Carbon Future

# Redefining electrochemical C–N coupling via electrolyte engineering

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Electrochemical synthesis offers a promising route powered by renewable electricity toward sustainable chemical manufacturing. Among the various electrosynthetic transformations reported thus far, C–N bond formation is particularly attractive because it enables the production of value-added chemicals like urea, amides, amines, and amino acids under mild conditions[1–4]. Compared with conventional thermochemical synthetic techniques, electrochemical C–N coupling offers several advantages, including operation under ambient conditions, modular reactor design, and compatibility with distributed energy systems. However, achieving selective and efficient C–N bond formation by electrosynthesis remains challenging because the reaction involves multiple competing pathways and highly reactive intermediates that are difficult to coordinate at the catalytic interface.

To date, electrochemical C–N coupling has been studied largely using a catalyst-centered framework, with major research efforts devoted to defect engineering, facet modulation, heterostructure construction, and active-site regulation[5–7]. Although these strategies have substantially improved catalytic performance, the catalyst surface represents only one component of the dynamic electrochemical interface. Catalyst surfaces fundamentally determine adsorption configurations, electronic structures, and accessible reaction pathways, while the surrounding electrolyte regulates the local environment in which these surface reactions occur. Electrochemical C–N coupling should therefore be understood as an interface-driven process governed by the cooperative effects of the catalyst and electrolyte. At such interfaces, reactant transport, solvation organization, proton availability, interfacial electric fields, and intermediate stabilization are directly controlled by the local electrolyte structure. Treating the electrolyte merely as an inert ion-conducting medium overlooks the significant roles of electrolytes in governing interfacial reaction dynamics.

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Herein we emphasize that electrolytes should be reconsidered as active interfacial architects rather than as passive spectators. Electrolytes fundamentally regulate the spatiotemporal probability of C–N coupling by reconstructing the local microenvironment. Recent studies suggest that electrolyte effects can be organized into four interconnected interfacial functions: reactant colocalization, proton choreography, intermediate traffic control, and direct participation in catalytic processes (**Fig. 1**). These functions are not mutually exclusive, as they can arise from shared physicochemical factors such as solvation, ion pairing, hydrogen-bond dynamics, and interfacial electric fields. Rather, they highlight complementary aspects of interfacial regulation: reactant colocalization emphasizes the spatial organization and effective proximity of coupling partners; proton choreography concerns the delivery and transfer of protons through the interfacial hydrogen-bond network; intermediate traffic control describes the mobility, residence, and assembly of reactive species within the interface; and direct participation refers to electrolytes that become active components of charge transfer or catalytic cycles.

Electrochemical C–N coupling is fundamentally a reactant co-reduction challenge that occurs within a confined interfacial environment. Carbon-containing and nitrogen-containing species exhibit distinct solvation, diffusion, and adsorption behaviors, and achieving synchronized interfacial availability is intrinsically difficult. Consequently, mismatched local concentrations of carbon and nitrogen frequently become kinetic bottlenecks. When nitrogen-containing intermediates accumulate while carbon species are insufficient, productive coupling becomes unlikely, and side reactions like hydrogen evolution dominate. Electrolyte engineering provides a unique opportunity to overcome this mismatch by reconstructing the local distributions of reactants near electrode surfaces. The use of mixed solvents, hydrophobic additives, and ionic-liquid-containing electrolytes can generate heterogeneous interfacial microenvironments that selectively enrich carbon reactants such as $CO_2$, simultaneously modulating the accessibility of nitrogen-containing species. Such local-concentration engineering is critical for tandem electrosynthetic pathways, in which carbon-derived and nitrogen-derived intermediates must coexist within narrow spatial and temporal windows to enable efficient coupling. Beyond simply increasing reactant solubility, electrolytes can also reorganize the interfacial structure to shorten the effective distance between reactive intermediates. For example,

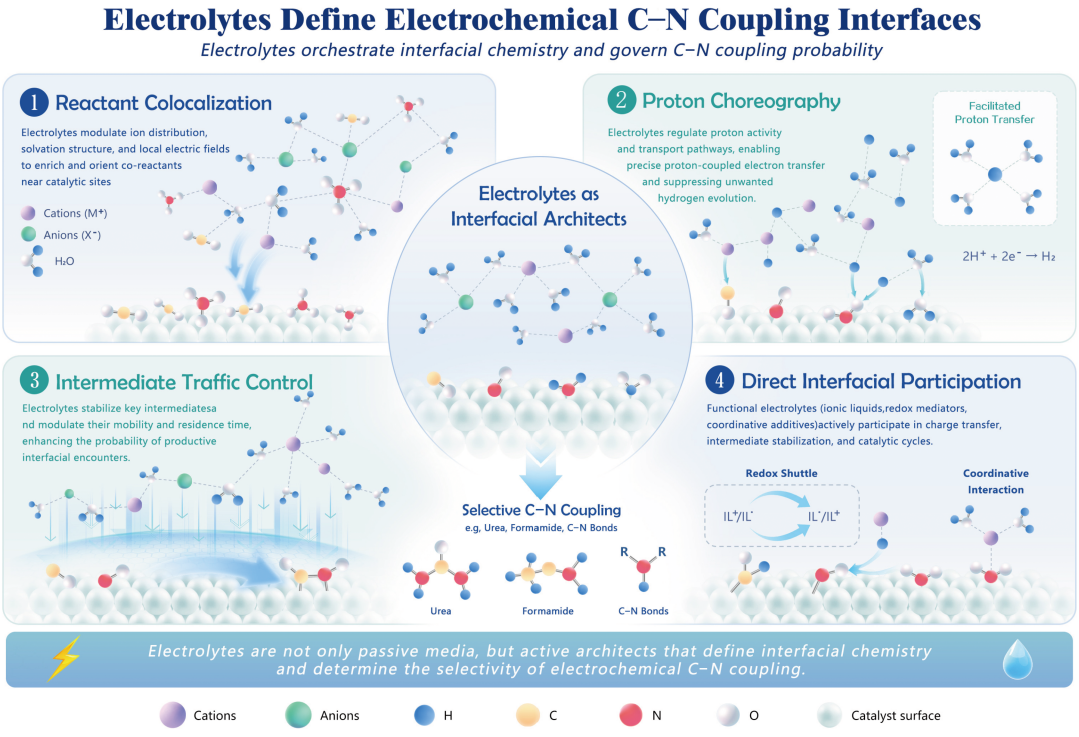


**Fig. 1. Electrolytes define electrochemical C–N coupling interfaces.**

ionic liquids with strong $CO_2$ affinities can promote interfacial $CO_2$ accumulation and enhance the local probability of encounters between carbon-containing and nitrogen-containing species[8–10]. These observations suggest that electrolytes are not merely passive media for reactant transport but are active regulators of interfacial reactant colocalization and coupling probability.

Selective electrochemical C–N coupling is fundamentally a proton-coupled electron-transfer challenge. Productive C–N bond formation requires precisely synchronized proton and electron delivery to highly reactive intermediates, whereas uncontrolled proton transfer frequently promotes hydrogen evolution or undesired hydrogenation pathways that suppress coupling selectivity. Electrolytes affect proton accessibility at electrochemical interfaces via hydrogen-bond networks, water activity, and proton-transport pathways. Electrolytes with strong hydrogen-bond-donating ability can stabilize reactive intermediates and alter reaction selectivity by suppressing undesired protonation pathways[11–13]. Similarly, both low-water-activity electrolytes and confined interfacial water structures can perturb proton transfer kinetics and reshape hydrogenation sequences. Importantly, the hydrogen-bond networks within the electrolytes may, in principle, function as dynamic proton shuttles that facilitate directional proton migration through Grotthuss-type transport[10]. Such "proton choreography" can influence the synchronization between electron transfer and intermediate hydrogenation, ultimately determining whether the reactive species undergoes productive C–N coupling or independent reduction pathways. Electrolytes thus govern the local proton environment that determines the course of interfacial proton-coupled electron-transfer dynamics.

Electrochemical C–N coupling is an intrinsically low-probability event that occurs between transient surface intermediates. Species such as *CO, *NO, and $*NH_2$ typically exist only at low surface coverages and brief lifetimes under normal operating conditions, making productive interfacial encounters inherently difficult. Extending the intermediate lifetime or increasing the local intermediate concentration can markedly enhance coupling selectivity. Electrolyte cations can substantially influence the interfacial electric fields and solvation structures, thereby altering the adsorption energetics and intermediate stability[14]. Alkali metal cations with different hydrated radii and polarization abilities may reshape the outer Helmholtz plane and stabilize specific adsorbed intermediates through electrostatic interactions. Such a cation-mediated interfacial assembly can shift the reaction pathways and alter the C–N coupling selectivity[15]. In addition, ion pairing and solvation-shell reconstruction may regulate the intermediate mobility and residence time near the catalytic sites. Electrolytes can be viewed as "intermediate traffic controllers" that govern the spatiotemporal dynamics of reactive species at electrochemical interfaces[16]. This article reframes the traditional understanding of electrolytes from simple charge carriers to active regulators of intermediate lifetimes and coupling probabilities.

In emerging electrosynthetic systems, the boundary between catalyst and electrolyte is becoming progressively blurred[17–19]. Functional electrolytes, including ionic liquids, redox mediators, and coordinative additives, may act as dynamic components of catalytic interfaces—participating in intermediate stabilization, charge transfer, and interfacial assembly—rather than serving merely as reaction media. For example, redox-active ionic-liquid systems have been reported to operate as dual-electron shuttles that facilitate intermediate generation and coupling at both electrodes, thereby fundamentally reshaping electrosynthetic pathways[20]. Rather than simply modifying the interfacial environment, these systems enable electrolytes to participate directly in catalytic cycles. This emerging view of electrolytes as active catalytic components expands conventional catalyst optimization toward electrolyte-integrated catalysis, in which catalyst and electrolyte properties are considered cooperatively as integral components of the catalytic interface. As increasingly complex electrosynthetic reactions

emerge, the design of catalytically non-innocent electrolytes becomes imperative to provide new opportunities for controlling reaction selectivity beyond the limitations of catalyst-centered approaches.

Despite the growing recognition of electrolyte effects in C–N electrosynthesis, the field still lacks a unified molecular framework to describe how electrolytes govern the interfacial reaction dynamics. Unlike catalyst surfaces, whose activity can often be determined by relatively well-defined descriptors, electrolyte effects remain difficult to predict because they emerge from collective phenomena, involving solvation, ion pairing, hydrogen-bond networks, proton transport, and interfacial electric fields. Taken together, the studies discussed above reveal emerging relationships between electrolyte properties and C–N coupling performance. Enhanced local availability of coupling partners, regulated proton-transfer environments, and altered ion–intermediate interactions can respectively influence productive encounters, competing protonation pathways, and intermediate stabilization, although these effects are strongly interconnected. While universal quantitative correlations remain unavailable, these trends provide a qualitative basis for connecting electrolyte properties with C–N coupling selectivity. For example, strong ion pairing may stabilize reactive intermediates, but can also suppress mass transport and reaction kinetics. Identifying and validating these descriptors will require integrating operando spectroscopy with molecular and ab initio molecular dynamics simulations to resolve the dynamic electrode–electrolyte interface under operating conditions.

Future electrosynthetic systems will likely rely on interface co-engineering strategies, in which catalysts and electrolytes will be designed cooperatively rather than independently. Practical electrolyte design must also balance interfacial performance with stability, cost, recyclability, membrane compatibility, and operation at technologically relevant current densities. Addressing these considerations will be essential for translating electrolyte engineering toward scalable C–N electrosynthesis. Beyond these practical considerations, future progress will require the development of quantitative descriptors and predictive models to establish rational relationships between electrolyte structures and catalytic outcomes. Integrating computational approaches, data-driven strategies, and high-throughput experiments may provide efficient platforms for exploring the multidimensional electrolyte design space and accelerating the discovery of optimized catalyst–electrolyte systems. Electrolytes may eventually evolve from passive reaction media into adaptive interfacial networks capable of dynamically responding to electric fields, reactant fluxes, and intermediate accumulations. Such programmable electrolyte interfaces could provide new opportunities for controlling complex multistep electrosynthetic reactions. These interfacial functions should be viewed as interconnected dimensions of electrolyte-mediated interfacial regulation. The same electrolyte properties, including solvation structure, ion pairing, hydrogen-bond dynamics, and interfacial electric fields, can simultaneously influence multiple aspects of the interface.

## References

[1] Jouny, M.; Lv, J. J.; Cheng, T.; Ko, B. H.; Zhu, J. J.; Goddard, W. A.; Jiao, F. Formation of carbon-nitrogen bonds in carbon monoxide electrolysis. *Nat. Chem.* **2019**, *11*, 846–851.

[2] Huang, D. S.; Qiu, X. F.; Huang, J. R.; Mao, M.; Liu, L. M.; Han, Y.; Zhao, Z. H.; Liao, P. Q.; Chen, X. M. Electrosynthesis of urea by using $Fe_2O_3$ nanoparticles encapsulated in a conductive metal-organic framework. *Nat. Synth.* **2024**, *3*, 1404–1413.

[3] Wang, H. G.; Cheng, Y. Y.; Wang, Y. Y.; Duan, R.; Zhou, M.; Liu, S. Q.; Zhao, W. L.; Qin, H. S.; Yang, J. H.; Peng, Y. G. et al. Imidazolium radical-mediated electron transfer enhances electrochemical C–N coupling for glycine synthesis. *Nat. Synth.* **2026**, *5*, 74–83.

[4] Hashmi, S. M.; Wang, Y. L.; Rehman, N.; Tan, X. Y.; García-Martínez, J.; Aiman, U.; Sajid, M.; Sun, Z. Y. Towards sustainable chemistry: Advances, challenges and opportunities in organic electrosynthesis. *Chin. J. Catal.* **2026**, *82*, 1–41.

[5] Xu, G. K.; Dong, C. Y.; Cai, X. C.; Kuang, J. H.; Xue, T. W.; Guo, Y. Y.; Wu, Y. Y.; Li, R. Q.; Shao, Z. Y.; Qiao, T. X. et al. Selective glycine electrosynthesis via C–N coupling enabled by synergistic Mott-Schottky heterojunction and oxygen vacancies. *Angew. Chem., Int. Ed.* **2026**, *65*, e5717711.

[6] Fan, Y.; Yan, Y. H.; An, Q. Z.; Xia, Z. C.; Pan, Y. P.; Lu, Y. X.; Zhu, Z. H.; Wang, R. Q.; Liu, Q. H.; Zou, Y. Q. et al. Electrochemical coupling of carbon monoxide and amine on iodide coordination stabilized $Cu^{\delta+}$ site. *Nat. Commun.* **2025**, *16*, 6917.

[7] Yin, Y. Y.; Ling, Z. N.; Liu, S. Q.; Wang, Y. Y.; Zhao, W. L.; Wang, H. G.; Yang, J. H.; Feng, R. J.; Zhang, S. P.; Xing, X. Q. et al. Efficient urea electrosynthesis from $CO_2$ and nitrate mediated by an ionic liquid bridge. *Nat. Sustain.* **2026**, *9*, 108–116.

[8] Yang, J. H.; Kang, X. C.; Jiao, J. P.; Xing, X. Q.; Yin, Y. Y.; Jia, S. Q.; Chu, M. G.; Han, S. T.; Xia, W.; Wu, H. H. et al. Ternary ionic-liquid-based electrolyte enables efficient electro-reduction of $CO_2$ over bulk metal electrodes. *J. Am. Chem. Soc.* **2023**, *145*, 11512–11517.

[9] Xiao, Y.; Yang, X.; Yang, Y. B.; Sun, C.; Shen, C.; Zhang, Y.; Han, L. L. CuAg alloy catalyst for modulating the activity of C–N coupling toward acetamide and urea synthesis via explicit pH-dependent water and induced ionic liquid cations models. *ACS Catal.* **2025**, *15*, 19552–19565.

[10] Muñoz, M.; Chen, M. S.; de Araujo Lima e Souza, G.; Simunovic, T.; Khokhar, V.; Qian, P. S.; Wainright, J.; Savinell, R.; Parnell, A.; Parnell, S. et al. Structured electrolytes facilitate Grotthuss-type transport for enhanced proton-coupled electron transfer reactions. *Proc. Natl. Acad. Sci. USA* **2026**, *123*, e2530367122.

[11] Zhang, H.; Raciti, D.; Hall, A. S. Disordered interfacial $H_2O$ promotes electrochemical C–C coupling. *Nat. Chem.* **2025**, *17*, 1161–1168.

[12] Liu, Z. Z.; Liu, Y. J.; Cai, L. J.; Ma, G. T.; Li, J. W.; Ding, Y. Q.; Chen, A. B.; Wang, N. N.; Shang, J.; Low, J. et al. The salting-out effect enables highly selective electrochemical ammoxidation of aldehydes to nitriles. *J. Am. Chem. Soc.* **2026**, *148*, 16965–16975.

[13] Wang, Y.; Zhang, X. D.; Li, P. S.; Wang, C. Y.; Hou, Y. Q.; Duan, R.; Ma, J.; Zhang, G. W.; Wang, X. H.; Liu, H. Z. et al. Proton-regulated C–N coupling for efficient amino acid electrosynthesis. *J. Am. Chem. Soc.* **2025**, *147*, 47370–47380.

[14] Wu, T. W.; Zhao, C. L.; Chen, W.; Sun, X. P.; Zhang, Y. N. Atomic-level insights into the cation-mediated electrocatalytic C–N coupling mechanism over Cu model catalyst. *J. Phys. Chem. Lett.* **2026**, *17*, 2418–2425.

[15] Yuan, Y.; Kou, M. M.; Zhao, J. M.; Zhao, J. S.; Yang, X. Regioselective electrocatalytic urea synthesis via spin-polarized PdCu/$TiO_{2-x}$ with oxygen vacancy engineering. *Carbon Hydrogen* **2025**, *27*, 344–353.

[16] Tu, X. J.; Zhu, X. R.; Bo, S. W.; Zhang, X. R.; Miao, R. P.; Wen, G. B.; Chen, C.; Li, J.; Zhou, Y. Y.; Liu, Q. H. et al. A universal approach for sustainable urea synthesis via intermediate assembly at the electrode/electrolyte interface. *Angew. Chem., Int. Ed.* **2024**, *63*, e202317087.

[17] Li, S. Y.; Liu, G. S.; Liu, C. H.; Fu, Y. F.; Fu, Y. X.; Xu, Y. F.; Li, C. Y.; Zhang, X. Q.; Xu, B. J.; Li, W. L. et al. Carbon defects enhanced TEMPO redox cycles for high-efficiency urotropine electrosynthesis. *Nat. Commun.* **2025**, *16*, 10578.

[18] He, Y. Q.; Mo, S. H.; Zeng, X.; Zhang, Y. H.; Nga, T. T. T.; Dong, C. L.; Yang, Y. L.; Lu, Z. R.; Zhang, Y. J.; Xia, Z. C. et al. Paired

electrolysis enables selective C–N coupling for the synthesis of nitrogenous aromatics. *Nat. Synth*., in press, DOI: 10.1038/s44160-026-01057-w.

[19] Wu, L. M.; Wang, R. H.; Li, Y. B.; He, L.; Sun, X. F.; Han, B. X. Electrolyte-regulated conversion of small resource molecules. *Angew. Chem., Int. Ed.* **2026**, *65*, e19095.

[20] Wang, H. G.; Zhou, M.; Wang, Y. Y.; Duan, R.; Qin, H. S.; Zhao, W. L.; Yin, Y. Y.; Yang, J. H.; Liu, S. Q.; Zhang, S. P. et al. Dual redox shuttles drive efficient formamide electrosynthesis. *J. Am. Chem. Soc.* **2026**, *148*, 8464–8473.

## Data availability

Not applicable.

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## Author Contributions

Y. Y. and Z. L.: Collect and analyze data; X. K. and B. H.: overall design and direction of the project; Y. Y., X. K., and B. H.: preparation of the manuscript.

## Competing interests

The authors declare no competing interests.

## Use of AI statement

None.