

Perspective

Catalyst design for electrochemical CO₂ reduction to ethyleneYuanjun Chen,¹ Rui Kai Miao,² Christine Yu,¹ David Sinton,^{2,*} Ke Xie,^{1,*} and Edward H. Sargent^{1,3,*}

SUMMARY

In electrochemical CO₂ reduction (CO₂R) into chemicals and fuels, it is a long-standing challenge to suppress the competing hydrogen evolution reaction (HER) and steer selectivity to a single valuable product. Ethylene is a desired model molecule in light of its large market size, range of applications from polymers to sustainable aviation fuel, and large present-day carbon intensity. The reaction pathways and reactivity of CO₂R rely on catalyst surface properties and local reaction environments. Here we review the mechanistic understanding of CO₂R to ethylene; we then discuss catalyst design strategies in light of the link between catalyst structure, reaction pathways, and ethylene production performance. We close with challenges in catalyst design and provide an outlook for further research directions to accelerate the rational design of catalysts.

INTRODUCTION

Ethylene is produced today at a rate of 150 million metric tons/year, the top hydrocarbon chemical produced worldwide. It goes to plastics, including polyethylene (which in turn is produced at a rate of 116 million metric tons per year), polyvinyl chloride (38 million metric tons per year), and polystyrene (25 million metric tons per year).¹ Ethylene is manufactured through steam cracking of naphtha derived from crude oil, and from ethane cracking.^{2,3}

Electrochemical CO₂ reduction (CO₂R) into chemical feedstocks provides an approach to transform waste CO₂ emissions into valuable products.^{4,5} When the reaction is powered using renewable electricity, these products can potentially be manufactured with a net-negative (cradle-to-gate) carbon intensity.^{6,7}

The electrochemical synthesis of ethylene via CO₂R relies on controlling surface properties and local catalyst environments to promote C–C bond coupling and steer the reaction pathway to ethylene while suppressing HER.^{8–11} Therefore, one of the primary challenges of electrochemical ethylene production is developing catalysts capable of simultaneously achieving high Faradic efficiency (FE), energy efficiency, conversion rates, and operational durability.

This Perspective focuses on catalyst design for electrochemical CO₂R to ethylene, particularly copper-based catalysts. We begin with the current understanding of the reaction mechanisms of CO₂R to ethylene. Then we summarize and discuss catalyst design strategies for promoting CO₂R to ethylene (Figure 1). We aim to establish relationships between catalyst structure and performance, utilizing current mechanistic explanations to support catalyst design and engineering. Building on this understanding, we conclude with new directions that could further enhance catalyst design principles for CO₂R to ethylene.

PROGRESS AND POTENTIAL

Electrochemical CO₂ reduction (CO₂R) offers a route to ethylene electrosynthesis. Developing efficient catalysts with high activity, selectivity, and stability is crucial to advance this technology. Numerous catalyst design strategies have been proposed to enhance CO₂R to ethylene, including engineering the size, crystal facets, morphology, and composition and tuning the local reaction environment. The rapid development of operando characterization and computation have deepened insight into reaction pathways. These new methods assist in the rational forward design of catalysts, reducing the need for trial-and-error approaches. The recent emergence of machine learning and high-throughput experimentation techniques promises to further accelerate catalyst design and discovery.



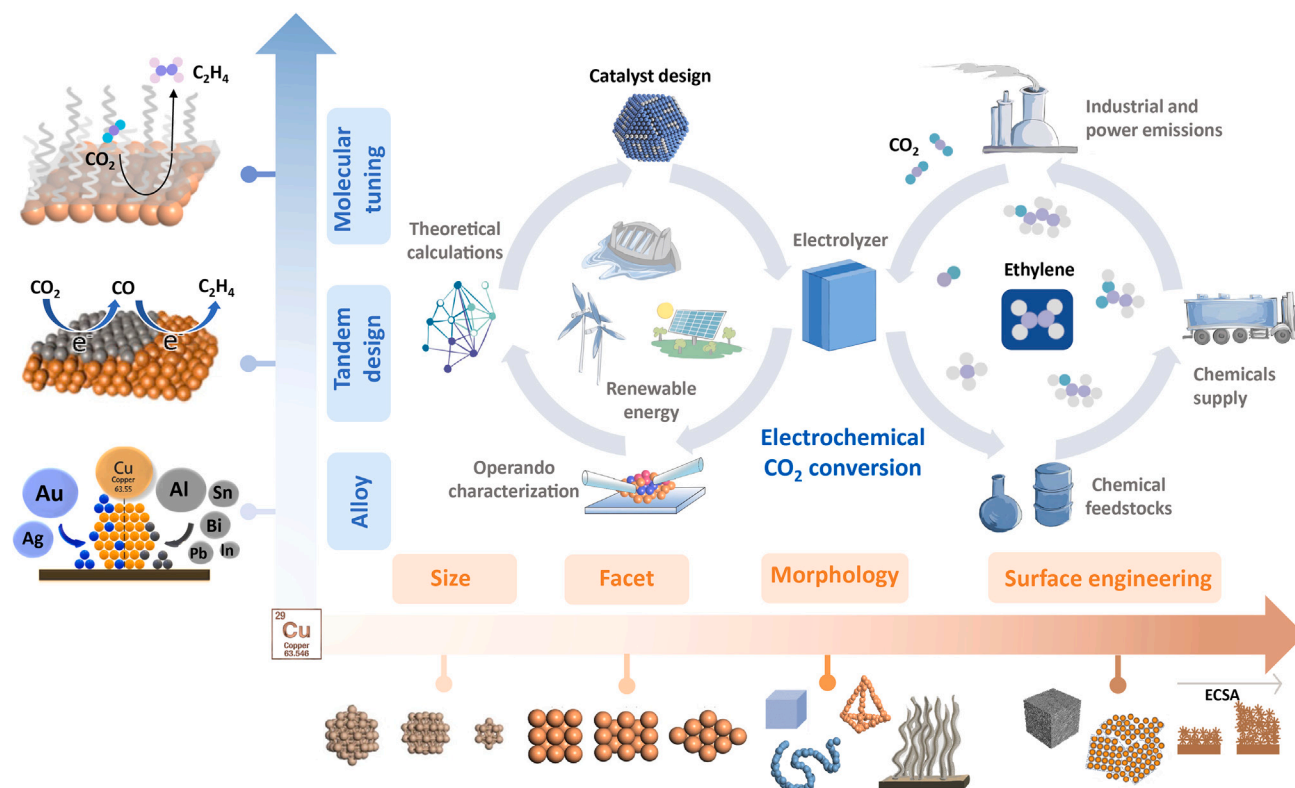


Figure 1. Catalyst design strategies for electrochemical CO₂ reduction to ethylene

Schematic of a closed carbon through electrochemical CO₂ reduction powered by renewably sourced electricity. Operando characterization and theoretical calculations techniques accelerate catalyst discovery and design. The catalyst design strategies encompass two dimensions: the first regulating the self-structure of copper catalysts, including size, crystal facets morphology, and surface engineering, while the second focuses on modifying copper-based catalysts through approaches such as alloying, tandem design, and molecular tuning.

PAST

The foundations of electrochemical CO₂R relies on multiple proton-coupled electron transfer reactions and numerous potential intermediates/products. CO₂R to ethylene necessitates a 12-electron transfer with proton coupling, which involves multiple possible intermediates, including *CO, *COCHO, *CHCOH, *OCHCH*O, and CH₂CH*O.^{12,13} The formation and reaction pathways of these intermediates are influenced by catalyst structure and local reaction environments; therefore, it is crucial to investigate mechanisms and pathways to design next-generation catalysts.

Despite the high complexity of CO₂ reduction mechanisms, most proposed pathways include CO₂ initially electrochemically reduced to CO*, a key intermediate for producing ethylene and other multicarbon (C₂₊) alcohols and oxygenates.^{14,15} The subsequent elementary steps and intermediates have been the primary focus of catalyst design. These specific steps determine selectivity toward ethylene or other C₂₊ alcohols and oxygenates. Summarily, the pathway of CO₂R to ethylene production can be categorized into three processes: CO₂ adsorption/activation, *CO intermediate formation, and C–C coupling steps (Figure 2).

The adsorption and activation of CO₂ are essential to the reduction process, since facilitating this process suppresses competing HER. There are two primary CO₂ adsorption states. One involves the formation of linear molecules through physical

¹Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA

²Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, ON M5S 3G8, Canada

³Department of Electrical and Computer Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA

*Correspondence: sinton@mie.utoronto.ca (D.S.), ke-xie@northwestern.edu (K.X.), ted.sargent@northwestern.edu (E.H.S.)
<https://doi.org/10.1016/j.matt.2023.12.008>

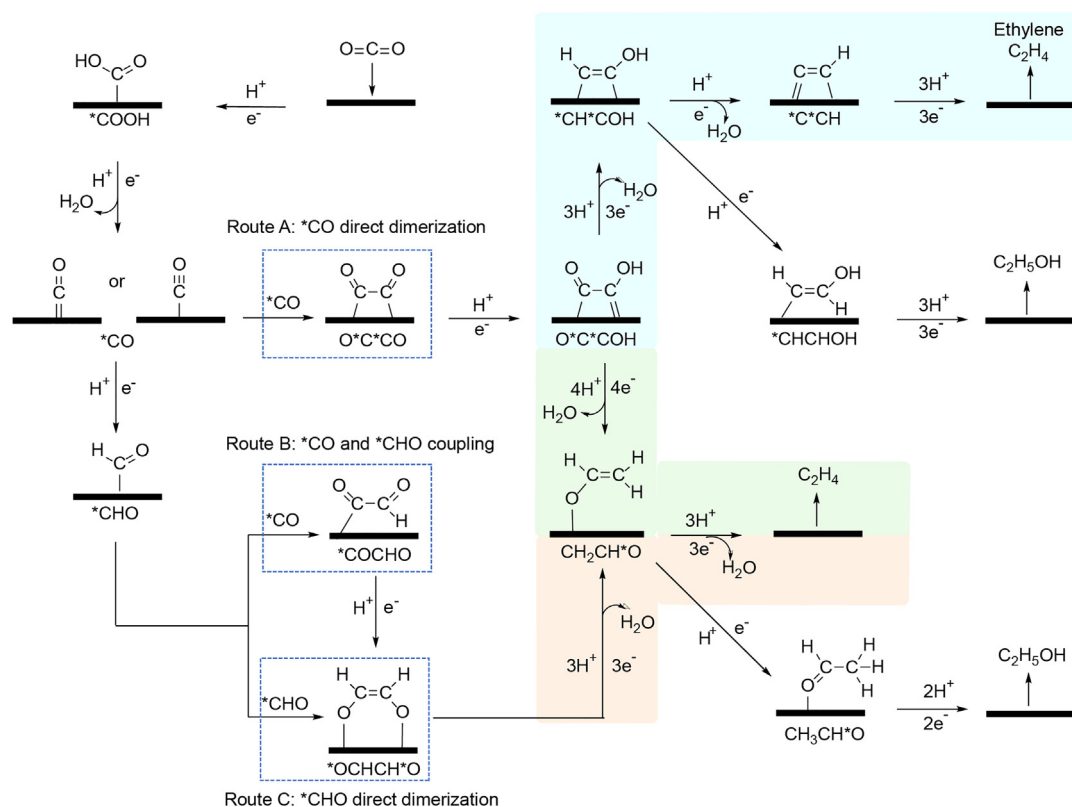


Figure 2. The possible pathways for electrochemical CO₂ reduction to ethylene

Ethylene production from CO₂ electroreduction via different C–C coupling routes, including *CO direct dimerization, *CO and *CHO coupling, *CHO direct dimerization, and subsequent reaction pathways highlighted in color.

Figure adapted with permission from Qu et al.,⁹ Springer Nature, copyright 2023; Nam et al.,⁴¹ Springer Nature, copyright 2020.

adsorption, while the other involves generating a charged CO₂^{δ-} intermediate through chemical adsorption. This CO₂^{δ-} intermediate forms by binding with the C atom on the catalyst when only electrons are involved in the activation process. However, when protons and electrons are involved in the CO₂ adsorption/activation process, a *COOH intermediate is formed, also with a C atom as the binding site, through a proton-coupled electron transfer (PCET) process. This is followed by the removal of the hydroxyl group and the formation of *CO, which can then be further converted into various products, including C₁ products (such as CO, CH₄, and CH₃OH) and C₂₊ products (C₂H₄, C₂H₅OH, CH₃COOH, and C₃H₇OH). In contrast, a *OCOH intermediate is formed when the O atom, instead of the C atom, binds on the catalyst, which is subsequently converted into formate.

The *CO intermediates greatly influence product selectivity. A low *CO adsorption energy on the catalyst surface (e.g., Au, Ag) typically results in the direct desorption of *CO and yields CO(g). A moderate *CO adsorption energy on the catalyst surface (e.g., Cu) leads to C–C coupling, facilitating the formation of ethylene and other C₂₊ products. Tuning the *CO coverage on the catalyst surface is an effective strategy to suppress HER and optimize the energy barriers of C–C coupling, thereby improving the CO₂-to-C₂₊ performance.^{16,17} It is worth noting that as *CO coverage increases, it diminishes the affinity of C atoms for the Cu surface. This reduced affinity promotes the formation of oxygenates, particularly acetate, rather than ethylene.^{18,19} Therefore, optimizing *CO coverage on the catalyst surface is a general strategy for maximizing ethylene selectivity.

Last, three C–C coupling routes are proposed (Figure 2). The first route involves the direct dimerization of adsorbed *CO intermediates, forming $^*CO^*CO$ ²⁰ and consequently $^*CO^*COH$ on Cu (100).²¹ The OH group in $^*CO^*COH$ intermediate disrupts the charge distribution balance inherent in the symmetrical structure of the $^*CO^*CO$ intermediate. This disruption can lead to the formation of two intermediates, $^*CH^*COH$ or CH_2CH^*O , depending on their interactions with protons and electrons. It has been proposed that $^*CH^*COH$ is the crucial intermediate responsible for producing both ethylene and ethanol.²² The *CCH intermediate is formed through the removal of the OH group from $^*CH^*COH$ species, which is subsequently hydrogenated to yield ethylene. When *CHCHOH is generated by hydrogenating $^*CH^*COH$, it can also be hydrogenated to produce ethanol. Alternatively, the hydrogenolysis of the CH_2CH^*O intermediate leads to ethylene production, while the hydrogenation of the CH_2CH^*O intermediate results in ethanol production. The second route involves coupling *CO and *CHO to generate *COCHO , which then hydrogenates to $^*OCHCH^*O$ and CH_2CH^*O , eventually yielding ethylene.^{23,24} The third proposed route involves the dimerization of *CHO intermediates to generate the $^*OCHCH^*O$, which subsequently forms the CH_2CH^*O intermediate through H_2O removal via a PCET process and yields ethylene.²⁵

The most efficient catalysts for ethylene production through CO_2R are Cu-based electrocatalysts. Cu stands as the sole heterogeneous catalyst that has the capacity to produce multicarbon products. Numerous factors influence CO_2R activity and selectivity, encompassing catalyst surface structure, morphology, and composition; and likewise, many strategies have been proposed to steer CO_2R product selectivity toward ethylene, focusing on engineering the size, crystal facet, morphology, and structure of Cu-based electrocatalysts.

The size effect of Cu-based electrocatalysts has been studied extensively.²⁶ Downsizing Cu nanoparticles increases the surface curvature and decreases the average coordination number of surface atoms. With the decrease of particle size (<5 nm), there is an increase in the activity and selectivity of H_2 and CO production, accompanied by a decrease in selectivity toward hydrocarbons, which are associated with a higher number of low coordination sites. In contrast, oversized catalysts have fewer exposed surface atoms and edge active sites, resulting in lower catalytic activity.

Early research findings suggest that the selectivity of C_{2+} products in catalysts is significantly influenced by the specific facet of Cu, with each facet favoring different product generations.²⁷ For example, Cu (100) was found to be conducive to ethylene production, while Cu (111) was more inclined to produce C_1 products. Cu (110) was proposed to favor the formation of C_2H_5OH and acetate.²⁸ Experiments and theoretical calculations have demonstrated that Cu (100) has a lower energy barrier for *CO dimerization compared with Cu (110) and Cu (111)²⁹; however, Cu (111) is the most stable facet of crystalline Cu. Thus, exposing and stabilizing more Cu (100) is highly desirable but challenging in practice.

Additionally, it has been reported that the surface energy of Cu (100) significantly decreases as the coverage of adsorbed species (including *CO , *COCHO , *COOH , etc.) increases during CO_2RR , while the surface energy of Cu (100) remains relatively stable when the coverage of *H species increases during HER. The adsorbed reaction intermediates on the Cu surface serve as capping agents that promote the generation of Cu (100). The presence of adsorbed species does not have a notable impact on the surface energy of Cu (111) in either the context of HER or

CO₂R.³⁰ Consequently, this finding provides a promising approach to induce the reconstruction of polycrystalline Cu surfaces into Cu (100) under CO₂R operational conditions.

Regulating the morphology of catalysts can tune the adsorption energy of intermediates and modify the local reaction environment, thereby steering the selectivity of CO₂R products. Some catalyst morphologies of note include nanocubes, nanowires, nanocages, core-shell structures, nanofoams, and nanoarrays. For instance, Cu nanowires with abundant step surfaces have shown outstanding ethylene selectivity, attributed to the lower *CO adsorption energy on adjacent active sites of the step surfaces compared with that of Cu (100), thereby lowering C–C coupling energy barriers.³¹ Cu nanoarrays have exhibited impressive performance and selectivity for ethylene production, mainly due to the induced tip effect and the altered local pH on the catalyst's surface. Cu nanowire arrays have been fabricated by electrochemical reduction of CuO nanowire arrays on Cu foil.³² These nanowire arrays exhibit elongated, densely packed structures that restrict OH[−] diffusion at the electrode surface, resulting in an elevation of the local pH at the electrode-electrolyte interface. This facilitates the formation of ethylene and suppresses the production of CH₄ and H₂.

The structure of Cu catalysts has also been a topic of intense interest, as improving the electrochemical active surface area (ECSA) and surface roughness enables local OH[−] formation and further increases local pH at the electrode-electrolyte interface. These effects can suppress HER and promote C–C coupling to produce ethylene and other C₂₊ products. Inspired by these observations, numerous efforts have been made to develop oxide-derived Cu materials to obtain higher ECSA, improve surface roughness, and construct grain boundaries.^{33,34}

PRESENT

Recent research has shifted attention from solely regulating the self-structure of copper catalysts to modifying both their electronic and geometric configurations and tuning the local reaction environment. These are achieved by implementing various catalyst strategies, including alloying, tandem design, and molecular tuning.

Incorporating other guest metals into Cu to form Cu-based catalysts can enhance CO₂R to ethylene production, primarily through geometric ensemble effects or electronic ligand and strain effects.¹⁵ Geometric ensemble effects arise from changes in the atomic arrangement of active sites, altering the interaction between intermediates and active sites. Beyond merely adjusting the number or configuration of specific atoms within an ensemble, this modification can also create bifunctional active sites, where neighboring metals assume distinct catalytic roles. For instance, it has been proposed that bifunctional active sites conducive to CO₂R could be established by introducing higher oxygen affinity metals. This would stabilize *COOH or *CHO intermediates by enabling both carbon and oxygen atoms to interact with the surface.³⁵ This contrasts with *CO, which usually binds to surfaces in an upright orientation primarily by the carbon atom. Another example is that the construction of isolated active sites could alter the proximity of intermediates, thereby influencing the selectivity.³⁶

The electronic effect is a result of heteroatom dopants (e.g., Au, Ag, Pd, Al, Zn, Sn) altering the electronic structure of the host metal (i.e., Cu). These dopants regulate the binding strength of the intermediate on the catalyst surface, thereby altering the

kinetics and energetics of CO₂R. The relationship between intermediate adsorption and the electronic structure of catalysts can be elucidated through d-band center theory.³⁷ Hybridization between metal d-bands and intermediate σ -orbitals gives rise to the formation of bonding and anti-bonding d- σ molecular orbitals. Shifting the metal d-band centers closer to the Fermi level elevates the energy level and reduces the electron occupancy of anti-bonding d- σ molecular orbitals. Consequently, this reinforcement enhances the d- σ bond between intermediates and metal catalysts. For example, the incorporation of Al into Cu to form a Cu–Al alloy catalyst effectively promotes ethylene production with an ethylene FE of 80% at a current density of 400 mA cm⁻² at -1.5 V vs. RHE.³⁸ This excellent performance was attributed to the high number of *CO adsorption sites and optimal *CO adsorption energy compared with those of other metal and bimetallic alloy catalysts. Additionally, water molecules near the Al atoms efficiently facilitated the conversion of *HOCCH to *CCH, reducing the energy barriers for ethylene formation and suppressing the production of competing alcohols, resulting in excellent activity and selectivity toward ethylene.

Constructing tandem catalysts is an effective approach to increase local CO coverage, which is essential to improving CO₂R to ethylene.³⁹ The widely used tandem catalysts for ethylene production consist of Cu and CO-producing guest metals (e.g., Au, Ag, Zn). The introduction of CO-producing guest metals effectively enhances the selective conversion of CO₂ to CO. This is due to two key factors: first, it generates a substantial CO coverage on the Cu surface. Second, it shortens the diffusion distance of CO intermediates, thereby increasing the availability of CO and improving the local CO concentration. An alternative type of tandem catalyst involves two distinct catalyst layers. One layer converts CO₂ into CO, while the other transforms CO into ethylene. The tandem catalyst configuration can improve local CO coverage, suppress competing HER and facilitate C–C coupling to promote ethylene production.

Selective production of target products necessitates control at each branching point in multiple PCET reaction process. This challenge is exacerbated by the linearly correlated adsorption energies of multiple intermediates, known as the linear scaling relations.^{8,40} In simpler terms, the adsorption energy of a specific intermediate cannot be altered without influencing others. For instance, a consequence of linear scaling relations, designing a catalyst with the optimal *COOH binding would lead to non-optimal *CO binding, and vice versa. This implies that the binding energies required for adsorption or activation will inevitably fall short of their optimum values unless these scaling relations are broken.

Organic molecules or inorganic compound additives, components that are not active sites but facilitate crucial steps by interacting with the catalyst surface, such as electrolytes, water and gas reactants, provide effective approaches to break scaling relations and enable control over the reaction pathways toward target products, thereby reducing overpotential and improving product selectivity in CO₂R.⁴¹ Commonly used organic molecule additives including pyridine-, imidazole-, and imine-based small molecules, *N*-heterocyclic carbenes (NHCs), 4-pyridyl ethyl mercaptan (4-PEM), *N*-substituted tetrahydro-bipyridine, ionic liquids, and polymers (e.g., polypyrrole, polyaniline, polydopamine). These additives can be incorporated into the catalyst surface through impregnation, chemical modification, and polymerization. Organic additives have applicable molecular properties, such as the electron density of the N atom (i.e., Bader charge analysis), electron donating/withdrawing capability (i.e., Hammett constant), and geometric constraints (i.e., steric hindrance). For instance,

the Cu-polyamine hybrid catalyst showed remarkable ethylene FE of $87\% \pm 3\%$ at -0.47 V. Raman measurements suggest that the presence of polyamine on the Cu surface leads to higher surface pH, higher CO content, and higher stabilization of intermediates, significantly promoting ethylene production.⁴² Coating an N-aryl-dihydropyridine-based oligomer film on the Cu surface improves the stabilization of an “atop-bound” CO intermediate, facilitating ethylene production with an ethylene FE of 72% and a full-cell energy efficiency of 20% in neutral media.⁴³

PROBLEMS

The production of a single product is a persistent challenge in the field. CO₂R is a highly complicated process involving multiple electron and proton transfer steps, a diverse array of intermediates, and various reaction pathways. Multiple pathways can lead to the same product, adding to the complexity of the process. The mechanisms for generating the same product can also differ significantly in different reaction environments, such as at high and low overpotentials. Many theory-driven studies have simplified the complex process of CO₂R by relying on a single key elementary step as a descriptor for the entire reaction pathway. However, these simplifications can reduce prediction accuracy and overlook optimal catalysts. In experimental studies, the design of electrocatalysts for CO₂R to produce specific products like ethylene has often been driven by trial-and-error rather than systematic and rational design.

Operando/*in situ* studies of CO₂R under operating conditions provide insight into the real active sites, reaction intermediates, and catalytic environments, which can provide experimental evidence to advance the understanding of reaction mechanisms and reveal the structure and catalytic properties relationship of catalysts.^{44–46} *In situ* Raman and infrared (IR) spectroscopies and online electrochemical mass spectroscopy can provide real-time insights into product formation as the electrode potential changes. These spectroscopic techniques and computational and *ex situ* experimental investigations hold great promise for gaining new mechanistic insights into the CO₂R. *In situ* Raman and IR spectroscopies provide platforms to detect intermediates such as *COOH, *CO, *CHO, and *OCCOH on Cu surfaces (Figure 3A).²¹ Additionally, broadband sum-frequency generation (BB-SFG) spectroscopy is a powerful tool to offer information associated with C–H and C–O bonds within relevant C₂₊ species.⁴⁷ However, the relatively weak binding energy and faster kinetics of crucial C₂ intermediates in the post-C–C coupling steps pose challenges for extracting their information using current operando techniques. This obstacle hinders the achievement of a complete understanding of the entire reaction mechanism. Therefore, there is a pressing need to develop operando characterization techniques with improved time and spatial resolution.

In situ X-ray absorption spectroscopy (XAS) and *in situ* grazing incidence X-ray diffraction (GIXRD) can monitor changes in catalysts' electronic structure and coordination environment. However, the information related to surface Cu is often obscured by the contributions from the bulk counterparts, potentially resulting in inaccurate conclusions about the real-time structure of catalysts. *In situ* electrochemical microscopy allows for visually observing structural variations in catalysts. However, this technique necessitates using flat electrodes, and its resolution falls short of providing atomic-level insights into the catalyst surface.

Numerous studies emphasize current density and product selectivity, but the crucial aspect of catalyst stability has not received requisite attention. It is essential to investigate the degradation mechanism of Cu-based catalysts in CO₂R and establish a

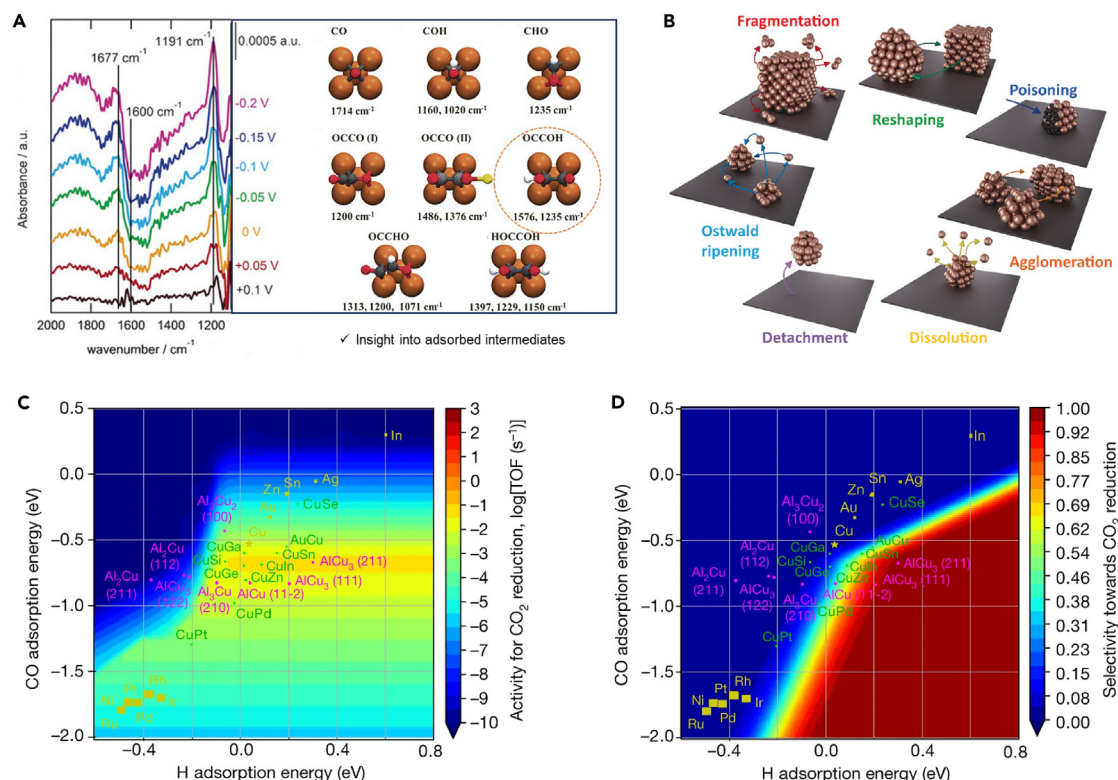


Figure 3. The challenges and opportunities of catalyst design for electrochemical CO₂ reduction to ethylene

(A) Insight into adsorbed intermediates for understanding of mechanism by *in situ* infrared spectroscopy. Reproduced with permission.²¹ Copyright 2017, Wiley-VCH.

(B) Schematic of degradation mechanisms of copper-based catalysts for electrochemical CO₂ reduction. Reproduced with permission.⁴⁸ Copyright 2020, Wiley-VCH.

(C and D) Screening of Cu and Cu-based compounds using computational methods.

(C) A two-dimensional activity volcano plots for CO₂ reduction.

(D) A two-dimensional selectivity volcano plot for CO₂ reduction. Reproduced with permission.³⁸ Copyright 2020, Springer Nature.

standardized procedure for assessing the stability of electrocatalysts (Figure 3B).⁴⁸ This procedure should consider parameters such as electrolysis time, applied potential, current density, electrolyte composition, electrode type, and desired product. Adopting such a method would streamline the benchmarking of catalysts, thereby enhancing the effectiveness of their evaluation and comparison.

POSSIBILITIES

It is imperative to comprehensively explore potential reaction mechanisms to lay the foundation for the rational design of electrocatalysts aiming to produce a specific product like ethylene. The emergence of automated screening methods that uses machine learning to guide DFT calculations represents a highly promising strategy for achieving exhaustive catalyst screening (Figures 3C and 3D).^{38,49} This may significantly accelerate catalyst discovery, laying the groundwork for informed and systematic catalyst design efforts. The combination of microkinetic modeling with DFT calculations can demonstrate the dominant species on the Cu surface, determine the turnover frequency of the reaction, and assess the selectivity toward desired products. The sensitivity analysis of individual model parameters, such as rate constants, equilibrium coefficients, and intermediate binding energies, can offer information about rate-limiting steps and other descriptors crucial for

designing more effective Cu catalysts and understanding the pathway toward C₁ products. More in-depth studies focusing on the C–C coupling steps and ethylene pathways are also much needed for catalyst design aimed at producing ethylene.

Additional dedicated efforts are needed to enhance further the temporal and spatial resolution of operando characterization techniques. For vibrational spectroscopy, such as Raman or IR, surface enhancement techniques improve resolution, even enabling single-molecule detection.⁵⁰ Sum-frequency generation (SFG) and second harmonic generation (SHG) spectroscopy allow atomic-level resolution to surface specificity owing to their exclusive activity in environments lacking inversion symmetry.⁵¹ For XAS, using a high-resolution fluorescence spectrometer enables the integration of fluorescence yield within a narrow range for a given fluorescence line, this allowing high-energy-resolution fluorescence-detected XAS (HERFD-XAS).⁵² This technique improves energy resolution by a factor of 2–5. This refined technique not only detects subtle features in XAS, such as the pre-edge, but also enables *in situ* monitoring of changes in the surface state.^{53,54}

Today it remains a challenge to distinguish signals related to intermediates on the substrate vs. in the electrolyte. Achieving clarity in monitoring intermediates requires further advancement in instrument detection capabilities. This includes upgrading detector sensitivity, optimizing power sources, and incorporating advanced laser sources.⁵⁵ Exploring faster data acquisition systems, and utilizing advanced data processing algorithms and software, offer the potential to extract ever more meaningful information from rapidly acquired data, also enabling enhanced resolution. Resolution improvement can be achieved by refining electrode substrate design and employing specialized electrochemical cell designs: these facilitate a more defined optical path, reducing the influence of electrolyte and electrode surface on the signals.

The challenge of distinguishing minority and bystander species within intermediates poses an opportunity of great interest and importance. Operando spectroscopy techniques are often limited by ensemble averaging, making them primarily sensitive to majority species within a sample. This limitation suggests a role for integrating machine learning methodologies⁵⁵ to distinguish subtle patterns and relationships within complex datasets. It has the potential to enable a more nuanced analysis of heterogeneous systems, facilitating the identification and characterization of minority species often overshadowed in ensemble averages. Acquiring precise, real-time structural information during CO₂R will contribute to deepened understanding of CO₂R reaction mechanisms and pathways, enabling catalyst design for targeted products.

Electrochemical systems to ethylene will continue to strive for higher energy efficiency, single-pass conversion, and operating stability. Systems to date have reached ethylene energy efficiency over 20% at industrially relevant current densities over 200 mA/cm². Achieving this energy efficiency in high single-pass conversion systems requires further progress. Looking at stability, catalysts today have shown operating lifespans of approximately a few hundred hours, while stability over 10,000 h is required for commercial applications. Studies of degradation mechanism of Cu-based catalysts in CO₂R will be crucial to progress in durability-science-driven advances.

Standard procedures and data acquisition to assess the activity and selectivity of CO₂R catalysts have been proposed, yet further efforts are needed.⁵⁶ Conducting long-term stability tests under real operational conditions for over 10,000 h is not a feasible or

realistic option for most academic labs. Accelerated degradation tests and procedures for stability assessment should be established to serve as benchmarks for catalyst stability. These benchmarks should be based on a fundamental understanding of catalyst degradation and reconstruction mechanisms⁴⁸ and consider parameters such as electrolysis time, applied potential, current density, electrolyte composition, electrode type, and desired product. This understanding should integrate real-time data obtained under operation conditions by *in situ* characterizations that observe local morphological, structural, and compositional changes of catalysts. Furthermore, theoretical calculations and computational simulations should have a mechanistic approach. This approach will advance the fundamental understanding of catalyst degradation and reconstruction mechanisms, improving catalyst stability through rational design to mitigate degradation and reconstruction during CO₂R.

The present-day viability of CO₂R technology is also limited by the off-target production of (bi)carbonate, formed when CO₂ reacts with OH⁻ in electrolytes. The single-pass conversion (SPC) of CO₂ is limited to 25% for CO₂R to ethylene.⁵⁷ CO₂ regeneration and separation from carbonate solutions or from cathodic and anodic streams has a severe energy penalty. A promising approach to mitigating carbonate formation and reducing CO₂ crossover involves substituting commonly used alkaline and neutral electrolytes with acidic ones (Figure 4A). However, kinetically favored HER typically outcompetes CO₂R in acidic media, resulting in poor CO₂R selectivity, particularly in the production of C₂₊ products.^{58,59} Despite some progress made in CO₂R to ethylene in acidic media, including regulating the structure of catalysts and tuning the local reaction environment, more efforts should be devoted to developing catalysts and systems to suppress HER and steer selectivity to ethylene.

Another possible avenue of research that has been proposed is a cascade system (Figure 4B) that converts CO₂ to CO and then to ethylene, driven by the rapid advancements in solid-oxide electrolysis cell (SOEC) technology for efficient CO₂ conversion to CO.^{60,61} This cascade system benefits from low energy cost and high SPC in both steps because CO does not react with OH⁻, thus avoiding the issues associated with carbonate formation. The technical challenges for the cascade step are to improve stability while maintaining the highest energy efficiency and productivity in the SOEC step and to achieve a highly efficient, selective, and stable CO-to-ethylene production process. Given that CO electroreduction (COR) shares similar mechanisms with CO₂R, most catalyst design strategies for CO₂R can be extended to COR. Certainly, there are still more differences between CO₂R and COR, such as local CO coverage and the adsorption behaviors of intermediates. These distinctions emphasize the need for further research of novel catalysts specifically designed for COR to ethylene conversion.

Catalysts for CO₂R from CO₂ capture solution is also an area with potential growth. Electrochemically converting CO₂ capture solutions circumvents the traditional costly step of generating high-purity CO₂ from CO₂ capture solutions. Thus, it holds great promise in reducing capital costs and improving overall ethylene production process efficiency. Direct (bi)carbonate reduction and amine-CO₂ adduct upgrading are two approaches for CO₂R from a capture solution (Figure 4C).^{62,63} The challenge for (bi)carbonate reduction lies in achieving sufficient CO₂ concentration on the catalyst surface and facilitating CO₂ adsorption and activation at a low local CO₂ concentration while suppressing HER. Moreover, the development of CO₂R from amine-based capture solutions requires catalyst design to break the N-C bond of the amine-CO₂ adduct and steer selectivity toward desired products. Systems should also be optimized to facilitate the mass transport of amine-CO₂ adducts to the catalyst surface.

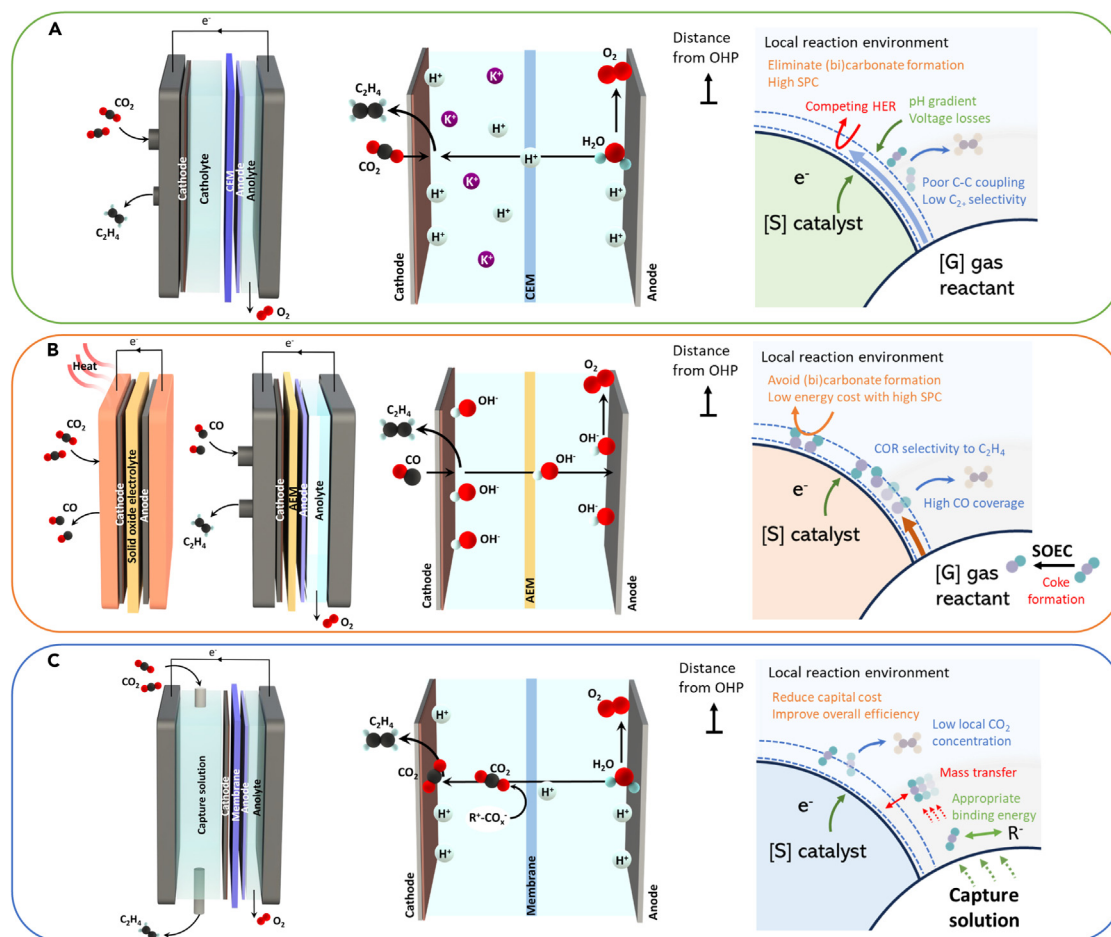


Figure 4. The perspective and challenges of catalyst design for recent technologies in electrochemical CO₂ reduction to ethylene

(A) Schematic illustration of CO₂R in an acidic electrolyte.

(B) Schematic illustration of cascade CO₂R-COR system. CO₂ reduction to CO in a solid-oxide electrolysis cell (SOEC) and CO reduction to ethylene in a membrane electrode assembly (MEA) electrolyzer.

(C) Schematic illustration of CO₂R from capture solution. In (bi)carbonate solutions, the protons in solution react with (bi)carbonate to *in situ* generate CO₂ at the catalyst surface to initiate CO₂R. In amine-based solutions, the amine-CO₂ adduct (R⁺-CO_x⁻) is directly reduced at the catalyst surface.

Figure adapted with permission from Ozden et al.,⁵⁷ Springer Nature, copyright 2022.

In conclusion, electrochemical CO₂R provides a promising and sustainable route for the electrosynthesis of ethylene and decarbonization of the petrochemical industry. To advance the commercial applications of CO₂R to ethylene technology, it is crucial to attain commercially relevant performance metrics across all aspects, encompassing cell voltage, current density, FE, energy efficiency, stability, and SPC. Achieving these metrics requires a holistic approach involving catalyst design, fundamental understanding, reactor engineering, and system optimization.

AUTHOR CONTRIBUTIONS

E.H.S., K.X., and D.S. supervised the project. Y.C., E.H.S., K.X., and D.S. conceived the idea. Y.C. wrote the manuscript. R.M. and C.Y. contributed to figures and manuscript editing. E.H.S., K.X., and D.S. reviewed and edited the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

- Geyer, R., Jambeck, J.R., and Law, K.L. (2017). Production, use, and fate of all plastics ever made. *Sci. Adv.* 3, e1700782.
- Amghizar, I., Vandewalle, L.A., Van Geem, K.M., and Marin, G.B. (2017). New trends in olefin production. *Engineering* 3, 171–178.
- Gao, Y., Neal, L., Ding, D., Wu, W., Baroi, C., Gaffney, A.M., and Li, F. (2019). Recent advances in intensified ethylene production—a review. *ACS Catal.* 9, 8592–8621.
- Jordaan, S.M., and Wang, C. (2021). Electrocatalytic conversion of carbon dioxide for the Paris goals. *Nat. Catal.* 4, 915–920.
- Hepburn, C., Adlen, E., Beddington, J., Carter, E.A., Fuss, S., Mac Dowell, N., Minx, J.C., Smith, P., and Williams, C.K. (2019). The technological and economic prospects for CO₂ utilization and removal. *Nature* 575, 87–97.
- De Luna, P., Hahn, C., Higgins, D., Jaffer, S.A., Jaramillo, T.F., and Sargent, E.H. (2019). What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science* 364, eaav3506.
- Bushuyev, O.S., De Luna, P., Dinh, C.T., Tao, L., Saur, G., van de Lagemaat, J., Kelley, S.O., and Sargent, E.H. (2018). What should we make with CO₂ and how can we make it? *Joule* 2, 825–832.
- Ross, M.B., De Luna, P., Li, Y., Dinh, C.-T., Kim, D., Yang, P., and Sargent, E.H. (2019). Designing materials for electrochemical carbon dioxide recycling. *Nat. Catal.* 2, 648–658.
- Qu, J., Cao, X., Gao, L., Li, J., Li, L., Xie, Y., Zhao, Y., Zhang, J., Wu, M., and Liu, H. (2023). Electrochemical carbon dioxide reduction to ethylene: from mechanistic understanding to catalyst surface engineering. *Nano-Micro Lett.* 15, 178.
- Li, L., Li, X., Sun, Y., and Xie, Y. (2022). Rational design of electrocatalytic carbon dioxide reduction for a zero-carbon network. *Chem. Soc. Rev.* 51, 1234–1252.
- Yan, T., Chen, X., Kumari, L., Lin, J., Li, M., Fan, Q., Chi, H., Meyer, T.J., Zhang, S., and Ma, X. (2023). Multiscale CO₂ electrocatalysis to C₂₊ products: reaction mechanisms, catalyst design, and device fabrication. *Chem. Rev.* 123, 10530–10583.
- Todorova, T.K., Schreiber, M.W., and Fontecave, M. (2019). Mechanistic understanding of CO₂ reduction reaction (CO₂RR) toward multicarbon products by heterogeneous copper-based catalysts. *ACS Catal.* 10, 1754–1768.
- Bagchi, D., Roy, S., Sarma, S.C., and C Peter, S. (2022). Toward unifying the mechanistic concepts in electrochemical CO₂ reduction from an integrated material design and catalytic perspective. *Adv. Funct. Mater.* 32.
- Wang, Y., Liu, J., and Zheng, G. (2021). Designing copper-based catalysts for efficient carbon dioxide electroreduction. *Adv. Mater.* 33, e2005798.
- Nitopi, S., Bertheussen, E., Scott, S.B., Liu, X., Engstfeld, A.K., Horch, S., Seger, B., Stephens, I.E.L., Chan, K., Hahn, C., et al. (2019). Progress and perspectives of electrochemical CO₂ reduction on copper in aqueous electrolyte. *Chem. Rev.* 119, 7610–7672.
- Huang, Y., Handoko, A.D., Hirunsit, P., and Yeo, B.S. (2017). Electrochemical reduction of CO₂ using copper single-crystal surfaces: effects of CO* coverage on the selective formation of ethylene. *ACS Catal.* 7, 1749–1756.
- Liu, X., Xiao, J., Peng, H., Hong, X., Chan, K., and Nørskov, J.K. (2017). Understanding trends in electrochemical carbon dioxide reduction rates. *Nat. Commun.* 8, 15438.
- Jin, J., Wicks, J., Min, Q., Li, J., Hu, Y., Ma, J., Wang, Y., Jiang, Z., Xu, Y., Lu, R., et al. (2023). Constrained C₂ adsorbate orientation enables CO-to-acetate electroreduction. *Nature* 617, 724–729.
- Li, J., Wang, Z., McCallum, C., Xu, Y., Li, F., Wang, Y., Gabardo, C.M., Dinh, C.-T., Zhuang, T.-T., Wang, L., et al. (2019). Constraining CO coverage on copper promotes high-efficiency ethylene electroproduction. *Nat. Catal.* 2, 1124–1131.
- Kim, Y., Park, S., Shin, S.-J., Choi, W., Min, B.K., Kim, H., Kim, W., and Hwang, Y.J. (2020). Time-resolved observation of C–C coupling intermediates on Cu electrodes for selective electrochemical CO₂ reduction. *Energy Environ. Sci.* 13, 4301–4311.
- Pérez-Gallent, E., Figueiredo, M.C., Calle-Vallejo, F., and Koper, M.T.M. (2017). Spectroscopic observation of a hydrogenated CO dimer intermediate during CO reduction on Cu(100) electrodes. *Angew. Chem. Int. Ed.* 56, 3621–3624.
- Cheng, T., Xiao, H., and Goddard, W.A. (2017). Full atomistic reaction mechanism with kinetics for CO reduction on Cu(100) from ab initio molecular dynamics free-energy calculations at 298 K. *Proc. Natl. Acad. Sci. USA* 114, 1795–1800.
- Garza, A.J., Bell, A.T., and Head-Gordon, M. (2018). Mechanism of CO₂ reduction at copper surfaces: pathways to C₂ products. *ACS Catal.* 8, 1490–1499.
- Goodpaster, J.D., Bell, A.T., and Head-Gordon, M. (2016). Identification of possible pathways for C–C bond formation during electrochemical reduction of CO₂: new theoretical insights from an improved electrochemical model. *J. Phys. Chem. Lett.* 7, 1471–1477.
- Ma, W., He, X., Wang, W., Xie, S., Zhang, Q., and Wang, Y. (2021). Electrocatalytic reduction of CO₂ and CO to multi-carbon compounds over Cu-based catalysts. *Chem. Soc. Rev.* 50, 12897–12914.
- Reske, R., Mistry, H., Behafarid, F., Roldan Cuenya, B., and Strasser, P. (2014). Particle size effects in the catalytic electroreduction of CO₂ on Cu nanoparticles. *J. Am. Chem. Soc.* 136, 6978–6986.
- Rossi, K., and Buonsanti, R. (2022). Shaping copper nanocatalysts to steer selectivity in the electrochemical CO₂ reduction reaction. *Acc. Chem. Res.* 55, 629–637.
- Hori, Y., Wakebe, H., Tsukamoto, T., and Koga, O. (1995). Adsorption of CO accompanied with simultaneous charge transfer on copper single crystal electrodes related with electrochemical reduction of CO₂ to hydrocarbons. *Surf. Sci.* 335, 258–263.
- Schouten, K.J.P., Qin, Z., Pérez Gallent, E., and Koper, M.T.M. (2012). Two pathways for the formation of ethylene in CO reduction on single-crystal copper electrodes. *J. Am. Chem. Soc.* 134, 9864–9867.
- Wang, Y., Wang, Z., Dinh, C.-T., Li, J., Ozden, A., Golam Kibria, M., Seifitokaldani, A., Tan, C.-S., Gabardo, C.M., Luo, M., et al. (2019). Catalyst synthesis under CO₂ electroreduction favours faceting and promotes renewable fuels electrosynthesis. *Nat. Catal.* 3, 98–106.
- Choi, C., Kwon, S., Cheng, T., Xu, M., Tieu, P., Lee, C., Cai, J., Lee, H.M., Pan, X., Duan, X., et al. (2020). Highly active and stable stepped Cu surface for enhanced electrochemical CO₂ reduction to C₂H₄. *Nat. Catal.* 3, 804–812.
- Ma, M., Djanashvili, K., and Smith, W.A. (2016). Controllable hydrocarbon formation from the electrochemical reduction of CO₂ over Cu nanowire arrays. *Angew. Chem. Int. Ed.* 55, 6680–6684.
- Li, C.W., Ciston, J., and Kanan, M.W. (2014). Electroreduction of carbon monoxide to liquid fuel on oxide-derived nanocrystalline copper. *Nature* 508, 504–507.
- Mariano, R.G., McKelvey, K., White, H.S., and Kanan, M.W. (2017). Selective increase in CO₂ electroreduction activity at grain-boundary surface terminations. *Science* 358, 1187–1192.
- Peterson, A.A., and Nørskov, J.K. (2012). Activity descriptors for CO₂ electroreduction to methane on transition-metal catalysts. *J. Phys. Chem. Lett.* 3, 251–258.
- Karamad, M., Tripkovic, V., and Rossmeisl, J. (2014). Intermetallic alloys as CO electroreduction catalysts—role of isolated active sites. *ACS Catal.* 4, 2268–2273.
- Nørskov, J.K., Abild-Pedersen, F., Studt, F., and Bligaard, T. (2011). Density functional theory in surface chemistry and catalysis. *Proc. Natl. Acad. Sci. USA* 108, 937–943.
- Zhong, M., Tran, K., Min, Y., Wang, C., Wang, Z., Dinh, C.T., De Luna, P., Yu, Z., Rasouli, A.S., Brodersen, P., et al. (2020). Accelerated discovery of CO₂ electrocatalysts using active machine learning. *Nature* 581, 178–183.
- Cao, B., Li, F.-Z., and Gu, J. (2022). Designing Cu-Based Tandem Catalysts for CO₂ Electroreduction Based on Mass Transport of CO Intermediate. *ACS Catal.* 12, 9735–9752.
- Birdja, Y.Y., Pérez-Gallent, E., Figueiredo, M.C., Göttle, A.J., Calle-Vallejo, F., and Koper, M.T.M. (2019). Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels. *Nat. Energy* 4, 732–745.
- Nam, D.H., De Luna, P., Rosas-Hernández, A., Thevenon, A., Li, F., Agapie, T., Peters, J.C.,

- Shekhah, O., Eddaoudi, M., and Sargent, E.H. (2020). Molecular enhancement of heterogeneous CO₂ reduction. *Nat. Mater.* *19*, 266–276.
42. Chen, X., Chen, J., Alghoraibi, N.M., Henckel, D.A., Zhang, R., Nwabara, U.O., Madsen, K.E., Kenis, P.J.A., Zimmerman, S.C., and Gewirth, A.A. (2020). Electrochemical CO₂-to-ethylene conversion on polyamine-incorporated Cu electrodes. *Nat. Catal.* *4*, 20–27.
43. Li, F., Thevenon, A., Rosas-Hernández, A., Wang, Z., Li, Y., Gabardo, C.M., Ozden, A., Dinh, C.T., Li, J., Wang, Y., et al. (2020). Molecular tuning of CO₂-to-ethylene conversion. *Nature* *577*, 509–513.
44. Handoko, A.D., Wei, F., Jenndy, Yeo, B.S., and Seh, Z.W. (2018). Understanding heterogeneous electrocatalytic carbon dioxide reduction through operando techniques. *Nat. Catal.* *1*, 922–934.
45. Li, X., Wang, S., Li, L., Sun, Y., and Xie, Y. (2020). Progress and perspective for in situ studies of CO₂ reduction. *J. Am. Chem. Soc.* *142*, 9567–9581.
46. Zhu, Y., Wang, J., Chu, H., Chu, Y.-C., and Chen, H.M. (2020). In situ/operando studies for designing next-generation electrocatalysts. *ACS Energy Lett.* *5*, 1281–1291.
47. Huang-Fu, Z.C., Song, Q.T., He, Y.H., Wang, J.J., Ye, J.Y., Zhou, Z.Y., Sun, S.G., and Wang, Z.H. (2019). Electrochemical CO₂ reduction on Cu and Au electrodes studied using in situ sum frequency generation spectroscopy. *Phys. Chem. Chem. Phys.* *21*, 25047–25053.
48. Popović, S., Smiljanić, M., Jovanović, P., Vavra, J., Buonsanti, R., and Hodnik, N. (2020). Stability and degradation mechanisms of copper-based catalysts for electrochemical CO₂ reduction. *Angew. Chem. Int. Ed.* *59*, 14736–14746.
49. Tran, K., and Ulissi, Z.W. (2018). Active learning across intermetallics to guide discovery of electrocatalysts for CO₂ reduction and H₂ evolution. *Nat. Catal.* *1*, 696–703.
50. Zhang, H., Duan, S., Radjenovic, P.M., Tian, Z.-Q., and Li, J.-F. (2020). Core-shell nanostructure-enhanced raman spectroscopy for surface catalysis. *Acc. Chem. Res.* *53*, 729–739.
51. Humbert, C., Noblet, T., Dalstein, L., Busson, B., and Barbillon, G. (2019). Sum-frequency generation spectroscopy of plasmonic nanomaterials: A review. *Materials* *12*, 836.
52. Wang, J., Hsu, C.-S., Wu, T.-S., Chan, T.-S., Suen, N.-T., Lee, J.-F., and Chen, H.M. (2023). In situ X-ray spectroscopies beyond conventional X-ray absorption spectroscopy on deciphering dynamic configuration of electrocatalysts. *Nat. Commun.* *14*, 6576.
53. Yang, Y., Louisia, S., Yu, S., Jin, J., Roh, I., Chen, C., Fonseca Guzman, M.V., Feijóo, J., Chen, P.-C., Wang, H., et al. (2023). Operando studies reveal active Cu nanograins for CO₂ electroreduction. *Nature* *614*, 262–269.
54. Feijóo, J., Yang, Y., Fonseca Guzman, M.V., Vargas, A., Chen, C., Pollock, C.J., and Yang, P. (2023). Operando high-energy-resolution X-ray spectroscopy of evolving Cu nanoparticle electrocatalysts for CO₂ reduction. *J. Am. Chem. Soc.* *145*, 20208–20213.
55. Stephens, I.E.L., Chan, K., Bagger, A., Boettcher, S.W., Bonin, J., Boutin, E., Buckley, A.K., Buonsanti, R., Cave, E.R., Chang, X., et al. (2022). 2022 roadmap on low temperature electrochemical CO₂ reduction. *J. Phys. Energy* *4*, 042003.
56. Clark, E.L., Resasco, J., Landers, A., Lin, J., Chung, L.-T., Walton, A., Hahn, C., Jaramillo, T.F., and Bell, A.T. (2018). Standards and protocols for data acquisition and reporting for studies of the electrochemical reduction of carbon dioxide. *ACS Catal.* *8*, 6560–6570.
57. Ozden, A., García de Arquer, F.P., Huang, J.E., Wicks, J., Sisler, J., Miao, R.K., O'Brien, C.P., Lee, G., Wang, X., Ip, A.H., et al. (2022). Carbon-efficient carbon dioxide electrolyzers. *Nat. Sustain.* *5*, 563–573.
58. Huang, J.E., Li, F., Ozden, A., Sedighian Rasouli, A., García de Arquer, F.P., Liu, S., Zhang, S., Luo, M., Wang, X., Lum, Y., et al. (2021). CO₂ electrolysis to multicarbon products in strong acid. *Science* *372*, 1074–1078.
59. Xie, Y., Ou, P., Wang, X., Xu, Z., Li, Y.C., Wang, Z., Huang, J.E., Wicks, J., McCallum, C., Wang, N., et al. (2022). High carbon utilization in CO₂ reduction to multi-carbon products in acidic media. *Nat. Catal.* *5*, 564–570.
60. Hauch, A., Küngas, R., Blennow, P., Hansen, A.B., Hansen, J.B., Mathiesen, B.V., and Mogensen, M.B. (2020). Recent advances in solid oxide cell technology for electrolysis. *Science* *370*, eaba6118.
61. Ozden, A., Wang, Y., Li, F., Luo, M., Sisler, J., Thevenon, A., Rosas-Hernández, A., Burdyny, T., Lum, Y., Yadegari, H., et al. (2021). Cascade CO₂ electroreduction enables efficient carbonate-free production of ethylene. *Joule* *5*, 706–719.
62. Lee, G., Li, Y.C., Kim, J.-Y., Peng, T., Nam, D.-H., Sedighian Rasouli, A., Li, F., Luo, M., Ip, A.H., Joo, Y.-C., and Sargent, E.H. (2020). Electrochemical upgrade of CO₂ from amine capture solution. *Nat. Energy* *6*, 46–53.
63. Sullivan, I., Goryachev, A., Digdaya, I.A., Li, X., Atwater, H.A., Vermaas, D.A., and Xiang, C. (2021). Coupling electrochemical CO₂ conversion with CO₂ capture. *Nat. Catal.* *4*, 952–958.