An ionic liquid-bridge strategy for selective and efficient urea electrosynthesis from CO_2 and nitrate

Yilin Wang,[1] Tao Shao,[1] Zhenwei Li,[1] Alex W. Robertson,[3] and Zhenyu Sun[1,2,*]

[1]State Key Laboratory of Organic-Inorganic Composites, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China
[2]School of Chemistry and Chemical Engineering/State Key Laboratory Incubation Base for Green Processing of Chemical Engineering, Shihezi University, Shihezi 832003, China
[3]Department of Physics, University of Warwick, Coventry CV4 7AL, UK
*Correspondence: sunzy@mail.buct.edu.cn

Received: November 7, 2025; Accepted: January 5, 2026; Published Online: January 9, 2026; https://doi.org/10.59717/j.xinn-mater.2026.100188

Citation: Wang Y., Shao T., Li Z., et al. (2026). An ionic liquid-bridge strategy for selective and efficient urea electrosynthesis from CO_2 and nitrate. *The Innovation Materials* **4**:100188.

Urea ($CO(NH_2)_2$) is a vital industrial product with an irreplaceable role in the production of agricultural fertilizers, pharmaceuticals, and basic chemicals. Conventionally, urea is synthesized under intense conditions via a two-step process: the Haber–Bosch process (N_2 and H_2 as feedstock to produce ammonia, 400–500°C, 10–20 MPa), followed by the Bosch–Meiser process (NH_3 and CO_2 as feedstock, 180–200°C, 15–25 MPa). These both consume a vast quantity of fossil fuels, accounting for more than 2% of global energy consumption, while emitting significant amounts of greenhouse gases (GHG). The size of this energy and GHG footprint is unsustainable. Research is now focused on developing low-emission, energy efficient, and sustainable routes for urea synthesis. A promising route is the direct synthesis of urea via renewably-driven electrochemistry, utilizing CO_2 and nitrogen-containing small molecules as feedstocks and bypassing the intermediate step of NH_3 formation.[1] This pathway not only avoids GHG emissions but actively converts the CO_2 into high-value-added chemicals, thus neatly addressing both energy and environmental challenges.

The electrochemical synthesis of urea was first achieved by Furuya and coworkers in 1995 through the co-reduction of CO_2 and nitrate/nitrite ions (NO_3^-/NO_2^-) on a copper-loaded gas diffusion electrode.[2] The C–N coupling is considered to be the critical step in the process. The adsorption and conversion of electrophilic *CO/*COOH (* denotes the adsorption site) species from CO_2 reduction and nucleophilic *NO/*NH_2 species from nitrogen precursor reduction control the reaction kinetics and selectivity. A direct coupling of *NO_2 and CO_2 followed by *CO_2NO_2 → *CO_2NH_2 → *$COOHNH_2$ → *$CONH_2$ → *$CONO_2NH_2$ → *$CO(NH_2)_2$ has also been reported to favor the formation of the desired C–N bond.[3]

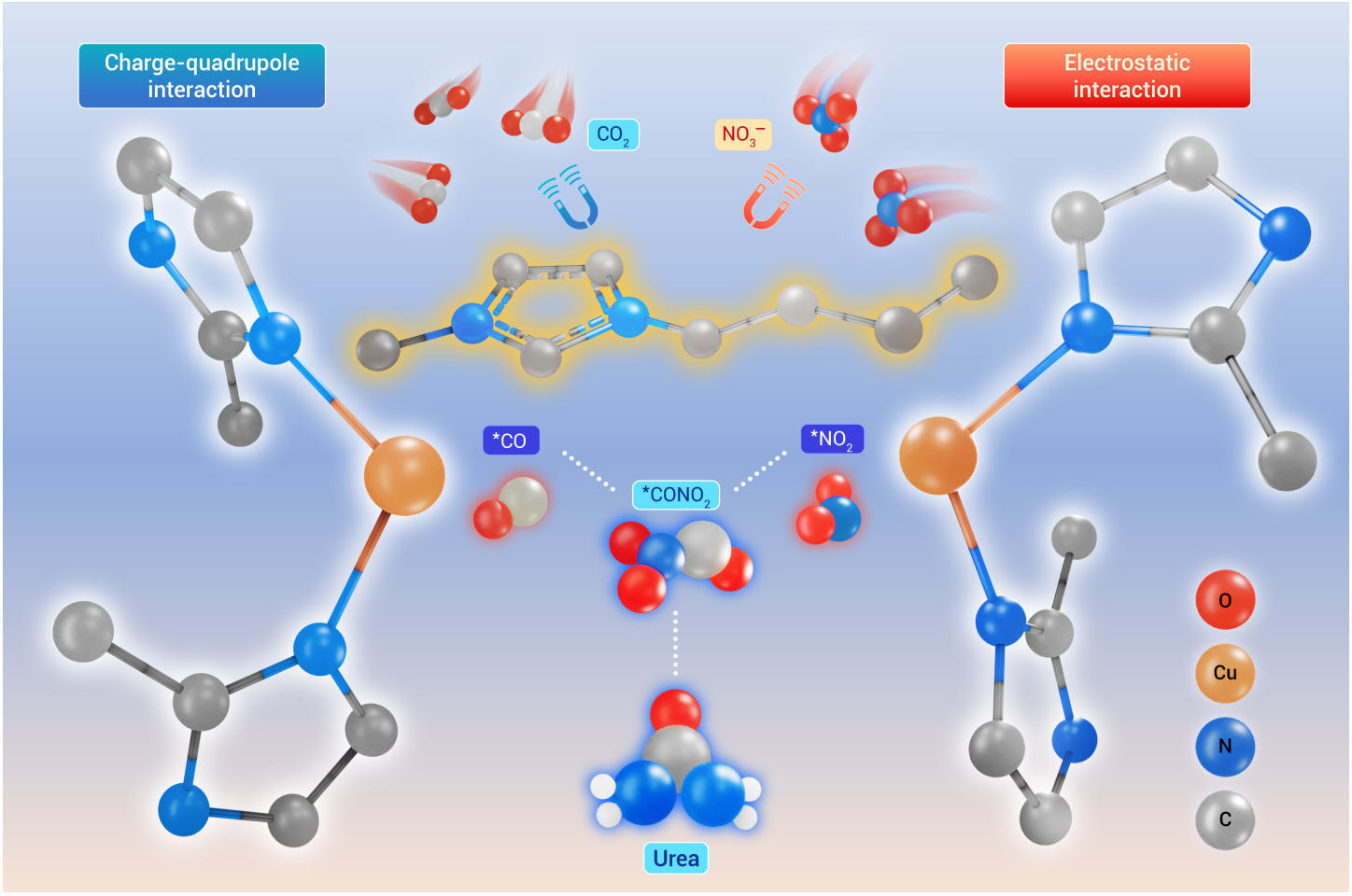

Figure 1. Schematic of interactions between reactants and IL@Cu-ZIF-8 for urea electrosynthesis.

Construction of a multi-active-center electrocatalyst, that can co-activate both CO_2 and NO_3^-/NO_2^-/NO to faciliate selective C–N coupling, would greatly assist in efficient urea synthesis. To this end, the kinetics of CO_2 reduction and NO_3^-/NO_2^-/NO reduction should be matched. Given the carbon-to-nitrogen stoichiometry of $CO(NH_2)_2$, a maximized urea selectivity tends to occur when the generation rate of C-based intermediates is tuned to approach half

of the formation rate of N-based intermediates. Equally importantly, the neighbouring active sites should act to effectively stabilize the carbon and nitrogen intermediates and facilitate C–N coupling by reducing its energy barrier. The formation of by-products from the competing reduction reactions (e.g., CH_4, CO, HCOOH, and CH_3OH from CO_2 reduction; NO_2^-, NH_2OH, NH_3, and N_2 from NO_3^- reduction; H_2 from proton/water reduction) also needs to be suppressed.

Compared to N_2, with its high triple bond energy of 941 kJ mol^{-1}, NO_3^- possesses a much lower bond energy (204 kJ mol^{-1}). This makes it easier to reduce to the key intermediate *NO, thus facilitating subsequent C–N coupling reactions to yield urea. Relative to NO and NO_2^- that are highly toxic and unstable, NO_3^- exhibits superior chemical stability and markedly lower toxicity. Therefore, urea electrosynthesis utilizing CO_2 and NO_3^- has recently triggered much interest. Among various metal catalysts, Cu stands out for its unique capability to bind *NO and *CO while exhibiting low affinity for *H species. Nevertheless, pure Cu catalysts display poor urea faradaic efficiency (FE) and also require application of strongly negative potentials; usually from –0.6 to –1.5 V versus (vs.) reversible hydrogen electrode (RHE). To address these limitations, several strategies have been adopted, including adjusting morphological structure, altering composition, regulating chemical state, and optimizing local microenvironments.[4] Despite these research efforts, Cu-based catalysts still suffer from poor long-term durability and slow urea yield rate.

Recently, Han et al. presented an innovative "ionic liquid (IL) bridge" strategy to enhance urea electrosynthesis.[5] The as-prepared catalyst (IL@Cu-ZIF-8) incorporated 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (BmimNTf$_2$) and Cu(II) into the zeolitic imidazolate framework-8 (Figure 1). It delivered a urea generation rate as high as 140 μmol h^{-1} cm^{-2} (42,000 mg h^{-1} g_{cat}^{-1}) and a urea FE of up to 55.3% at an applied potential of –0.5 V (vs. RHE). 94% of the FE was retained even after 100 hours of continuous electrolysis. In particular, 0.53 g of pure urea was attained after 5 hours of electrolysis on a 25-cm^2 electrode with the cathodic current above 1.8 A and yield rate exceeding 0.1 g h^{-1}, which underscores its potential for practical application. It was found that urea production was siginificantly affected by the cation structure rather than the anion, with limidazolium cations with a C(2)–H atom being more effective in boosting urea yield.

Electrochemical impedance spectroscopy and kinetic isotope effect measurements suggested a higher *H coverage on the surface of IL@Cu-ZIF-8 compared to Cu-ZIF-8. Molecular dynamics simulations, validated by attenuated total reflection surface enhanced infrared absorption spectroscopy, confirmed strong and specific interactions between the $Bmim^+$ and reactants and intermediates. A possible reaction pathway was proposed based on density function theory calculations: $*CO + *NO_2 \rightarrow *CONO_2 \rightarrow *CONOOH \rightarrow *CONO \rightarrow *CONOH_2 \rightarrow *CON \rightarrow *CONH \rightarrow *CONH_2 \rightarrow *CO(NH_2)_2 \rightarrow$ urea. The calculated potential determining steps were $*CO_2 \rightarrow *COOH$ for CO_2 reduction reaction and $*NO_3 \rightarrow *NO_3H$ for NO_3^- reduction reaction. Mechanism studies revealed the IL on the catalyst acted as a dynamic molecular bridge, efficiently connecting active copper centers and reactant molecules via charge-quadrupole, electrostatic, and hydrogen bonding interactions. This configuration optimally confines and concentrates the reactants near the active sites, thereby enhancing the generation of key *CO and *NO intermediates and bringing them into closer proximity. Concurrently, the IL effectively inhibited the hydrogen evolution reaction, as evidenced by a lower kinetic isotope effect and a higher Gibbs free energy for hydrogen adsorption.

By lowering the energy barriers for the critical steps in the formation of key intermediates, this IL-based strategy significantly increased the efficiency of the electrocatalytic reactions required for urea production. In conclusion, this work provides an effective strategy for designing advanced electrocatalysts to expedite complex reactions involving multi-step and multi-proton/electron transfers. This IL-bridge protocol can be applied to other electrocatalytic reactions, paving the way for more sustainable chemical synthesis and energy conversion opportunities. However, whether the IL and Cu(II) in the catalyst will retain stability after longer electrolysis, such as over 100 h, or at higher current densities, exceeding the 110.5 mA cm^{-2} reported, needs to be further explored.

The electrocatalytic coupling of C–N bonds for urea synthesis holds great promise for broadening application prospects. Using NO_3^- as a reactant offers an ingenious way to integrate two energy-intensive processes—urea synthesis and wastewater denitrification—into a sustainable pathway. However, most electrocatalysts were tested under ideal lab conditions with high-concentration nitrate and high-purity CO_2. In reality, nitrogen-containing wastewater has much lower nitrate levels (e.g., ~200 ppm) and a more complex composition. To reduce reliance on purified reagents and accelerate commercial production, it is crucial to directly use actual wastewater or simulate realistic wastewater environments and industrial waste gases (such as CO_2 from coal-fired power plants). In addition, to meet the demands of industrial-scale application, the design and development of electrocatalysts that can sustain extended cycles (thousands to tens of thousands of hours) at high current densities (exceeding 200 mA cm^{-2}) will be crucial. Integrating alternative sources like N_2, CO, and formic acid could lead to new reaction systems, expand candidate feedstock materials, and enhance process sustainability. Combining additional energy sources (e.g., pulsed electrolysis) into the urea production process could improve energy efficiency. The yields of urea could also be further enhanced by integrating electrocatalytic oxidative coupling of CO and NH_3 at the anode.

REFERENCES

1. Wang J., Yao Z., Hao L., et al. (2022). Electrocatalytic coupling of CO_2 and N_2 for urea synthesis. *Curr. Opin. Green Sustainable Chem.* **37**:100648. DOI:10.1016/j.cogsc.2022.100648
2. Shibata M., Yoshida K. and Furuya N. (1995). Electrochemical synthesis of urea on reduction of carbon dioxide with nitrate and nitrite ions using Cu-loaded gas-diffusion electrode. *Electroanal. Chem.* **387**:143–145. DOI:10.1016/0022-0728(95)03992-P
3. Hu B., Lu R., Wang W., et al. (2025). Directing the C–N coupling pathway enables efficient urea electrosynthesis. *J. Am. Chem. Soc.* **147**:21764–21777. DOI:10.1021/jacs.5c04483
4. Xu M., Zhang H., Lv X., et al. (2025). Selective urea electrosynthesis from CO_2 and nitrate on spin-polarized atomically ordered PdCuCo. *Adv. Mater.* **37**:2505286. DOI:10.1002/adma.202505286
5. Yin Y., Ling Z., Liu S., et al. (2025). Efficient urea electrosynthesis from CO_2 and nitrate mediated by an ionic liquid bridge. *Nat. Sustain.* Early View DOI:10.1038/s41893-025-01703-9

FUNDING AND ACKNOWLEDGMENTS

The authors acknowledge the financial support from the Joint Funds of the National Natural Science Foundation of China (U24B20201) and National Natural Science Foundation of China (22372007, 21972010). The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

AUTHOR CONTRIBUTIONS

Y.W., and T.S. co-wrote the draft. T.S. helped draw the figure. Z.S. supervised and revised the manuscript. Z.L. and A.R. helped polish the language. All authors contributed to the article and approved the submitted version.

DECLARATION OF INTERESTS

The authors declare no competing interests.

LEAD CONTACT WEBSITE

Zhenyu Sun https://www.x-mol.com/groups/ZhenyuSun