

## Perspective

## Electrochemical urea synthesis

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## SUMMARY

Enabling the electrification of the chemical industry is crucial for the sector's transition toward zero emissions and a sustainable future. Approximately 2% of the globally used energy is dedicated to fertilizer production, including urea. The electrochemical synthesis of urea from a nitrogen source and CO<sub>2</sub> based on renewable energy can contribute to reaching the ambitious goal of sustainable production with close to zero emissions. However, the current state of technology remains at a low readiness level and a small scale. The majority of studies in the field employ electrode surface areas in the order of 1 cm<sup>2</sup> and achieve moderate current efficiencies of <50%. They are mostly operated in batch mode in H-cells, which are prone to mass transport limitations, leading to a restriction of the achievable current density. In this perspective, we analyze the main challenges regarding highly efficient and scalable reactors for continuous production. We identify knowledge gaps and potential pitfalls. Finally, we propose guidelines to rapidly bridge the gap between fundamental research and industrial application.

## INTRODUCTION

Worldwide research on greenhouse gas (GHG) reduction strategies not only highlights the urgency of fighting global warming but also underscores the collective determination to find innovative solutions for a sustainable future. A major contribution of about 12% of anthropogenic GHG emissions is caused by agricultural production. In particular, the synthesis of nitrogen fertilizer causes about 2% of the energy used worldwide with urea as the dominant nitrogen-based fertilizer with an annual production of about 76 Mt, which accounts for 50% of nitrogen-based fertilizers.<sup>1–3</sup> Exploring opportunities for sustainable urea production is therefore pivotal for reducing the environmental impact while addressing the challenge of meeting growing global fertilizer demand. Today, urea is produced from CO<sub>2</sub> and NH<sub>3</sub> with carbamate as an intermediate in the Bosch-Meiser process. The required ammonia is produced in the Haber-Bosch process, and 42% of the annual ammonia production is directly converted to urea.<sup>3</sup> CO<sub>2</sub> originates as a by-product from steam methane reforming (SMR), which is employed to supply H<sub>2</sub> to the Haber-Bosch process.<sup>4</sup> Both the Haber-Bosch and Bosch-Meiser processes are characterized by their high operational demands: the former requires temperatures of 400–650°C and pressures of 100–400 bar, while the latter operates at around 190°C and pressures of 140–175 bar.<sup>5,6</sup> One approach to decrease GHG emissions for urea production is to valorize green hydrogen from water electrolysis instead of gray hydrogen from SMR. Another approach is the substitution of the Haber-Bosch and Bosch-Meiser process with an alternative technology.

Prominently featured in literature are photo-catalytic, plasma-catalytic, homogeneously catalyzed, biological, and electrochemical ammonia synthesis.<sup>7–10</sup> The

## CONTEXT &amp; SCALE

To provide food for a growing world population, an increasing amount of nitrogen-based fertilizers is needed to satisfy agricultural production capacities. Due to the high production volume of fertilizers, about 2% of the worldwide energy demand is directed toward their synthesis. Among the nitrogen-based fertilizers, urea is the most dominant product, with a share of 50%. Today, significant efforts are directed toward electrochemical synthesis as an electrified and sustainable technology to produce urea. However, at the current stage, this technology is far from application. A transition and broadening of the research focus from fundamental research on catalyst design toward reactor and process design at scale is paramount to advance this research field. This perspective addresses analytical challenges, highlights research gaps in catalyst and reactor design, and sheds light on the requirements for a feasible process to give guidance and directions for future research work.



latter approach has especially resonated in the scientific community, as electrochemical conversions may directly be driven via electricity from renewable resources. Scalability, milder reaction conditions in terms of pressure and temperature, but also the potential for decentralized production at a small scale are characteristics of electrochemical processes, which further contribute to their attractiveness.<sup>11</sup> For a long time, electrochemical dinitrogen reduction to ammonia demonstrated positive developments with the prospect of improving the energy efficiency by operating at room temperature, atmospheric pressure, with water as a solvent, and, if based on green electricity, CO<sub>2</sub> emission-free.<sup>12</sup> However, no major breakthrough has been achieved as of now. The triple bond of N<sub>2</sub> remains sluggish despite numerous attempts to design suitable catalysts.<sup>13</sup> Due to the inert nature of the dinitrogen molecule, many studies struggle with low reaction rates and false positives, which lead to an overestimation of reaction rates and current efficiencies (CEs).<sup>14</sup> These false positives are mainly based on unknown NO<sub>x</sub> impurities brought into the system via the N<sub>2</sub> gas supply.<sup>14–16</sup> Thus, the feasibility of reducing N<sub>2</sub> in aqueous media remains a significant challenge. Presently, the most promising approach is the non-aqueous lithium shuttle method, which has already demonstrated successful conversion of dinitrogen into ammonia.<sup>17</sup> However, the low energy efficiency remains to be a central obstacle on the way to a practical implementation.<sup>17</sup>

Accordingly, the focus of research shifts toward different nitrogen sources than N<sub>2</sub>, such as NO<sub>3</sub><sup>−</sup>, NO<sub>2</sub><sup>−</sup>, or NO. They exhibit a higher reactivity due to a lower bond energy in comparison with the N<sub>2</sub> triple bond.<sup>18</sup> Unfortunately, these substrates show limited potential for a conversion process to ammonia, which will be elucidated in detail in this work. Thus, the field of direct electrochemical conversion of oxidized nitrogen species (NO<sub>3</sub><sup>−</sup>, NO<sub>2</sub><sup>−</sup>, and NO) and CO<sub>2</sub> into urea as an added-value product emerged.<sup>19–21</sup> The research on electrochemical urea synthesis is still in its infancy, and research efforts are mainly focused on novel catalysts and materials. Transferring the reduction of nitrogen species to urea synthesis requires overcoming unique challenges. In particular, the multi-step co-reduction of two substrates into one product is a challenge. The development of catalysts that are both efficient and selective, capable of minimizing the generation of numerous by-products and ensuring stable operation under mild conditions, is essential. Consequently, acquiring a deep understanding of the reaction mechanism is crucial. Furthermore, it is necessary to develop electrochemical cells in which both liquid and gaseous transport of the reactants are optimized for this co-reduction and which at the same time enable a sufficiently high yield and energy efficiency, and scalability. Nonetheless, rapid and efficient development of electrochemical urea synthesis must incorporate a holistic view of the entire electrochemical cell to avoid dead ends.

This perspective seeks to contribute to the advent of electrochemical urea synthesis by consolidating research findings, highlighting areas for improvement, and addressing the main challenges ahead. Existing knowledge gaps and white spots are identified that require further investigation. Catalysis research must be accompanied by electrochemical engineering to transition from laboratory-scale experiments to large-scale applications. By considering industrial conditions and value chains, we identify critical barriers to commercial-scale application.

## ELECTROCHEMICAL UREA SYNTHESIS

In addition to the electrochemical approach for urea synthesis, various technologies such as biomass conversion, plasma-assisted methods, electromagnetic field

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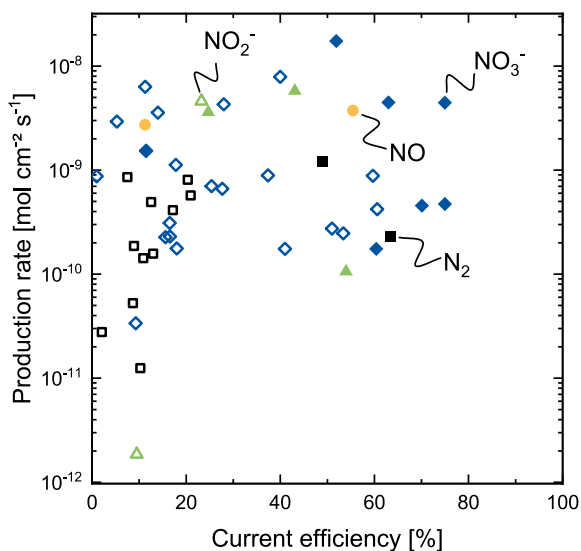
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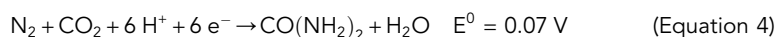
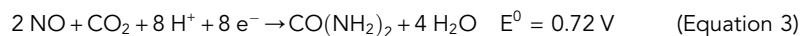
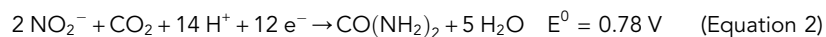
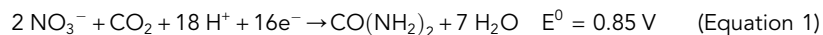
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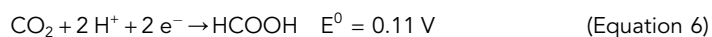
**Figure 1. Comparison of production rate and CE for electrochemical urea synthesis from different nitrogen sources**

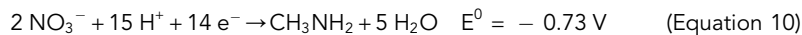
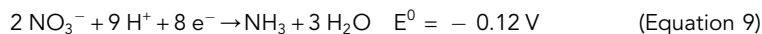
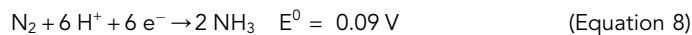
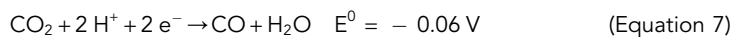
Data points that are not validated with more than one detection method are depicted with open symbols. Full symbols indicate double detection of urea by two independent methods, indicating more reliable measurements. In 28% of the shown studies urea formation was verified by double detection. References are given in the [supplemental information \(Table S8\)](#).

induction, and photo-catalytic processes have been explored.<sup>22–25</sup> All of these technologies have been little researched so far, which makes comparison and identification of their main challenges difficult. In this perspective, we thus exclusively focus on electrochemical techniques. To provide an overview of the achievements in electrochemical urea synthesis [Figure 1](#) summarizes a selection of results obtained with  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}$ , and  $\text{N}_2$  as nitrogen source. The selection is based on all publications until November 2023, where both the geometric area-specific production rates in  $\text{nmol cm}^{-2} \text{s}^{-1}$  and CEs were specified or could be calculated (see [Table S8](#)). In the following sections, figures of merit for electrochemical urea synthesis based on the oxidation state of the nitrogen species will be presented and critically discussed. The individual half-cell reactions toward urea are listed in [Equations 1, 2, 3, and 4](#).



Common side reactions that decrease the CEs in electrochemical urea synthesis are given in [Equations 5, 6, 7, 8, and 9](#).<sup>26,27</sup> An extended list can be found in the [supplemental information \(Table S4\)](#).





### Remarks on the choice of nitrogen source

The selection of the nitrogen source for urea electrolysis presents a challenge, balancing factors such as thermodynamics, kinetics, and practical considerations. Based on the standard potential,  $\text{NO}_3^-$  would be the best option. However,  $\text{NO}_3^-$  also requires the highest number of  $\text{H}^+$  per urea molecule. When taking water splitting at the anode into account, the reaction of NO is thermodynamically favorable as it has the lowest changes in Gibbs free energy per molecule of urea (Table S3). As seen in Figure 1 and discussed in the following sections, higher current densities can be achieved with  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and NO compared with  $\text{N}_2$ . The inert nature of  $\text{N}_2$  compared with other nitrogen sources in electrochemical reactions has been observed in electrochemical  $\text{NH}_3$  and is in accordance with the expectations.<sup>28</sup>

From a practical point of view,  $\text{N}_2$  and NO are gaseous species unlike  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , which are supplied within the electrolyte. The latter allows for a decoupled tailoring of the mass transport of the nitrogen source and  $\text{CO}_2$ . Regardless of the nitrogen source, since urea can either be present in liquid solution or as a solid,<sup>29</sup> a liquid phase within the cell setup is necessary. This calls for a sophisticated design of zero-gap cell setups, which are usually utilized to achieve a low cell voltage. More details are discussed in engineering and cell design. Although  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and NO exhibit a much higher reactivity, they are not as freely available as  $\text{N}_2$ . This has to be considered for a potential application and is further discussed in holistic process evaluation.

### Recent progress in electrochemical urea synthesis

#### Nitrate

Between 1995 and 2003, Shibata et al.<sup>30–32</sup> published a seminal series of studies on electrochemical urea synthesis with  $\text{NO}_3^-$  and nitrite as nitrogen sources. Different metals (Cr, Mo, Mn, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, In, Tl, Sn, and Pb) were screened on gas diffusion electrodes (GDEs). Their catalytic performance was assessed in a batch electrolysis cell with stationary electrolytes. Although the CE was up to 29% for nitrate reduction, nitrite was identified to be the substrate achieving higher CEs.<sup>30,31</sup> As a result, the focus of research following these publications shifted to the reduction of nitrites. 15 years later, Saravanakumar et al.<sup>33</sup> excavated the simultaneous reduction of nitrate and  $\text{CO}_2$  again. Using  $\text{TiO}_2$  nanoparticles as the catalyst on an indium tin oxide-coated glass slide in an H-cell, urea was obtained with a CE of 40% and a production rate of  $52.38 \text{ nmol cm}^{-2} \text{ s}^{-1}$ , forming mainly ammonia and carbon monoxide as by-products. Gas chromatography (GC) was used to analyze carbon reduction products, while urea was detected by the urease assay. The urease assay involves the enzymatic decomposition of urea to ammonia and subsequent quantification of ammonia via indophenol-blue method. This production rate was not achieved again in subsequent studies in the literature. More recently, Shin et al.<sup>34</sup> were able to synthesize urea with a CE of 51.9% at a production rate of  $17.41 \text{ nmol cm}^{-2} \text{ s}^{-1}$ , which is in the same order of magnitude as the study

mentioned before (Figure 1). Based on the experience of low production rates in urea synthesis from dinitrogen, the authors intended to use nitrate as substrate. To increase CE and production rate, the authors used GDEs in a flow cell containing copper(I)oxide nanoparticles with atomic scale spacing, thereby improving the urea synthesis from H-cell research. Sensitized for impurities and difficulties in liquid analytics the authors validated product quantification by implementing several methods for product analysis. Gaseous products were analyzed via GC, while C–N coupled liquid products were detected using nuclear magnetic resonance (NMR). Carbon-containing liquid products were analyzed via high-performance liquid chromatography (HPLC) and ionic compounds via ion chromatography.<sup>34</sup> The application of multiple quantification assays marks an important milestone in electrochemical urea synthesis because it increases the reliability of results as discussed in the introduction and dinitrogen (N<sub>2</sub>). To date, the highest CE known to the authors was published by Luo et al.<sup>35</sup> A CE of 75% and a production rate of 0.47 nmol cm<sup>-2</sup> s<sup>-1</sup> with a GDE in combination with a flow cell and a copper-zinc hybrid catalyst were achieved. Improving the catalyst to a “3D hybrid catalyst,” they reported a slightly lower CE of 63% but with a production rate of 4.47 nmol cm<sup>-2</sup> s<sup>-1</sup>. Luo et al. used the diacetylmonoxime (DAMO) method and NMR for urea quantification to verify their results (Figure 1). A notable shift in research focus can be observed when comparing publications concentrating on nitrate or nitrite reduction. In the early 20<sup>th</sup> century, there was a predominant emphasis on nitrite reduction, largely influenced by the findings of Shibata et al.<sup>30</sup> Nowadays, research tends to prioritize nitrate reduction, as it offers fewer analytical challenges, which will be elaborated on in dinitrogen (N<sub>2</sub>). Additionally, nitrates are a more readily available substrate.

#### Nitrite (NO<sub>2</sub><sup>-</sup>)

As previously noted, Shibata et al.<sup>30,31,36–38</sup> found nitrite to exhibit enhanced CE in comparison with nitrate. By contrast, the present literature does not show a distinct pattern of nitrite outperforming nitrate as a nitrogen source, as depicted in Figure 1. Zhang et al.<sup>39</sup> directly compared nitrite and nitrate using the same iron-nickel-based catalyst and observed a only marginally higher production rate and CE for nitrite. In the aforementioned works of Shibata et al., GDEs were coated with different metal catalysts and evaluated for their performance in reducing CO<sub>2</sub> and nitrites to urea. Many recently published works, around 20 years later, are based on this series. The Shibata series has inspired catalyst and electrolyte selection, but also the method for urea quantification, which is the enzymatic urease assay. In most of the recently published results, the high CE for urea of up to 55%,<sup>36</sup> obtained with zinc and cadmium catalysts could not be achieved with zinc oxide<sup>40</sup> or other catalyst materials.<sup>39,41,42</sup> One reason for the deviance originates from the quantification methods employed, which will be discussed in detail in analytical methods and reliability. An exception is the work of Zhang et al.,<sup>43</sup> who used a cobalt-nickel oxide on graphdiyne catalyst with a production rate of 913.2 μg h<sup>-1</sup> in an H-cell. They reported a CE of 64.3% with a nitrogen selectivity of 86% and a carbon selectivity of 100%. However, it is unclear how the carbon selectivity was calculated, as the specific formula is not provided and a CE toward CO of more than 20% under the reaction conditions is reported. A comparable high CE of 54% was reported by Akther et al.<sup>44</sup> for an iron(III)-tetrasulfophthalocyanine catalyst. The production rate was reported to be 1.06 nmol cm<sup>-2</sup> s<sup>-1</sup>, which is an order of magnitude lower than reported for most nitrite-based systems. A CE of 43.1% with a production rate of 5.78 nmol cm<sup>-2</sup> s<sup>-1</sup> was achieved by Cao et al.<sup>45</sup> with a Cu-TiO<sub>2</sub> catalyst in an H-cell. A similar production rate of 4.6 nmol cm<sup>-2</sup> s<sup>-1</sup> with a CE of 23.3% was achieved by Meng et al.<sup>40</sup> on ZnO in an H-cell. Meng et al.<sup>40</sup> were one of a few author groups that used HPLC instead of spectroscopic methods to determine the urea

concentration. Overall, most publications using nitrite as a nitrogen source focus on developing new catalysts. The electrochemical characterization is carried out almost exclusively in H-cells with electrode surfaces in the order of  $1 \text{ cm}^2$ .

#### Nitric oxide (NO)

NO has scarcely been investigated as a nitrogen source in literature compared with  $\text{N}_2$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$ . Huang et al.<sup>46</sup> report a CE of 11.26% with a production rate of  $4.67 \text{ nmol cm}^{-2} \text{ s}^{-1}$ .  $\text{CO}_2$  and NO were supplied to a GDE with zinc as a catalyst in a flow cell. A different approach was pursued by Shi et al.,<sup>47</sup> who investigated the use of flue gas as a carbon and nitrogen source. They synthesized formic acid from flue gas containing  $\text{CO}_2$ . Formic acid was then electrochemically processed with NO, which is also present in flue gas, to form urea. The CE was 55.45%, while a production rate of  $3.75 \text{ nmol cm}^{-2} \text{ s}^{-1}$  was achieved. In comparison to the previously described work, they used an H-cell approach without a GDE and gold-copper Janus nanoparticles as catalyst. Besides the two experimental works, there is a theoretical study by Wan et al.<sup>48</sup> investigating the co-reduction of NO and CO on various metals by density functional theory (DFT) calculation. They found Co to be a good catalyst in theory and also contribute to a more fundamental understanding of NO's potential as a nitrogen source by providing a possible reaction pathway. To the best of our knowledge, Co has not been experimentally investigated until now. In summary, investigations of NO as a nitrogen source in the literature are limited compared with  $\text{N}_2$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$ . This could be because NO's toxicity requires increased safety measures and laboratory equipment. Considering the future availability of nitrogen sources, NO holds potential significance due to emerging processes, such as plasma-driven nitrogen oxidation, which may serve as a NO source.<sup>49</sup>

#### Dinitrogen ( $\text{N}_2$ )

Urea synthesis from  $\text{N}_2$  is even more challenging than electrochemical ammonia synthesis, as it combines simultaneous dinitrogen and  $\text{CO}_2$  reduction. Concerning the detection of false positives, the same challenges as in electrochemical ammonia synthesis apply. Thus, the same rigorous protocols are needed to obtain unambiguous results and prevent significant contamination with more reactive species such as NO,  $\text{NO}_2^-$ , or  $\text{NO}_3^-$  within the experimental setup. This requires extensive cleaning procedures to remove contamination, control experiments with argon instead of  $\text{N}_2$ , reproducibility of the results, a minimum production rate, and quantitative isotope-labeled  $^{15}\text{N}_2$  experiments.<sup>14–16</sup> A series of five research articles on electrochemical  $\text{N}_2$  has been published by Yuan et al.<sup>50–54</sup> The highest reaction rate is  $1.2 \text{ nmol cm}^{-2} \text{ s}^{-1}$  with a CE of about 49%. Metal-organic frameworks with Co were employed as the catalyst. A  $3 \text{ cm}^2$  electrode was used in an H-cell. The DAMO method and NMR were utilized to analyze the samples regarding the urea content.<sup>54</sup> Only Zhang et al.<sup>55</sup> have achieved a higher CE of 63.5% with a catalyst named ZnMn-N,Cl. This is attributed to a pre-poisoning strategy using CO to suppress side reactions such as hydrogen evolution. The reaction rate was  $0.23 \text{ nmol cm}^{-2} \text{ s}^{-1}$  in an H-cell with a  $1 \text{ cm}^2$  electrode. Urea was quantified using the DAMO and urease decomposition method.<sup>55</sup> Especially in recent publications, experimental protocols have gotten increasingly sophisticated. Some of the studies nearly fulfill every criterion for reliable data. One important step for contamination control is a suitable scrubber for the removal of any  $\text{NO}_x$  contamination. However, there is no information regarding the pretreatment of the  $\text{N}_2$  (and  $^{15}\text{N}_2$ ) gas<sup>56–61</sup> or a combination of a base trap (NaOH/KOH) and an acid trap ( $\text{H}_2\text{SO}_4$ ).<sup>50–55,62</sup> This scrubber combination is known to be less efficient for the removal of problematic NO contamination due to low solubility in acid and base solution. To circumvent this, the recommended scrubber of choice is  $\text{KMnO}_4$  for the oxidation of NO.<sup>14</sup>

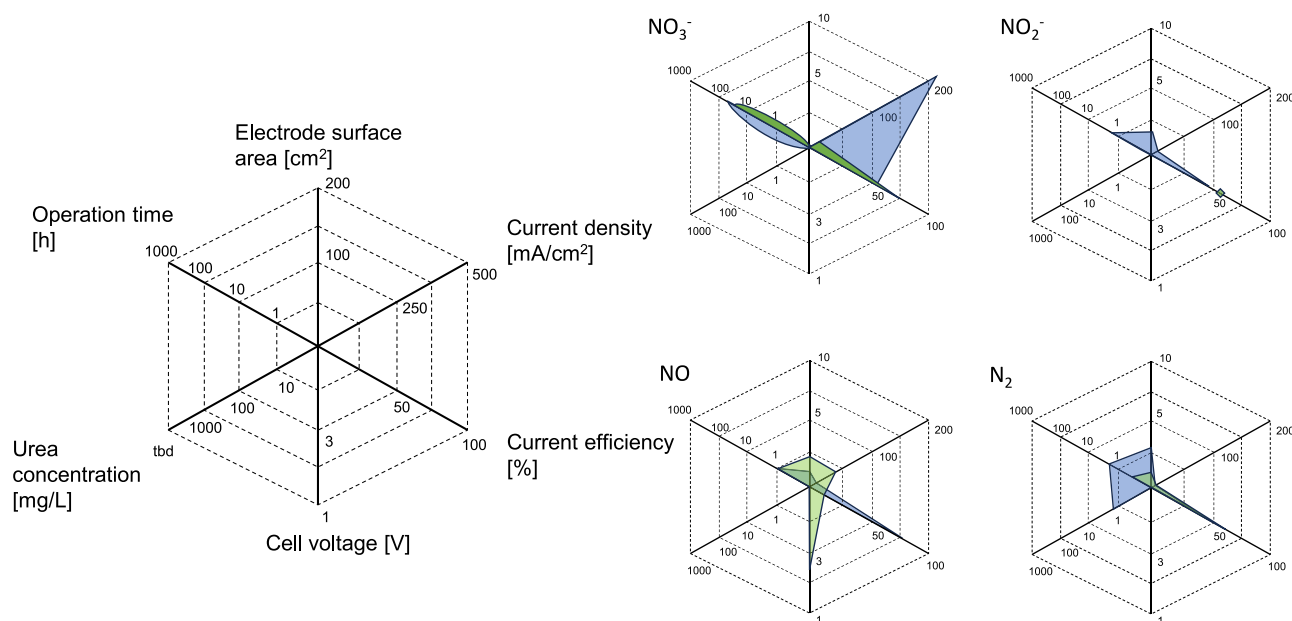
Hence, current results in the literature should be validated by fulfilling all necessary precautions.

### Urea synthesis through C–N coupling mechanism

In the one-step electrochemical synthesis of urea, controlling side reactions is crucial due to the simultaneous presence of multiple substrates. Effective catalysts must specifically favor urea synthesis while reducing unwanted reactions like the reduction of only the carbon or nitrogen sources and avoiding electrolyte decomposition, such as the hydrogen evolution reaction. The proximity of C–N coupling is essential for urea formation. So far, the mechanisms have been studied on several different catalyst materials. The choice of catalyst up to date was based on properties such as oxygen vacancies and modifiable electronic properties, and from experience with catalysts applied in CO<sub>2</sub> reduction. A systematic study of catalysts, driven by modeling studies, will contribute to a better mechanistic understanding and advancement of the field. Zhong et al.<sup>63</sup> discussed the mechanism of urea formation extensively. Due to the C=O, N≡N, or N=O bonds, the kinetics are generally sluggish.<sup>63</sup> Shibata et al.<sup>30</sup> demonstrated experimentally that urea forms only when both NO<sub>2</sub><sup>−</sup> or NO<sub>3</sub><sup>−</sup> and CO<sub>2</sub> are present at the electrode; adding potential intermediates such as NH<sub>3</sub> or CO to the electrolyte did not result in urea, indicating that necessary intermediates must be generated directly at the electrode surface. CO<sub>2</sub> is absorbed in aqueous NH<sub>3</sub>-solutions and forms carbonates instead of desired urea.<sup>64,65</sup> Recent studies explored the reaction mechanism for urea formation by using DFT calculations. By comparing the proposed reaction mechanisms for NO<sub>2</sub><sup>−</sup> or NO<sub>3</sub><sup>−</sup> to urea, different pathways appear for different catalyst materials. In general, the performance of electrochemical C–N coupling using NO<sub>3</sub><sup>−</sup> is lower than when NO<sub>2</sub><sup>−</sup> is used, because of sluggish kinetics of the conversion from nitrates to nitrites.<sup>63</sup> In the urea formation, \*NO and \*CO are critical surface intermediates for the C–N coupling.<sup>66</sup> Qiu et al.<sup>67</sup> calculated that the coupling of two \*NO with \*CO to \*ONCONO occurs first, followed by the protonation to urea. Liu et al.<sup>66</sup> presented a mechanism involving alternating C–N coupling and protonation of the N-atom steps. Luo et al.<sup>35</sup> proposed a similar alternating coupling and protonation mechanism but included the coupling of intermediate forms \*NO<sub>2</sub> and \*CO<sub>2</sub> which are in an even higher oxidation state. The mechanism underscores the limitations of urea formation arising from C–N coupling and suggests that the balance between coupling and protonation could be beneficial in tuning urea formation, a hypothesis that requires further exploration.

### Critical discussion and white spots

A spotlight in the field of electrochemical urea synthesis must be pointed toward the parallels to electrochemical dinitrogen reduction to ammonia, particularly in terms of analytical challenges and false positives. As previously described, no significant breakthrough has been made in the low-temperature direct reduction of dinitrogen for years, and research has mainly focused on the development of new catalysts on a very small scale. In principle, this approach is suitable for determining suitable catalysts for processes with a low technology readiness level. However, catalyst screening should not lead to a multitude of different catalyst modifications of the same material. Similar research efforts in other research fields show an overall low outcome of this methodology.<sup>68,69</sup> The focus should rather be on a broad screening of different materials, for example in the publications of the Shibata et al.<sup>30–32,36–38</sup> series. As discussed in [engineering and cell design](#) a focus on electrochemical systems and cells that lead to scalable devices must be considered from the beginning. For example, when using CO<sub>2</sub> as a substrate, researchers should use GDEs to overcome mass transport limitations. The majority of research articles describe the



**Figure 2. Spiderweb diagram for data reporting**

Data report in the form of a spiderweb diagram with the most important experimental parameters for better comparability of literature results. Smaller diagrams are zoomed in to show the data more accurately.  $\text{NO}_3^-$ : blue,<sup>34</sup> green<sup>35</sup>;  $\text{NO}_2^-$ : blue,<sup>45</sup> green<sup>43</sup>; NO: blue,<sup>47</sup> green<sup>46</sup>;  $\text{N}_2$ : blue,<sup>54</sup> green.<sup>55</sup>

synthesis and characterization of the materials in detail, but important parameters such as catalyst loading or reactor volume are missing. Several key metrics need to be included in the publications for a rapid advancement toward a higher technology readiness level, such as the electrode surface area, current density, CE, cell voltage, urea concentration, and operation time. We therefore recommend using the spider web diagram proposed in Figure 2 for better comparability and a quick assessment of the strengths and weaknesses of individual studies. The parameters current density, CE, and cell voltage were selected to evaluate the electrochemical performance and efficiency, while the electrode area and operation time are suitable for an evaluation regarding scale-up and process stability for a future industrial process. The urea concentration indicates measurement accuracy and reliability of the results in a preliminary phase but also provides relevant data for necessary downstream applications for the concentration of urea in industrial applications. We have deliberately not included the previously frequently used production rate in the diagram as it can be calculated with given current density and CE. At the same time, we believe that the current density is the more appropriate parameter as the use of different units and reference values, such as surface area or catalyst mass, make comparability by production rate challenging. The scale was chosen to be adequate for research and development toward industrially relevant operating parameters. The use of this diagram is illustrated with research data from the nitrogen source-specific subsections. Given today's low technology readiness level of electrochemical urea synthesis, the scales on the spider web diagram showing literature results were adjusted compared with those on the proposed diagram to ensure readability.

The incomplete reporting of data impedes the reproduction of results, although this is one of the most essential quality features in science.<sup>70</sup> The importance of standards for experiments and reports has already been pointed out for a similar situation in the field of battery research<sup>68</sup> or  $\text{CO}_2$  reduction.<sup>71</sup> We do not believe it is



currently possible to standardize experiments for electrochemical urea synthesis with respect to the setup. However, a consensus for standardized publication is required. Therefore, we suggest that every publication should at least report the six most important electrochemical performance parameters shown in [Figure 2](#). Arguably, energy efficiency is an essential figure of merit and should be included as technology evolves. Moreover, the definition of minimal requirements for an experimental procedure would improve the comparability between research groups. Chen et al.<sup>72</sup> suggested the use of a benchmark catalyst for the identification of differences in experimental setups. As there is no accepted and commercially available catalyst for electrochemical urea synthesis, a catalyst that synthesizes ammonia and CO from  $\text{NO}_3^-$  or  $\text{NO}_2^-$  and  $\text{CO}_2$  could be used. Although this would not improve comparability with regard to urea synthesis itself, possible variations due to the experimental setup and cell design could be identified. Other than the experimental setup, the importance of reliable detection of urea needs to be emphasized. The analytics concerning urea became a focus within the last 2 years as quantitative and qualitative detection in electrolyte samples is more challenging than previous literature suggested.<sup>73–76</sup> Methods that could point to false positives should be avoided and findings with outdated methods should be evaluated with this in mind. Therefore, a critical discussion of the urea quantification methods is necessary.

## CHALLENGES AND OPPORTUNITIES

### Analytical methods and reliability

Developing detection methods for a new field of research can be challenging, especially for low target substance levels and the abundance of by-products. In the field of electrochemical urea synthesis, three groups have developed and proposed analytical protocols to be followed.<sup>74–76</sup> Fortunately, the research field can benefit from methods that have already been developed and applied in different applications, including clinical diagnostics, environmental monitoring, and the food industry. Francis et al.<sup>77</sup> provided a comprehensive summary of the methods employed in those applications. The most relevant methods in the field of electrochemical urea synthesis are the urease method, DAMO method, NMR, HPLC, or HPLC combined with mass spectroscopy (HPLC-MS). Even if the detection limit is of decisive importance, it plays a subordinate role in the field of electrochemical urea synthesis. This can be attributed to the similar detection limits of 0.52 (urease), 0.14 (DAMO), 0.55 (NMR), and 0.42 ppm (HPLC) of those methods and to the primary challenge of ensuring reliable detection in the presence of an array of by-products.<sup>75</sup> Consequently, the differences characterizing the individual detection methods will be examined here.

The dominating methods in electrochemical urea synthesis are spectroscopic, which can be divided into direct and indirect measurements. For indirect methods, urea is first converted enzymatically into ammonia by urease. Subsequently, the urea concentration can be determined from the difference in ammonia concentration before and after the conversion (e.g., by indophenol-blue method). The most used direct method is the DAMO method, which is based on the formation of a complex by the reaction of DAMO and urea. The correct and appropriate application of both methods offers challenges and pitfalls.

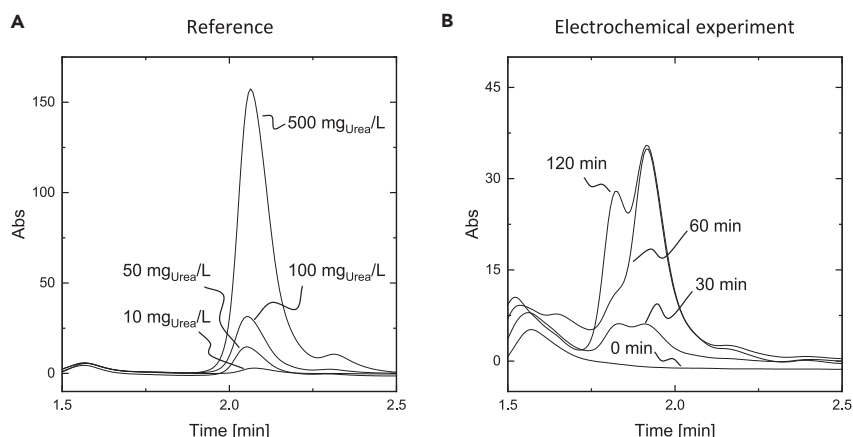
The influencing factors on the urease method include the pH value, temperature, conversion, activity, and concentration of the enzymes, the presence of metal ions, and most importantly, the presence of  $\text{NO}_2^-$  and  $\text{NH}_4^+$  ions in the

solution.<sup>46,76,78</sup> Ammonia and therefore  $\text{NH}_4^+$  ions are commonly reported as side products in electrochemical urea synthesis. Therefore, the correct and reliable application of the urease method is difficult, and the method should only be used in combination with a second method for validation.

The DAMO method has fewer influencing parameters compared with the urease method. Most metal ions in low concentration do not influence the measurement accuracy.<sup>76</sup> Additionally, Li et al.<sup>76</sup> have investigated how the by-products of electrochemical urea synthesis ( $\text{CH}_3\text{OH}$ ,  $\text{HCOOH}$ ,  $\text{HCHO}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$ ) affect the method and found no influence up to a concentration of  $10 \text{ mmol L}^{-1}$ . However, some reducing reagents as well as thiourea and thiosulfate were found to interfere.<sup>77</sup> Most notably nitrite, which leads to a significant underestimation for concentrations above  $1 \text{ mmol L}^{-1}$ .<sup>76</sup> This was confirmed by Huang et al.,<sup>75</sup> who found the critical  $\text{NO}_2^-$  concentration to be 20 ppm. The effect of nitrite is highly significant for two reasons: if used as a nitrogen source for the reaction, it is naturally present in elevated concentrations in the samples. Secondly, nitrate will be reduced to nitrite preceding the further reduction to urea. Hence, nitrite will be present in experiments with nitrate. The DAMO method should therefore be used with caution, and side effects from by-products, especially nitrite, should not be underestimated.

A method often used for qualitative evidence of urea is NMR. An advantage of urea detection with NMR is the low influence of by-products and metal ions.<sup>75</sup> Additionally, similar to electrochemical ammonia synthesis, NMR can be applied for control experiments with isotope-labeled molecules.  $^1\text{H}$ -NMR can be utilized for isotope-labeled measurements of  $^{15}\text{N}$ , while  $^{13}\text{C}$ -NMR can be used for  $^{13}\text{C}$ -labeled experiments.<sup>76</sup> A drawback of this technique is the need for suppression of water, which is time-consuming and difficult to operate.<sup>75</sup> Li et al.<sup>76</sup> developed a method to circumvent the need for water suppression for qualitative identification, yet they recommend not using it for quantitative detection. Another disadvantage of NMR that has hardly been considered in literature is the influence of the electrolyte, as described by Yuan et al.<sup>74</sup> The carbon-oxygen-bond peaks of carbonate and bicarbonate can interfere with the urea carbon-oxygen-bond peak. Carbonate and bicarbonate are naturally present when using  $\text{KHCO}_3$ , the most common electrolyte in electrochemical urea synthesis. Distinguishing between (bi)carbonate peaks and the urea carbon-oxygen-bond peak is essential for reliable urea detection. Disregarding the (bi)carbonate peak can lead to a false-positive result of a  $^{13}\text{C}$ -NMR measurement, especially when using  $^{13}\text{C}$  nitrogen as described by Yuan et al.<sup>74</sup> An alternative to the aforementioned detection methods can be urea quantification by HPLC.<sup>40,46,73,79</sup> HPLC can be combined with MS to assign urea to a peak in the chromatogram and to confirm the presence of urea in the system. Yuan et al.<sup>74</sup> have developed a method to quantitatively detect isotope-labeled urea using a liquid chromatography-mass spectrometry (LC-MS) method and recommend using LC-MS as the best detection method. However, the authors emphasize that for reliable detection at least two detection methods should be combined and additionally isotope-labeled control experiments should be used. HPLC and HPLC-MS currently appear to be the most reliable methods for measuring urea from electrochemical systems. The influence of by-products and components present in the system such as nitrite or metal ions is reported to be minimal.

We have studied electrochemical urea synthesis on zinc and copper with nitrite and nitrate as nitrogen sources and found an influence of by-products on HPLC measurements for our system. [Figure 3A](#) shows chromatograms of reference samples and [Figure 3B](#) samples from electrochemical experiments. The reference samples



**Figure 3. Exemplary HPLC chromatogram for urea quantification**

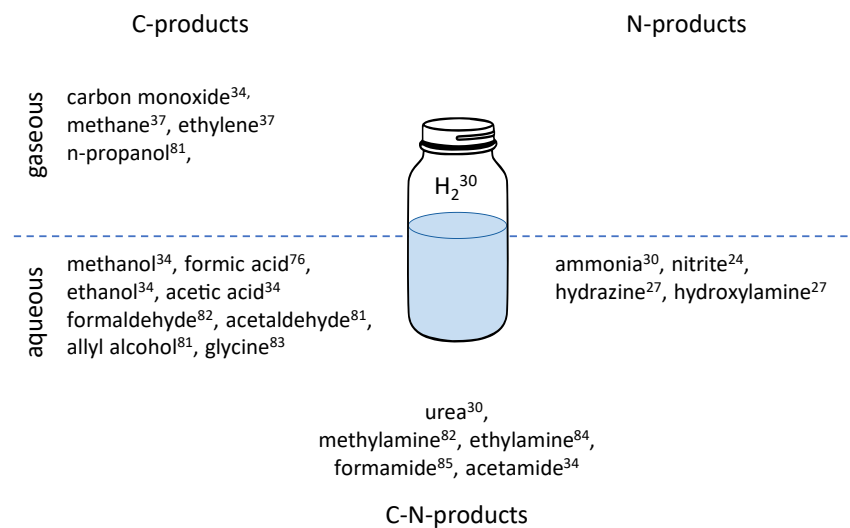
(A and B) Exemplary HPLC chromatogram of (A) urea concentrations of 10, 50, 100, and 500 mg L<sup>-1</sup> in electrolyte (0.2 mol KHCO<sub>3</sub> + 0.02 mol KNO<sub>2</sub>) and (B) samples of electrochemical urea synthesis of 0, 30, 60, and 120 min. (Reaction conditions: catholyte: 0.2 mol KHCO<sub>3</sub> + 0.02 mol KNO<sub>2</sub>; anolyte: 0.1 mol H<sub>2</sub>SO<sub>4</sub>; catalyst: zinc; current density: 20 mA cm<sup>-2</sup>; electrode area: 25 cm<sup>2</sup>; electrolyte volume: 250 mL; and details of HPLC method are given in the [supplemental information](#)).

consist of urea in concentrations from 10 to 500 mmol l<sup>-1</sup> in a 0.2 mol KHCO<sub>3</sub> + 0.02 mol KNO<sub>2</sub> electrolyte. In comparison, the chromatogram of the experiment samples indicates the formation of side products during electrolysis but no urea formation. Depending on the applied HPLC method, by-products can influence the precise quantification of urea by overlapping peaks or even lead to false-positive results. The issue and occurrence of an unknown side product are also described by Yuan et al.<sup>74</sup>

The large number of possible by-products at CEs below 100% (Figure 4) makes analysis challenging in general. This is due to two reasons: firstly, not all possible reaction products are known, and secondly, different methods have to be combined to quantify all by-products. An overview of the most frequently used analytical methods in electrochemical urea synthesis with their advantages and disadvantages is given in Table 1.

### Engineering and cell design

Current literature on electrochemical urea synthesis mainly focuses on catalyst development for carbon and nitrogen activation and subsequent C–N coupling.<sup>78</sup> However, for the different substrates, the reactor must be carefully designed to mitigate mass transfer limitations, kinetic overpotentials, and ohmic resistances, whereas selectivity and current density must be maximized. In the following, requirements for the electrochemical cell will be discussed, focusing on the different substrates used in the urea electrolysis. When using CO<sub>2</sub> as the carbon source, mass transport during electrolysis is a challenge. Additionally, nitrate or nitrite may only be available in low concentrations from waste streams, and thus, mass transfer will be highly relevant here as well. Several key factors have to be considered for an energy-efficient reactor with a high production rate, including electrode arrangement, flow distribution, the choice of ion exchange membrane, and reactor design as shown in Figure 5. The reactor should provide efficient mass transfer of reactants and products, and a practical implementation in scalable systems should be considered. This includes using GDEs, as well as flow cells with reasonable electrolyte gaps, to overcome limitations in solvated CO<sub>2</sub> availability and to enhance overall mass



**Figure 4. Side products in electrochemical urea synthesis**

Depiction of possible products in the simultaneous reduction of carbon species and nitrogen species to aim for urea production.<sup>30,34,37,75,80–84</sup>

transport. In literature, the majority of publications employ H-type cells with electrode surface areas in the order of  $1 \text{ cm}^2$ .<sup>33,85–87</sup> Since the solubility of  $\text{CO}_2$  in water is low and the solubility of nitrogen compounds, such as nitrogen oxide, is even less, GDEs should be used to overcome mass transport limitations. As in  $\text{CO}_2$  reduction reaction, flow cells can be leveraged to increase mass transport.<sup>46,88</sup> Thus, GDEs will be fundamentally important in electrochemical urea synthesis systems from  $\text{CO}_2$ , both when the nitrogen source is used in an ionic form and especially when nitrogen is used in a gaseous form. GDEs have multiple functions, including efficient mass transport of reactant gases ( $\text{CO}_2$  and nitrogen compounds) and facilitating electrochemical reactions at the electrode-electrolyte interface. The choice of GDE material, catalyst loading, ionomer, ionomer-catalyst ratio, and the design of the microporous layer can significantly affect the overall performance and durability of the system.<sup>89</sup> As shown by Kim et al.,<sup>90</sup> the ionomer has a tremendous impact on product selectivity in  $\text{CO}_2$  reduction, and it will also have an impact on the electrochemical urea synthesis. Likewise, the supporting electrolyte, namely the cations, must be considered as they are known to be of high influence.<sup>91</sup> Recent work in electrochemical  $\text{CO}_2$  reduction additionally highlights the importance of humidity in the feed gas stream<sup>92</sup> and pH changes in the boundary layer.<sup>93</sup> At last, the reaction system must also be optimized with respect to temperature.<sup>94</sup> A liquid electrolyte is needed to remove the formed product urea, as urea dissolves in aqueous media and can be removed from the reactor, but also to supply ionic substrates such as nitrate and nitrite. Ionic migration across the ion exchange membrane must be considered and balanced with the electrode reactions to obtain a stable operation.<sup>95</sup> In the following paragraph ion migration will be considered for the case of nitrate reduction, with the arguments applying for nitrite as well. In general, the reactor can be operated with three different ion exchange membranes: cation exchange membrane (CEM), anion exchange membrane (AEM), or bipolar membrane (BPM). The different reactor designs are depicted in Figure 6.

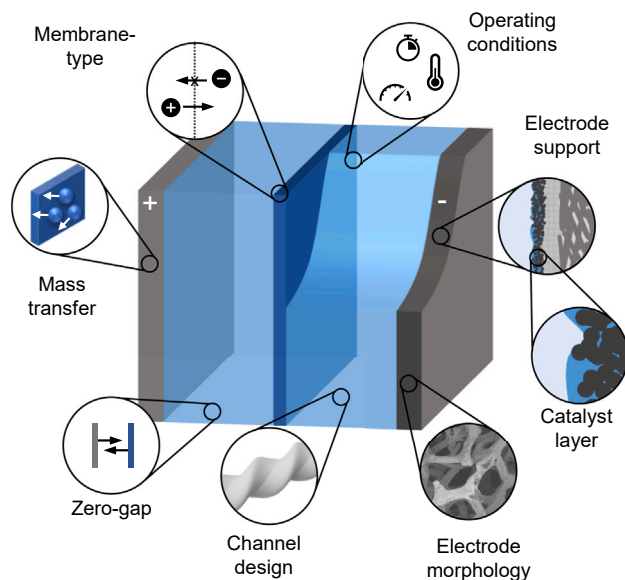
In a CEM-based cell, positively charged ions will migrate across the membrane toward the cathode. Since protons are consumed at the cathode, they must be replenished from the anolyte. Otherwise, a pH shift will take place in the catholyte

**Table 1. Comparison of urea quantification methods**

	Urease	DAMO	NMR	HPLC/HPLC-MS
Main advantage	facile and easy-to-use detection via UV-vis measurements	facile and easy-to-use detections via UV-vis measurements; few influencing by-products	isotope labeling possible	identification of side products by MS; isotope labeling possible by MS
Main disadvantage	reproducibility is difficult; many influencing factors especially in enzymes	not applicable to many systems because of nitrite interference; time-sensitive (heating and cooling time)	water suppression and resulting measurement time; quantification difficult	separation of side products and urea in column challenging
Main known interfering components	nitrite; ammonia	nitrite; reducing agents like thiourea and thiosulfate	water; carbonate; bicarbonate	unknown

Comparison of urea quantification methods regarding their respective main advantages, disadvantages, and interfering components.

compartment. Acidic conditions at the anode will supply the desired protons, which necessitates acidic oxygen evolution reaction (OER) with iridium oxide as a rare and cost-intensive catalyst. Additionally, when nitrate and nitrite are used as substrate, more protons are consumed than will migrate through the CEM, which is evident from Equations 1 and 2. Thus, the pH of the catholyte will increase unless controlled externally. This effect will be a challenge independent of the ion exchange membrane type. Using AEM for urea synthesis, alkaline instead of acidic OER may be implemented as an anode reaction, and hydroxide ions will migrate through the membrane. In this case, cost-effective non-noble metal catalysts, such as nickel oxide hydroxide or nickel-iron oxides, could be used. Unfortunately, depending on nitrate concentrations and membrane selectivity, nitrate and carbonate migration from catholyte to anolyte competes with hydroxyl ion migration. This setup might work by using the electrolyte in a single-pass mode, consecutively passing the anolyte and the catholyte. Thereby, the loss of nitrate could be mitigated. The mixing of hydrogen and oxygen gas needs to be considered to avoid creating an explosive gas mixture. Hence, produced oxygen from the anolyte needs to be removed before the electrolyte can be fed into the catholyte chamber to produce urea.<sup>96</sup> However, this reactor design presents challenges, as loss of CO<sub>2</sub> at the anode and oxidation of nitrite are possible. BPMs can be implemented as a remedy to undesired ion cross-over discussed in CEM and AEM. By working with independent conditions on both electrolytes, alkaline pH would be preferred for using non-precious metals in alkaline OER. In addition, nitrate cross-over will be mitigated. Nonetheless, pH control of the catholyte is still needed to maintain a constant value due to the imbalance of protons consumption and replenishment. Inspired by electrochemical CO<sub>2</sub> reduction, a bicarbonate solution could be used as CO<sub>2</sub> source.<sup>97–99</sup> The cathode must then be in contact with an acidic ion exchange membrane (either CEM or CEM-side of a BPM) to locally shift the chemical equilibrium from bicarbonate and dissolved CO<sub>2</sub>, which can then be reduced. As suggested in the literature, BPMs are the choice to reduce CO<sub>2</sub> loss.<sup>100,101</sup> Electrochemical urea synthesis with bicarbonate can then be operated in zero-gap assembly (Figure 6D). This approach circumvents the implementation of GDEs, which are prone to salt precipitation and flooding.<sup>102</sup> Zero-gap assemblies are additionally favorable for maximized energy efficiency, as they eradicate ohmic loss from electrolytes.<sup>95</sup> In terms of urea synthesis, it is important to couple the above-discussed steps with optimization steps that aim at the coupling of carbon and nitrogen species. Currently, no clear trends can be seen in the parameter optimization of catalyst loading, binder recipe, or excess of CO<sub>2</sub> for urea synthesis. Nevertheless, the catalyst choice is important to enable an efficient C–N coupling. Therefore, the use of bimetallic catalysts could be beneficial, as shown by Luo et al.<sup>35</sup> Tuning the ratio of metals or the size of metallic regimes could be parameters to adjust the efficiency of C–N coupling. Likewise, adjustments in catalyst loading and ionomer-to-binder ratio might be crucial steps to balance the reduction



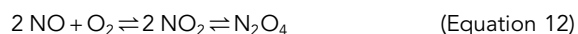
**Figure 5. Engineering approaches for improved performance**

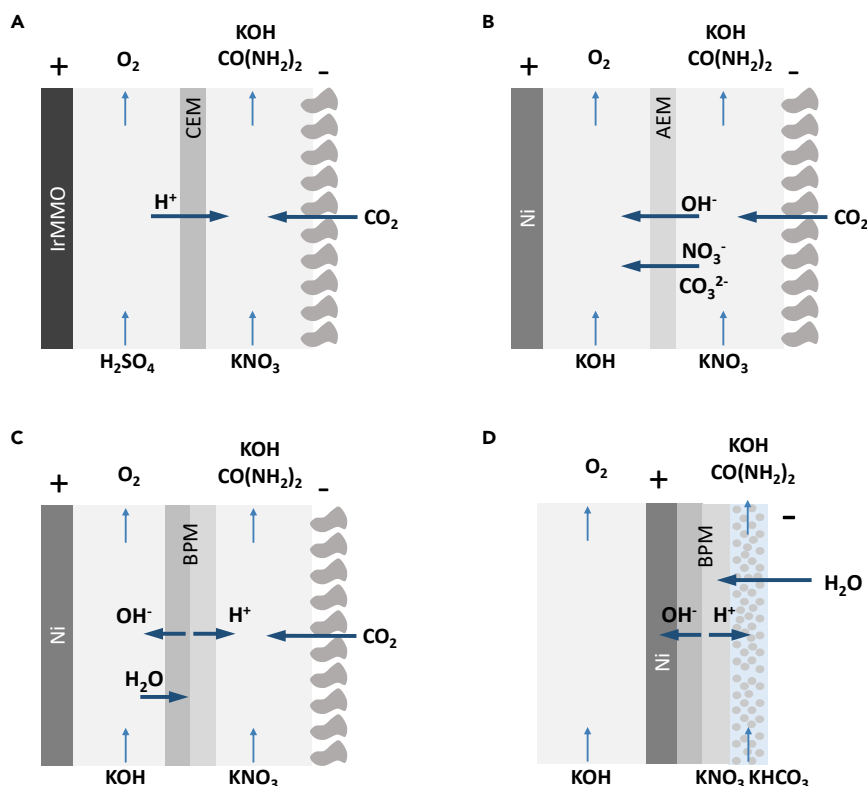
Schematic depiction of relevant engineering aspects in electrochemical urea synthesis.

and protonation of substrates and the coupling of the intermediates. The combination of zero-gap assembly and bicarbonate reduction shows promise in enhancing the energy efficiency and stability of electrochemical urea synthesis. As stated, mass transfer limitations in the liquid phase can be a challenge, especially for low substrate concentrations. Careful engineering by tuning fluid flow velocity and implementing static mixers in the electrolyte channel are tools to overcome low currents. 3D structured and high-surface areas additionally provide means to counteract diffusion limitations. Metal foams are frequently employed and have been proven to be effective. Once stable operating conditions are found, the OER anode reaction may be substituted by another value-added reaction to maximize electron economy in a paired synthesis.

### Holistic process evaluation

To gauge whether electrochemical urea synthesis can be relevant outside of academic research, even considering all recommendations from [engineering and cell design](#), the integration into current process chains, up- and downstream processes, and economical aspects need to be considered. These challenges are rarely addressed by current publications in this field. However, without rigorous studies but by considering industrial nitrogen chemistry and basic thermodynamics, electrochemical urea synthesis currently seems to have only limited use cases. Nitrate is one of the most frequently used substrates. Today, nitrates are industrially produced from nitric acid ( $\text{HNO}_3$ ) in the Ostwald process. The Ostwald process consists of a three-step synthesis, starting with the catalytic combustion of ammonia ([Equations 11 and 12](#)) and subsequent absorption of  $\text{NO}_2$  into water ([Equation 13](#)), while the  $\text{NO}$  is recycled and the acid is concentrated by distillation.<sup>103</sup>

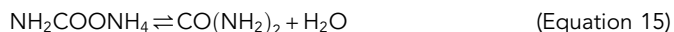
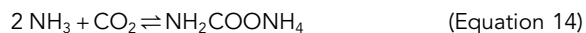




**Figure 6. Reactor designs**

Scheme of different possible reactor designs using (A) CEM, (B) AEM, (C) BPM, and (D) zero-gap assembly.

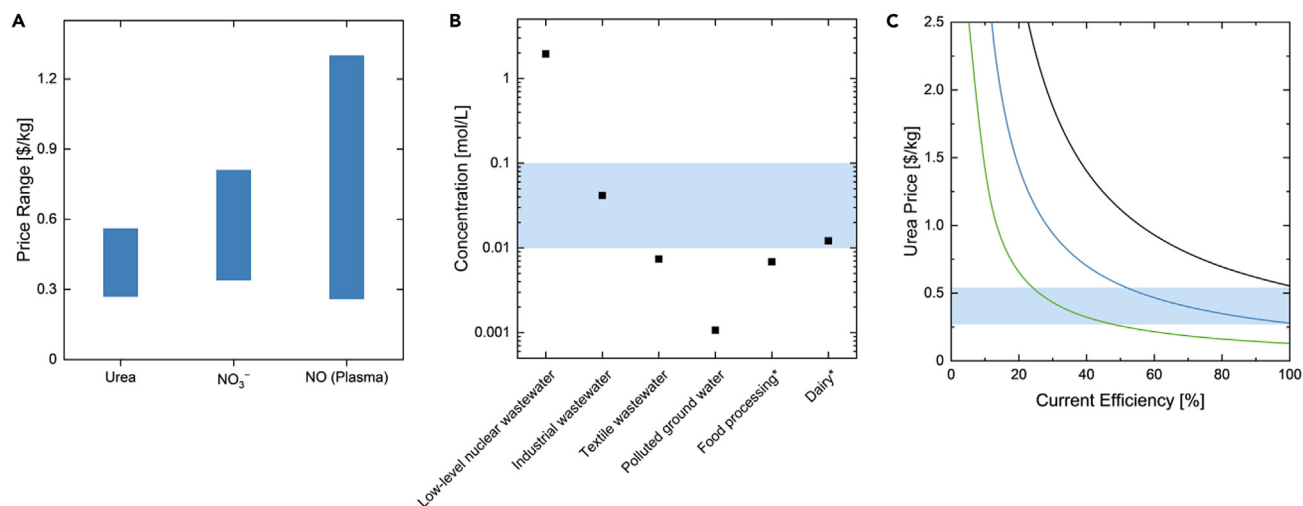
In conventional urea synthesis, ammonia and  $\text{CO}_2$  react to ammonium carbamate (Equation 14), which decomposes at high temperatures into urea and water (Equation 15).<sup>103</sup> In both cases, the synthesis uses ammonia as a reagent.



Accordingly, as seen in Figure 7, the price for both is in a similar range of about 0.27–0.56 \$  $\text{kg}^{-1}$  for urea<sup>104–107</sup> and 0.34–0.81 \$  $\text{kg}^{-1}$  for nitrates.<sup>104–107</sup> Therefore, there is no financial incentive to convert nitrates into urea, especially since both are mainly used as fertilizers.<sup>103</sup>

Nitrites are not traded on a similar scale as nitrates. Hence, industrial prices are not easily accessible. Most nitrites are less stable than nitrate and are produced either from nitrate or by absorption of NO in hydroxide solutions.<sup>108</sup> As mentioned before, nitric oxide is currently produced with ammonia as a reagent. Hence, it is very unlikely that the economic prospects of NO or  $\text{NO}_2^-$  are any more promising.

There are alternative ways to obtain  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , or NO that one could consider for electrochemical urea synthesis. The most prominent ones are NO from plasma reaction or flue gas and  $\text{NO}_2^-$  or  $\text{NO}_3^-$  from wastewater. The first upstream process could provide nitrogen oxide for a price of about 0.77 \$  $\text{kg}^{-1}$  (assuming an electricity price of 0.03 \$  $\text{kW}^{-1} \text{h}^{-1}$  and a specific energy of 2.8  $\text{MJ mol}^{-1}$ )<sup>49,109</sup> (Equation S4). Additionally, NO from a plasma reactor can also be absorbed into liquid solution



**Figure 7. Market price comparison, substrate availability, and product price range**

(A) Current prices of urea, and nitrate.<sup>104–107</sup> The price range of nitric oxide from the plasma pathway is estimated for a range of 0.02–0.05 \$ kW<sup>-1</sup> h<sup>-1</sup>. (B) Nitrate concentrations in different wastewaters. For nitrogen sources labeled with a star (\*) the information for the total nitrogen content was converted assuming 100% nitrate. The blue area labels nitrate concentrations dominantly applied in the literature. (C) Urea prices dependent on the CE for a current density of 100 mA cm<sup>-2</sup>. The blue box represents the current urea price range. The curves correspond to different cell voltages (black: 3.0 V, blue: 1.5 V, green: 0.6 V).

(e.g., KOH) to generate NO<sub>2</sub><sup>-</sup> and subsequently NO<sub>3</sub><sup>-</sup>. A proof-of-concept coupling with electrolysis to NH<sub>3</sub> has already been demonstrated in literature.<sup>110,111</sup> The short start-up and shutdown time of plasma reactors would be advantageous for coupling electrochemical urea synthesis with renewable energy, which could be suitable for decentralized production. Advancement from fundamental research to application accompanied by improvements in energy efficiency could enable the plasma pathway as a suitable precursor for electrochemical urea synthesis.<sup>49</sup>

Alternatively, the use of an urea electrolyzer for downstream treatment of industrial flue gas from power plants, vehicles, and factories can be implemented. Shi et al.<sup>47</sup> showed that nitric oxide can be successfully converted into urea. Up to date, research in this field is limited and further studies are necessary to make an assessment. Due to the required shift to renewable electricity, power plants will produce fewer flue gas in the long term, lowering the potential impact of this technology. A similar concept that could be feasible is the electrochemical treatment of wastewater.<sup>112,113</sup> This application could be possible for urea synthesis, but the nitrogen content is low except for nuclear wastewater, as shown in Figure 7.<sup>114</sup> Accordingly, experimental studies should be conducted at similar concentration levels if this application is envisioned, but only very few studies utilize a concentration lower than 0.1 mol/L. Hence, there is little information regarding the conversion rate at low concentrations. It should be kept in mind that an upstream process for obtaining nitrate from wastewater would be a competing concept due to the similar price range and application of nitrate and urea. Hence, electrochemical conversion followed by a urea downstream process needs to be more economical than (non-reactive) nitrate removal.

Based on these considerations, N<sub>2</sub> as a nitrogen source would be ideal as it is readily available at low cost. However, as discussed before, N<sub>2</sub> as the nitrogen source is the most challenging electrochemical synthesis route to urea. Without a suitable upstream process or a drastic change in the industrial nitrogen landscape, it is very unlikely for electrochemical urea synthesis to be industrially relevant in the near future.

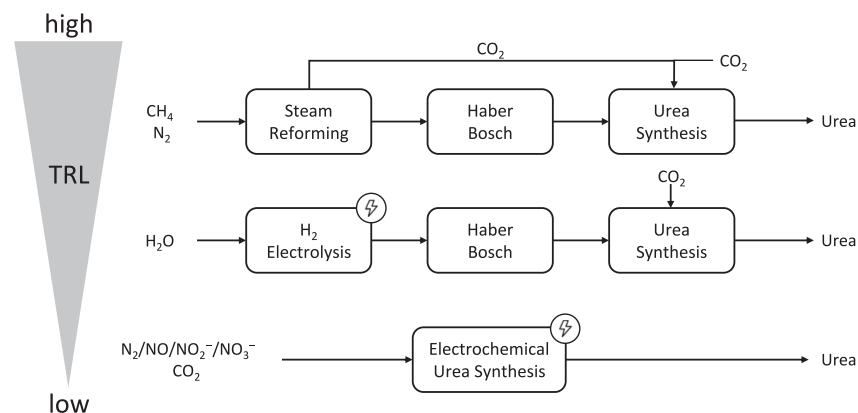


Moving from upstream to the performance of the electrolysis process itself, an estimation using Faraday's law gives insight into the operating conditions that electrochemical urea synthesis would have to reach. Depending on the cell voltage, the urea price can be calculated as a function of the CE (according to [Equations S5–S7](#)). The reduction of nitrate is used for an exemplary calculation. The theoretical cell voltage is calculated from the Gibbs free energy as a reference (see [calculations S1 and S2](#)). For nitrate reduction from  $\text{KNO}_3$ , this yields a cell voltage of approximately 0.6 V. As seen in [Figure 7](#), a cell voltage of less than 3 V at 100% CE and  $100 \text{ mA cm}^{-2}$  is required to reach current urea price levels. When assuming the minimal cell voltage of about 0.6 V, a CE of about 22% is required. As already mentioned in [electrochemical urea synthesis](#), a CE of 51% with a current density of  $115 \text{ mA cm}^{-2}$  was achieved by Shin et al.<sup>34</sup> By taking the cathodic potential, electrolyte, and membrane conductivity into account and by assuming a good catalyst for OER, an overall cell voltage of 2.2 V can be estimated (see [Equation S8](#)). This corresponds to a urea price of  $0.924 \text{ \$ kg}^{-1}$ . Chemical prices are subject to change, especially with the transition toward sustainable production, but it illustrates the importance of improving the CE and minimizing cell voltage when looking at a potential application and shows the gap to the current nitrogen value chain.

The downstream of urea from electrochemical synthesis must also be considered, as electrochemical  $\text{CO}_2$  reduction has shown its impact on the process costs of electrolysis products.<sup>80,115</sup> The thermodynamic minimum to separate urea is the difference in Gibbs free energy of solid and liquid urea (in aqueous solution). The value of  $6.86 \text{ kJ mol}^{-1}$ <sup>116</sup> for this dissolution process is small compared with the Gibbs free energy difference of the synthesis reaction itself, ranging from 490 to  $930 \text{ kJ mol}^{-1}$  depending on the nitrogen source. However, depending on the impurities and the separation method, the actual energy requirement is orders of magnitude higher.<sup>80</sup> Therefore, it is meaningful to develop and evaluate separation concepts at early stages to assess the economic impact,<sup>117</sup> especially regarding the potential application for wastewater nitrate conversion. In the case of electrochemical urea synthesis, the gas and liquid phases can contain all products of  $\text{CO}_2$  reduction in addition to the side products of urea synthesis. Although urea can be supplied in liquid solution or as a solid, the conventional downstream process involves evaporation and subsequent prilling. For electrochemical urea synthesis, this requires a separation of ions from the liquid phase. A suitable process for this separation task could be electrodialysis.<sup>118</sup> At last, when discussing the electrification of the chemical industry, a very prominent process alternative is the generation of green hydrogen from water electrolysis for the Haber-Bosch process as seen in [Figure 8](#).

This will allow the current high-capacity plants ( $>2,000 \text{ Mt d}^{-1}$ <sup>1103</sup>) to be kept without changing the current value chain, except for the  $\text{CO}_2$  source. These plants have been subject to optimization for several decades, which results in a specific energy of 24.8 GJ to produce urea from coal or natural gas via the ammonia route.<sup>119</sup> For electrochemical urea synthesis a CE of 100% with a cell voltage of about 1 V is required to achieve a similar specific energy input.

All these factors combined, which go beyond catalyst research and engineering aspects, result in a high technological and economical entry barrier as an alternative to the current large-scale value chain. However, electrochemical urea synthesis still holds promise for meaningful application if the process is tailored toward the advantages of an electrochemical process. Therefore, research efforts need to put a greater emphasis on scenarios like small-scale decentralized production, utilization of low-concentration waste streams (e.g., wastewater treatment or flue gas



**Figure 8. Comparison of different process routes**

Comparison of different process routes to urea with a rough classification regarding sustainability and technology readiness level.

treatment), and bicarbonate reduction. Especially the latter could be a suitable follow-up process for direct air capture. Further details and promising results on urea from waste nitrogen are given in a life-cycle assessments by Luo et al. With low-cost renewable electricity, electrosynthesis of urea would release less CO<sub>2</sub> equivalents per kg of urea than conventional production technologies.<sup>35</sup>

## CONCLUSIONS AND OUTLOOK

Electrochemical urea synthesis as a process that utilizes nitrogen and CO<sub>2</sub> to produce urea is an attractive concept. Skipping several energy-intensive production steps would be a major step toward sustainable fertilizer production. However, current research efforts do not appropriately address the current challenges within this field. On a laboratory scale, catalyst screenings must be operated at relevant conditions. Moreover, the analytical methods still need refinement to reliably detect urea without any susceptibility to false positives. Here, in particular, lessons should be learned from electrochemical ammonia synthesis. The majority of experimental work is conducted in simple H-cell setups with small electrode areas. As seen in other research fields, such as CO<sub>2</sub> reduction, the electrode, reactor, and cell design can have a major impact on performance. These engineering aspects are currently not focused on and leave room for improvement. Moreover, they are important for the prospect of scaling up the process and reaching commercial applications. From today's point of view, there are process routes for electrochemical urea synthesis that are more promising than others. The use of N<sub>2</sub> would be ideal, but today's catalysts lack sufficient activity. On the other hand, without substantial changes in the current nitrogen value chain, there are very few economically feasible sources for NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>. The use of electrochemical urea synthesis as a downstream process for wastewater or flue gas treatment possibly provides low-cost access to reactive nitrogen sources. With the current development of plasma reactions, NO could also become a key nitrogen component for electrochemical fertilizer production. These potential nitrogen sources should be kept in mind, and research efforts should be directed accordingly. Lastly, downstream processing, although rarely considered, needs to receive more attention. Hence, an economic assessment of electrochemical urea synthesis is presently not possible, and target performance parameters cannot yet be defined. Taking a broader perspective on the necessary research steps toward an application could help to address the question if, how, and when electrochemical urea will be part of a sustainable nitrogen economy.

## SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.joule.2024.04.004>.

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## AUTHOR CONTRIBUTIONS

Y.K., Y.S.T., and W.P. contributed equally to this work. Conceptualization: Y.K., Y.S.T., W.P., R.K., and M.W.; writing – original draft: Y.K., Y.S.T., and W.P.; writing – review and editing: U.S., R.-A.E., R.K., and M.W.; supervision: R.-A.E., U.S., R.K., and M.W.; funding acquisition: R.-A.E., U.S., R.K., and M.W.

## DECLARATION OF INTERESTS

The authors declare no competing interests.

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