Strategies in catalysts and electrolyzer design for electrochemical CO₂ reduction toward C_{2+} products

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In light of environmental concerns and energy transition, electrochemical CO₂ reduction (ECR) to value-added multicarbon (C_{n+}) fuels and chemicals, using renewable electricity, presents an elegant long-term solution to close the carbon cycle with added economic benefits as well. However, electrocatalytic C-C coupling in aqueous electrolytes is still an open challenge due to low selectivity, activity, and stability. Design of catalysts and reactors holds the key to addressing those challenges. We summarize recent progress in how to achieve efficient C-C coupling via ECR, with emphasis on strategies in electrocatalysts and electrocatalytic electrode/reactor design, and their corresponding mechanisms. In addition, current bottlenecks and future opportunities for C_{2+} product generation is discussed. We aim to provide a detailed review of the state-of-the-art C-C coupling strategies to the community for further development and inspiration in both fundamental understanding and technological applications.

INTRODUCTION

The excessive release of carbon dioxide (CO₂) into atmosphere has triggered serious environmental consequences and also presents an urgent and potentially irreversible threat to human societies (1, 2). As the atmospheric CO₂ concentration increased sharply from 270 ppm (parts per million) in the early 1800s to 403.1 ppm in July 2015, a worldwide consensus on recycling the carbon footprint emitted by human activities has been reached (3, 4). To realize the close loop for carbon footprint, one potential approach is to shift the dependence of current energy and chemical industries away from fossil fuels into renewable sources such as solar and wind (5–8). However, the fraction of energy from those renewable sources is only limited to 30% owing to their intermittent nature, unless approaches for large-scale energy storage become available (9). Hence, as an alternative, capture of CO₂ from point sources such as power plants, followed by conversion into chemical feedstocks and fuels, is more practically viable (9–12). Electrocatalytic CO₂ reduction (ECR) using renewable electricity represents an elegant long-term solution due to the mild operation conditions required for the conversions, in which value-added products could be selectively produced (13). As schematically illustrated in Fig. 1, in this process, the electrochemical electrolyzer converts CO₂ and water into chemicals and fuels powered by renewable electricity. The resulting fuel is capable of long-term storage and can also be distributed or consumed, giving off CO₂ as the main waste, which will be captured and fed back to the reactor to close the loop. Moreover, the resulting small-molecule chemical feedstocks [e.g., carbon monoxide (CO) and formate] from ECR can be used as raw materials for more complicated chemical synthesis.

However, CO₂ is a quite stable linear molecule with a strong C=O bond (750 kJ mol⁻¹) (14), making it difficult for electrochemical conversion. Thus, it requires a high activation barrier, which, in turn, leads to significant overpotentials (15). Furthermore, ECR in an aqueous electrolyte involves multi-electron/proton transfer processes together with a number of different possible reaction intermediates and products (16–18), making it highly complex. Table 1 summarizes the half electrochemical thermodynamic reactions of the main ECR products, including CO, methane (CH₄), methanol (CH₃OH), formic acid (HCOOH), ethylene (C₂H₄), ethanol (CH₃CH₂OH), and so on, together with their corresponding standard redox potentials (19). In general, during an ECR process, CO₂ molecules first undergo ad sorption and interaction with atoms on the catalyst surface to form *CO₂*, followed by various stepwise transfer of protons and/or electrons toward different final products. For example, CH₄ is believed to form through the following pathways: CO₂ → *COOH → *CO → *CHO → *H₂O → *H₂O → *H₂O → CH₄ + *O → CH₄ + *OH → CH₄ + H₂O (20).

Figure 2A summarizes the Faradaic efficiency (FE) under different production rates (current density) for the reported ECR electrocatalysts, which represents the product selectivity of the reaction (21–43). Notably, while the state-of-the-art electrocatalysts can transform CO₂ into C₂ products (CO or formate) with over 95% FE under high production rate (>20 mA cm⁻² for H-type cell and >100 mA cm⁻² for flow cell) (9,21,22,25,28,44,45), the highly selective (>90%) and efficient production of more available multicarbon (Cₙ⁺) chemicals has not been realized so far. This is due to the fact that coupling to C₂⁺ products requires arrival and adsorption of several CO₂ molecules to the surface, stepwise transformation, and spatial positioning (13). To be specific, as shown in Fig. 2B, the subsequent reactions of *CO intermediates determine the final C₂⁺ products of ECR. In general, C₂H₆ and CH₂COO⁻ share the same *CH₂ intermediate, which is generated from the proton-coupled electron transfer steps of *CO. Further protonation of *CH₂ gives *CH₃ intermediate, which leads to the formation of C₂H₄ via *CH₃ dimerization. Unlike C₂H₆ generation, *CH₂COO⁻ is formed by CO insertion into *CH₂. The *CO dimerization is the rate-determining step for C₂H₄, CH₃CH₂OH, and n-propanol (n-C₃H₇OH) formation. After a series of electron transfer and protonation steps, the *CO–CO dimer forms the *CH₂CHO intermediate, which serves as the selectivity-determining step for C₂H₄ and C₂H₂O. In addition, it was found that reducing *CH₂CHO to C₂H₄ has lower energy barrier than transforming *CH₂CHO to...
C₂H₅OH (46), which may explain the higher FE for C₂H₄ over C₂H₅OH on most copper catalysts. Furthermore, stabilized C₂ intermediates could transfer to n-C₃H₇OH via CO insertion. The complex and uncontrollable reaction pathways during C₂+ chemical formation are mainly due to many more permutations to the protonation sites, along with the possible involvement of nonelectrochemical step (19, 47). As such, the design of highly selective electrocatalysts is a prerequisite for specific C₂+ product formation at high yield. In this review, we aim to highlight the recent progress on strategies in electrocatalyst design for selective C₂+ product generation via ECR. We also provide a summary of the understandings of related mechanisms. Electrode and reactor design will also be emphasized to show how to achieve efficient, stable, and large-scale operation of ECR. Furthermore, we will discuss the remaining challenges and future opportunities for electrochemical conversion of CO₂ into value-added C₂+ chemicals.

Electrocatalytic transformation of CO₂ into chemical fuels and feedstocks is a potential technology to achieve a carbon-neutral energy cycle (11). However, the FE of C₂+ products is still far from practical application, where state-of-the-art catalysts allow production of C₂ products with around 60% FE (13, 33), while the C₃ production is limited to less than 10% FE (48, 49). Reductive coupling of CO₂ to C₂+ products requires heterogeneous catalysts with highly coordinated morphological and electronic properties (50, 51). The catalytic surface needs to break the scaling relations between the intermediates (47, 52, 53). Moreover, to achieve C–C bond formation, the absorbed reaction intermediates at the catalyst surface must be in close proximity to one another. Furthermore, the pathway from the initially adsorbed intermediate toward a specific C₂+ product needs to be well controlled because of the multiple proton-assisted electron transfer steps. Considering the high complexity of CO₂ reduction toward C₂+ products, electrocatalysts should be carefully tailored to increase the selectivity. According to the intermediate species and chemical compositions, we categorize C₂+ products into multicarbon hydrocarbons and oxygenates (4, 54). To approach highly efficient electrocatalysts for specific C₂+ molecule production, several catalyst design strategies, such as heteroatom doping, crystal facet regulation, alloy/dealloying, oxidation state tuning, and surface ligand control, have been demonstrated (35, 41, 55–61). Optimal design should rationally consider the aforementioned effects and maximize the benefits. Otherwise, understanding what active-site motifs lead to such a unique catalytic behavior may further shine a light on precise catalyst design for C–C coupling. Hence, how to design ECR catalyst toward specific products (multicarbon hydrocarbons and oxygenates) and the related mechanism will be discussed in this part.

MULTICARBON HYDROCARBONS
C₂+ hydrocarbons, such as C₂H₄, are nexus chemicals for a variety of chemical industries, such as polyethylene production (62, 63). Besides, it could be directly used as the fuel for welding or a mixed component in natural gas (12). Hydrogenation of CO (Fischer–Tropsch synthesis) and CO₂ has been used to produce C₂+ hydrocarbons for a long time in industrial scale but challenged by high energy consumption and environmental impact (64). In stark contrast, electrochemical CO₂ reduction using renewable energy provides a cleaner and more sustainable route. Great effort has been made to develop efficient electrocatalysts toward C₂+ hydrocarbons (32, 33, 65–70).

Binmetallic electrocatalysts have been widely investigated to break the scaling relationship during electrochemical CO₂ conversion, which
can stabilize the key intermediate and lower the overpotential and, thus, in turn, increase the selectivity (71–74). While a series of alloy materials including Au-Cu, Ag-Cu, Au-Pd, and Cu-Pt have been demonstrated for high efficiency C₂ production by stabilizing the critical intermediate (73, 75), the alloy effect toward C₂ hydrocarbon formation seems to be more complex (76). For example, in the Cu-Ag bimetallic system, the product distribution can be easily controlled by tuning the surface atomic ratio of Ag and Cu (77). The surface Cu-rich sample is preferred for hydrocarbon production, while the products of the surface Ag-rich one are dominated by CO, highlighting the importance of atomic ratio for alloyed ECR electrocatalysts. The geometric effect caused by the local atomic arrangement can significantly affect the binding strength of the intermediates. Gewirth and co-workers (36) showed that Cu–Ag alloys from additive-controlled electrodeposition exhibited ~60% FE for C₂H₄ in an alkaline flow electrolyzer (Fig. 3, A and B). In this case, optimized C₂H₄ selectivity can be achieved by morphology and Ag-loading tuning. The Ag sites were believed to play the role of a promoter for CO formation during ECR. Then, the optimal availability of the CO intermediate could help the C–C coupling in the neighboring Cu. Besides, Ag can also promote the formation of Cu₂O during the Cu-Ag catalyst synthesis (Fig. 3C), resulting in enhanced C₂H₄ production efficiency. This synergy opens up new possibilities for developing C–C coupling catalysts. Furthermore, the mixing pattern of different metals in the alloy system could also determine the distribution of ECR products. Using Pd-Cu alloy as an example (Fig. 3D), Kenis and co-workers (71) demonstrated that a phase-separated Pd-Cu catalyst can offer the highest selectivity (~50%) for C₂H₄ compared with its ordered and disordered counterparts. According to the d-band theory, typically, transition metal with a lower d-band center shows weaker binding of the in situ generated intermediates on the metal surfaces (78). While phase-separated Pd-Cu alloy exhibited similar catalytic selectivity and activity for CO with Cu nanoparticles (NPs), it offered completely different binding strength toward intermediates by Pd tuning. As shown in Fig. 3E, phase-separated Cu-Pd alloy showed the lowest-lying d-band center, whereas that of Cu NP is the highest. It suggests that the phase-separated Cu-Pd alloy had the lowest binding strength for the CO intermediate. This observation implies that the geometric and structure effect may play a greater role than the electronic effect for improving the hydrocarbon selectivity in the phase-separated Cu-Pd alloy case. To date, only pure copper or copper-based alloy shows superior selectivity and activity for electrochemical reduction of CO₂ to C₂ hydrocarbons. Thus, it is very necessary to develop a novel electrocatalyst for C₂ hydrocarbon production from ECR. Inspired by CO₂ hydrogenation, a preliminary study demonstrated that Ni-Ga alloy with different phases could be used for C₂H₄ generation (79). It showed that Ni₃Ga₃ film could reduce CO₂ to C₂H₄ and ethane (C₂H₆). Although the FE toward C₂H₄ hydrocarbons is less than 5%, it may open new lines for electrocatalyst screening toward C–C coupling based on the alloy effect.

Besides alloy effect, manipulating the oxidation states is another major principle to tune the performance of electrocatalysts, which can affect the local electronic structure of the material. The first example for the oxidation state tuning of catalyst is to use oxide-derived materials. The residual oxygen species on the surface or subsurface of catalyst after in situ reduction can regulate the oxidation state of the metal center. For example, plasma-oxidized Cu showed more than 60% selectivity toward C₂H₄, which was ascribed to the reduction-resistant Cu⁺ (37). To confirm that Cu⁺ is the key parameter for high ethylene selectivity, we performed control experiments using different plasma (Fig. 4A). In situ hard x-ray absorption spectroscopy further showed that the residual oxides in the (sub)surface layer are stable against reduction condition, with a significant amount of Cu⁺ species.

### Table 1. Half electrochemical thermodynamic reactions of the main ECR production, together with their corresponding standard redox potentials (V versus reversible hydrogen electrode (RHE)).

| Products                  | Equation                        | Acid   | $E$ (V) | Equation                        | Acid   | $E$ (V) |
|---------------------------|---------------------------------|--------|---------|---------------------------------|--------|---------|
| Hydrogen                  | $2H^+ + 2e^- \rightarrow H_2$  | 0.000  |         | $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ | 0.000  |         |
| Carbon monoxide           | $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ | -0.104 |         | $CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^-$ | -0.094 |         |
| Methane                   | $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ | 0.169  |         | $CO_2 + 6H_2O + 8e^- \rightarrow CH_4 + 8OH^-$ | 0.159  |         |
| Methanol                  | $CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$ | 0.016  |         | $CO_2 + 5H_2O + 6e^- \rightarrow CH_3OH + 6OH^-$ | 0.006  |         |
| Formic acid/formate       | $CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$ | -0.171 |         | $CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-$ | -0.063 |         |
| Ethylene                  | $2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$ | 0.085  |         | $2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^-$ | 0.074  |         |
| Ethane                    | $2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_4 + 4H_2O$ | 0.144  |         | $2CO_2 + 10H_2O + 14e^- \rightarrow C_2H_4 + 14OH^-$ | 0.068  |         |
| Ethanol                   | $2CO_2 + 12H^+ + 12e^- \rightarrow CH_3CH_2OH + 3H_2O$ | 0.084  |         | $2CO_2 + 9H_2O + 12e^- \rightarrow CH_3CH_2OH + 12OH^-$ | 0.074  |         |
| Acetic acid/acetate       | $2CO_2 + 8H^+ + 8e^- \rightarrow CH_3COOH + 2H_2O$ | 0.098  |         | $2CO_2 + 5H_2O + 8e^- \rightarrow CH_3COO^- + 7OH^-$ | 0.065  |         |
| n-Propanol                | $3CO_2 + 18H^+ + 18e^- \rightarrow CH_3CH_2CH_2OH + 5H_2O$ | 0.095  |         | $3CO_2 + 13H_2O + 18e^- \rightarrow CH_3CH_2CH_2OH + 18OH^-$ | 0.073  |         |
remaining after 1 hour of reduction at relatively high potentials of \(-1.2\) V versus reversible hydrogen electrode (RHE). Furthermore, electroreduction of copper from a sol-gel copper oxychloride verified again that stabilized surface Cu\(^+\) species could improve the selectivity of \(\text{C}_2\text{H}_4\) (61). The oxidation state of a copper catalyst under different applied potentials was tracked using time-resolved in situ soft x-ray absorption spectroscopy. The initial transition step from Cu\(^{2+}\) to Cu\(^+\) is very quick; however, the further electrochemical reduction of Cu\(^+\) species to Cu\(^0\) is much slower. Around 23% of Cu\(^+\) species remain even after 1-hour constant reduction under \(-1.2\) V versus RHE (Fig. 4B). Mechanistic studies revealed that the interface between Cu\(^+\) and Cu\(^0\) leads to electrostatic attraction between intermediates since the C atom of \(^*\)CO@Cu\(^+\) is positively charged, whereas that of \(^*\)CO@Cu\(^0\) is negatively charged (80), which, in turn, promotes the C–C bond formation and thus produces \(\text{C}_2\text{H}_4\) hydrocarbons. In addition to oxide-derived materials, copper nitride (Cu\(_3\)N) was also used to achieve (sub)surface Cu\(^+\) species to decrease the dimerization energy barrier of \(^*\)CO (81). In addition, compared with oxide-derived Cu, Cu\(_3\)N-derived Cu\(^+\) species are even more stable (Fig. 4C). As a result, the nitride-derived copper catalyst exhibits an FE of 39 ± 2% for \(\text{C}_2\text{H}_4\), outperforming the pure Cu (23%) and oxide-derived Cu (28%). Analogous to the abovementioned Cu\(^+\)/Cu catalytic system, boron has been used as a heteroatom dopant to introduce and stabilize Cu\(^{\delta^+}\) (41). The average oxidation state of copper can be controlled from +0.25 to +0.78 by changing the concentration of boron dopant. Projected density of states showed that the electrons transferred from copper to boron, leading to a dopant-induced positively charged copper sites. The boron-doped copper showed an increased formation energy of \(^*\)CHO intermediate and, thus, suppressed the reaction pathway toward \(\text{C}_1\) products. In addition, it can increase the selectivity toward multicarbon hydrocarbons by decreasing \(^*\)CO dimerization reaction energy (Fig. 4D). By optimizing the average surface oxidation state of copper, a high \(\text{C}_2\) FE of \(~80\)% with \(~53\)% \(\text{C}_2\text{H}_4\) could be achieved under an average copper oxidation state of +0.35 (Fig. 4E). To date, the active sites on copper have been identified as Cu\(^0\), Cu\(^{\delta^+}\), and/or their interface for ECR in different studies (39, 41, 42, 81, 82). However, what is the active site is still being debated. While the heteroatom doping–induced Cu\(^{\delta^+}\) catalysts have been demonstrated to be very active for ECR toward \(\text{C}_2\) products, the synergistic effect from the simultaneously generated defects and interfaces should also be considered. Hence, systematic in operando characterizations should be developed to identify the active center on copper surface and monitor the potential in situ transformation of the active sites under reaction conditions. Besides, the stability of the positively charged copper is another concern under electrochemical reduction conditions. How to synthesize catalysts with stable Cu\(^{\delta^+}\) sites remains a challenge.

Apart from the electronic structure, oxide-derived materials can also lead to morphology or structure evolution during the in situ reduction process. From the perspective of morphology or structure, the enhanced electrochemical performance of oxide-derived electrocatalysts has been attributed to the formation of active grain boundaries, edges, and steps (83–85). Yeo and co-workers (83) reported the selective C–C coupling on electrodeposited Cu\(_2\)O films with different thicknesses (Fig. 4F). In situ Raman spectroscopy revealed that the surface of
the Cu$_2$O films was reduced to stable metallic Cu$^0$ during ECR (83). As a result, metallic Cu$^0$ has been confirmed as the catalytic active center instead of Cu$^+$ species or the Cu$^+$/Cu$^0$ interface. In the process of reducing Cu$_2$O to metallic Cu$^0$, the catalyst surface is likely to in situ form steps, edges, and terraces. It was pointed out that the formed steps and edges are more active than the terraces, originating from their stronger binding with $^*$CO, which can further hydrogenate $^*$CO to $^*$CHO or $^*$CH$_2$O. Besides, edge Cu atoms are a promoter to boost $^*$CHO and $^*$CH$_2$O formation. Previous work suggested that $^*$CHO and $^*$CH$_2$O intermediates are more favorable for C–C coupling than $^*$CO in kinetics (86). By regulating the surface morphology, the chemisorption energies of the $^*$CHO and $^*$CH$_2$O intermediates can be optimized. In this study, the authors found that the FE of C$_2$H$_4$ decreased from 40 to 22% when they increased the thickness of Cu$_2$O thin film from 0.9 to 8.8 $\mu$m. This is due to the concentration of low coordinated Cu that increased with the increase in Cu$_2$O thickness. These undercoordinated atoms can strongly bind with H and, thus, are more preferred for hydrogen evolution than C–C coupling. This work demonstrated that the oxide-derived copper catalyst can significantly enhance the C$_2$H$_4$ selectivity via surface morphology reconstruction instead of introducing charged Cu$_{\delta^+}$ species. Using the oxide-derived catalysts, ethane (C$_2$H$_6$) has also been selectively produced with the help of palladium(II) chloride (PdCl$_2$) additive in electrolyte (34). It showed that the adsorbed PdCl$_x$ on the surface of Cu$_2$O-derived Cu played a vital role for C$_2$H$_6$ evolution. Specifically, CO$_2$ was firstly reduced to C$_2$H$_4$ at the Cu$_2$O-derived active Cu sites, and then the formed C$_2$H$_4$ would be hydrogenated with the assistance of adsorbed PdCl$_x$ to produce C$_2$H$_6$. The FE of C$_2$H$_6$ increased from <1 to 30.1% with the assistance of PdCl$_2$. This work suggests that the combination of the well-defined ECR catalyst and electrolyte additive may open up new opportunities for specific C$_2^+$ product generation.

Morphology and/or structure regulation represents another alternative strategy to modulate catalytic selectivity and activity. Controlling the size, shape, and exposed facets of catalyst has been widely demonstrated for ECR performance improvement (58, 87, 88). For example, the Cu(100) facet is intrinsically preferred for C$_2$H$_4$ generation, while the dominated product from the Cu(111) catalyst is methane (CH$_4$) (87). In a study of Cu nanocrystals with various shapes and
sizes, Buonsanti and co-workers (58) revealed a nonmonotonic size dependence of the C2H4 selectivity in cube-shaped copper nanocrystals (Fig. 5A). Intrinsically, cubic Cu nanocrystals exhibited higher C2H4 activity and selectivity than spherical Cu nanocrystals owing to the predominance of the (100) facet. The smaller crystal size of cubic Cu could offer higher activity because of the increased concentration of low-coordinated surface sites, such as corners, steps, and kinks. However, the stronger chemisorption of low-coordinated sites was accompanied by higher H2 and CO selectivity, resulting in lower overall hydrocarbon FE. On the other hand, the ratio of edge sites to plane sites decreased with the increase in particle sizes, which also affects the performance of C2H4 production. The authors demonstrated that intermediate-sized copper nanocubes with a 44-nm edge length displayed the highest C2H4 selectivity due to the optimized balance between particle size and the density of edge sites. Furthermore, morphology can also affect the local pH and mass transport during ECR. It has been demonstrated that the high local pH in the vicinity of catalyst surface, which is caused by the in situ generated OH−, suppresses the proton-involved reaction pathway. As a result, C2H2 hydrocarbon formation through CO dimerization could be enhanced, and CH4 formed through COH intermediate might be inhibited. Copper nanowire arrays (Fig. 5B) have been demonstrated to achieve increased local pH (68). As a commonly used electrolyte, CO2 saturated potassium bicitonate (KHCO3) solution will quickly neutralize the local OH− (HCO−3 + OH− = CO−3 + H2O) and decrease the local pH. With an elongated microstructure, the diffusion of HCO−3 into the Cu nanowire arrays can be somehow undermined so that the neutralization effect for local OH− will be suppressed to some degree. On the basis of a similar principle, copper meshes with precisely controlled mesopores (Fig. 5C) demonstrated enhanced FE for C2H4 or C2H6 production (32). It showed that the local pH in the electrode surface could be increased by narrowing the pore width, resulting in decreased C2 product FE and enhanced C2 product FE. Besides, by increasing the pore depth, the major reduction product could be tuned from C2H4 to C2H6. The FE of C2H6 was as high as 46%. Since the chemicals have been confined inside the pores during ECR, prolonged retention time of the key intermediates caused by the deeper pores has been explained as the main reason for the high selectivity toward saturated C2 hydrocarbon. Cul-derived Cu nanofibers also showed high selectivity toward C2H6 (FE = 30% at −0.735 V versus RHE) (89). The anisotropic morphology and high surface roughness of Cul-derived Cu nanofibers can improve the trapping efficiency of absorbed H2 and thus increase the FE of C2H6.

Catalyst surface modification using small molecules is another well-known strategy to improve the electrochemical performance of ECR. This strategy can influence the microenvironment near the catalyst surface, which may stabilize the key intermediates due to the interaction between surface ligand and intermediate. Amine has been reported as a modifier to promote ECR (35). Various amino acids, including glycine (Gly), dl-alanine (Ala), dl-leucine (Leu), dl-tryptophan (Tyr), dl-arginine (Arg), and dl-tryptophan (Trp), have been investigated to study their effects on copper nanowires (35). As shown in Fig. 5D, all amino acid–based ligands were capable of improving the selectivity of C2+ hydrocarbons. Such an enhancement suggests that −COOH and −NH2 functional groups in amino acid are probably responsible for the enhanced selectivity of ECR. Previous reports illustrated that the adsorption of amino acids on the Cu surface was achieved through both −COOH and −NH2 groups (35, 90). Stearic
acid (C₁₇H₃₅COOH, RCO₂H), which contains only the ─COOH group, was selected to identify the role of ─COOH. Other modifiers, such as α-anthraquinone diazonium salt (AQ), o-nitrobenzene diazonium salt (PhNO₂), and dodecyl mercaptan (C₁₂H₂₅SH, RSH), which contain neither ─COOH nor ─NH₂ groups, were also investigated. However, all of them were not positive for C₂⁺ hydrocarbon FE improvement (Fig. 5E). Theoretical calculations indicated that ─NH₃⁺ groups in the adsorbed zwitterionic glycine could stabilize *CHO intermediate due to their strong interaction, such as hydrogen bonds. Introduction of halide ions into the electrolyte is another way to modify the catalysts (91, 92). As shown in Fig. 5F, C₂H₄ production rate on plasma-activated Cu could be significantly increased with the assistance of halide additives. It was shown that I⁻ ion is more active than Br⁻ and Cl⁻, in agreement with the corresponding adsorption energy of I⁻, Br⁻, and Cl⁻ on the Cu(100) facet (91). Besides halides, hydroxide ion also showed a positive effect on C₂H₄ selectivity. Recently, Sargent and co-workers (33) reported the CO₂-to-C₂H₄ conversion with ~70% FE using concentrated potassium hydroxide (KOH) electrolyte (up to 10 M) in a flow cell. As shown in Fig. 5G, the onset potential of CO and C₂H₄ in 10 M KOH electrolyte was much lower compared to that in 1 M KOH. Furthermore, the Tafel slopes (Fig. 5H) of C₂H₄ formation decreased with the increase of hydroxide concentration (135 mV decade⁻¹ in 1 M KOH and 65 mV decade⁻¹ in 10 M KOH), suggesting the transmutation of the overall rate-determining step. Density functional theory (DFT) results proved that the presence of concentrated hydroxides could lower the binding energy of the CO intermediate and also increased the charge imbalance between two carbon atoms in adsorbed OCCO intermediates. As a result, the OCCO intermediate would be further stabilized through a stronger dipole attraction, leading to lower activation energy barrier for CO dimerization, which will then improve the overall performance.
**MULTICARBON OXYGENATES**

C$_2$ oxygenates such as ethanol (CH$_3$CH$_2$OH) are another major category of highly valuable ECR products. Industrial synthesis of ethanol is an energy-intensive process, which also consumes a large amount of ethylene or agricultural feedstocks (40). Thus, electrocatalytic production of ethanol or other C$_2$ oxygenates from CO$_2$ makes a lot of economic and environmental sense. Since ethanol generation from ECR shared a penultimate intermediate with C$_2$H$_4$ that is *C$_2$H$_3$O (43), selective hydrogenation of this intermediate could switch ECR pathways from C$_2$H$_4$ to alcohols (64). However, in most systems, the selectivity toward C$_2$ oxygenates is much lower than hydrocarbons (31, 37, 39, 41, 42, 67). Thus, in this section, we will highlight the electrocatalyst design strategies that can achieve impressive C$_2$ oxygenate FE of over 25%.

As discussed above, well-designed bimetallic catalysts can improve the selectivity and activity for C$_2$ hydrocarbon production. A similar but not identical strategy has also been used to improve the electrocatalytic performance for C$_2$ oxygenates (38, 93, 94). For instance, Ag-incorporated Cu-Cu$_2$O catalysts exhibited tunable ethanol selectivity, and the highest ethanol FE was 34.15% (95). The bifacial boundary in the phase-blended Ag-Cu alloy, instead of Ag/Cu atomic ratio, was identified as the key factor for selective production of ethanol. Since the Cu site is very close to the Ag site in a phase-blended pattern (Ag-Cu$_2$O$_{30}$), the formation rate of ethanol intermediates for the phase-blended sample could be promoted in comparison to the phase-separated one (Ag-Cu$_2$O$_{50}$), leading to a better ethanol generation performance. Besides ethanol, Cu-Ag bimetallic NPs have also been demonstrated to convert CO$_2$ to acetate with the addition of benzoiazole (93). At −1.33 V versus RHE, the FE of acetate was 21.2%. Two possible reaction pathways were proposed in this case: One is based on CO dimerization, and the other one is upon CO insertion, highlighting the critical role of CO intermediate formation on active Ag sites. A similar observation was reported in Cu-Zn catalysts (Fig. 6, A and B) for ethanol production (38). By tuning the content of Zn in Cu-Zn Cu alloyed catalysts, the ratio of ethanol versus C$_2$H$_4$ FE could be well controlled in the range of 0.48 to 6, suggesting the importance of CO-evolving sites for C$_2$ oxygenate formation. Formation of alloyed catalysts might induce the strain effect on the matrix material, which may not be desired sometimes. Thus, a direct route toward bimetallic catalysts might be more suitable for some target products. Jaramillo and co-workers (96) constructed a simplified Au-Cu bimetallic system, synthesized by direct deposition of gold NPs onto a polycrystalline Cu foil, to investigate the tandem catalysis effect. The bimetallic Au-Cu exhibited synergistic selectivity and activity toward C$_2$$_2$$_2$, outperforming pure copper and gold, and Au-Cu alloy. Compared with Cu foil, the bimetallic Au-Cu system showed increased local CO concentration due to the presence of Au NPs (Fig. 6C) that were active for CO generation. Since gold is not active for CO reduction, the enhanced C$_2$$_2$, alcohol production rate on Au-Cu bimetallic catalysts was ascribed to a tandem catalysis mechanism. Specifically, gold NPs could generate a high local CO concentration near the Cu surface. Next, the abundant local CO molecules can be further reduced to C$_2$$_2$, alcohols by Cu.

Selective exposure of crystal facets for electrocatalysts has been demonstrated as an effective and straightforward approach to achieving enhanced FE toward specific ECR products and an important way for fundamental understanding. Simple but scalable synthesis of single-crystal catalysts is challenging. Inspired by the galvanostatic charging-discharging (GCD) procedure for batteries, our group developed a metal ion cycling method (Fig. 6D) to selectively expose the crystal facet of a Cu catalyst (42). After 100 GCD cycles, a dense Cu nanocube array was formed on the Cu foil with exposed (100) facets (Fig. 6, E to G). The 100-cycle catalyst presented an overall C$_2$, alcohol FE of more than 30% and a corresponding C$_2$, alcohol current density of more than 20 mA cm$^{-2}$. However, the 10-cycle Cu with a lower ratio of the (100) facet only offered a C$_2$, alcohol FE of ~10%. DFT simulation confirmed that the Cu(100) and stepped (211) facets were more favorable for C-C coupling over Cu(111), as shown in Fig. 6H. A model catalyst, epitaxial Cu film with different exposed facets, has been used to determine the active-site motifs toward C$_2$$_2$, oxygenate production (Fig. 6I) (97). Since it is statistically less likely for a CO$_x$ dimer to be adjacent to H$_x$ atoms on a surface with fewer neighbors, lower-coordinated Cu sites could suppress the formation of hydrocarbons and lead to improved C$_2$$_2$, oxygenate FE because it is more difficult to hydrogenate C-C coupled ECR intermediates on its surface (97). In the epitaxial Cu film study, the authors confirmed that the ECR on the Cu(751) facet showed improved oxygenate/hydrocarbon ratio. This enhancement could be ascribed to the surface Cu atom geometry of different Cu facets and the corresponding lower average coordinated number (Fig. 6J), where Cu atom coordinated, respectively, with two, four, and six nearest neighbors on Cu(751), Cu(100), and Cu(111) facets. In situ morphology reconstruction has also been used to improve C$_2$$_2$, oxygenate FE. An active cube-like Cu catalyst was developed by Yang and co-workers (98), which showed improved C-C coupling performance. In detail, monodisperse Cu NPs (6.7 nm) with different loadings were deposited onto carbon paper support as a catalyst for ECR. Obviously, increased FE of C$_2$$_2$, oxygenates was observed with the increase in Cu NP loading. It was shown that densely packed Cu NPs under high loading conditions underwent in situ morphological transformation during ECR, in which cube-like morphologies were largely formed (Fig. 6K). This newly formed structure was found to be more electrocatalytically active. Tafel analysis suggested that CO dimerization was the rate-determining step for C$_2$ product formation, whereas that of n-propanol showed a discrete pathway in this catalytic system. Nanodendritic copper is another example that shows the importance of morphology control for C$_2$$_2$, oxygenate production (99). Briefly, the total FE of the well-defined copper nanodendrite (Fig. 6L) for C$_2$$_2$, alcohol was about 25% at −1.0 V versus RHE. An impressive n-propanol FE of 13% could be achieved at −0.9 V. Considering the high activity of Cu atom, copper-based catalysts always suffer from structural degradation during ECR, especially at high overpotential, which, in turn, leads to poor stability. However, such a nanodendritic copper exhibited good stability for alcohol production, showing an alcohol FE of ~24% over 6 hours.

Defects of electrocatalysts, such as atom vacancies and dopants, show the possibility of adsorbing unconventional ECR intermediates and, thus, selectively enhancing the corresponding pathway toward oxygenates (29, 43, 100). Taking C$_2$H$_3$O as an example, which is the potential penultimate intermediate for ethylene and ethanol production, Sargent and co-workers (43) studied the role of defects in a core-shell Cu electrocatalyst in detail. They theoretically showed that the reaction energy barriers for ethylene and ethanol formation were similar in the early C-C coupling stage (0.5-V overpotential) (Fig. 7A). Under such a condition, the introduction of copper vacancy would slightly increase the energy barrier for ethylene formation, yet it showed no influence on the ethanol generation (Fig. 7B). However, as shown in Fig. 7C, copper catalysts with vacancy and subsurface sulfur dopant...
Fig. 6. Alloy, morphology, and structure effects on ECR catalysts for efficient C₂+ oxygenate production. (A to C) Alloy effects. (A) Maximum FE of ethanol and C₂H₄ and the FE ratio of ethanol and ethylene on various Cu-Zn alloys. (B) Partial current density of ethanol on various Cu-Zn alloys. (A) and (B) are reproduced with permission from the American Chemical Society (38). (C) CO₂ reduction and CO evolution rates on gold, copper, and the Au-Cu bimetallic system. Reproduced with permission from the Nature Publishing Group (96). (D to G) Morphology or structure effects. (D) Schematic illustration of metal ion cycling method. (E and F) SEM images of 100-cycle Cu before (E) and after (F) the prereduction under ECR conditions. (G) TEM and selected-area electron diffraction suggested that Cu(100) were exposed and (H) free energy for *OCCO and *OCCHO formation on Cu(100), Cu(111), and Cu(211) facets. (D) to (G) are reproduced with permission from the Nature Publishing Group (42). (I) Ratio of oxygenates and hydrocarbons as a function of potential on Cu(111), Cu(751), and Cu(100). (J) Coordination numbers for Cu(111), Cu(100), and Cu(751). (I) and (J) are reproduced with permission from the National Academy of Sciences (97). (K) Scheme of the transformation process from Cu NPs to cubic-like copper. Reproduced with permission from the National Academy of Sciences (98). (L) SEM images of nanodendritic copper before and after ECR. Reproduced with permission from the American Chemical Society (99).
could significantly increase the energy barrier for the ethylene route, making it thermodynamically unfavorable. However, such a modification showed a negligible effect on the ethanol pathway. This phenomenon was further experimentally verified. A core-shell structured Cu$_2$S-Cu with abundant surface vacancies (Cu$_2$S-Cu-V; Fig. 7D) was synthesized. The ratio of alcohol to ethylene increased from 0.18 on bare Cu NPs to 0.34 on vacancy-free Cu$_2$S-Cu and then to 1.21 on Cu$_2$S-Cu-V, although the total FE of C$_2$+ products for all catalysts remained similar (Fig. 7E). This observation indicated that the promotion of alcohol selectivity was associated with the suppression of ethylene production, consistent with the DFT result. In addition, defect engineering plays a more important role for metal-free carbon catalyst since pure carbon materials are inactive for ECR. Dopants such as nitrogen and boron have been used to alter the electronic structure of a carbon-based catalyst (31, 43, 100). For example, nitrogen-doped nanodiamond (NDD) film on silicon substrate was devolved by Quan et al. (29) for selective acetate production from ECR (Fig. 7F). The acetate onset potential was as low as −0.36 V versus RHE using an NDD catalyst, and the FE for acetate was more than 75% in a potential range from −0.8 to −1.0 V versus RHE.
origin of such an impressive improvement, NDD/Si electrodes with different nitrogen contents or nitrogen species were prepared and investigated (Fig. 7G). The authors concluded that the superior performance of the NDD/Si catalyst for ECR could be attributed to its high overpotential for hydrogen evolution and N doping, where N-sp3C species was highly active for acetate production. Electrokinetic data and in situ infrared spectrum revealed that the main pathway for acetate formation might be CO2 → *CO2* → *(COO)2* → CH3COO−. Besides nitrogen, boron is another well-explored heteroatom to regulate the electronic structure of nanodiamond. However, boron-doped nanodiamond (BDD) preferentially reduced CO2 to formaldehyde or formate (101). Furthermore, Quan and co-workers (102) demonstrated that boron and nitrogen co-doped nanodiamond (BND) showed synergistic effect on ECR, which could overcome the limitation of BDD and then selectively produce ethanol. BND1, BND2, and BND3 catalysts with different nitrogen contents and similar boron doping levels were prepared. As shown in Fig. 7H, the highest selectivity of ethanol up to 93% could be achieved on the BND3 catalyst at −1.0 V versus RHE, which has the highest nitrogen doping. Theoretical calculation illustrated that the C−C coupling process on BND was thermodynamically favorable, where the boron atom promoted the capture of CO2 and nitrogen dopant facilitated the hydrogenation of intermediate toward ethanol. Although heteroatom-doped nanodiamond was capable of converting CO2 into multicharbon oxygenates with high selectivity, its ECR activity is very limited because of the slow charge transfer process (current density is less than 2 mA cm−2). Graphene-based material might be a potential solution to overcome the shortcomings of diamond-based catalysts. Theoretically, the edge pyridinic N sites in the graphene layer have been taken as the active sites for C−C coupling (103). This is due to the fact that the presence of pyridinic N at edge sites could convert CO2 into CO, which can be further coupled into C2, molecule (Fig. 7I). For example, the *C2O2* intermediate could be stabilized in nitrogen-doped carbon in which the two C atoms are bonded to the pyridinic N and its adjacent C atom, respectively (103). The theoretical prediction was then validated using nitrogen-doped graphene quantum dot (NGQD) catalysts (31). After the pulverization of nitrogen-doped graphene sheets (1 to 3 μm) (Fig. 7J), 1- to 3-nm NGQDs were obtained in which the density of pyridinic N at edge sites was increased by three orders of magnitude. At −0.78 V versus RHE, the maximum FE for C2, oxygenates could reach up to 26%. In addition, as shown in Fig. 7K, the partial current density for C2, oxygenates is close to 40 mA cm−2 at −0.86 V versus RHE, which is much higher than that of the modified nanodiamond. In comparison, N-free graphene quantum dots and N-doped graphene oxide, which show much lower edge site pyridinic N, primarily yielded H2, CO, and formate.

**DESIGN OF THE ELECTROREDUCTION CELL**

Beyond electrocatalysts, electrode and catalytic reactor architecture design present another effective route to boost the ECR performance, especially for production rate and energy efficiency. Significant improvements have been made on design and fabrication of novel electroreduction systems to achieve highly efficient C2, production. In this section, we will discuss the ECR electrode/reactor design in detail.

**Electrolyzer design**

H-type cells are extensively used in lab-scale tests, considering their facile assembly, easy operation, and low cost. The cells are equipped with independent cathode and anode chambers that are connected by an ion-exchange membrane (104, 105). The primary disadvantage of this H-type cell is the low CO2 solubility in aqueous electrolyte, which is only 0.034 M under ambient conditions, leading to limited CO2 reduction current densities of *j* < 100 mA cm−2 (64). Moreover, other intrinsic drawbacks, including a limited electrode surface area and a large interelectrode distance, have failed to meet the growing research requirements (105, 106). For C2, product generation, H-type cells usually show low selectivity under high overpotentials, e.g., 32% for ethylene at −0.98 V versus RHE (107), 13.1% for n-propanol at −0.9 V versus RHE (99), and 20.4% for ethanol at −0.46 V versus RHE (108), due to the seriously competitive hydrogen evolution.

To address the above issues, the flow reactor was proposed (15, 109). In flow cells, gaseous CO2 stream can be directly used as feedstock at cathode, thus leading to significantly improved mass diffusion and production rate (104, 110). Figure 8A shows the typical architecture of a flow cell, where a polymer electrolyte membrane (PEM) served as the electrode separator that is sandwiched between two flow channels. The catalyst is immobilized onto a gas diffusion electrode (GDE) to serve as the cathode electrode, in which gaseous CO2 is directly fed. The catholyte, such as 0.5 M KHCO3, is continuously flowed within the thin layer between the catalyst electrode and PEM. In addition, the anode side is typically circulated with an aqueous electrolyte for oxygen evolution reaction (43, 110). Compared with H-type cells, these membrane-based flow cells show much superior ECR performance. For example, Sargent and co-workers (43) evaluated the ECR performance of the Cu2S-Cu-V catalyst in both H-type cell and flow cell, as depicted in Fig. 8 (B to E). Using H-type cells, the maximum FE for C2, products was 41% with a total current density of ~30 mA cm−2 under −0.95 V versus RHE. However, the FE for C2, products increased to 53% with a total current density easily exceeding 400 mA cm−2 under −0.92 V versus RHE in a flow system. Such a significant performance improvement using the flow reactor can be ascribed to the enhanced CO2 diffusion and suppressed side reactions, mainly originating from the local gas-electrolyte-catalyst triple-interface architecture.

The zero gap cell is another emerging class of electrolyzers, which further removes the flow channels in flow cells and presses two electrodes together with an ion-exchange membrane in between. This configuration could significantly decrease mass transfer and electron transfer resistance and thus improve energy efficiency, making it more feasible in practical applications (110). The reactants fed to the cathode can be either CO2-saturated catholyte or humidified CO2 stream. Water vapor or aqueous electrolyte is mandatorily fed to the anode for proton release to compensate the charge for the CO2 reduction species (111). Gutiérrez-Guerra et al. (109) evaluated the performance of the Cu-AC hybrid catalyst in the zero gap cell and reported that acetaldehyde is the main product with a high selectivity of 60%. As another advantage of this device, it is very easy to pressurize the reactant flow and significantly enhance the local CO2 concentration, thus resulting in large current densities and high reaction rates (110). However, the accelerated ion exchange rate in zero gap cells tends to acidify the catholyte, shifting the reaction toward H2 evolution instead of CO2 reduction (112). To tackle this problem, Zhou and co-workers (112, 113) inserted a buffer layer with a circulating aqueous electrolyte between the cathode and membrane to maintain the proper pH near the cathode for CO2 reduction reaction. Although various C2, products were detected on the basis of the zero gap cells, including acetone, ethanol, and n-propanol, the FEs are still relatively low. Most
reported studies always focus on C₁ products that involve fewer numbers of proton and electron transfers during the reduction reaction. Therefore, the feasibility of the zero gap cell for C₂⁺ products is still under debate (110).

Moreover, microfluidic electrolytic cells (MECs) are a kind of highly attractive electrolyzer configuration developed by Kenis and co-workers (39, 114). In this device, the membrane is replaced by a thin space (<1 mm in thickness) filled with flowing electrolyte stream to separate the anode and cathode. The CO₂ molecules could quickly diffuse into the electrode-electrolyte interface near cathode, and the two fixed GDEs are flushed by flowing electrolyte. Compared to membrane-based flow cells, MECs not only avoid the high membrane cost but also mitigate water management, which particularly refers to the anode dry-out and cathode flooding when operated...
at high current densities owing to the osmotic drag of water molecules along with proton transport from anode to cathode across the membrane (115). As far as we know, despite the noticeable merits and achievements, a minimal number of studies have achieved C₂⁺ products in the original MECs. This is probably caused by the “floating” effect that protons formed in the anode are easily drained from the cathode vicinity or washed away by the flowing electrolyte, rather than participating in the multiple proton required C₂⁺ formation reaction. The speculation could be confirmed by the following instance. In 2016, Kenis and co-workers (31) reported the successful reduction of CO₂ to C₂⁺ products on a modified and membrane-containing MEC, in which NGQDs could reduce CO₂ molecules to C₂⁺, with 55% FE (31% for ethylene, 14% for ethanol, 6% for acetate, and 4% for n-propanol) at an applied potential of −0.75 V versus RHE in 1 M KOH solution. It is important to point out that an electrolyte environment could significantly affect the product selectivity as well. For example, Jiao and co-workers (30) synthesized a nanoporous Cu catalyst and then tested its ECR performance using different electrolytes (KHCO₃, KOH, K₂SO₄, and KCl) in a membrane-based MEC. They revealed that the CO₂ reduction in alkaline electrolyte (KOH) exhibits the highest C₂⁺ selectivity and current density, as shown in Fig. 8 (F and G). At −0.67 V versus RHE in 1 M KOH electrolyte, the obtained FE for C₂⁺ reaches up to 62% with a partial current density of 653 mA cm⁻², which is among the highest current densities that have ever been reported in electrochemical CO₂ reductions toward C₂⁺ products. Ethylene (38.6%), ethanol (16.6%), and n-propanol (4.5%) are the main C₂⁺ products with a small amount of acetate. They also pointed out that there is a strong correlation between the calculated surface pH and FE for C₂⁺ products: The higher the surface pH, the higher current densities and C₂⁺ products yield, as depicted in Fig. 8H. The theoretical calculation proposed that the near-surface OH⁻ ions could strongly facilitate C–C coupling (31).

In addition to the electrolyzer configuration, the electrolyte applied in different electrolyzers could also substantially alter the final ECR products. As we mentioned above, highly alkaline KOH solutions are always used in flow cells with excellent performance rather than in anode cells. It is ascribed to the fact that KOH electrolyte could provide higher electrolyte conductivity, decrease ohmic resistance between the thin electrolyte coating on catalyst and bulk electrolyte, and further decrease the required overpotentials for C₂⁺ formation (31). The DFT results further confirm that the presence of OH⁻ ions could lower the energy barrier for CO dimerization, thus boosting the C₂⁺ formation and suppressing the competition from C₁ and H₂ formation (30, 33). However, alkaline KOH could not be used as electrolyte in H-type cells. This is because CO₂ streams will rapidly react with KOH solutions and lastly create a bicarbonate solution with neutral pH in H-type cells (30). In flow cells, however, once the CO₂ diffuses through the GDE, the CO₂ molecules will be consumed at the triple boundary phase (CO₂-catalyst-electrolyte) to form reduced products immediately. Besides, the poor buffering capacity of the electrolyte is able to rapidly increase the pH around the electrode in stationary electrolyzer configurations, whereas the flowing electrolyte will refresh the surface and minimize the pH fluctuation in the electrolyte (33, 116).

As aforementioned that ECR is a diffusion-controlled reaction, high reaction pressure could also significantly enhance the bulk and interface CO₂ concentration. The common high-pressure reactors are similar to the stainless steel autoclave, in which high-pressure CO₂ (up to 60 atm) could be introduced into the cell, leading to a remarkable increase in both the FE and the current density of C₂⁺ (117, 118). Sakata and co-workers (119) showed that the current density could be improved to 163 mA cm⁻² under 30 atm on a Cu electrode with ethylene as the major product. Many metal catalysts (e.g., Fe, Co, and Ni), with no activity for C₂⁺ production at ambient pressure, could reduce CO₂ to ethylene, ethane, propane, and other high-order C₂⁺ products at elevated pressures. It has been demonstrated that the selectivity of the products markedly depends on the CO₂ pressure in the manner of altering CO₂ availability at the electrode surface (117, 120). The main reduced products are altered from H₂ to hydrocarbons (C₂⁺ included) and lastly to CO/HCOOH with increased CO₂ pressure. Notably, the CO₂ pressure should be carefully monitored because excessive high or low CO₂ pressures would induce superfluous or limited CO₂ diffusion rate, which tends to favor the production of CO/HCOOH or H₂. Only a compatible amount of intermediate CO and current density that generated on the electrode surface could facilitate the C–C coupling reaction and enhance C₂⁺ product selectivity (119).

**Structure of a GDE**

Designing a novel electrode with advanced structures is another important direction to enhance the selective C₂⁺ production. In early stage, the working electrodes are nonporous metal foils and suffer from sluggish mass transfer (26, 105). As a result, GDE was proposed to alleviate the poor cell performance by providing hydrophobic channels that facilitate CO₂ diffusion to catalyst particles (121). The conventional GDE usually comprises a catalyst layer (CL) and a gas diffusion layer (GDL), as shown in the lower part of Fig. 8A (30, 33). The gas-liquid-catalyst interface formed in GDE is crucial to improve the cell performance. The GDL assembled with porous materials (typically carbon paper) could provide abundant CO₂ pathways and ensure rapid electrolyte diffusion rate. It also acts as a low-resistance transportation medium for protons, electrons, and reduction products from the CL into the electrolyte (121). Drop casting, airbrushing, and electrodeposition are the common technologies for preparation of GDEs (122). Catalysts assembled with GDEs have been intensively investigated in CO₂ electroreduction to C₂⁺ products. Notably, the aforementioned flow cells with favorable performance are all coupled with GDEs. As early as 1990, Sammells and co-workers (123) reported that Cu-coated GDEs achieved high FE of 53% for ethylene with a high density of 667 mA cm⁻². Enhancing the selectivity of ethylene and ethanol is a major challenge that is always coproduced on Cu-based catalysts because of their very similar mechanistic reaction pathways. Moreover, it is important to point out that the elevated productivity and selectivity of ethylene compared to ethanol have been observed on Cu-based GDE (25, 36). Gewirth and co-workers (36) showed an excellent FE of 60% for ethylene and a suppressed FE for ethanol of 25% on electrodeposited Cu–Ag GDE, when the total current density reached ~300 mA cm⁻² at −0.7 V versus RHE. It is a rare work that achieved such a high selectivity at a large current density. This finding suggests that a GDE-incorporated electrode provides a promising avenue for tuning the reaction pathways, in which the selectivity of reduced products can be obtained at high current densities.

The stability of GDEs is also a significant issue that should be addressed because stable long-term operation is essential to realize practical application for flow cells. Despite the outstanding CO₂-to-C₂⁺ performance achieved with GDEs, the stability is still poor due to the weak mechanical adhesion of the catalyst, GDL, and binder layers (77, 124). The carbon surface of GDL might change from hydrophobic to hydrophilic during the electrochemical reaction due to the oxidation reaction that occurred at elevated overpotentials, which leads to
the flooding in GDL and obstructed CO2 diffusion pathways (33). To solve this problem, researchers integrated hydrophobic scaffold of polytetrafluoroethylene (PTFE) into GDEs. Compared to hydrophilic Nafion, a hydrophobic PTFE layer renders a superior long-term stability (33). Sargent and co-workers (33) assembled a Cu catalyst between the separated PTFE and carbon NPs, in which the hydrophobic PTFE layer could immobilize the NPs and graphite layers, thus constructing a stable electrode interface (Fig. 8, I and J). As a result, the FE for ethylene production was increased to 70% in 7 M KOH solution at current densities of 75 to 100 mA cm−2. The life span of this flow reactor was extended to more than 150 hours with negligible loss in ethylene selectivity, which is 300-fold longer than traditional GDEs, as shown in Fig. 8K. Such a sandwich structure has been demonstrated to be an excellent GDE design. For example, Cui and co-workers (124) designed a trilayer structure with an active electrode layer clipped by two hydrophobic nanoporous polyethylene films. The outer hydrophobic layers could slow down the electrolyte flux from the bulk solution, leading to stable, high local pH around the working electrode. Optimization of the interlayer space, which can improve CO2 transport and adsorption, is also important in such a design (124). Recently, carbon nanotubes have also been integrated into the GDEs because of their high porosity, good conductivity, and hydrophobicity, which could facilitate electron and mass transportation (77).

Despite the exciting progresses on ECR, strategies for low-cost, large-scale C2+ product generation are rarely present (125). At this stage, the challenges and opportunities are concurrent to understand the reaction mechanisms of ECR and commercialize this promising technology.

SUMMARY AND OUTLOOK

As an elegant solution to close the carbon loop and store intermittent renewable energy, such as wind and solar, substantial progresses have been made to achieve efficient CO2 conversion in the past decades. While the understanding of the processes associated with ECR has come a long way since its early days (126), the C–C coupling via ECR toward C2+ products is still far from ready for practical application. In this review, we took a detailed look at the current strategies that can promote the selectivity and production rate for C2+ products via ECR, including fine-catalyst tuning, electrolyte effects, electrochemical conditions, and electrochemical electrode/reactor design.

Despite all the effort put into ECR, there are still many problems with the current catalysts and ECR system that must be addressed before commercializing ECR. First, as the dominating catalyst to realize efficient C–C coupling, Cu suffers from serious stability issues, especially in aqueous electrolyte, and can rarely survive for 100 hours due to their high atom mobility, particle aggregation, and structure deterioration under ECR conditions. Thus, how to achieve long-term stability using a Cu-based catalyst is still an open challenge. Anchoring the Cu-based catalyst on specific support with strong interaction might be a reliable strategy to preserve the catalyst structure/morphology and thus provides enhanced life span. Furthermore, using a polymer membrane electrolyte to replace the aqueous solution during ECR can probably further improve the stability of the Cu-based catalyst. In addition, from the perspective of catalysts, in situ/in operando characterization techniques and theoretical modeling should also be used to monitor and understand the catalyst performance decay, thus, in turn, suppressing the degradation and poisoning of catalyst to the lowest levels. Another important issue of ECR catalysts that should be addressed is to make the synthesis protocol viable for mass production. To this end, streamlining the synthetic procedures using widely available feedstocks is preferred.

Second, the generated C2+, oxygenated from ECR are usually mixed with solutes (e.g., KHCO3 and KOH) in the electrolyte for traditional H- or flow-cell reactors, which, however, requires extra separation and concentration processes to recover pure liquid fuel solutions in practical applications. At the same time, the evolved C2+, hydrocarbons are also mixed with H2 and residual CO2. Thus, a costly separation process is indispensable for current ECR technology, which further hinders ECR from practical application. Therefore, how to directly and continuously produce pure liquid fuel solutions and pure gas hydrocarbons, particularly with high product concentrations, is highly desirable for the practical deployment of ECR. We thus predict the rising importance of direct generation of pure products via ECR in the near future, which may take the ECR technology much closer to market (127).

Third, while the formation of C–O and C–H bonds, such as ethanol, acetic acid, and ethylene, in ECR technology has been heavily studied, exploration of other types of products is also important for ECR technology and shows economical interest. For example, recently, Han and co-workers (128) reported the production of 2-bromoethanol by ECR. The in situ formation of C–Br bond transforms the product from ethanol to 2-bromoethanol, which is an important building block in chemical and pharmaceutical synthesis and shows higher added value. Thus, beyond the current well-studied C2+, products, we believe that targeting of other rarely explored products such as oxalic acid (129) and synthesis of more complex C2+ molecules such as cyclic compounds is another promising route for future ECR research.

Last but not least, novel electrode and reactor designs such as waterproof GDE, liquid-flow cells, and PEM cell should be widely adopted to boost the ECR production rate to commercial level (>200 mA cm−2). However, the large discrepancy in electrocatalytic activity is always observed when electrocatalysts are applied to the full cell test. Therefore, more systematic studies should be performed to minimize the gap between half-cell studies and full-cell device application to bring the ECR from lab-scale test to practical use.

In summary, electrochemical CO2 reduction offers good opportunity for us to deal with the environmental issue from greenhouse gases emitted by human activities. It also shows the possibility to achieve clean fuels and chemicals using renewable energy. While many challenges remain for ECR technology at the current stage, especially for the C–C coupling process, it is believed that with continued research and development on both catalyst optimization and cell perfection, the perspective of a real-world CO2 electrolysis for clean fuel and chemicals will be realized in the near future.

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