR, which they attribute to the favorable formation of ion pairs of smaller halides with its corresponding cations, inhibiting the availability of cations at the OHP (Figure 4c). Buffering anions can act as proton donors that can either favor the formation of hydrocarbons, such as methane, or promote the competing HER.⁷⁹ During reduction reactions, the change in local pH impacts the equilibria of buffering anions,⁶² which makes bicarbonate a CO₂ reservoir due to alkaline local pH shift.⁸⁰ Understanding the role of anions for urea electrosynthesis would clarify the challenges that need to be addressed regarding the optimum anionic environment and also the necessity of pretreatment of nitrate-rich wastewater.

5. COMPLEMENTARY IN SITU AND ONLINE TECHNIQUES FOR UREA ELECTROSYNTHESIS

Having established the importance of catalyst structure and electrolyte composition for urea electrosynthesis, we now turn our attention to exploring how these effects can be studied using coupled analytical techniques. As we stated in the previous section, electrochemical reactions occur within the EDL, which is a region that typically extends a few angstroms to tens of nanometres.¹⁴ Given these dimensions, surface-sensitive techniques are indispensable for probing localized phenomena driving electrochemical urea synthesis. This combination of techniques allows us to extract information about the formation of intermediates, adsorbates, byproducts, and local changes of both the catalyst and electrolyte.

In situ attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) and Raman spectroscopy can give complementary information on the potential dependent formation of the C–N bond during urea electrosynthesis. Li et al.⁸¹ employed both techniques to understand the mechanism of the co-reduction of CO₂ and NO₃[−] on nitrogen-doped carbon catalysts. Using ATR-SEIRAS, they

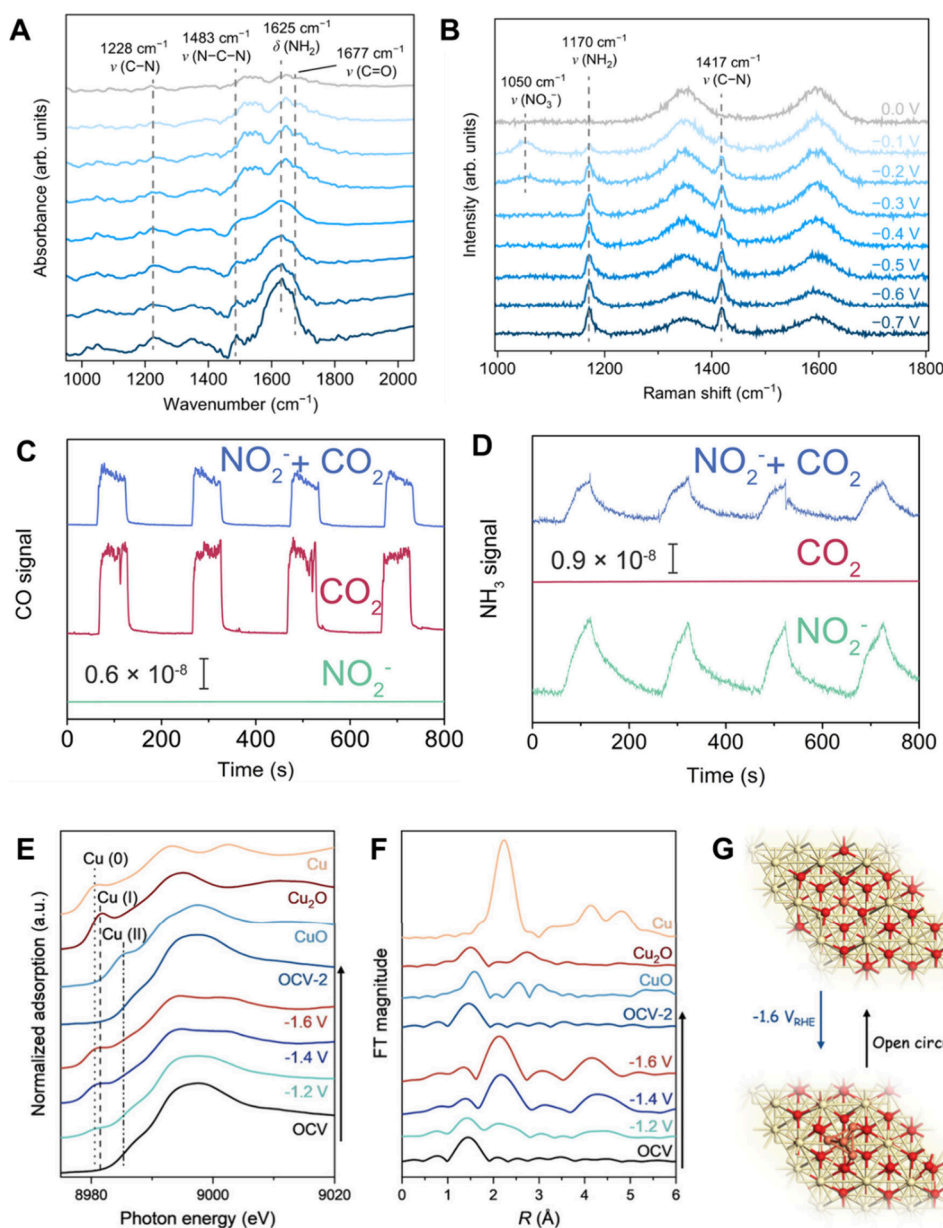


Figure 5. Results from different complementary in situ and online techniques for urea electrochemical synthesis: (a) in situ ATR-SEIRAS and (b) Raman spectroscopy. Reproduced from ref 81. Available under a CC-BY license. Copyright 2024 Springer Nature. Online differential mass spectrometry for (c) CO and (d) NH₃. Reproduced with permission from ref 84. Copyright 2021 Elsevier. In situ (e) XANES and (f) EXAFS with (g) the scheme of Cu agglomeration made from EXAFS results. Reproduced with permissions from ref 83. Copyright 2023 Wiley-VCH.

detected the potential-dependent emergence of bands at 1228 and 1483 cm⁻¹, which they assigned to C–N and N–C–N bonds from urea, respectively (Figure 5a). They also confirmed the formation of a C–N bond with in situ Raman spectroscopy through the emergence of a band at 1417 cm⁻¹ (Figure 5b). These spectroscopic techniques have primarily been used to probe the occurrence of bond formation for urea electrosynthesis, unveiling the reaction mechanism. However, they can also be applied to explore thermodynamic and kinetic aspects of simultaneous CO₂RR and NO₃RR by correlating the evolution of key bands with applied potential and current densities.⁸² In situ spectroscopies can help optimize both electrolyte composition²³ and catalyst design⁸³ for promoting the formation of the desired adsorbates in urea synthesis.

The comprehension of the C–N coupling step is important, but understanding the potential-dependent occurrence of side

reactions that form byproducts from the independent reduction of CO₂RR and NO₃RR is crucial to optimize urea synthesis. In this regard, online differential electrochemical mass spectrometry (DEMS) can be employed to evaluate the potential-dependent formation of volatile products. Meng et al.⁸⁴ employed DEMS to track the formation of the byproducts CO and NH₃ formed from the independent reduction CO₂ and NO₂⁻, respectively (Figures 5c and d). Thus, DEMS is a powerful technique to elucidate reaction mechanisms and investigate which conditions lead to undesired reaction pathways, allowing us to avoid them.

The dynamics of the local coordination of the active site plays a major role in tuning the catalyst activity for an electrochemical reaction. In situ X-ray absorption spectroscopy (XAS) is a powerful technique to extract dynamic information, as it correlates the local coordination environment of the active

site with its activity to the electrochemical formation of urea. Wei et al.⁸³ employed in situ XAS to evaluate the dynamics of the X-ray absorption near edge spectra (XANES) as well as the *R*-space extended XAS fine structure spectra (EXAFS) of a Cu single atom on a CeO₂ support for urea synthesis (Figures 5e and f). They found that, under cathodic conditions, Cu single atoms aggregate, forming clusters (Figure 5g). This study on urea synthesis,⁸³ along with other recent works on the individual reduction of CO₂^{85,86} and NO₃[−],^{63,87} exemplifies how XAS techniques are already very elucidative tools to monitor the catalyst dynamics under electrochemical conditions. With the advancement of synchrotron facilities, XAS can now provide time-resolved insights, enabling an accurate understanding of reaction conditions that lead to catalyst degradation, which would be valuable for urea electrosynthesis.

We recommend the use of in situ spectroscopic techniques to study the molecular mechanisms on electrodes with a well-known distribution of active sites. These investigations will be essential to designing more efficient catalysts for electrochemical C–N coupling. This approach allows us to obtain detailed insights into the surface-dependent activity of the catalyst.⁵⁴ We also encourage the employment of surface-sensitive techniques coupled with electrochemistry experiments, allowing us to monitor the dynamics of the catalyst during urea electrosynthesis.

6. CHALLENGES AND OPPORTUNITIES IN ACTIVE SITE AND ELECTROLYTE ENGINEERING

The number of studies reporting new catalysts for urea electrosynthesis has grown exponentially over the last five years, as reflected in numerous recent reviews.^{1–3,5,7,15–18,88} In this section, we summarize key strategies currently employed for active site and electrolyte engineering to enhance electrosynthesis of urea, highlighting promising directions and opportunities for future research in the field. From the catalyst perspective, it is important to consider the need for combining different active sites that can promote different steps in the C–N coupling process from CO₂RR and NO₃RR. We highlight three strategies that address this challenge in different way (Figure 6): bimetallic catalysts, single-atoms alloys, and metal oxide catalysts. For electrolyte engineering, we highlight the study of the role of alkali cations in stabilizing key intermediates for urea synthesis.

By combining different metals, we can modulate electronic and geometric properties that can promote key steps in urea synthesis. In this regard, Luo et al.²² reported the use of a Zn/Cu hybrid catalyst to promote urea synthesis (illustrated in Figure 6a). They showed with both in situ spectroscopies and DFT studies that the combination of these two metals facilitates urea synthesis because they promote different key steps: the formation of *CO₂NO₂ occurs on Zn sites, while the *CO₂NH hydrogenation step is more favorable on Cu sites. Considering that multiple steps need to be favored by the catalyst surface, high-entropy alloys (HEAs) are also promising, since they consist of randomly distributed multi-metallic alloys that offers a wide range of unique sites. A recent work of Plenge et al.⁸⁹ theoretically evaluated a HEA for catalytic NO and CO reduction for C–N coupling, where they found a ternary AuCuPd as an optimum site at equal CO/NO partial pressures. The study of HEAs for the electrochemical co-reduction of CO₂ and NO₃[−] is a promising but still unexplored alternative for urea synthesis.

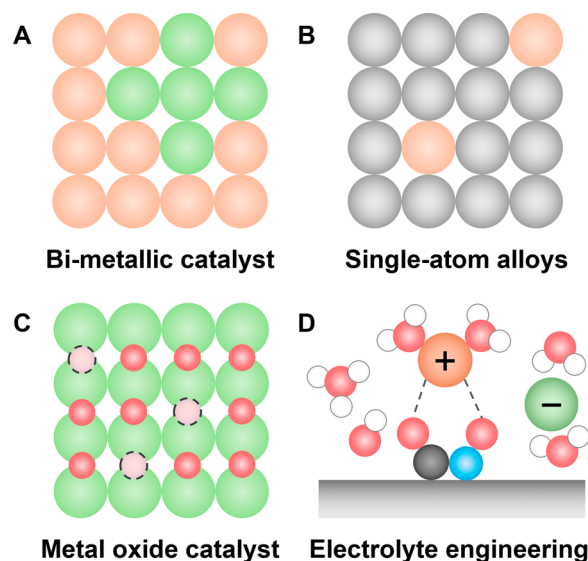


Figure 6. Illustration of different strategies and opportunities to study electrochemical synthesis of urea from carbon dioxide and nitrate reduction reactions: (a) bimetallic, (b) single atom, (c) oxygen vacancies in metal oxide catalysts, and (d) electrolyte engineering.

Single atom alloys (SAAs), which consist of a matrix of host metals with atomically dispersed dopant metallic atoms (Figure 6b), are also a compelling alternative for active site engineering, allowing us to obtain a surface with unique catalytic properties and different active sites promoting the desired electrochemical steps. Wang et al.²⁵ evaluated the activity of Cu single atoms in Ru for urea electrochemical synthesis. Using DFT analysis, they attributed the enhanced activity of Cu–Ru SAA to the occurrence of C–N coupling through *NO₂ + CO₂ on Cu–Ru sites, while the hydrogenation of *CO₂NH occurs on Ru–Ru sites. More detailed experimental investigations on the roles of different active sites of SAA in the C–N coupling mechanisms for urea synthesis are still needed.

Metal oxides under electrochemical reduction conditions are usually thermodynamically unstable, which leads to the formation of metal–oxide interfaces,⁹⁰ oxygen vacancies,⁹¹ and defects⁹² that can serve as active sites for electrochemical reactions.⁹³ Meng et al.⁸⁴ employed oxygen-vacancy-rich porous ZnO nanosheets for the electrosynthesis of urea from the co-reduction of NO₂[−] and CO₂ (illustrated in Figure 6c). They showed that oxygen vacancies boost urea formation and attributed this catalytic activity to the production of *COOH and *NH₂ adsorbates for C–N coupling through the occupation of oxygen vacancies by CO₂ and NO₂[−] species, which was not confirmed by in situ techniques. Anastasiadou et al.⁹⁴ evaluated mixed Zn and Cu oxides with different ratios for urea electrosynthesis, promisingly showing that optimized Faradaic efficiency could be obtained when employing CuO₅₀ZnO₅₀, which they attributed to possible electronic effects. The underlying cause of this enhanced activity remains unclear and can be investigated with coupled in situ and online techniques.

Another strategy for engineering active sites to promote key steps required for urea synthesis is to integrate multiple approaches, such as oxygen vacancies and single atoms.⁹⁵ Zhang and co-workers employed Zn single atoms anchored on oxygen vacancy (OV)-rich indium oxide (Zn₁/In₂O_{3–x}) to synthesize urea from CO₂ and NO₃[−] reduction.⁹⁵ Using in situ

FTIR and DFT calculations, they assigned distinct roles to the proposed active sites. They attributed the enhanced activity of their catalyst to a tandem mechanism through which Zn–OV sites favor the conversion of NO_3^- into adsorbed $^*\text{NH}_2$ while In–OV sites reduce CO_2 to $^*\text{CO}$. The $^*\text{CO}$ spontaneously migrates to Zn–OV, enabling C–N coupling through the formation of adsorbed $^*\text{CONH}_2$.

On the electrolyte side, Tu et al.²³ recently demonstrated that an alkali metal cation is needed to activate the C–N coupling via $^*\text{CO} + ^*\text{NO}$ (Figure 2c), as M^+ stabilizes both intermediates (Figure 6d). They reported that urea synthesis from the co-reduction of NO_3^- and CO_2 follows the trend of alkali cations: $\text{Li}^+ < \text{Na}^+ < \text{Cs}^+ < \text{K}^+$. Interestingly, Gerke et al.⁹⁶ reported the same trend for urea synthesis on Au under constant potential electrolysis. They also explored the use of a pulsed potential regime to desorb hydrogen, hinder the HER, and facilitate mass transport. Understanding the critical phenomena within the EDL that promote C–N coupling opens the door to evaluating additional electrolyte aspects, such as buffering anions and the time-dependent formation of intermediates, that can be explored alongside pulsed electrolysis.

Addressing the challenges and opportunities in active site and electrolyte engineering for sustainable urea electrosynthesis requires a multifaceted approach. By utilizing catalysts with complementary active sites, we can promote key steps in C–N coupling, as demonstrated by recent advances. At the same time, tailoring the electrolyte composition and employing dynamic electrochemical strategies, such as pulsed potentials, can optimize the EDL environment, minimizing competing reactions. Together, these strategies pave the way for enhancing urea electrosynthesis efficiency by deepening our understanding of fundamental interactions between catalyst, electrolyte, and reaction intermediates.

7. SUMMARY AND OUTLOOK

We provide an overview of the key aspects to consider for enabling urea synthesis from the co-reduction of CO_2 and NO_3^- . Although this topic is gaining increasing attention, we shed light on an often-overlooked aspect: the need for fundamental research conducted under well-defined electrode and electrolyte conditions. We encourage the review of the current literature on the activity of single crystals for both CO_2 and NO_3^- to gain insights into the structure sensitivity of catalysts for urea synthesis, along with their further application for the co-reduction of CO_2 and NO_3^- . We also evaluate the effects of electrolyte species on both reactions and how we can explore them for urea synthesis. This approach is critical to rationally design the structures of both catalysts and electrolytes.

We highlight different strategies that have been employed for both the active site and electrolyte design to optimize urea electrosynthesis. To correctly assign the roles of different aspects of both catalyst and electrolyte in urea electrosynthesis, we emphasize the importance of utilizing advanced coupled in situ and online techniques under well-known experimental conditions. Thus, we will be able to gain valuable insights into the role of different parameters that impact the co-reduction of CO_2 and NO_3^- for C–N coupling, paving the way for the development of more efficient systems for optimized urea electrosynthesis.

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Notes

The authors declare no competing financial interest.

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