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Advancing electrocatalytic CO₂ reduction: key strategies for scaling up to industrial applications

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Electrocatalytic CO₂ reduction (eCO₂RR) to high value-added C₂₊ products offers a highly promising pathway toward carbon neutrality and sustainable energy storage. However, the limited activity of current catalysts and the suboptimal configuration of reaction systems hinder the achievement of high C₂₊ selectivity and long-term operational stability, falling short of industrial application requirements. In this review, we take a unique perspective to examine recent advances in the functional design of catalysts and the optimization of reactor systems. We highlight that rational catalyst design can enhance C₂₊ product selectivity, while optimization of reactor components can improve system stability. The integration of innovative technologies with system-level optimization holds great potential to advance the scalability and economic feasibility of eCO₂RR. This review bridges the gap between fundamental research and industrial application of eCO₂RR, offering critical insights to guide its development as a practical and scalable technology.

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1. Introduction

Over the past few decades, rising CO₂ emissions from fossil fuel combustion have posed potential threats to the global climate, such as ocean acidification, extreme weather events, and droughts.^{1,2} High concentrations of CO₂ can also lead to health risks and water security challenges.³ The rapid increase in CO₂ emissions has prompted scientists and governments to collaborate on achieving net-zero emissions and developing efficient CO₂ conversion technologies. eCO₂RR into highly value-added chemicals and fuels using renewable energy is a promising method to reduce carbon emissions and support the development of a sustainable society.^{4–7}

A typical CO₂ electrolyzer consists of a cathode chamber and an anode chamber separated by an ion exchange membrane. The eCO₂RR occurs at the cathode, while the oxygen evolution reaction (OER) usually occurs at the anode (Fig. 1).⁸ CO₂, being a fully oxidized and thermodynamically stable molecule, poses several significant challenges for electrochemical conversion. Firstly, eCO₂RR is a thermodynamically uphill reaction with a high activation barrier, necessitating a sufficient overpotential to drive the reaction and make CO₂ conversion feasible.⁹ Over 16 products have been reported from eCO₂RR, such as carbon monoxide, methane, methanol, formate, ethylene, ethanol, acetate, and *n*-propanol.^{10–13}

Secondly, eCO₂RR involves multiple electron/proton transfer steps, with electrons and protons supplied by water.¹⁴ This proton-assisted process involves various intermediates and products, complicating the control of product selectivity.¹⁵ In aqueous electrolytes, the competing hydrogen evolution reaction (HER) can inhibit the formation of reduced products, further complicating eCO₂RR.¹⁶ Therefore, achieving effective eCO₂RR relies on the rational design of catalysts to minimize side reactions and enhance selective production of reduced products.

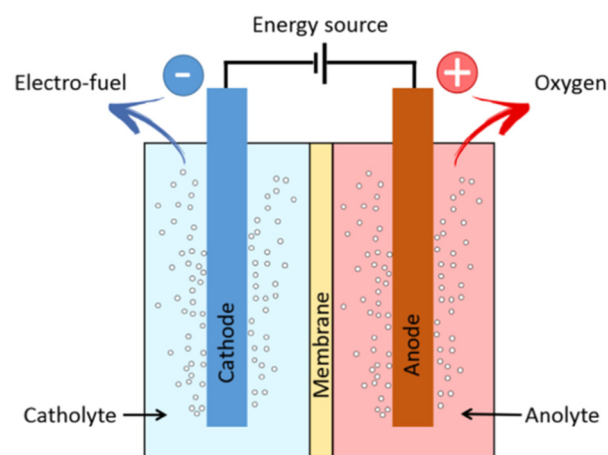


Fig. 1 A typical schematic of an ion-conducting membrane based CO₂ electrolyzer.⁸ Reprinted with permission. Copyright 2016 Elsevier.

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To date, only Cu-based catalysts have demonstrated the capability to efficiently convert CO₂ into valuable C₂₊ products *via* electrocatalysis. As a result, extensive research has focused on the rational design of Cu-based catalysts to achieve desirable activity and stability. In this review, we not only summarize the commonly adopted strategies for catalyst design, but also discuss the development of CO₂ electrolyzers ranging from laboratory-scale reactors to systems with industrial application potential. This review aims to provide an in-depth perspective on how to bridge the gap between fundamental research and scalable industrial implementation in the field of eCO₂RR.

2. Cu-based electrocatalyst

Among the state-of-the-art eCO₂RR catalysts, copper is the only metal capable of reducing CO₂ into hydrocarbons and alcohols.¹⁷ Therefore, numerous approaches, including alloying,^{18–22} oxide-derived copper (OD-Cu),^{23–25} grain boundaries (GBs),^{26,27} and morphology modification,^{28–30} have been developed to increase the capability of the Cu-based catalysts. The main technique of these approaches is to create specific ensembles with controllable selectivity towards the targeted products (*e.g.* ethylene and methane). The revealed reaction mechanism and catalytic behaviors may further shine a light for development of Cu-based electrocatalysts.

2.1. Alloy effects

Single-metal catalysts often produce only C₁ (*e.g.*, CO, HCOOH) products (*e.g.*, Au, Sn and Bi) and suffer from undesirable HER (*e.g.*, Pt and Pd), or exhibit low product selectivity due to the diverse reaction pathways of Cu.^{31–33} Consequently, many researchers have focused on alloying other metals with Cu. This approach aims to optimize the electronic structure and local coordination environment of Cu atoms, alter the adsorption strength of key intermediates, and expose new active sites, thereby enhancing the formation of multi-carbon products.^{34,35} Additionally, bimetallic catalysts can enhance CO coverage on the catalyst surface, promoting C–C coupling towards C₂₊ products (*e.g.*, C₂H₄, and C₂H₅OH).³³ Therefore, alloying strategies play a crucial role in modulating the reaction pathways of eCO₂RR.³⁶

The alloying effect on the formation mechanisms of C₁ and C₂₊ products is complex. Under severe cathodic conditions (*i.e.*, cathodic potentials > −1.1 V *vs.* reversible hydrogen electrode, RHE), CH₄ production tends to outcompete C₂H₄. This is because CH₄ formation requires a higher overpotential and faster kinetics.³⁷ In the CuAg alloy system, many studies reported CH₄ as the main reduced product. For instance, studies have shown that Ag–Cu surfaces, due to low-coordination sites, strongly bind with *CO, inhibiting CO–CO coupling and resulting in lower selectivity towards C₂H₄ (Fig. 2a and b).³⁸ Ag-modified Cu nanowires (Cu₆₈Ag₃₂) exhibit more than three times the CH₄ activity and selectivity compared to pristine Cu nanowires. *In situ* characterizations reveal that the

dynamic reoxidation/reduction-driven atomic interdiffusion of Cu sites facilitates the CuAg alloying (Fig. 2c). The induced tensile strain strengthens the binding with *CHO intermediates, promoting further reduction and suppressing undesired HER.³⁹ Furthermore, as both Cu and Ag have valence d-states, the catalytic performance of CuAg catalysts is in principle determined by their electronic structure. The interface interaction between Cu and Ag alters the surface electronic structure and tailors the adsorption strength of *CO on the catalytic surface (Fig. 2d). Consequently, *CO tends to convert into CH₄ before desorbing from the Cu surface.⁴⁰ Conversely, for the CuAg alloy system that produces C₂₊ products, the CO₂ reduction pathway follows a tandem catalysis mechanism. Ag sites are more favorable for CO production, which enriches CO at neighboring Cu sites and promotes C–C coupling towards C₂₊ products such as ethylene and ethanol.^{41,42} For example, Gewirth and co-workers reported that a CuAg alloy prepared by additive-controlled electrodeposition achieves 60% ethylene selectivity and 25% ethanol selectivity (Fig. 2e). The high selectivity for C₂₊ products results from the stabilization of the Cu₂O overlayer and optimization of CO intermediates availability at Cu sites through Ag doping in the alloy system.¹⁸ Zheng and co-workers reported that the introducing Ag facilitates electron transfer from Cu to Ag, creating electron-deficient Cu sites. This enhances the adsorption of key intermediates in the ethanol reaction pathway, such as *CH₃CHO and *CH₃CH₂O, resulting in excellent ethanol selectivity (Fig. 2f).⁴³

Additionally, the mixing modes of bimetallic catalysts influence the product distribution in eCO₂RR. Kenis and co-workers demonstrated that phase-separated PdCu catalysts achieve the highest ethylene selectivity (~50%) compared to both ordered and disordered counterparts.⁴⁴ The lower d-band center of these phase-separated catalysts, compared to Cu NPs, indicates the weaker CO intermediate binding. This suggests that geometric and structural effects play a more significant role than electronic effects in enhancing product distribution.⁴⁴ Jaramillo and colleagues reported that gold nanoparticles on polycrystalline copper foil follow a tandem catalysis mechanism, showing superior synergistic catalytic activity and selectivity compared to gold, copper, and CuAg alloys.⁴⁵ In summary, alloying strategies open new avenues for enhancing the conversion of eCO₂RR to target products, but different structures and interfaces will give different electronic states for different products selectivity.

2.2. Oxidation states

Beyond alloying strategies, modulation of the oxidation state also affects the activity and selectivity of eCO₂RR. For oxide-derived Cu (OD-Cu), the oxidation state of the metal centers is effectively maintained by residual oxygen species on the surface or subsurface of the catalyst after *in situ* reduction. These oxidized Cu species serve as active sites for eCO₂RR, facilitating C–C coupling to form C₂₊ products. For example, plasma-oxidized Cu can achieve ethylene selectivity exceeding 60%.⁴⁶ Comparative experiments with various plasma treat-



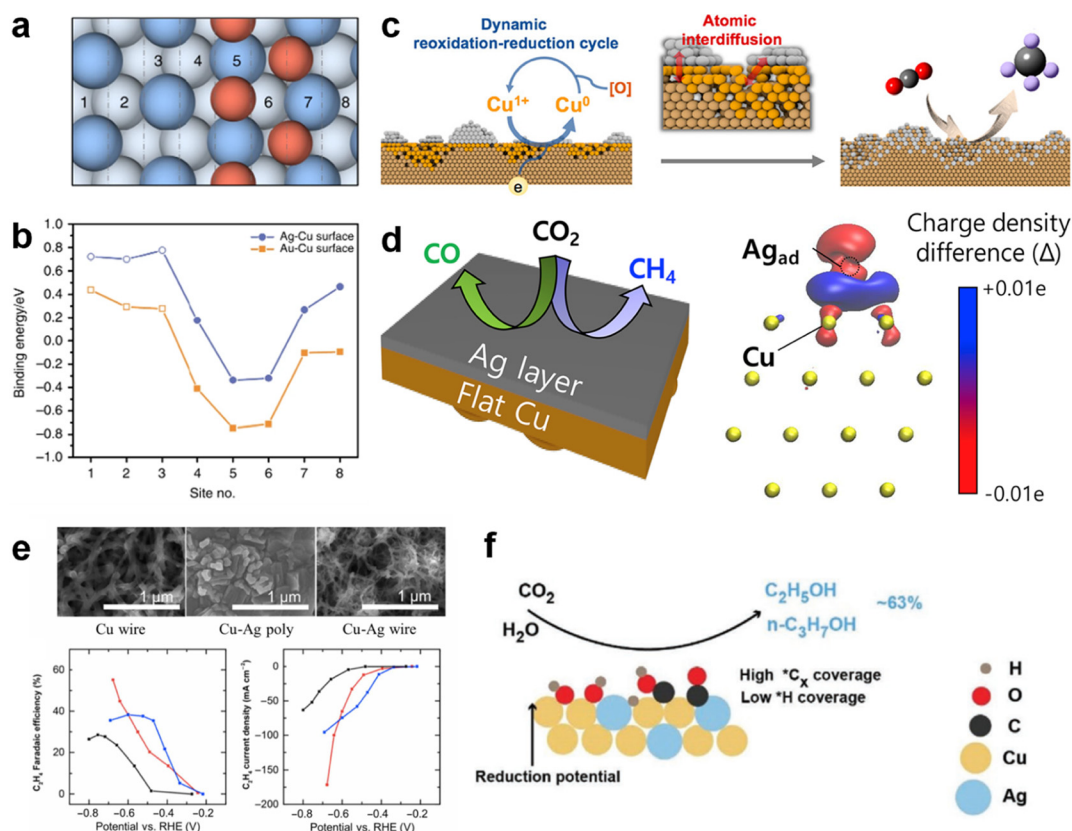


Fig. 2 Alloy effect of electrochemical CO₂ reduction. (a) Top view of the unit cell used for computational investigations (blue: top layer Ag or Au atoms; light blue: bottom layer Ag or Au atoms; orange: Cu atoms). The site numbers show the position and chemical environment of the binding sites.³⁸ Reprinted with permission. Copyright 2019 Springer Nature. (b) Energy diagram for CO adsorption on the Ag–Cu surface (blue line) and Au–Cu surface (orange line).³⁸ Reprinted with permission. Copyright 2019 Springer Nature. (c) The dynamic reoxidation/reduction-driven atomic interdiffusion processes of Cu sites.³⁹ Reprinted with permission. Copyright 2020 American Chemical Society. (d) The optimized Cu/Ag layered catalyst for eCO₂RR-to-CH₄ conversion.⁴⁰ Reprinted with permission. Copyright 2020 Elsevier. (e) The scanning electron microscopy (SEM) images and corresponding C₂H₄ FE of CuAg bimetallic electrocatalysts from additive-controlled electrodeposition.¹⁸ Reprinted with permission. Copyright 2018 American Chemical Society. (f) Illustration of the eCO₂RR process on the Cu₃Ag₁ catalyst.⁴³ Reprinted with permission. Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

ments confirm the crucial role of Cu⁺ in the conversion of eCO₂RR to C₂H₄ (Fig. 3a).⁴⁶ Sargent and colleagues used *in situ* soft X-ray absorption spectroscopy to monitor the oxidation state of copper over time under eCO₂RR conditions.⁴⁷ The sol-gel materials effectively slow the electrochemical reduction of oxidized copper species, stabilizing Cu⁺ species under cathodic potentials (Fig. 3b).⁴⁷ The catalyst achieves an ethylene partial current density of 160 mA cm⁻² and an ethylene-to-methane ratio of 200 (Fig. 3c). However, after one hour of continuous operation, only 23% of Cu⁺ species can be effectively preserved (Fig. 3b). Theoretical analyses have further explained why OD-Cu leads to the production of ethylene and ethanol. Research indicates that 4-(6)-coordinated Cu adatoms and Cu₃^{δ+}O₃ leads to tethering CO₂, while metastable near-surface oxygen atoms in fcc-(111) or (100)-like Cu matrix promote C–C coupling, thereby enhancing the formation of C₂₊ products.⁴⁸ Nevertheless, the poor stability of oxidized Cu^{δ+} species under high current densities poses significant challenges for the widespread application of OD-Cu. To enhance the stability of

oxidized Cu^{δ+} species, Fang and colleagues developed a one-step surface coordination method to synthesize ultrastable and hydrophobic Cu^{δ+}, achieving a C₂ faradaic efficiency (FE) of 90.6% at a partial current density of 453.3 mA cm⁻² (Fig. 3d and e). Spectroscopic and computational results indicate that Cu(II) carboxylate coordination species on the catalyst surface can effectively stabilize active Cu^{δ+} species.⁴⁹ Additionally, heteroatom doping can also stabilize Cu^{δ+} species. For example, the average oxidation state of copper can range from +0.25 to +0.78 by varying the boron doping content.⁵⁰ PDOS analysis shows that electron transfer from Cu to boron creates a negatively charged Cu site, increasing the formation energy of *CHO while lowering the reaction barrier for *CO dimerization (Fig. 3f). These findings provide new insights into enhancing the stability of active Cu^{δ+} species during eCO₂RR.

However, *in situ* reduction of OD-Cu can also cause morphological and structural changes, making the identification of its true active sites a subject of ongoing debate.^{51–53} For instance, Cu⁺, mixed oxidation states (Cu^{δ+}) of Cu (*e.g.*, Cu²⁺



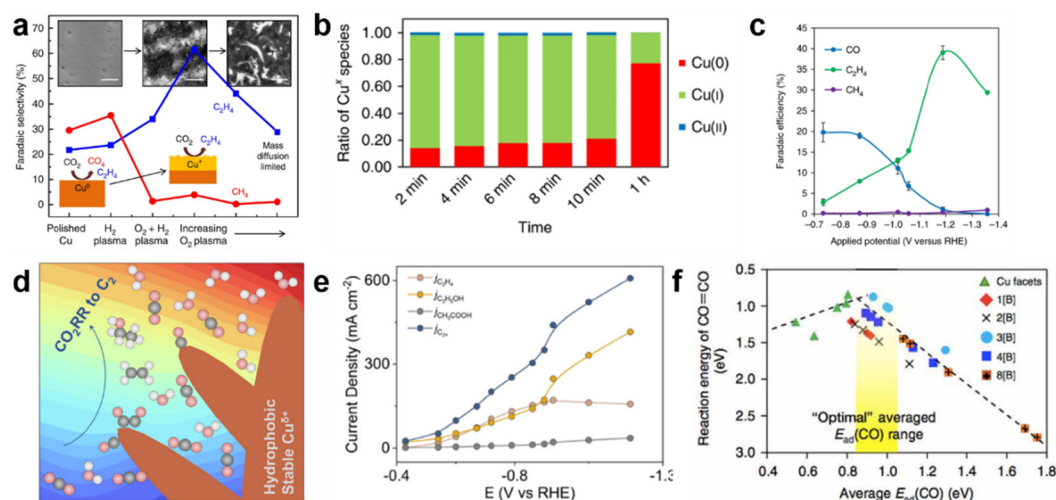


Fig. 3 Oxidation states manipulation for eCO₂RR. (a) Summary of the C₂H₄ selectivity of different plasma-activated Cu electrocatalysts.⁴⁶ Reprinted with permission. Copyright 2016 Springer Nature. (b) Ratio of Cu oxidation states relative to the reaction time at -1.2 V vs. RHE for electro-redeposited Cu.⁴⁷ Reprinted with permission. Copyright 2018 Springer Nature. (c) Reduced products of eCO₂RR on electro-redeposited Cu.⁴⁷ Reprinted with permission. Copyright 2018 Springer Nature. (d) Illustration of the eCO₂RR process on the ultrastable and hydrophobic Cu^{δ+} catalyst.⁴⁹ Reprinted with permission. Copyright 2023 American Chemical Society. (e) Current density distribution of the ultrastable and hydrophobic Cu^{δ+} catalyst.⁴⁹ Reprinted with permission. Copyright 2023 American Chemical Society. (f) Boron doping was able to change the average absorption energy of CO in the copper surface and lower the CO-CO dimerization energy.⁵⁰ Reprinted with permission. Copyright 2018 Springer Nature.

and Cu⁺) or their interface have been identified as the active sites for promoting CO-CO coupling in OD-Cu during eCO₂RR.^{46,54} Conversely, another study suggests that metallic Cu is the active site in bulk Cu catalysts, attributing this to the instability of subsurface oxides under negative cathodic potentials.⁵⁵ Additionally, the active site of Cu nanoparticles (NPs) is reported to be metallic Cu nanograin, as investigated through the structural dynamics during the life cycle of Cu NPs using liquid cell scanning transmission electron microscopy.⁵⁶ Therefore, the real active sites and structural evolution of OD-Cu under eCO₂RR reaction conditions remain unclear.

2.3. Grain boundaries

Grain boundaries (GBs), as structural defects, can create significant structural perturbations in their vicinity, inducing dislocations in the GBs region and leading to lattice strains (either compressive or tensile strains). In other words, GBs can generate high-energy surfaces through stabilized dislocations, which are thermodynamically favorable for catalysis.⁵⁷ To enhance the selectivity for multi-carbon products, various strategies have been developed to engineer GBs structures. These structures can adjust the adsorption energy of key intermediates on the catalyst surface, thus enhancing product selectivity.^{58,59} For example, Chen *et al.* used PVP as an additive to control the growth rate of Cu during electrodeposition, resulting in Cu with abundant GBs (Fig. 4a). This catalyst achieves 70% selectivity for ethylene and ethanol across a wide potential range.²⁶ Han and colleagues found that the oxide/hydroxide crystals in HQ-Cu (containing Cu, Cu₂O, CuO) and AN-Cu (containing Cu, Cu(OH)₂) fragment into nanosized irregular Cu grains under applied cathodic potentials (Fig. 4b).

This fragmentation results from oxidation-reduction cycling, which not only creates a complex GBs network but also exposes various high-index facets. These structural features facilitate C-C coupling, thereby enhancing the selectivity for C₂₊ products.²³ Huang *et al.* prepared La₂CuO₄ nanobamboo perovskites with abundant twin boundaries, achieving a 60% faradaic efficiency (FE) for ethylene. The high ethylene selectivity is attributed to the active (113) surface with inherent strain effects (Fig. 4c).²⁷ Therefore, designing and constructing unique GBs structures is highly beneficial for eCO₂RR reactions.

In complex GBs systems, single strategy often fails to meet practical needs in catalyst design. Combining multiple structural defects as active sites is often necessary to construct complex GBs structures, where various structural characteristics synergistically enhance the activity and stability of catalysts.^{47,61,62} For OD-Cu, the active Cu⁺ species inevitably undergoes electrochemical reduction to bulk metallic Cu at high current densities,⁶³ leading to poor selectivity for C₂₊ products. This presents a significant challenge for the effective utilization of OD-Cu. However, research indicates that abundant nanograin boundaries can enhance the stability of catalyst morphology and Cu⁰/Cu⁺ interfaces under high polarization and high current densities, preventing catalyst reconstruction and improving catalytic stability (Fig. 4d).⁶⁰ Moreover, nanograin boundaries and Cu⁰/Cu⁺ interfaces can increase *CO adsorption strength, promoting CO-CO coupling toward C₂₊ products.^{56,64} Therefore, constructing intricate structures assemblies with abundant nanograin boundaries and Cu⁰/Cu⁺ interfaces in Cu-based catalysts holds promise for achieving efficient eCO₂RR to C₂₊ products. Additionally, oxygen vacancies, a well-known defect, are widely employed to tailor the properties of catalysts.^{2,65,66} For example, due to their

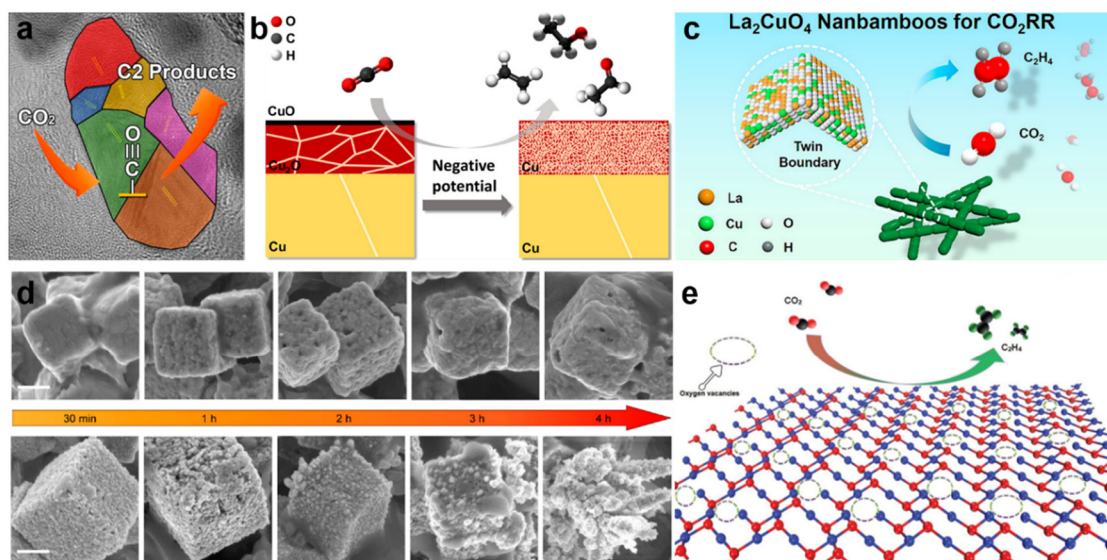


Fig. 4 Grain boundaries for eCO₂RR. (a) Illustration of the eCO₂RR process on the grain boundaries-rich Cu catalyst.²⁶ Reprinted with permission. Copyright 2020 American Chemical Society. (b) The fragmentation process of oxide/hydroxide crystals into nanosized irregular Cu grains under the applied negative potentials.²³ Reprinted with permission. Copyright 2020 American Chemical Society. (c) The La₂CuO₄ nanobamboo (La₂CuO₄ NBs) perovskite with rich twin boundaries showing a high FE of 60% toward ethylene.²⁷ Reprinted with permission. Copyright 2021 American Chemical Society. (d) SEM images of dynamic structure evolution for Cu₂O(CO) and Cu₂O electrocatalysts during eCO₂RR.⁶⁰ Reprinted with permission. Copyright 2023 American Chemical Society. (e) Schematic of electrocatalytic reduction of CO₂ on Vo-rich CuO_x-Vo surface to C₂H₄.⁶¹ Reprinted with permission. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

weakly bounded electrons, oxygen vacancies serve as excellent Lewis base sites to enhance the binding affinities of key intermediates (such as *CO and *COH), thereby promoting the production of C₂ (Fig. 4e).⁶¹ Moreover, a higher concentration of oxygen vacancies near active sites is favorable for activating CO₂ molecules, lowering the reaction barrier for target products.⁶⁷ Therefore, integrating oxygen vacancies with grain boundaries and interface engineering is likely to modulate the surface electronic structure and concentration of active sites, thus accelerating reaction kinetics. However, effectively constructing oxygen vacancies and interface structures on catalyst surface remains highly challenging. Gaining a deeper understanding of the synergistic interactions between oxygen vacancies and interface structures will offer valuable guidance for the rational design of catalysts.

2.4. Morphology modification

The morphology of Cu nanostructures, such as size, shape, and crystal facets, significantly impacts the selectivity of eCO₂RR towards multi-carbon products.^{28,68,69} The Cu(100) facet favors ethylene production, whereas the Cu(111) facet promotes methane production.⁶⁹ Buonsanti *et al.* synthesized Cu nanocrystals with varying sizes and shapes using a consistent colloidal method. The results demonstrated that cubic Cu nanocrystals exhibit higher ethylene selectivity than spherical ones, primarily due to the dominant presence of the Cu(100) facet.²⁸ Among the cubic Cu nanocrystals, those with a 44 nm edge length exhibit the highest eCO₂RR activity and ethylene selectivity compared to cubes with edge lengths of 24 nm and 63 nm, revealing a non-monotonic size-dependent selectivity in cubic

Cu nanocrystals (Fig. 5a).²⁸ Mild plasma treatment introduces oxygen/chlorine ions into Cu nanocubes, the surface and sub-surface oxygen species could influence the binding strength of CO on the surface, promoting the formation of multi-carbon products such as ethylene, ethanol, and isopropanol.⁷⁰ Song *et al.* reported that branched CuO nanoparticles achieve over 70% ethylene selectivity after activation. Compared to the cubic morphology, the initial branched CuO structure forms highly active interfaces and junctions in-between during activation, resulting in a large surface area and high local pH (Fig. 5b).⁷¹ Yang and colleagues demonstrated that densely packed Cu NPs, after undergoing structural rearrangement during the eCO₂RR reaction, transform into a mixture of highly active cubic particles and smaller nanoparticles. At lower overpotentials (−0.53 V vs. RHE), selective formation of C₂–C₃ products can be achieved.⁷²

Additionally, when high-curvature structures such as nanoneedles and nanodendrites are involved, they significantly impacts the catalyst's structure and catalytic mechanism.⁷⁴ For instance, nanoneedles can promote the nucleation of smaller gas bubble,⁷⁵ facilitating field-induced reactant concentration.^{76,77} The high local electric field can cause the accumulation of charged cations, stabilizing reaction intermediates and enhancing eCO₂RR activity.⁷⁸ Edward *et al.* reported that the morphology of Cu derived from a sol-gel is controlled by electro-redeposition. Depending on the applied potentials, different structural morphologies, including nanoclusters, nanoneedles, nanowhiskers, and nanodendrites, appear sequentially (Fig. 5c). This growth results from the simultaneous dissolution and redeposition process of Cu ions from the bulk phase.⁴⁷ Inspired by gas-trapping phenomenon observed in spiders, hier-



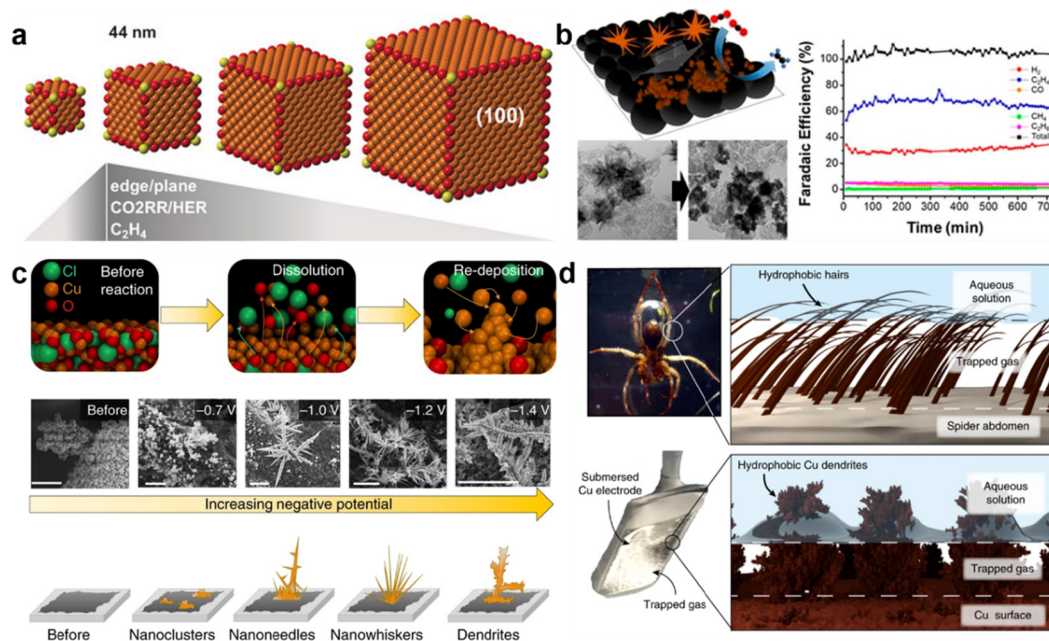


Fig. 5 Morphology effect for eCO₂RR. (a) Schematic of a non-monotonic size-dependence of the selectivity in cube-shaped copper nanocrystals.²⁸ Reprinted with permission. Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Schematic illustrating the transformation process of branched CuO NPs on conductive carbon materials during activation.⁷¹ Reprinted with permission. Copyright 2019 American Chemical Society. (c) Schematic of the electro-growth process, whereby simultaneous dissolution and redeposition of Cu results in structured deposits.⁴⁷ Reprinted with permission. Copyright 2018 Springer Nature. (d) The plastron effect: the use of a hydrophobic surface to trap a layer of gas between the solution–solid interface. This is illustrated on a diving bell spider for subaquatic breathing and on a hydrophobic dendritic Cu surface for aqueous CO₂ reduction.⁷³ Reprinted with permission. Copyright 2019 Springer Nature.

archically structured Cu dendrites undergo surface hydrophobic treatment with 1-octadecanethiol. The treated electrodes can capture CO₂ gas at the electrolyte-electrode interface, forming a triple-phase boundary (Fig. 5d), which effectively suppresses HER and promotes eCO₂RR reactions.⁷³ In summary, the morphology effect offers a promising paradigm for the design and development of Cu-based electrocatalysts.

3. The CO₂ electrolyzer

There are three main configurations for CO₂ electrolyzers: H-cells, flow cell, and membrane electrode assembly (MEA).

3.1. H-cells

Most initial performance evaluations of eCO₂RR and catalyst screening are typically conducted using an H-cell. This system involves three electrodes: the working electrode and reference electrode are placed in the cathode chamber, while the counter electrode is fixed in the anode chamber. The cathode and anode chambers are separated by an ion-exchange membrane (Fig. 6).^{79,80} This simple setup facilitates rapid catalyst screening. CO₂ is bubbled into the cathode chamber to maintain a CO₂-saturated electrolyte. Although some eCO₂RR catalysts have shown excellent performance in H-cells (Table 1), their practical application is constrained by several factors. The CO₂ concentration near the catalyst is limited by its solu-

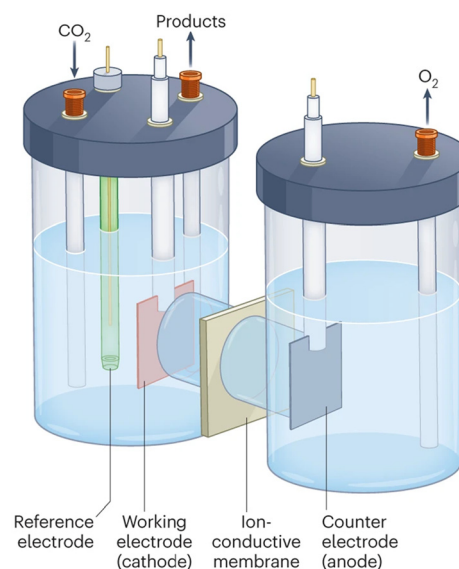


Fig. 6 Schematic illustration of three-electrode H-cells.⁸⁰ Reprinted with permission. Copyright 2023 Springer Nature.

bility (approximately 34 mM at room temperature), resulting in mass transport constraints, which cap the maximum operating current at below 100 mA cm⁻².^{81,82} eCO₂RR performance testing is typically conducted under neutral conditions to



Table 1 The reported performance of eCO₂RR in different CO₂ electrolyzer

Electrolyzer	Catalyst	Electrolyte	V (vs. RHE/full-cell voltage)	Total current density (mA cm ⁻²)	Stability (h)	Main product (FE)	Ref.
H-cell	Cu NPs	0.1 M KHCO ₃	1.7 vs. Ag/AgCl	7.5	—	C ₂ H ₄ (92.8%)	99
	Carbon-supported Cu	0.1 M KHCO ₃	−0.6 V _{RHE}	1.5	16	Ethanol (91%)	100
	Cu NPs	0.1 M KHCO ₃	−0.81 V _{RHE}	12.8	—	<i>n</i> -Propanol (5.9%)	72
	Nitrogen-doped nanodiamond	0.5 M NaHCO ₃	−0.8 to −0.1 V _{RHE}	~7	3	Acetate (77%)	101
	Sn coupled with defective CuO	[Bmim]BF ₄ /H ₂ O	−2.0 V vs. Ag/Ag ⁺	67	36	Methanol (88.6%)	102
	CuAg	0.1 M KHCO ₃	−1.1 V _{RHE}	40	17	CH ₄ (50%)	22
	Ni/Fe-NC	0.5 M KHCO ₃	−0.7 V _{RHE}	9.5	>30	CO (98%)	103
	3D core-shell porous-structured Cu@Sn	0.5 M KHCO ₃	−0.93 V _{RHE}	16.52	15	Formate (100%)	104
	DVL-Cu@GDL	0.5 M KCl	—	150	55	C ₂ H ₄ (74%)	105
	Graphite/carbon NPs/Cu	7 M KOH	0.55 V _{RHE}	55–70	150	C ₂ H ₄ (70%)	93
Flow cell	Cu/Cu ₂ O	1 M KOH	−0.66 V _{RHE}	200	50	Ethanol (56%)	106
	CuAl ₂ O ₄ /CuO	1 M KOH	—	200	150	Ethanol (41%)	107
	<i>b</i> -Cu ₂ O/Cu	1 M KOH	−1.3 V _{RHE}	1000	16	<i>n</i> -Propanol (7.1%)	108
	Hg-CoTPP with N-doped graphene	1 M KOH	−0.8 V _{RHE}	420	360	CO (~100%)	109
	Grain boundary-enriched bismuth	1 M KHCO ₃	−0.77 V _{RHE}	450	—	Formate (97%)	110
	CuGa ₂	1 M KOH	−0.3 V _{RHE}	21.4	24	Methanol (78%)	111
	Cu ₁ Sm-O _x	1 M KOH	−1.35 V _{RHE}	500	24	CH ₄ (65%)	112
	CuGaO ₂ nanosheet	1 M KOH	−2 V _{RHE}	1000	5	CH ₄ (68–55%)	113
	F-Cu	0.1 M KHCO ₃	−3.7	316	35	C ₂ H ₄ (55.6%)	114
	CuO nanoplate	0.5 M KHCO ₃	−3.2	200	—	C ₂ H ₄ (80%)	105
MEA	Cu ₃ Sn	1 M KOH	−3	900	48	Ethanol (40%)	115
	Copper(II) phthalocyanine	0.05 M KHCO ₃	−4.2	190	110	CH ₄ (56%)	116
	Cu nanoparticles supported on N-doped carbon	0.1 M KHCO ₃	−4	230	50	CH ₄ (60%)	117
	Ni-NCB	0.1 M KHCO ₃	−2.8V	8300	6	CO (90%)	118
	Porous Ag	0.1 M KHCO ₃	—	500	25	CO (74%)	119

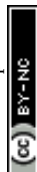
avoid side reactions, such as carbonate formation in alkaline electrolytes and HER in acidic electrolytes.⁸⁰ However, the eCO₂RR reaction and pathways are highly dependent on the local reaction microenvironment, which influences the reaction energetics on the catalyst surface.^{79,83} Consequently, catalysts developed in H-cells may perform significantly differently under industrial conditions due to variations in reaction microenvironments. Furthermore, impurities deposition on the catalyst surface can affect the eCO₂RR reaction pathways, leading to catalyst deactivation.^{84,85} Therefore, alternative testing systems are needed to evaluate the catalyst performance under industrially relevant eCO₂RR conditions.

3.2. Flow cells

To address the challenges of low CO₂ solubility, low current density, and mass transport limitations in H-cells, gas diffusion electrodes (GDEs) have been developed. GDEs significantly shorten the diffusion path of CO₂ to the electrode surface (approximately 50 nm), enhancing mass transport efficiency and enabling the industrial application of eCO₂RR.^{83,86} Unlike H-cells, flow cells can effectively utilize alkaline electrolytes, which are unsuitable for H-cells. GDEs allow separation of the CO₂ flow field from the liquid electrolytes, maintaining a high local pH on the catalyst surface, which inhibits HER and pro-

motes C–C coupling.^{87–89} This configuration allows for high product selectivity at high current densities, positioning flow cells as a potential replacement for H-cells in eCO₂RR performance testing. In the flow cell configuration (Fig. 7a), the catholyte and anolyte circulate through the cathode and anode chambers, respectively. The cathode and anode chambers are separated by an ion exchange membrane. Gaseous CO₂ is continuously supplied to the cathode catalyst.^{90,91}

Current research on eCO₂RR catalysts has transitioned from H-cells to flow cells. The complexity of flow cell configurations has driven the evolution of catalyst material design into a multifaceted approach, encompassing the catalyst, the local microenvironment, and the overall system (Table 1). The catholyte can regulate the local microenvironment on the catalyst surface, optimizing CO₂ conversion efficiency (Fig. 7b). For example, Dinh *et al.* showed that a high concentration of KOH electrolyte can significantly reduce the onset potential for eCO₂RR.⁹³ Chen and colleagues reported that Cu-polyamine in a strong alkaline electrolyte (10 M KOH) can achieve an 87% FE for ethylene.⁸⁷ Elevated pH levels can reduce H coverage on the catalyst surface, thus inhibiting HER. This enhanced catalytic activity can, in turn, lower the cell voltage, thereby improving energy efficiency (Fig. 7c). Although strong alkaline electrolytes can accelerate the formation of multi-carbon products,⁹³



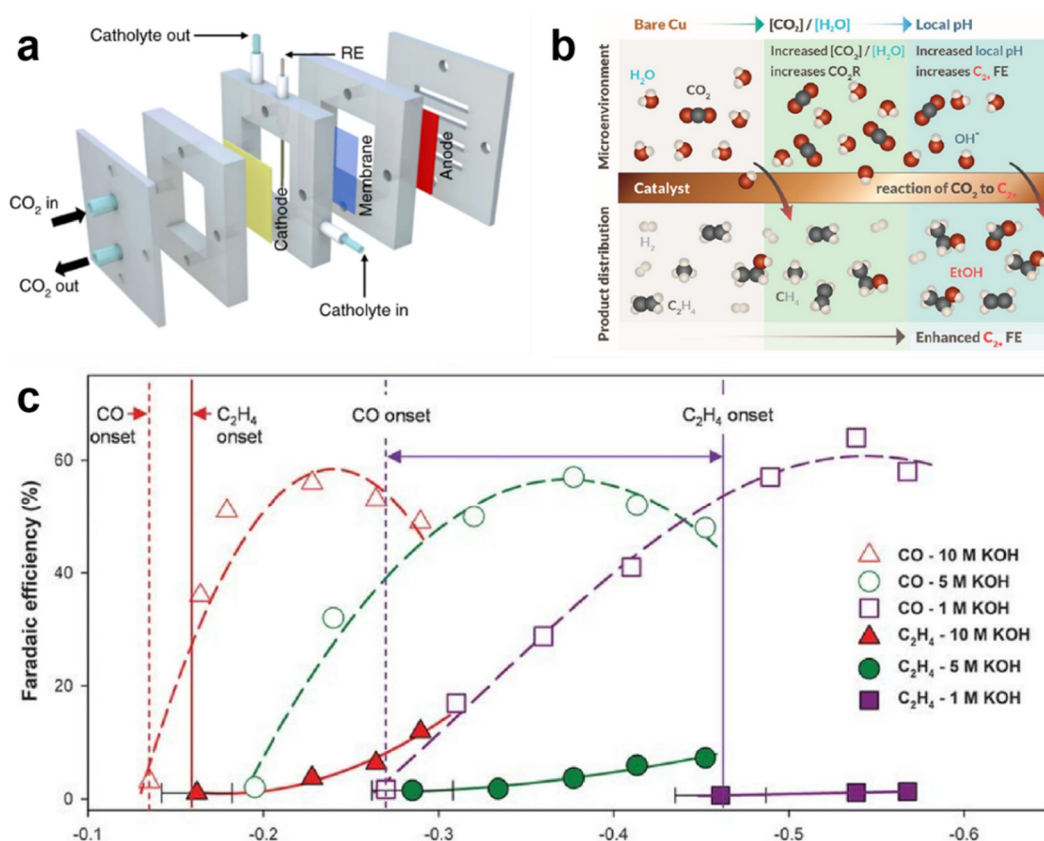


Fig. 7 (a) Schematic illustration of flow cells.⁹¹ Reprinted with permission. Copyright 2019 Springer Nature. (b) Schematic illustration of the local microenvironment and its effect on eCO₂RR selectivity.⁹² Reprinted with permission. Copyright 2022 American Chemical Society. (c) C₂H₄ and CO FE showing the reduction of C₂H₄ onset potential with increasing KOH concentrations.⁹³ Reprinted with permission. Copyright 2018 The American Association for the Advancement of Science.

they also lead to low CO₂ utilization efficiency and irreversible electrolyte acidification,^{94,95} creating challenges for optimal performance. In acidic electrolytes, the FE of HER side reaction is typically 20% or higher, making it energy-intensive and inhibitory to the eCO₂RR reaction.⁹⁶ To address these issues, neutral electrolytes like potassium bicarbonate have been employed, though product selectivity of eCO₂RR in neutral electrolyte is lower than in alkaline environments.^{97,98} Overall, the flow cell configurations overcome the limitations of H-cells, facilitating the large-scale application of eCO₂RR.

3.3. MEA electrolyzer

In a flow cell, liquid electrolytes in the cathode and anode chambers create high resistance, lowering the overall energy efficiency of the system. To tackle this issue, a practical approach is to remove the liquid electrolyte between the electrodes, leading to the development of the membrane electrode assembly (MEA).¹²⁰ An MEA operates as a dual-electrode zero-gap cell, with a polymer electrolyte membrane sandwiched between the anode and cathode. The electrolyte circulates through the porous anode without the need for a reference electrode. Humidified CO₂ is continuously supplied to the cathode's GDE (Fig. 8a). Compared to flow cells, the MEA configuration leverages the gas diffusion electrode (GDE) of a flow cell, mini-

mizing the electrolyte usage by enabling direct contact between the catalyst layer and the ion exchange membrane. This design mitigates cell resistance, boosts energy efficiency, and enhances cell stability, making it more feasible for practical applications.⁹⁵

The formation of multi-carbon products in an MEA electrolyzer has yet to be extensively studied (Table 1). Gabardo *et al.* demonstrate the potential for multi-carbon product formation in an MEA reactor by sputtering Cu onto a porous PTFE membrane as the catalyst and adjusting the reaction temperature to 40 °C, achieving 30% ethylene selectivity.¹²¹ Gong *et al.* reported that oxygen-rich ultrathin CuO nanoplate arrays could achieve 80% ethylene selectivity at a current density of 200 mA cm⁻² (Fig. 8b). Compact evaporated Cu films and stable nanostructures effectively prevent GDL flooding during eCO₂RR testing, enhancing the long-term stability of the catalyst.¹⁰⁵ Zheng *et al.* reported that a low-entropy Cu₃Sn catalyst maintains stability for over 48 h at industrial-scale current densities, with 40% ethanol selectivity (Fig. 8c).¹¹⁵ Gu *et al.* constructed a defect-rich surface by electrodepositing Cu in a CO-rich atmosphere, significantly promoting CO₂ conversion to ethanol, achieving 70% FE for C₂₊ alcohols at a partial current density of 100 mA cm⁻². In a 30 h stability test, the MEA electrolyzer produces 500 mg of C₂₊ alcohols per cm² of catalyst (Fig. 8d).¹²² In summary, MEA electrolyzers may offer better

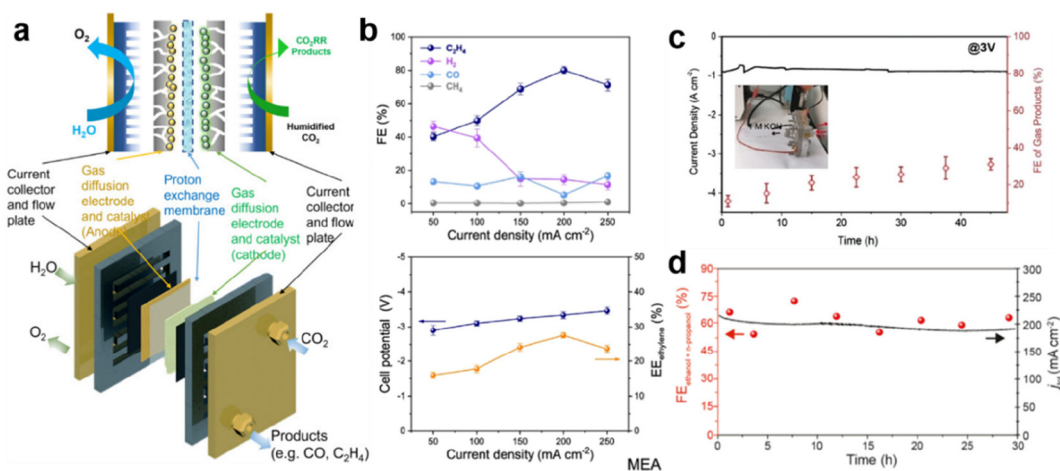


Fig. 8 (a) Schematic of membrane-electrode assembly for eCO₂RR.¹²⁰ Reprinted with permission. Copyright 2022 Elsevier. (b) Gas product FEs, cell potential and energy efficiency for C₂H₄ of the DVL-Cu@GDL catalyst in an MEA electrolyzer.¹⁰⁵ Reprinted with permission. Copyright 2022 Springer Nature. (c) The long-term stability test of Cu₃Sn in 1 M KOH at 3 V.¹¹⁵ Reprinted with permission. Copyright 2021 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) eCO₂RR to ethanol using Cu-DS catalyst in a MEA system during 30 h of electrolysis under a full-cell voltage of 3.5 V.¹²² Reprinted with permission. Copyright 2021 Elsevier.

stability than flow cells and H-cells, making them more attractive for commercial applications.

4. Mechanistic insights

In-depth investigation of the reaction mechanism is crucial for the rational design of Cu-based electrocatalysts. By elucidating the nature and dynamic evolution of active sites during the eCO₂RR reaction, mechanistic insights can provide a theoretical foundation for the functional design of catalysts, thereby avoiding inefficient and blind screening processes and enabling the precise development of high-performance catalytic materials. Currently, most mechanistic studies of eCO₂RR rely on *ex situ* characterization methods.^{25,41,123} However, under practical eCO₂RR conditions, the structure and active sites of catalysts can undergo significant dynamic transformations.¹²⁴ For instance, in Cu-based catalysts, it has been traditionally believed that oxidative Cu^{δ+} species are inevitably reduced to metallic Cu under cathodic potentials, making metallic Cu widely regarded as the dominant active phase.¹¹⁴ Nevertheless, recent *in situ* Raman spectra studies have revealed the presence of oxidative Cu^{δ+} species, such as Cu₂O and Cu-OH species, even under strongly reducing conditions.^{114,124} These species can originate not only from the precursor but also form dynamically on the surface of metallic Cu NPs during eCO₂RR conditions. Moreover, theoretical calculations have shown that oxidative Cu^{δ+} species can promote C-C coupling more effectively, thus favoring the formation of C₂₊ products.^{47,124} This suggests that metallic Cu is not the sole active site, and oxidative Cu^{δ+} species may play a more critical role under practical eCO₂RR conditions.

Most mechanistic studies to date have been conducted at low current densities, whereas industrial eCO₂RR systems typically operate at high current densities (>200 mA cm⁻²).^{74,94}

Under such industrially relevant conditions, the stability and behavior of oxidative Cu^{δ+} species remain ambiguous. On one hand, conventional *in situ* electrochemical cells often suffer from high internal resistance, limiting their capacity to sustain high current operation.¹¹⁴ On the other hand, extensive gas evolution at high current densities interferes with signal acquisition, preventing accurate detection of transient active species. Furthermore, these cells do not realistically simulate the operating environment of practical CO₂ electrolyzers. Changes in any component, such as electrolyte composition, catalyst layer structure, membrane type, or gas-liquid-solid triple-phase boundaries, can significantly affect eCO₂RR performance, complicating mechanistic interpretation.¹²⁵ To better mimic industrial conditions, it is imperative to develop *in situ*-compatible electrolyzer systems capable of operating at high current densities. Given that MEA-based electrolyzers are widely used in practical applications, *in situ* characterizations in MEA reactors have emerged as a promising platform for studying the dynamic evolution of catalysts under realistic operating conditions. However, due to the close contact between the catalyst layer and the membrane, Raman spectroscopy often fails to capture useful signals. In this context, *in situ* X-ray absorption spectroscopy (XAS), with its element-specific sensitivity and ability to resolve atomic-scale structural changes, presents a powerful alternative. XAS enables real-time tracking of catalyst structural evolution under operational conditions, paving the way for deeper mechanistic understanding and the targeted design of advanced eCO₂RR catalysts.

5. System optimization in eCO₂RR

5.1. Electrolyte engineering

The choice of electrolyte plays a fundamental role in dictating CO₂ solubility, proton availability, and the stabilization of key



reaction intermediates. Optimizing the electrolyte composition is crucial for achieving high faradaic efficiency (FE) towards C_{2+} products while minimizing side reactions such as the HER. Electrolyte pH strongly influences the reaction pathway of CO_2 electroreduction. A neutral or slightly alkaline pH is often preferred because it maintains sufficient CO_2 availability while suppressing excessive HER. For example, potassium bicarbonate ($KHCO_3$) is a commonly used neutral electrolyte that ensures moderate proton availability and stable catalyst performance. Conversely, strongly alkaline electrolytes (e.g., KOH) accelerate CO_2 depletion near the electrode due to rapid carbonate formation, which reduces eCO_2RR efficiency.³⁷ Bipolar membranes (BPMs) have been extensively studied as a means to decouple the pH at the cathode and anode, thereby optimizing reaction conditions for both CO_2 reduction and oxygen evolution. BPMs generate local proton gradients, which can facilitate selective eCO_2RR to C_{2+} products by stabilizing key intermediates such as CO dimer species. Studies have shown that BPM-integrated systems can significantly enhance ethylene and ethanol production rates while preventing catalyst degradation.¹²⁶ Adding alkali metal cations (e.g., K^+ , CS^+ , or Rb^+) to the electrolyte has been found to enhance C_{2+} selectivity. These cations interact with adsorbed CO intermediates, stabilizing them and promoting C–C coupling.¹²⁷

Thus, electrolyte optimization remains a powerful approach for enhancing C_{2+} product formation in eCO_2RR , ensuring high selectivity while mitigating competing side reactions.

5.2. Gas diffusion electrodes

In an H-cell, the catalyst is typically deposited on a substrate such as carbon paper, glassy carbon rods, or directly on a

metal foil as the working electrode. In aqueous electrolytes, this setup leads to sluggish mass transfer and low eCO_2RR reaction rates.^{128,129} To enhance eCO_2RR performance, GDEs have been introduced, enabling CO_2 to diffuse directly to the electrode–electrolyte interface.¹³⁰ GDEs typically consist of a gas diffusion layer (GDL) and a catalyst layer (Fig. 9a).^{93,131} This structure forms a three-phase interface where the liquid electrolyte and gaseous CO_2 coexist in the catalyst layer.¹³⁰ The GDL contains a dense carbonaceous network that serves as a porous support for the catalyst layer. This dense network, typically made from carbon fibers like carbon paper or PTFE, ensures mechanical stability and facilitates efficient gas transport. The dense carbon network in the GDL plays a crucial role in forming a stable and efficient interface for the electrochemical reactions in eCO_2RR systems.¹³² The GDLs are typically treated with PTFE to enhance hydrophobicity, effectively preventing water infiltration. The nanoporous structure of the GDL ensures the transport of CO_2 gas to the catalyst layer. Maintaining GDE hydrophobicity is crucial during the eCO_2RR reaction.^{133,134} Loss of hydrophobicity can cause electrolyte permeation into GDL pores, leading to flooding within the GDL. This obstructs CO_2 diffusion, inhibiting eCO_2RR and promoting HER.^{135,136} Therefore, GDE stability is critical for long-term stability testing of CO_2 electrolyzers.

To overcome these challenges, researchers have incorporated hydrophobic PTFE frameworks into GDEs. Compared to carbon paper-based GDEs, hydrophobic PTFE exhibits better long-term stability during eCO_2RR testing. Sargent *et al.* sputtered Cu NPs onto porous PTFE and coated the catalyst surface with carbon nanoparticles and graphene to enhance conductivity, thereby creating a stable electrode interface (Fig. 9b). This setup achieved 70% ethylene selectivity at current den-

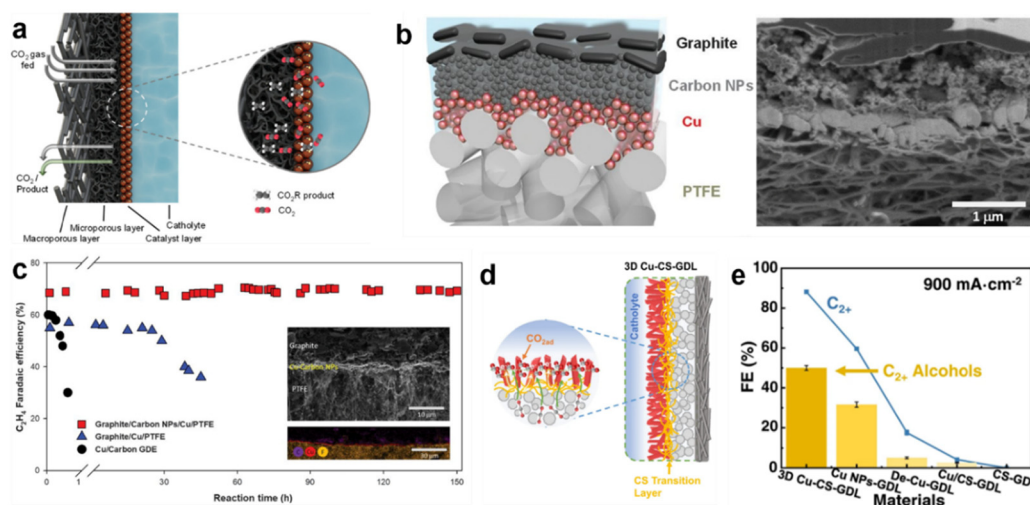


Fig. 9 (a) Schematic of an eCO_2RR GDE cathode and its fundamental components.¹⁰ Reprinted with permission. Copyright 2024 American Chemical Society. (b) Structure of the polymer-based gas diffusion electrode.⁹³ Reprinted with permission. Copyright 2018 The American Association for the Advancement of Science. (c) The long-term stability test of polymer-based gas diffusion electrode.⁹³ Reprinted with permission. Copyright 2018 The American Association for the Advancement of Science. (d) Schematic of 3D Cu-CS-GDL electrode.¹³⁷ Reprinted with permission. Copyright 2023 Springer Nature. (e) The FE of C_{2+} products and C_{2+} alcohols on different GDEs at a current density of 900 $mA\ cm^{-2}$.¹³⁷ Reprinted with permission. Copyright 2023 Springer Nature.

sities of 75 to 100 mA cm⁻² in 7 M KOH electrolyte, with extended long-term stability testing up to 150 h without decay—300 times longer than traditional GDEs (Fig. 9c).⁹³ This GDE design has demonstrated structural superiority. Additionally, Han *et al.* coupled GDEs with 3D nanostructured catalysts to design a 3D Cu-chitosan (CS)-GDL electrode. CS acts as a transition layer between the Cu catalyst and the GDL (Fig. 9d). The highly interlaced network promotes the growth of 3D Cu films, facilitating rapid electron transfer and reducing mass transfer limitations. This structure achieved 88.2% C₂₊ selectivity at a current density of 900 mA cm⁻² (Fig. 9e).¹³⁷ These advancements in GDE design underscore the importance of creating a stable and efficient interface for electrochemical reactions, highlighting the critical role of dense carbonaceous networks and hydrophobic treatments in achieving high performance and long-term stability in eCO₂RR systems.

6. Conclusion and outlook

In summary, eCO₂RR represents a key pathway for sustainable carbon management, and ongoing research is focused on overcoming the challenges of catalyst design, system optimization, and product selectivity. Further advancements in understanding reaction mechanisms, developing efficient catalysts, and optimizing system configurations are essential to enable large-scale deployment of eCO₂RR technology for the production of high-value chemicals and fuels.

Despite extensive efforts in eCO₂RR systems, several issues remain that must be addressed before commercialization. These issues primarily revolve product selectivity, stability, understanding of reaction mechanisms, and energy efficiency. The specific details are as follows:

(1) While C₁ products like CO and formate can achieve nearly 100% selectivity at high current densities, the selectivity for multi-carbon products remains insufficient for industrial applications. Although multi-carbon products could ideally serve as direct fuels, their high separation costs and the mixture of various gaseous and liquid products make them impractical for continuous supply in downstream reactions. Future efforts should focus on designing catalysts that improve the selectivity for single products, making them more practical for industrial applications.

(2) Industrial-scale eCO₂RR technology demands long-term stability. Challenges such as catalyst deactivation and the electrowetting effect of the GDL hinder the advancement of eCO₂RR technology. Therefore, ensuring the long-term operation of Cu-based catalysts in reactors remains a significant challenge. Anchoring catalysts onto superhydrophobic and highly stable GDLs could improve the stability of CO₂ electrolyzers.

(3) Previous mechanistic studies have generally concentrated on H-cell setups at the lab scale, which may not be applicable to flow cells and MEA reactors. The significant differences in current densities and configurations between flow cells, MEA reactors, and H-cells indicate that conventional

in situ reaction cells may not accurately reflect the reaction processes in flow cells and MEAs. Therefore, developing appropriate *in situ* flow cell and MEA systems is essential for elucidating the true reaction mechanisms under realistic eCO₂RR conditions.

(4) In terms of electrolyzer design, conventional flow cells suffer from high internal resistance, resulting in elevated energy consumption and limiting their suitability for industrial-scale applications. As a result, research should shift toward the structural optimization of MEA electrolyzers. Although MEA systems offer advantages such as lower cell resistance, and higher energy efficiency, they face challenges in long-term stability. One of the major issues is membrane degradation, which leads to increased cell resistance, localized overheating, and diminished catalytic activity. Therefore, the development of highly durable membrane materials is essential for advancing the practical application of MEA systems. In addition, operational parameters within MEA systems, such as temperature and pressure, significantly influence overall performance. Introducing elevated temperature and pressure conditions can accelerate reaction kinetics and enhance catalytic activity. Lastly, given that the energy efficiency of current MEA electrolyzers typically remains below 50%, future studies should focus on strategies to reduce the overall cell voltage and improve C₂₊ product selectivity, thereby enhancing the energy efficiency of the system.

Although significant progress has been made, addressing these key issues is crucial for the commercial viability of eCO₂RR technologies. Focusing on these areas will facilitate the transition of eCO₂RR from laboratory research to large-scale industrial applications.

Author contributions

Yimin Wu conceived and supervised the project. L. W. and Y. A. W. wrote the manuscript. All authors made comments and revised the manuscript.

Conflicts of interest

The authors declare no competing interests.

Data availability

No primary research results, software or code have been included.

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