Carbon Dioxide and Nitrate Electrocatalytic C-N Coupling for Sustainable Production of Urea

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Abstract: The electrocatalytic co-reduction of carbon dioxide (CO_2) and nitrate (NO_3^-) for urea synthesis under environmental conditions offers a promising solution for achieving sustainable environmental management. Besides, electrochemical urea synthesis is an alternative approach for cleaner production of urea compared to the conventional urea industrial production process with high energy consumption and pollution. However, lower urea yield, lower selectivity and unclear C-N coupling reaction mechanism are still the main challenges to its largescale application. In this review, we focus on accurate and reliable detection methods and evaluation criteria for urea products, recent progress on CO_2 and NO_3^- electrocatalytic co-reduction synthesis of urea, rational design of high-performance electrocatalysts, and C-N coupling reaction mechanism of urea electrochemical synthesis under atmospheric conditions. This review could contribute to the development of electrochemical urea synthesis via effective remediation of CO_2 and NO_3^- .

Keywords: urea synthesis; C-N coupled system; electrocatalytic co-reduction; reaction mechanism; multiphase electrocatalysts

1. Introduction

Carbon Capture and Utilization (CCU) is a promising solution for converting CO_2 into valuable chemical products, reducing the greenhouse effect caused by its emission into the atmosphere, and achieving "carbon peaking and carbon neutrality" [1,2]. Not only may CCU be used with C/H/O-based reactants, but it can also be used to synthesize useful compounds other than simple carbon species [3,4]. For example, the addition of nitrogen can form C-N bonds and generate organic nitrogen compounds [5]. These products have a variety of chemical and biological activities, are very important chemical intermediates or raw materials, have broad application prospects and market value is therefore very important [6]. Of particular importance is the production of urea using the electrocatalytic co-reduction C-N coupling of naturally occurring molecules and environmental pollutants, such as CO_2 and NO_3^- , as sources of C and N [7,8] (Figure 1).

Compared with the traditional energy-intensive process for urea synthesis, this approach reduces the dependence on fossil fuels and CO_2 emissions, which not only enables the effective use of CO_2 but also helps to control water pollution and ultimately achieve the efficient green synthesis of urea, which is of high significance for climate change mitigation and environmental protection [9]. However, this attractive approach is still in its infancy, yields and selectivity of the target product are still low, and it faces many problems in terms of economic efficiency, so there is still a long way to go to achieve industrialization [10,11]. The logical design of electrocatalysts, the benefits of utilizing nitrate as an N source, the reaction mechanism of C-N coupling, and precise and dependable detection techniques for the products of electrocatalytic urea production have also received little attention in reviews [12].

This review includes an overview of the developments in the field of electrochemical urea synthesis research, the rational design of high-performance electrocatalysts, the reaction mechanism of C-N coupling in the electrochemical urea synthesis under ambient conditions, and the more precise and reliable detection of lower urea yields. We also provide an overview of the primary challenges facing multiphase electrocatalytic urea production. This work also aims to stimulate future research towards the overall enhancement of C-N coupling system performance and product efficiency, by looking ahead to the research direction and development opportunities in this sector. The advancement of electrochemical urea production in industry is aided by this review.





Figure 1. Cleaner production of urea from the catalytic coupling of CO₂ and nitrate.

2. Advances in Electrocatalytic C-N Coupling Research

2.1. Urea Product Detect Techniques and Reliable Quantification

The electrocatalytic co-reduction C-N coupling of CO_2 and NO_3^- to synthesize urea is not only a promising strategy for carbon neutrality and wastewater treatment, but also a promising approach for energy-saving and sustainable urea synthesis. However, the performance of the current electrocatalyst shows low activity. The reaction system needs to be optimized while the reaction mechanism is still unclear, resulting in a low yield and selectivity of urea. Therefore, such low concentrations of urea are very susceptible to interference during the test [13]. To evaluate the quality of urea more accurately, urea detection methods and the advantages and disadvantages of each method have been reviewed, to provide guidance for researchers to choose the appropriate urea detection method. The main testing methods for urea products are the urease decomposition method, diacetyl monoxime method (DAMO), high-performance liquid chromatography (HPLC), and ¹H nuclear magnetic resonance (¹H NMR) [5,13–15]. In addition, possible interferents (liquid byproducts or dissolved metal ions) generated during urea synthesis have an impact on the quantification of urea detection when the urea concentration is at the nmol/µmol level.

Specifically, NO_2^- and NH_4^+ had a significant interfering effect on urea quantification, and the presence of ions such as Co^{2+} , Fe^{2+} and Mn^{2+} also led to inaccurate detection of urea concentrations [13,16]. Furthermore, differences in urease activity produced by different batches, possible NH_4^+ loss during heating, and the inhibition of NH_4^+ determination by colorimetric methods by high urease concentrations may have an impact on the quantitative urea test.

Reducing substances such as NO_2^- and S_2O_3 , thiourea, thiosulfate, etc. can also interfere with the accuracy of urea quantification when determining urea content by the DAMO method [17,18]. The ¹H NMR method's detection limit for urea testing is 0.42 ppm. Temperature, pH, and solvent all affect the signal intensity of active hydrogen, which can distort test findings. One benefit of using ¹H NMR for quantifying urea is that the presence of metal ions or byproducts does not have a substantial impact on the measurement of urea since each compound's hydrogen atoms have a distinct chemical coordination environment [13]. When testing urea concentration by HPLC, a 5 μ m NH₂ column is usually used, with acetonitrile-water as the mobile phase [19]. This method has the advantages of high resolution, good reproducibility, and less interference from impurities. The presence of CO2 reduction intermediates such as HCOO⁻, CH₃OH and CH₃CH₂OH, NO₃⁻ reduction by-products NH₄⁺ and NO₂⁻, and C-N coupling by-products (e.g., formamide and acetamide) does not significantly interfere with the accurate quantification of urea by HPLC [20,21]. The sensitivity, versatility, ease of use, chemical information, speed of analysis and immunity to interference of the assays were objectively assessed and compared based on a thorough examination of the different assays mentioned above, as shown in Figure 2. The single urea quantification methods all have drawbacks and are difficult to quantify accurately for trace amounts of urea. Therefore, synergistic methods may be the development trend to retain the advantages of detection to overcome the defects of detection and to achieve accurate quantification. Fortunately, high-performance liquid chromatography-mass spectrometry (HPLC-MS) can avoid these problems and is considered a more suitable method for urea quantification at this stage.



Figure 2. Comparison of four common urea testing methods [22].

2.2. The Progress of Electrocatalytic Co-Reduction of Carbon Dioxide and Nitrate for Urea Synthesis

Electrochemical urea synthesis has shown promising potential in the field of energy and environmental sustainability. Previous studies have focused on the development of CO_2 and different nitrogen-containing species (e.g., NO_3^- , NO_2^- , NH_3 , N_2 and NO) for urea synthesis.

In previous reports of electrocatalytic synthesis of urea, the most studied N sources are NH₃ and N₂. However, there are disadvantages to using NH₃ and N₂ as N sources [23]. Additional processes such as NH₃ collection and air separation of N₂ elevate the cost and show lower Faraday efficiency (FE) [24]. There are several benefits to using NO₃⁻ as a source of N. First, NO₃⁻ is widely distributed in the natural world, particularly in industrial wastewater. Unlike other N sources, which require additional processes and energy consumption to obtain, NO₃⁻ is readily available as an environmental waste [25]. Secondly, the maximum concentration of NO₃⁻ in drinking water should be limited to less than 10 mg/L because excessive NO₃⁻ ingestion may cause disease. Therefore, using NO₃⁻ as an N source can achieve high-value conversion of environmental pollutants, solving the environmental problems caused by NO₃⁻ and converting waste into valuable chemicals, which is extremely beneficial to environmental sustainability [26,27]. In addition to this, the chemical stability of N₂ and the low solubility of N₂ in the electrolyte require a large amount of energy to activate the reactants and carry out the coupling reaction [28]. In this respect, the N=O bond dissociation energy of NO₃⁻ (204 kJ mol⁻¹), contrasts with that of the N=N bond (941 kJ mol⁻¹) [29,30]. Therefore, electrochemical reduction of CO₂ and NO₃⁻ to synthesize urea offers a promising and feasible solution for pollution and carbon reduction.

Researchers have made outstanding contributions to the investigation of electrocatalytic CO_2 and nitrate coreduction to urea. However, the low yield and selectivity of urea remain the most important problems to be solved in this direction (Table 1). Electrocatalytic co-reduction systems need to achieve current densities of hundreds of mA/cm⁻² and >50% selectivity of the target product to be economically viable for the electrosynthesis of urea [7,31,32]. Consequently, the design and preparation of superior electrocatalysts is an important measure to improve the yield and selectivity of urea electrosynthesis. This review focuses on the recent studies and electrocatalysts (precious metal catalysts, transition metal catalysts, single-atom catalysts, carbon-based catalysts and surface defects) used for electrocatalytic CO_2 and NO_3^- synthesis of urea under ambient conditions, providing some references for the design and preparation of high-performance electrocatalysts.

Table 1. Comparison of recently reported work on the synthesis of urea by electrocatalytic CO_2 and NO_3^- correduction.

Electrocatalyst	Urea Yield	FE _{Urea} (%)	Reference
Fe(a)@C-Fe ₃ O ₄ /CNTs	$1341.3 \pm 112.6 \ \mu g \ h^{-1} \ m {g_{cat}}^{-1}$	16.5 ± 6.1	[33]
CoPc-COF@TiO2 NTs	$1205 \ \mu g \ h^{-1} \ cm^{-2}$	49	[34]
F-CNTs	$6.36 \text{ mmol } h^{-1} g_{cat}^{-1}$	18	[35]
Cu ₂ O (ds)	$7541.9 \ \mu g \ h^{-1} \ m g_{cat}{}^{-1}$	51.97 ± 0.8	[36]
MoO _x /C	1431.5 ug $h^{-1} mg_{cat}^{-1}$	27.7	[37]

Ru-Cu CF	$151.6 \text{ ug } \text{h}^{-1} \text{ cm}^{-2}$	25.4	[38]
Core-shell Cu@Zn	$7.29 \ \mu mol \ cm^{-2} \ h^{-1}$	9.28	[39]
Cu ₁ -CeO ₂	52.84 mmol $h^{-1} g_{cat.}^{-1}$	-	[40]
Fe-Ni-DASC	20.2 mmol $g^{-1} h^{-1}$	17.8	[41]
In (OH) ₃ -S	533.1 $\mu g h^{-1} m g_{cat}^{-1}$	53.4	[9]
Cu-N-C	-	28	[42]
AuPd	$204.2 \ \mu g \ m g^{-1} \ h^{-1}$	15.6	[21]
Vo-InOOH	592.5 μ g h ⁻¹ mg _{cat} ⁻¹	51	[18]

2.2.1. Precious Metal Catalysts

In addition to being crucial for electrocatalysis, precious metals and alloys have demonstrated exceptional performance in the co-reduction of CO₂ and NO₃⁻ to produce urea by electrocatalysis. To synthesize carbon dioxide-coupled NO₃⁻ to urea in a highly selective and active manner, Qin et al. [38] developed an electrode via in-situ deposition that was anchored to a three-dimensional copper foam (Ru/Pt/Pd-Cu CF). Remarkably high yield and selectivity (urea yield of 151.6 μ g h⁻¹ cm⁻² and FE of 25.4%) were obtained at a low potential of -0.3 V vs. Ag/AgCl using the noble metal alloy catalyst. The reason for this excellent performance is that the presence of Ru in the Ru/Pt/Pd-Cu CF facilitates the generation of *NH₂ and provides strong adsorption energy for the stabilization of the *COOH intermediate [38]. Wang et al. [21] synthesized AuPd nanoalloy electrocatalysts for the simultaneous reduction of CO₂ and NO₃⁻ under ambient conditions. Besides, the synthesized catalysts showed excellent catalytic performance with urea production rates up to 204.2 μ g mg⁻¹ h⁻¹ and FE of 15.6%. Although precious metals have excellent performance, their expensive price limits their wide application. The preparation of alloys of precious metals with other inexpensive metals is one of the promising methods for utilizing precious metals. This is because the excellent catalytic properties of precious metals can be retained and the amounts of precious metals used can be reduced.

2.2.2. Transition Metal Catalysts

Transition metals are widely studied in the field of electrocatalysis due to their unique outer electronic structure [43,44]. With an optimized urea yield rate and FE over Cu@Zn [39], the self-supported core-shell Cu(a)Zn nanowires demonstrated excellent performance in urea electrosynthesis, reaching 7.29 µmol cm⁻² h⁻¹ and 9.28% at -1.02 V vs RHE, respectively. According to research by Seokmin et al. [36], copper (Cu) with atomicscale spacing (ds) between copper facets can greatly increase the electrochemical urea synthesis efficiency of CO₂ and NO₃⁻. By varying the degree of lithiation on each sample, they were able to create ds between the Cu faces in four different Cu samples with varying ds values. Out of the four samples, Cu with ds close to 6 Å exhibited superior electrocatalytic performance (Figure 3d-f), yielding 7541.9 µg h⁻¹ mgcat⁻¹ and 115.25 mA cm⁻² at 0.41 V_{RHE} for urea. The urea yield of this compound is 444.7 $\mu g h^{-1} m g_{cat}^{-1}$ and its partial current density is 1.96 mA cm⁻², which is significantly higher than bare Cu, and also has a stability of up to 50 h [36]. Transition metals are the most promising alternative to precious metal catalysts. Thus, the design and preparation of excellent transition metal catalysts has a highly broad development prospect. The design of superior transition metal catalysts should emphasize the active site of the catalyst, the modulation of the electronic structure, and the adsorption-desorption with the reactants. A strategy to improve urea selectivity using a hybrid catalyst (Zn/Cu) is reported by Luo et al. [45]. The catalytically active sites of the two transition metals were able to independently stabilize the key intermediates *CO₂NO₂ and *COOHNH₂ required for urea formation through a relay catalytic mechanism. At 1,000 parts per million of NO₃⁻ in wastewater, the catalyst demonstrated a 75% FE, while producing 16 µmol h⁻¹ cm⁻². Zhao et al. [46]. reported a CuWO₄ catalyst with natural bimetallic sites for high urea productivity (98.5 \pm 3.2 µg h⁻¹ mg⁻¹ cat) with high FE (70.1 \pm 2.4%). Additionally, it was established that the electrosynthesis of urea is dependent on the C-N coupling of *NO2 and *CO intermediates on the CuWO4 surface.

2.2.3. Single-Atom Catalysts

Due to their maximum surface atom utilization and controllable physicochemical properties, single-atom catalysts have drawn increasing attention in multiphase catalytic conversion reactions, such as electrochemical CO_2 reduction, N_2 reduction, and O_2 reduction [47–49]. For the first time, Leverett et al. [42] reported on the electrochemical synthesis of urea from CO_2RR and NO_3 ⁻RR using Cu SACs. The urea was produced at a current density of -27 mA cm⁻² at -0.9 V versus the reversible hydrogen electrode, with a FE of 28%, and demonstrated that the critical parameter's catalytic activity is dependent on *COOH, which determines the importance of urea. Wei et al.'s work [40] also affirmed the superior performance of Cu single atoms for the electrocatalytic reduction

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of NO_3^- and CO_2 for urea synthesis. Cu SACs modified on a CeO₂ carrier were used to catalyze the synthesis of urea. The average urea yield was 52.84 mmol h^{-1} gcat⁻¹ (-1.6 V vs RHE).

A diatomic catalyst with Fe-Ni bonds has been shown by Zhang et al. [41] to greatly increase the electrochemical urea synthesis's efficiency. Compared to isolated diatomic and monatomic catalysts, the bound Fe-Ni pair served as an efficient site for coordinated adsorption and activation of various reactants, improving the critical C-N coupling both thermodynamically and kinetically. An order of magnitude better results was obtained in urea synthesis than in the previous process, with a high yield of 20.2 mmol h^{-1} g⁻¹ and a corresponding FE of 17.8% [41]. Despite the excellent performance of atomically fractionated catalysts, there are still limitations such as complex preparation procedures, the multiple demands for instruments, and the tendency to aggregate leading to a decrease in catalytic activity. Therefore, the design of single-atom catalysts should focus on utilizing simpler preparation methods and improving the stability of single-atom catalysts.

2.2.4. Carbon-Based Catalysts

The development of carbon-based catalysts has been instrumental in the electroreduction synthesis of urea due to the wide availability and economic feasibility of carbon as compared to metallic elements. Because of their high electrical conductivity and enormous specific surface area, carbon compounds have garnered a lot of interest. Because doping causes a surface charge distribution, doping carbon materials with heteroatoms (such as N, B, and F) is thought to be an effective technique for improving their electrocatalytic characteristics [50,51]. Fluorine-rich surface carbon nanotubes (F-CNTs) with an undamaged inner carbon nanotube wall that facilitates effective charge transfer between the inner and exterior walls were described by Liu et al. [35]. With an efficiency of 6.36 mmol h^{-1} gcat⁻¹ and a FE of 18%, F-CNTs catalyzed the production of urea from NO₃⁻ and CO₂ under ambient circumstances. In addition to being good electrocatalysts, CNTs are also effective co-catalysts and loading materials for catalytic active sites [52,53]. For instance, a liquid-phase laser irradiation technique was described by Geng's group [33] to create symbiotic graphitic carbon-encapsulated amorphous iron and iron oxide nanoparticles (Fe(a)@C-Fe₃O₄/CNTs) on carbon nanotubes. With a maximal urea production of 1341.3 \pm 112.6 μ g h⁻¹ mgcat⁻¹, a FE of 16.5 ± 6.1%, and outstanding stability, Fe(a)@C-Fe₃O₄/CNTs demonstrated remarkable electrocatalytic activity for urea synthesis utilizing NO₃⁻ and CO₂. It is noteworthy that biomass is renewable and carbon-rich source material, so the conversion of waste biomass into carbon materials during the design of carbon catalysts may be economically feasible and has a broad application prospect. Carbon materials can also be used as co-catalysts to enhance the metal-catalyzed reactivity. Graphene-loaded In_2O_3 was created by Mao et al. [54] to demonstrate superior electrocatalytic activity in the production of urea. It was discovered that the dispersion effect of graphene, which completely exposed the active sites of In₂O₃, was primarily responsible for the notable increase in the catalytic activity of In₂O₃.

2.2.5. Defect Engineering Catalysts

It has been reported in the literature that surface defects lead to the generation of off-domains of charge. The ability to change the coordination environment on the surface of metal catalysts facilitates the adsorption and activation of active substances [55–57]. Consequently, several studies have suggested creating oxygen vacancies on the surface of oxides based on metals to aid in the electrocatalytic co-reduction of CO_2 and NO_3^- for the manufacture of urea. For instance, Yu et al. [9] demonstrated effective oxygen vacancy-deficient indium hydroxide electrocatalytic urea synthesis, leading to selective C-N coupling and exceptional electrocatalytic urea synthesis activity. It was discovered that the potential-determining stage of the whole urea production process is $*CO_2NH_2$ protonation. Consequently, urea synthesis was increased by the application of flawed engineering to lower the energy barrier of $*CO_2NH_2$ intermediate protonation. Additionally, the poorly designed catalyst yielded 592.5 μ g h⁻¹ mgcat⁻¹ of urea and had a high FE of 51.0% [18]. Heteroatom doping can also introduce abundant oxygen vacancies into oxide electrocatalysts. Cao et al. [58] demonstrated that doping low-valent Cu into TiO₂ nanotubes can produce oxygen vacancy-rich catalysts. The primary cause of the catalyst's high activity is the ability of oxygen vacancies and defects to alter the electronic structure of the active sites on the catalyst surface, which lowers the energy barrier for the conversion of $*CO_2NH_2$ to $*COOHNH_2$.

2.3. Proposed Reaction Mechanisms

The secret to creating effective electrocatalysts and raising urea yield and selectivity is to examine the C-N coupling reaction mechanism in the electrocatalytic co-reduction of CO_2 and NO_3^- for urea production. These days, density functional theory (DFT) computations and potent in situ characterization techniques are the primary tools used in research on the C-N coupling reaction mechanism. In the NO_3^- and CO_2 co-reduction urea electrosynthesis

reaction system, based on comparative experimental results, most reports indicate that the electrocatalytic CO_2 and NO_3^- co-reduction synthesis of urea originates from the reaction between *CO and *NH₂ intermediate species. The results suggest that the electrocatalyst can facilitate the reaction between CO_2 -to-*CO and NO_3^- -to-*NH₃, which is effective for urea synthesis [37–39].

Zhang et al. [33] investigated the mechanism of C-N coupling on electrocatalysts $Fe(a)@C-Fe_3O_4/CNTs$ by the in-situ Fourier transform infrared (FT-IR) test. Suggesting that certain urea can form Fe^{2+} -urea complexes by way of N atoms on the N-H group and oxygen atoms on the C=O group coordinating with Fe^{2+} . The in-situ FT-IR measurements showed that the C-N coupling was successfully realized via the coupling process of CO₂ and NO₃⁻ catalyzed by $Fe(a)@C-Fe_3O_4/CNTs$. In addition, the authors used DFT calculations to reveal the catalytic reaction mechanism of urea synthesis [45,46,59]. The authors created surface structure models for C+Fe₃O₄, carbon-coated crystalline Fe(a)@C, and carbon-coated amorphous Fe (Fe(a)@C) based on the structural properties. Then, it was found that in these three models, *CO₂ could be reduced to *CO and *NO₃ to *NH₂. The direct conversion of *CO₂ to *CO at the C+Fe₃O₄ surface is more energetically advantageous than in the other models. As a transition step, *CO₂ is electrically reduced to *COOH via a proton-coupled electron transfer (PCET) phase. An important step in the urea-producing process is the production of *NH₂, which shows how easy it is to decrease NO₃⁻. As can be seen from the free energy profile for this reaction, the reduction of NO₃⁻ to *NH₂ is a spontaneous process for all three models. The Fe(a)@C site is more likely to produce *NH₂ since it has the lowest energy. In this case, the coupling of *NH₂ and *CO should entail the desorption of the active intermediate and the selection of the coupling site.

The work of Yu et al. [39] also confirms the above idea. The sole carbonaceous product that CO_2 electroreduction produces without nitrate addition is CO. NH_4^+ is the primary nitrogenous product formed by NO_3^- electroreduction after CO_2 is eliminated. Figure 3a,b demonstrate that FE_{CO} and FE_{NH4}^+ from the $CO_2 + NO_3^-$ electroreduction combination are much lower than those from CO_2 and NO_3^- electroreduction, respectively, pointing to a possible competitive link between the synthesis of CO/NH_4^+ and urea. Notably, substituting CO_2 with CO or NO_3^- with NH_4^+ did not result in the production of urea (Figure 3c). A series of in situ characterizations were performed in order to reveal the reaction pathway for the electro-synthesis of urea on Cu@Zn. On-line DEMS signal intensity decreased under CO_2 and NO_3^- conditions (Figure 3d,e), indicating a competitive relationship between CO and NH_2 . Fourier transform infrared spectroscopy, also known as an attenuated complete reflection in situ ATR-FTIR, shows the signals for sole CO_2 , sole NO_3^- , and mixed electroreduction (CO_2 and NO_3^-). Typical intermediate peaks were seen under the CO_2 atmosphere (*CO at 2060 cm⁻¹ and *COOH at 1360 and 1210 cm⁻¹), as Figure 3f illustrates. Peaks of *NO (1310 cm⁻¹), *NO₂ (1210 cm⁻¹), and NH_4^+ (1140 cm⁻¹) are seen during NO_3^- electroreduction. It is noteworthy that the *CO peak vanishes under CO_2 and NO_3^- , whereas the standard C-N bond is seen at 1420 cm⁻¹.



Figure 3. (a) FE_{CO} for the electrochemical reduction of CO₂ and the mixture. (b) FE_{NH4+} for the electrochemical reduction of NO₃⁻ and the mixture. (c) FE_{urea} for the electroreduction of mixtures. DEMS spectra of (d) CO and (e) NH₂ signals. (f) In situ ATR-FTIR spectra [39].

The production of *CONH₂ as the main intermediate is essential for the synthesis of urea. Qin et al. [37] detected the reaction intermediate by in situ ATR-FTIR to speculate on the reaction pathway of NO₃⁻ and CO₂ coreduction for the synthesis of urea at the MoO_x/C electrode [37]. At every potential, typical peaks were found at 1420 cm⁻¹, indicating the successful production of the C-N bond in the *CONH₂ intermediate. Subsequently, DFT calculations based on free energy diagrams with the lowest energy routes disclosed the principles of urea generation. More specifically, *NO₂ intermediates with an adsorption free energy of -2.04 eV are produced when NO₃⁻ reduction initiates the urea production process. Interestingly, the *CO₂NO₂ intermediate is formed when *NO₂ and CO₂ are more favorably linked. Then, with a rise in adsorption free energy of 1.38 eV, the hydrogenation of *CO₂NO₂ to *CO₂NOOH is a potential energy limiting step. This is kinetically more favorable than the potential energy limiting step on MoO₃ (from *CO₂NOOH to *CO₂NO), with a 1.86 eV rise in free energy. A further reduction route produces a succession of intermediates, *CO₂NO, *CO₂NHOH, *CO₂NH, *CO₂NH₂ and *COOHNH₂, from the CO₂NOOH intermediate.

Interestingly, the creation of the *CONH₂ intermediate is thought to be a crucial step in many electrocatalytic systems, even though the protonation of *COOHNH₂ to *CONH₂ is an exothermic phase with a free energy loss of -1.77 eV. *CONO₂NH₂ is created when *CONH₂ thermodynamically and spontaneously combines with another *NO₂ intermediate. The result of this is the creation of *CO(NH₂)₂. As a result, CO(NH₂)₂ can be produced as a final product with selectivity. Moreover, searching theoretically for effective electrocatalysts to co-reduce CO₂ and NO₃⁻ to urea is a plausible strategy. The theoretical study of urea electrosynthesis, which was based on the projector augmented wave approach using the Vienna Ab initio Simulation Package, employed DFT simulations that resembled the urea creation process. The Perdew-Burke-Ernzerh of functional with the generalized gradient approximation and the projector-augmented plane-wave approach was used to model the exchange-correlation potentials and the ion-electron interactions, respectively. In conclusion, there is an ongoing

debate on the specific chemical pathways and crucial intermediates involved in electrocatalytic C-N coupling, and more investigation is required to determine the mechanism behind the production of urea.

As shown in Figure 4, the main mechanism of the electrochemical synthesis of urea is the co-reduction of CO_2 and NO_3^- through a series of PECT and chemical processes (C-N coupling) [60]. The initial conversion of CO_2 and NO_3^- by PECT results in intermediates such as $*CO_2$, *CO, *COOH, $*NO_2$, *NO, $*H_2NOH$, *NH and $*NH_2$, which are further transformed to C-N intermediates by C-N coupling. Different intermediates to begin the coupling are a crucial step in the synthesis of urea. C-N coupling may be classified into one-step and two-step methods [18].



Figure 4. The general mechanisms in formation of organonitrogen compounds by electrochemical C-N coupling [61].

3. Conclusions and Outlook

The production of urea by the electrocatalytic C-N coupling of NO_3^- and CO_2 is an environmentally friendly and sustainable technology that is powered by clean, renewable energy sources and can support the global N and C balance. This study included a summary and presentation of the product testing and evaluation criteria, research progress, design of the electrocatalyst, and reaction mechanism for the electrocatalytic co-reduction of NO_3^- and CO_2 to urea. In most current circumstances, the side reaction still performs better than the C-N coupling. The reaction mechanism of electrocatalytic urea synthesis is still controversial and it is difficult to theoretically guide the design of efficient catalysts. Besides, the active sites of urea formation and the proposed intermediates are still uncertain. Therefore, an outlook on the existing problems and efforts in the electrocoupling synthesis of urea is summarized.

The practical implementation of urea electrosynthesis still faces several obstacles. For instance, the existence of extremely competitive side reactions such as CO, H₂, and ammonia results in an unsatisfactory C-N coupling efficiency. The electrochemical synthesis of urea is an integrated multistep process involving proton-coupled electron transfer and C-N coupling steps. Designing catalysts with dual metal sites may be a promising approach as the optimal efficiency for the reduction of CO₂ and NO₃⁻ cannot be simultaneously achieved with a single metal active site. Therefore, methods such as surface defect engineering, construction of transition metal alloys or heterojunctions, heteroatom doping, and the use of bimetallic or multimetal catalysts are hopeful avenues for optimizing the electrochemical synthesis of urea. The selectivity and activity of electrocatalytic urea synthesis are significantly restricted by intense competition with the hydrogen evolution reaction (HER) in aqueous solutions. Selecting a suitable electrolyte for efficient electrochemical urea synthesis could significantly improve urea yield and FE_{Urea}. Using a high-concentration LiCl solution as the electrolyte, the salt precipitation effect can simultaneously inhibit HER and provide sufficient active hydrogen for the co-reduction of CO_2 and NO_3^- in urea synthesis. Additionally, ionic liquids with high solubility and affinity for gaseous reaction molecules could be promising electrolyte candidates for electrochemical urea synthesis. Apart from advancing strategies for the rational design of electrocatalysts and electrolyte optimization, reactor configuration remains a bottleneck that needs to be addressed. Liquid flow cells equipped with gas diffusion electrodes are considered effective reactors for gas-solid interface catalytic reactions, providing sufficient contact between gaseous reactants and catalyst surfaces, effectively enhancing the solubility and diffusion rate of gas reaction molecules, thereby improving the electrochemical urea synthesis process.

Further research into the mechanism is necessary for the design of electrocatalysts in the future and for increasing the yield of urea synthesis, particularly in the areas of C-N coupling and by-product generation. In situ characterization techniques play a crucial role in probing the reaction mechanism. Different characterization techniques have different functions, and combining different in situ characterization techniques can make up for the deficiencies existing in a single characterization technique. Consequently, it is anticipated that the development of a network of complimentary in situ characterization methods will offer a more thorough understanding of the C-N coupling reaction mechanism. In order to monitor important intermediates throughout the C-N coupling reactive active sites at the atomic level, more sophisticated in-situ testing methods have been developed. These methods include in-situ Raman spectroscopy, in-situ mass spectrometry, and in-situ Fourier transform infrared spectroscopy. The electrochemical reduction reaction process and the reaction intermediates' transformation mechanism may be thoroughly studied with the aid of these in situ characterization approaches, which can also offer a solid scientific foundation for enhancing the catalysts' catalytic efficacy and product selectivity.

Furthermore, theoretical computations' capacity to investigate the reaction system's atomic-level specifics holds enormous promise for improving our comprehension of how C-N bonds are formed. DFT calculations are widely utilized in the study of multielectron systems. With the advancement of DFT calculations, combining DFT with experimental characterization can be a more effective approach to investigate the thermodynamic properties, active sites, and reaction mechanisms of catalysts for a range of electrocatalytic reactions. Several investigations have demonstrated the critical significance DFT plays in researching reaction processes and forecasting sophisticated catalysts. Convincingly, DFT combined with experiment can eliminate trial and error during catalyst exploration and pave the way for the design of novel advanced electrocatalysts.

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