Electrocatalytic Pathways to the Formation of C–N Bonds

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ABSTRACT: The electrochemical synthesis of organonitrogen compounds characterized by the presence of C–N bonds has emerged in the past few years as an appealing alternative for the industrial-scale production of these compounds. Given their high industrial and societal importance, finding sustainable production methods is crucial. However, their production depends on the Haber Bosch process, which has a substantial environmental impact. In response to these challenges and recognizing the scientific challenge of making C–N bonds on an electrochemical interface, there is a notable surge in interest from the scientific community. This review summarizes some of the latest contributions to electrochemical C–N bond formation (urea, amides, and amines) concerning catalyst development and reaction mechanism elucidation.

KEYWORDS: electrocatalysis, nitrogen chemistry, carbon dioxide electroreduction, C–N coupling, organonitrogen compounds, electrosynthesis

1. INTRODUCTION

Organonitrogen compounds, organic compounds composed of one or more nitrogen atoms, find a wide range of applications, including fertilizers, CO₂ adsorbents, pharmaceuticals, surfactant manufacturing, and the production of large polymers such as nylon for cookware and fabrics. The diversity of applications positions the organonitrogen compounds within the chemicals with the highest industrial production volume. For instance, urea, a widely used fertilizer, reaches an annual production of 187.8 million metric tons, and this production volume is expected to grow by 2% per annum.¹ The significance of organonitrogen compounds is also evident in the pharmaceutical sector, as 80% of top-selling pharmaceuticals feature C–N bonds.

The current synthesis methods for most organonitrogen compounds heavily rely on fossil fuels both as a source of energy and as raw materials (carbon, hydrogen, and nitrogen). The nitrogen source, ammonia, is particularly unsustainable due to the emissions associated with the Haber-Bosch process. This process is responsible for 1.9 t of CO₂ per metric ton of NH₃ produced and consumes 1 to 2% of the world’s annual energy output.² For these reasons, there is a need to provide the chemical industry with alternative, greener, and sustainable production technologies for synthesizing organonitrogen compounds.

A promising approach to address this challenge involves the utilization of electrochemical techniques. With these methods, renewable energy can be directly used as a driving force to enable the formation of C–N bonds. Moreover, the use of electrochemistry offers other advantages.³ It allows operation at milder temperatures and pressures while generating less waste than conventional approaches. To enhance the sustainability of this technology, an intriguing avenue is to combine electrochemistry with waste and widely abundant substrates, such as CO₂ and reactive forms of nitrogen (Figure 1). CO₂ is still the cheapest and most available source of carbon that can be converted into valuable and commodity chemicals.⁴

Due to the environmental importance of the substrates, products, and technologies, the general interest in developing electrochemical methods for synthesizing organonitrogen compounds has emerged in the past few years.⁵–⁸ While enzymatic and molecular catalytic systems for C–N bond formation have been recently reported,⁹ electrocatalytic systems are more translatable to the industry and, therefore, more heavily investigated.⁶ Predominantly, the research efforts are focused on urea electrosynthesis, which is not surprising, given the industrial importance of this compound.

This review aims to provide a concise overview of the current advancements in the electrosynthesis of amides and amines. Urea will be addressed individually because of its
notable significance. As the simplest amide, urea serves as a model molecule for investigating the process of C–N bond formation within an electrochemical environment. The discussion will more specifically focus on the catalyst advancements in terms of rational design and the elucidation of reaction mechanisms in the synthesis of the reviewed organonitrogen compounds.

2. UREA ELECTROSYNTHESIS

Urea is one of the simplest compounds with C–N bonds. Its annual production is estimated to be ca. 200 million tons. Due to its high nitrogen content, most of it is used in the agricultural sector as a nitrogen-based fertilizer. Other uses of urea include animal feed, urea–formaldehyde resins, emollients for skin care, and reductant for diesel engines, commonly known as “AdBlue”. Furthermore, urea’s usage expands further to polymers and pharmaceuticals by reacting with alcohols and malonic esters to form urethane and barbituric acids.4

Currently, urea is produced via the Bosch-Meiser process, but this process suffers from high energy input (150–200 °C and 100–200 atm) and CO2 emissions. Even though the CO2 used in the urea synthesis is recycled from the NH3 synthesis from Haber-Bosch, the amounts of CO2 are still not fully mitigated. Thus, the industry and the scientific community are looking into alternative routes, such as electrochemistry, that can contribute to synthesizing green fertilizers.

The first widely available source of nitrogen that comes to our minds for the electrosynthesis of organonitrogen compounds is nitrogen (N2). Several works have reported urea as a product of the coreduction of N2 and CO2.10,11 The first barrier for this reaction is the substantial energy required to dissociate the nitrogen triple bond (941 kJ mol−1). Despite the intense research into the nitrogen reduction reaction, the only promising results have been obtained in nonaqueous media via lithium or calcium-mediated nitrogen reduction.12,13 In aqueous media, the reported efficiencies are very low and often lack reliability due to sample contamination by adventitious N species.14 Unfortunately, similar contaminations can occur during the electrochemical reduction of N2 and CO2. Reactive nitrogen such as nitrate (NO3−) and nitrite (NO2−) are interesting substitutes to overcome this problem. Dissociating the N≡O bond demands substantially less energy than the N≡N bond (607 kJ mol−1 compared to 941 kJ mol−1, respectively). Moreover, NO3− and NO2− are significantly more soluble in water than N2 (40,000-fold higher).15

mitigating concerns of external contaminations. The utilization of NO3− and NO2− is also environmentally crucial, given their prevalence as contaminants in freshwater. Elevated levels of NO3− and NO2− in drinking water can lead to severe health issues such as methemoglobinemia and clinical cyanosis (blue baby and stomach cancer).16

The first reports on urea electrosynthesis from CO2 and NO3−/NO2− were documented with various metal catalysts in 0.2 M KHCO3 by Shibata et al.17,18 After screening a wide range of metals, Cu, Ag, Zn, Cd, In, Sn, Ti, Pb, Au, and Pd were identified as capable of synthesizing urea. Cu, Zn, Ag, and Cd were found to produce urea at Faradaic efficiencies (FE) higher than 30% using NO2− as a nitrogen source. The authors attributed the metals’ ability to synthesize urea to their ability to form CO and NH4+ according to reactions R1–R3. The authors refer to the hypothetical NH3 and CO intermediates as precursors (pre). Note that these species were not experimentally identified by the authors, and their form is unknown (e.g., adsorbed species, radicals).

\[
\text{NO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightarrow \text{NH}_3\text{(pre)} + 2\text{H}_2\text{O} \quad \text{(R1)}
\]

\[
\text{CO}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{CO}\text{(pre)} + \text{H}_2\text{O} \quad \text{(R2)}
\]

\[
\text{CO}\text{(pre)} + 2\text{NH}_3\text{(pre)} \rightarrow \text{NH}_2\text{CONH}_2 \quad \text{(R3)}
\]

In an effort to optimize the catalytic performance for urea electrosynthesis, (bi)metallic catalysts with favorable active sites were fabricated (Figure 2).

The rational design of a catalyst with dual active sites represents a strategic approach to enhancing the efficiency of a complex chemical reaction composed of two individual processes. In the intricate landscape of catalysis, where selectivity is paramount, the incorporation of dual active sites allows for a finely tuned reaction pathway. By strategically placing distinct active sites, each tailored to promote a specific subreaction, the catalyst can precisely initiate and guide the sequential steps of the overall process. This design not only facilitates the simultaneous activation of two individual reactions but also enables the coordination of the reaction intermediates and their spatial interactions. Such intricately engineered catalysts play a pivotal role in unlocking the full...
potential of tandem reactions, offering a pathway toward a better reaction selectivity and overall catalytic efficiency in complex chemical reactions.

Feng et al. developed Te-doped Pd nanocrystals with improved FE compared to plain Pd. The authors assigned that to an improved CO$_2$ adsorption and NH$_3$ production caused by the Te doping and a consequent electron transfer from Te to Pd. A diatomic non-noble electrocatalyst with bonded Fe-Ni pairs was developed, reaching an FE of 17.8% (Figure 3a). The authors suggested that the tailoring of the bridge sites of the Fe-Ni pairs boosts the urea synthesis intrinsically by facilitating the C–N coupling process and effectively suppressing the hydrogen evolution. Meng et al. synthesized Cu@Zn electrodes, which reached ca. 10% FE for urea. The authors supported that an electron transfer from the Zn shell to the Cu core takes place, enabling the coupling of the proposed CO$_{ads}$ and NH$_2$$_{ads}$ intermediates. Their theoretical calculations showed that this electronic transport promotes the formation of intermediates and further reduces their coupling energy barrier, improving the catalytic performance of urea electrosynthesis. A recent study on CuO$_{x}$ZnO$_{y}$ revealed that the nature of the metals on the catalysts is important, but different ratios between these metals can also significantly affect the catalytic activity toward the reaction. All the CuO$_{x}$ZnO$_{y}$ compositions tested showed higher Faradaic efficiencies for urea than those of ZnO or CuO. Remarkably, CuO$_{0.6}$ZnO$_{0.4}$ showed the highest with 41% at −0.8 V versus RHE.

An In(OH)$_3$-S catalyst with well-defined {100} facets delivered a Faradaic efficiency of 53.4% for urea via enabling the direct C–N coupling between NO$_2$$_{ads}$ and CO$_2$$_{ads}$ intermediates. This work suggests that a hole accumulation layer is developed by the capture of electrons by CO$_2$, and the resulting p-type In(OH)$_3$ repels protons and inhibits the competing hydrogen evolution.

The design of catalysts with defects is gaining momentum due to the improved efficiencies that have recently been reported with such low-coordinated sites. The first study reporting urea electrosynthesis with such materials included a

Figure 2. Summary of some reported Faradaic efficiencies to urea starting from NO$_2$/NO$_3$ and CO$_2$. Data from refs 17–31.

Figure 3. Different catalyst design approaches for urea electrosynthesis: introduction of oxygen vacancies, designing dual atom catalyst, inducing structural defects. (a) Product distributions of CO$_2$RR, NO$_3$RR, and urea synthesis on Ni-SAC, Fe-SAC, I-FeNi-DASC (isolated), and B-FeNi-DASC (bonded) at −1.4 V vs RHE. Adapted with permission from ref 25. Copyright 2022 Nature Publishing Group. (b) Faradaic efficiency for different products over the AuCu self-assembled nanofiber at −1.55 V (vs Ag/AgCl) and (c) selectivity of NH$_3$, urea, and byproduct (e.g., N$_2$) of the AuCu SANFs at −1.55 V (vs Ag/AgCl) for 2 h. Adapted with permission from ref 19. Copyright 2022 Elsevier. (d) Urea yields in Vo-InOOH; (e) urea synthesis performance in Vo-InOOH compared with InOOH at −0.5 V vs RHE. Adapted from ref 29. Copyright 2022 American Chemical Society.
TiO$_2$-Nafion electrode that reached an FE of 40%. The work did not focus on the catalyst design but highlighted the catalyst’s importance in converting NO$_3^-$ to NH$_3$. Au/Cu alloys were synthesized to modulate Cu’s coordination state and electronic structure by the presence of structural defects. The improved catalytic performance (FE of 25%) was credited to the facile adsorption of the CO$_2$ and NO$_2^-$ reactants on the electrocatalyst surface (Figure 3b, c). Using Cu-TiO$_2$ as an electrocatalyst, a FE efficiency of 43% was reached from the coreduction of CO$_2$ and NO$_2^-$.

The authors attributed the enhanced performance to the low coordinated Cu sites and improved adsorption of the CO$_2$ and NO$_2^-$ reactants on the Cu and Ti sites of the oxygen vacancy-rich anatase TiO$_2$, respectively. The proximity of CO$_{2\,\text{ads}}$ and NH$_{2\,\text{ads}}$ intermediates was demonstrated to be beneficial for the subsequent reaction to urea formation.

Introducing oxygen vacancies into the electrocatalyst has been adopted as a strategy to improve the electrocatalytic activity of a specific material. Oxygen vacancy-rich ZnO porous nanosheets were prepared by Meng et al. and compared to ZnO. A FE of 23.26% at −0.79 V versus RHE was reached and attributed to the surface oxygen vacancies. The authors suggest that NO$_2^-$ binds to the catalyst’s surface via the oxygen, filling the oxygen vacancy space. A multistep proton-coupled electron transfer is then suggested to take place and form the proposed NH$_{2\,\text{ads}}$ intermediate. Meanwhile, the oxygen from CO$_2$ is inserted in the vacancy and converted to a COOH$_{\text{ads}}$ intermediate after the one-step proton-coupled electron transfer process. Finally, urea is proposed to be formed by coupling the two adsorbed intermediates.

Introducing oxygen vacancies to InOOH has also been shown to enable a selective C–N coupling toward urea electrosynthesis with an FE of 51.0% (Figure 3d, e). The activity was accredited to a reconfigured electronic structure of the In surface active sites that leads to a lower energy barrier for the protonation of CO$_2$NH$_{2\,\text{ads}}$ to COOHNH$_{2\,\text{ads}}$. Wang et al. explored CeO$_2$ and speculated that oxygen vacancies stabilize the N-intermediate species while inhibiting their hydrogenation and facilitating the C–N coupling.

According to the first reports of urea electrosynthesis from CO$_2$ and NO$_3^-$ by Shibata et al., the pathway follows a 14-electron reduction process. However, the exact mechanism is not fully established yet. Most of the experimental reports support the initial theory of Shibata et al. that urea formation is derived from the reaction between CO$_{2\,\text{ads}}$ and NH$_{2\,\text{ads}}$, intermediate species. For example, by studying CO$_2$ and NO$_3^-$ at Cu@Zn catalysts by in situ Fourier transform infrared spectroscopy, Meng et al. showed the disappearance of the CO$_2$ peak at 2060 cm$^{-1}$ during the NO$_3^-$ and CO$_2$ coreduction and the appearance of the C–N bond signal at 1420 cm$^{-1}$. These observations support the initially proposed mechanism. In another electrocatalytic system (ZnO), the authors proposed a urea formation pathway by coupling COOH$_{\text{ads}}$ and NH$_{2\,\text{ads}}$, intermediates from observation with in situ diffuse reflectance infrared Fourier transform spectroscopy. Their results showed the formation of the C–N bond at 1440 cm$^{-1}$ only in the presence of CO$_2$ and NO$_3^-$, strengthening previous investigations showing that urea cannot be formed by CO and NH$_3$ species.

When CO$_2$ was tested without NO$_3^-$ in the electrolyte, a peak was present at 1210 cm$^{-1}$, attributed to COOH$_{\text{ads}}$. However, in the presence of NO$_3^-$ this peak was not visible. Even though the proximity of the prominent NO$_3^-$ peak at 1220 cm$^{-1}$ can be a reason for the COOH$_{\text{ads}}$ disappearance, the authors consider its absence an indication of a COOH$_{\text{ads}}$ intermediate. On the other hand, the study of Guo et al. showed that replacing the CO$_2$ carbon source with HCOOH does not yield urea but formamide. Through a series of in situ spectroscopy experiments (Raman, infrared absorption spectroscopy), quasi in situ electron paramagnetic resonance, and online differential electrochemistry mass spectrometry (DEMS) combined with theoretical calculations, they support that the C–N formation for formamide follows a coupling of CHO$_{\text{ads}}$ and NH$_{2\,\text{ads}}$ intermediates. This highlights the importance of the NH$_{2\,\text{ads}}$ species for this C–N product formation. An important observation was found by Krzywda et al. when studying urea synthesis on Cu surfaces using Raman spectroscopy. Simultaneous with the reduction of NO$_3^-$ and CO$_2$, the authors identified the formation of Cu–C–N-like species. This observation shows that cyanide formation and cyanide intermediates cannot be excluded during urea synthesis.

As urea electrosynthesis has been proven highly potential-dependent, different potentials can lead to other reaction intermediates. It was shown that at more negative potentials, where the formation of urea is low, the reaction proceeds via a desorbed CO. A recent density functional theory (DFT) study revealed that Cu can bind NO$_{2\,\text{ads}}$ and CO$_{\text{ads}}$ but not H$_{\text{ads}}$. CO$_{\text{ads}}$ + N$_{\text{ads}}$ and CONH$_{\text{ads}}$ + N$_{\text{ads}}$ were identified as the two possible C–N couplings that lead to urea formation via further hydrogenation. However, urea formation has not been proved experimentally by the coreduction of CO and NO. Lv et al. studied urea electrosynthesis on a catalyst with a semiconducting behavior. DFT calculations concluded that the critical step of the C–N coupling originates from the reaction between NO$_{2\,\text{ads}}$ and CO$_{\text{2\,\text{ads}}}$ intermediates. Yang et al. reported similar findings, revealing that higher kinetic barriers are present with the coupling of CO$_2$ intermediates (i.e., COOH$_{\text{ads}}$ and CO$_{\text{ads}}$) and the same nitrogen-based intermediates. Barrier decomposition analysis revealed that the favorable kinetics of the CO$_2$ involved C–N coupling resulting from the lower deformation energies of the two reacting fragments and their interaction. The observed attractive interaction is caused by the charge transfer from the nitrogen-based intermediate to CO$_2$. This study further highlighted that the kinetics of the coreduction reaction are correlated to the deformation energy of the nitrogen-based intermediate. A recent report on the Cu/Zn hybrid catalysts showed 75% efficiency toward urea. The authors proposed a relay catalysis mechanism in which $^*$CO$_2$NO$_2^-$ (assumed the key intermediate for C–N coupling) preferentially forms on Zn sites, and the subsequent protonation step to generate $^*$COOH$\text{NHz}_2^-$ benefits from a lowered reaction energy on nearby Cu sites.

When NO$_2^-$ is used as the nitrogen source for urea synthesis, urea is suggested to be formed via an intermediate generated after the reduction of NO$_2^-$ (e.g., NO$_2^-$, NH$_3$). Urea synthesis starting from CO$_2$ and NO studied with in situ FTIR and DFT calculations disclosed an NH$_{2\,\text{ads}}$ intermediate. The authors observed a vibrational feature at 1465 cm$^{-1}$, which was ascribed to the C–N bond formation along with the existence of N–H vibration bands at ca. 1410 and ca. 1150 cm$^{-1}$. Furthermore, the proposed pathway through an intermediate generated after the reduction of NO$_3^-$ (e.g., NO, NH$_3$), and before NH$_3$ production, is further supported by the recent study of Li et al.. The authors studied the...
simultaneous electroreduction of CO$_2$ and NH$_3$ on a Cu catalyst and reported the formation of formamide and acetamide but no urea.

Regardless of these recent developments in the field, the mechanism of urea electrosynthesis is still debated, and further research is needed to clarify the underlying reaction pathways. Different pathways are responsible for the formation of the various C–N bond species. On the basis of early studies on C–N bonds as well as on the reduction of NO$_3^-$, the reaction pathways are very likely dependent not only on the starting substrate combination but also on the electrocatalyst (and its composition), the applied potential, and electrolyte conditions.$^{34,44}$

3. OTHER AMIDES

The formation of C–N bonds through urea electrosynthesis raises the prospect of synthesizing other compounds containing the –CONH$_2$ functional group. This can be achieved by utilizing carbon precursors besides CO$_2$, like methanol$^{45}$ or formic acid,$^{35}$ but also the source of nitrogen.$^{34}$ (Figure 4). Despite the range of opportunities, only a few examples exist in literature, which will be summarized in the coming paragraphs.

Jiao and co-workers$^{34}$ pioneered an exhaustive study of the synthesis of amides for the electrosynthesis of acetamide via coelecrotoreduction of NH$_3$ and CO on Cu electrodes. To enhance selectivity toward specific C$_2$ products like acetate, the authors used CO instead of CO$_2$ as the carbon source. Remarkably, the achieved FE was up to 38%, coupled with a partial current density of 114 mA cm$^{-2}$ at $-0.68$ V versus RHE in a flow cell configuration. Furthermore, by employing various amine sources, the authors successfully achieved high FEs in the electrochemical synthesis of different acetamides. Specifically, N-methylacetamide (FE = 42%), N-ethylacetamide (FE = 34%), and N,N-dimethylacetamide (FE = 36%) were synthesized in a separate study.$^{38}$ A lower FE of 30% for formamide was attained using low-coordinated Cu nanocubes. In this case, the starting materials were HCOOH and NO$_3^-$, and the reaction was observed at a lower overpotential of $-0.4$ V versus RHE. Li and Kornienko$^{45}$ conducted a study where the synthesis of formamide and acetamide from CO$_2$ and NH$_3$ on Cu and CuO electrodes was reported. However, the resulting FE did not exceed 1% for formamide and 10% for acetamide.

A successful route for formamide synthesis involved using methanol (CH$_3$OH) as a carbon source achieved by its reduction in combination with ammonia as the nitrogen feedstock.$^{36}$ By screening various metals, the authors identified Pt, Ni, and Fe as effective catalysts for formamide production. Among these, Pt exhibited superior performance, featuring a 40% FE at a current density of 100 mAm$^{-2}$. The reasons behind Pt’s impressive performance were elucidated through theoretical investigations and isotope-labeled in situ electrochemical characterizations. These efforts unveiled that the efficient production of formamide can be attributed to the moderate binding affinity of reaction intermediates on PtO$_x$ substrate.

Similarly to what was observed for urea electrosynthesis, the formation of different amides seems to have a complex mechanism, very likely dependent on the electrocatalyst, reaction conditions, and substrate. Combining isotope-labeled in situ ATR-SEIRAS, DEMS, and DFT experiments, Guo et al.$^{35}$ substantiated the coreduction mechanism of HCOOH and NO$_3^-$ (Figure 5 and 6). The authors proposed that forming formamide involves coupling $^\ast$CHO and $^\ast$NH$_2$ intermediates.$^{48}$

On the other hand, Li and Kornienko propose that acetamide synthesis necessitates a pre-existing C$_2$ intermediate and, therefore, follows a similar pathway to the acetate synthesis pathway.$^{42}$ This hypothesis is also endorsed by Jouny et al.$^{34}$ The authors showed through theoretical investigations on Cu surfaces that the acetamide formation happens through nucleophilic attack of NH$_3$ on a $^\ast$C$\equiv$C$\equiv$O intermediate, which is formed during electrocatalytic CO reduction. Their hypothesis was validated through a series of control experiments, including labeled CO experiments and varying OH$^-$ concentrations. A rise of acetate compared to acetamide was observed with higher OH$^-$ concentrations. Since the acetate formation happens through the nucleophilic attack of the OH$^-$ on the same ketene intermediate, the OH$^-$ is likely competing.

![Figure 4. Faradaic efficiencies for different amines and amides electrosynthesis from different C- and N-substrates. Data from refs 42, 45–50.](image-url)
with NH₃. This nucleophilic attack was also considered critical for synthesizing different acetamides with different amine sources.²⁴ By testing various amine nucleophiles in combination with CO reduction, the authors saw that the respective N-substituted acetamides were produced with activity and selectivity comparable to those of acetamide in the NH₃ case.

Regarding formamide electrosynthesis, initial investigations suggest shared mechanistic intermediates with formate, signifying nucleophilic NH₃ attack on a *CO₂ intermediate.⁴² The employment of a thicker Cu catalyst layer strengthened this theory, leading to amplified acetamide production due to increased C₂ intermediates available for coupling with NH₃. However, formamide selectivity deviates from this trend.

When starting from CH₃OH and NH₃ on a Pt surface, the production of formamide is believed to follow a different pathway.⁴⁵ Two possible pathways are proposed. The first entails aldehyde from alcohol dehydration reacting with NH₃ to yield a hemiaminal, subsequently dehydrated into formamide. The second pathway involves the aldehyde as the intermediate of CH₃OH oxidation, reacting with NH₃ to form aldime via a hemiaminal intermediate. This aldime is then oxidized to a nitrile and subsequently hydrolyzed into formamide. Corroborating the presence of the aldehyde intermediate, formamide is detected upon substituting CH₃OH precursor with formaldehyde. The absence of ammonia prompts the conversion of the formaldehyde intermediate into formic acid.

### 4. ELECTROSYNTHESIS OF AMINES

In recent studies, there has been a focus on the synthesis of various amide products, along with the emergence of amines as another significant group of compounds. These amines are being synthesized by coreducing diverse carbon and nitrogen precursors. Notably, Wang and colleagues⁴⁶ demonstrated the production of methylamine using a molecular electrocatalyst composed of cobalt β-tetraaminophthalocyanine (CoPc-NH₂) supported on carbon nanotubes. The authors reported a FE of 13% at ca. −0.9 V versus RHE with a partial current density of 3.4 mA cm⁻². This catalytic performance remained stable over 16 h, exhibiting an average FE of 12%.⁴⁶ Further employing the same catalyst and utilizing different nitrogenous reagents, the researchers extended their investigations to encompass a variety of N-methylamines, including amines and nitro compounds like nitrobenzene.⁴⁶ This work yielded noteworthy outcomes, including the formation of N-methylaniline with an FE of 6%, formaldehyde hydrazone with 8.6%, methyl hydrazine with 0.6%, and methylamine with 2.0%, all at an approximate potential of −0.9 V versus RHE. The same authors reported the synthesis of ethylamine from CO₂ and NO₃⁻ using an oxide-derived Cu catalyst with an FE of 0.3% and a current density of 0.26 mA cm⁻² at −1.0 V RHE.⁴⁷

Kim et al.⁴⁹ incorporated the utilization of oxalic acid as the carbon source for C–N coupling studies and successfully synthesized glycine (NH₂CH₂COOH) over a Cu–Hg electrocatalyst (Figure 7a, b). They reported an FE of 43% with 39 mA cm⁻² at −1.2 V RHE. Similarly to CO₂, oxalic acid is a CO₂ reduction product and is often generated in the presence of aprotic electrolytes. The researchers postulate that the effectiveness of the Cu–Hg catalyst arises from the facile desorption of intermediates such as glyoxylic acid (HOOC-CHO) and NH₂OH, enabling efficient coupling to form glyoxylic oxime (HOOCCHNOH), which is subsequently reduced to glycine. The authors further highlight the

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**Figure 5.** Potential-dependent in situ ATR-SEIRAS using formic acid as the C source and (a) ¹⁴NO₃⁻ and (b) ¹⁵NO₃⁻ as the N source. (c) Quasi in situ EPR trapping of carbon radical. # indicates the carbon radical. (d) Online DEMS for nitrite reduction. (e) Schematic illustration of formamide generation pathway on the ER–Cu surface. (f) ¹H NMR spectra of the controlled experiment using 0.2 M NH₃·H₂O or 0.02 M NH₃·H₂O as a N source, respectively. (g) GC–MS spectrum uses 0.02 M NO₂ as the N source. * indicates characteristic peaks of formamide. Reproduced from ref 48. Copyright 2022 American Chemical Society.

**Figure 6.** Schematic illustration of the pathway to formamide according to ref 48.
Figure 7. (a) Faradaic efficiencies of glyoxylic acid, glycolic acid, glycine, and hydrogen after 400 C charge accumulation at four different applied potentials (@1.2, @1.4, @1.6 and @1.8 V vs Ag/AgCl) in a 15 wt % H2SO4 aqueous electrolyte containing 0.25 M oxalic acid and 0.25 M NaNO3. (b) Faradaic efficiencies of the products at four different molar ratios of oxalic acid and nitrate (2:1, 1:1, 1:2, 1:3, total concentration was fixed). Adapted with permission from ref 49. Copyright 2021 John Wiley and Sons. (c) Electrochemical coreduction of CO2 and NO3− to synthesize acetaldoxime and ethylamine. Adapted with permission from ref 47. Copyright 2022 Elsevier.

The critical C−N bond-forming step for methyamine formation is the nucleophilic attack between formaldehyde and hydroxylamine intermediates. These intermediates are part of the pathways for electrocatalytic conversions: CO2-to-methanol and NO3−-to-NH3, respectively. This C−N coupling reaction leads to formaldoxime (H2C=NOH) formation, followed by its electrochemical reduction to CH3NH2. To validate this theory, the researchers conducted a series of experiments. Instead of CO2, CO or formaldehyde were employed, as these species were identified as intermediates in the CO2-to-methanol pathway. Methyamine was detected in both cases, but when methanol was the carbon source, methyamine production did not occur. This implies that formaldehyde is the primary C intermediate for the C−N coupling process. Similarly, methyamine was produced when NO3−, NO, or hydroxylamine were used as nitrogen precursors, which are along the pathway of electrochemical NO3− reduction to NH3. Conversely, using NH3 as the nitrogen source did not yield methyamine. This suggests that hydroxylamine is the probable N intermediate for C−N coupling.

The pathway for ethylamine formation generated from NO3− and CO2 reduction catalyzed by an oxide-derived Cu electrocatalyst was reported by Tao et al. In accordance with the authors, acetaldehyde reacts with the NH2OH intermediate derived from NO3− reduction, giving rise to the acetaldoxime (CH2CHNOH) intermediate, which is eventually transformed into ethylamine (Figure 7c). Acetaldehyde and NH2OH are reaction intermediates for electrochemical CO2 reduction to ethanol and NO3 reduction to NH3+, respectively. The authors’ mechanistic analysis revealed that the overall yield of ethylamine faces limitations due to the competitive reduction of acetaldehyde to ethanol and NH3OH to NH3.

Kim et al. proposed an electrochemical glycine synthesis process involving glyoxylic oxime generation and reduction, facilitated by a hydroxylamine intermediate. To substantiate their hypothesis, the authors conducted a sequence of experiments. They examined glycine formation in the presence of glyoxylic acid and either hydroxylamine or ammonia. The outcomes indicated that glycine materialized solely in the presence of hydroxylamine. The proposed reaction pathway encompasses an initial 2-electron reduction step converting oxalic acid to glyoxylic acid along with a 6-electron reduction step of nitrate to hydroxylamine. Subsequently, glyoxylic oxime is formed by the nucleophilic attack of hydroxylamine on the electrophilic carbon center of glyoxylic acid and coupled with dehydration. Lastly, a 4-electron reduction converts glyoxylic oxime into glycine.

5. CONCLUSIONS

This review summarizes some of the latest scientific discoveries on the electrochemical C−N coupling. The discussion encompasses an overview of the most efficient catalysts and the mechanistic developments for various amides and amines. Figure 8 presents a comprehensive visual representation of all mechanistic insights covered in this review. Due to the nascent stage of the studies, data from in situ techniques are currently limited. Figure 8 highlights the molecules identified experimentally using in situ techniques.

Without any doubt, the electrosynthesis of urea is the most targeted reaction, probably due to its molecular simplicity and industrial relevance. However, even with the simplest molecules, such as urea and acetamide, it is clear how complex the C−N bond formation is. And that is not surprising, considering the complexity of the reactions involved. The coreduction of CO2 and NO3− reduction highly depends on electrode material, solution pH, and even substrate concentration. The possible products and intermediates are
numerous, so making these reactions selective is challenging. Despite the remarkable efforts of the scientific community on the topic, to pursue the electrochemical synthesis of organo-nitrogen compounds with higher complexity and in a selective manner, such as ethylamine or glycine, we have to understand the catalytic sites, the interfacial properties, and the reaction mechanism. Even though the development of amides and amines synthesis is still in its early stages, with the gathered data, there is an opportunity to enhance the catalyst materials for a more selective and efficient process. From the current catalysts under review, it is apparent that incorporating oxyphilic catalyst sites, such as the oxygen vacancies found in ZnO,\textsuperscript{22} InOOH,\textsuperscript{29} or CeO\textsubscript{2},\textsuperscript{33} proves to be a promising strategy for activating NO\textsubscript{3}/2\textsuperscript{−} species. Heterojunctions, like Cu-TiO\textsubscript{2},\textsuperscript{23} have demonstrated efficiency in activating CO\textsubscript{2} and NO\textsubscript{3}/2\textsuperscript{−} at the different binding sites. Another viable approach involves electron transfer through the use of a second metal, such as the Cu@Zn\textsuperscript{30} or Te–Pd\textsuperscript{35} to facilitate C–N coupling reactions by activating and stabilizing the carbon intermediate. Additionally, it is crucial not to overlook the competitive reaction of H\textsubscript{2} evolution. Suppression of this reaction can be achieved by incorporating bridge sites or employing p-type materials, like In(OH)\textsubscript{3}.\textsuperscript{30} In summary, by leveraging the insights gained from the current data, we can work toward optimizing catalyst materials and strategies for a more effective synthesis of amides and amines.

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**Figure 8.** Schematic representation of the pathways proposed for (a) urea, (b) amine, and (c) amide formation. The mechanisms are shown according to the refs 29, 34–36, 40, 42, and 45–50.
Author Contributions
The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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