A brief review of electrocatalytic reduction of CO₂—Materials, reaction conditions, and devices

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Abstract
Global warming caused by the rapid increase in atmospheric CO₂ concentration is regarded as one of the most serious problems faced by human being. Electrochemical CO₂ reduction (ECR) is one promising strategy that can fix CO₂ in a mild and clean manner combined with sustainable energies. However, the ECR performance is highly dependent on the catalysis system because of the difficulty in CO₂ activation, low mass transfer, poor product selectivity, and competitive hydrogen evolution reaction (HER). The binding strength of electrocatalysts toward carbon intermediates is the crucial factor for ECR performance. Furthermore, the reaction conditions and the configurations of devices are also of significance for ECR efficiencies. Here, we briefly reviewed the effects of electrocatalyst materials, as well as the reaction conditions, coupled anodic reactions, and devices on the ECR. Moreover, challenges and some perspectives for large-scale applications are included.

1 | INTRODUCTION
Electrochemical CO₂ reduction (ECR) is considered as one of the most promising approaches to convert CO₂ to valuable products and to help solve the energy and environmental crisis. ECR generally proceeds at benign reaction conditions under ambient temperatures and pressures, which greatly benefits the large-scale applications. As the power of ECR, electricity can be derived from renewable energies, such as solar energy, tide, and wind. These renewable energies would be stored as chemical energies in high value-added chemicals upon the ECR process, which could be an ideal choice for energy conversion and storage technology for high energy densities and low costs. Considering the rapid increase of CO₂ concentration in the atmosphere (from 270 ppm in the 1800s to 401 ppm in 2015), ECR...
technologies have attracted increasing interest in recent years (see the publication numbers per year, Figure 1).

An intractable issue for ECR is that the inert CO$_2$ molecular is fully oxidized and thermodynamically stable, resulting in the difficulty of linear CO$_2$ activation. Large energy barrier should be overcome to form CO$_2$•$^-$ intermediate, which requires a negative potential of −1.90 V vs the standard hydrogen electrode (SHE). The specific adsorption of CO$_2$ on electrodes and proton-electron transfer steps are more thermodynamically favorable with less-negative potentials. However, these steps in ECR are a multi-electron transfer process leading to complex reaction pathway. Common reduction products of ECR are carbon monoxide (CO, 2-electron transfer) and formic acid/formate (HCOOH/HCOO$^-$, 2-electron transfer). Some organic chemicals with deeper reduction states like methanol (CH$_3$OH, 6-electron transfer), methane (CH$_4$, 8-electron transfer), ethylene (C$_2$H$_4$, 12-electron transfer), and ethanol (C$_2$H$_5$OH, 12-electron transfer) can also be produced from ECR process. Due to the similar potentials of half-reactions, the products may be composed of multiple carbon compounds, and hence, the control of product selectivity should be deeply studied. Half reactions on the cathode are summarized in Table 1 (pH = 7, 25°C, 1 standard atmospheric pressure). Notably, the equilibrium electrode potential (−0.42 V vs SHE at pH = 7) of the hydrogen evolution reaction (HER) is also presented in Table 1, showing a close potential to those of ECR reactions. This leads to the inevitable competition of HER with ECR in the aqueous system and the formation of an undesirable side product, H$_2$. Suppressing HER is also of great significance for ECR investigations. Moreover, in the respect of profits of practical applications, the current density should at least exceed hundreds of milliampere/cm$^2$ and the overpotential should be low for high energy efficiency. The design of nanostructured electrocatalysts can improve ECR and has been reviewed in many previous papers. However, a suitable catalyst only reduces the activation energy barrier of the reactions, but the other factors such as the mass transfer (temperatures, pressures, solubility, etc), the counter anodic reaction, and the configurations of the ECR electrolyzer can also thermodynamically and kinetically influence the efficiency of the ECR. In the following part of this review, the effects of these physical chemistry factors toward the performance and recent studies of ECR reactions will also be discussed.

2 FUNDAMENTALS OF ECR REACTIONS

2.1 The parameters in ECR reactions

The performance of electrocatalysis can be quantitatively measured for several fundamental parameters, such as the onset potential, the Faradaic efficiency (FE), the energy efficiency (EE), and the current density.

Onset potential means the practical potential, where the difference between equilibrium potential and onset potential is defined as overpotential.

Faradaic efficiency implies the selectivity of products, and it can be calculated by the following equation (Equation 1):

$$\eta = \frac{a n F}{Q}$$  \hspace{1cm} (1)

where $a$ is the number of transferred electrons; $n$ is the amount of the specific product (mol); $F$ is the Faraday’s constant ($F = 96485$ C mol$^{-1}$); $Q$ is the quantity of the charge consumed in reduction (C).

The energetic efficiency (EE) is a parameter reflecting the utilization of overall energy toward the desired product. EE can be calculated by the equation below:

$$\eta_{\text{energetic}} = \frac{E_{\text{eq}}}{E_{\text{eq}} + \eta} \times \eta_{\text{Faradaic}}$$  \hspace{1cm} (2)

where $E_{\text{eq}}$ and $\eta$ are the equilibrium potential and overpotential, respectively.
The current density refers to the current per unit area of the geometric surface (mA cm\(^{-2}\)). It reflects the kinetics of reduction, implying the possibility of large-scale applications. The current density of specific products can be calculated by multiplying the total current density and the corresponding FE.

### 2.2 The mechanism of ECR reaction

The ECR process involves three major steps occurring at the interface between cathode and electrolyte. The first step is the chemical adsorption of CO\(_2\) molecules on the surface of electrocatalysts. Then, the electrons transfer and/or protons migrate to cleave C-O bonds with the formation of related intermediates. Finally, these intermediates rearrange to products and desorb from the surface of the catalyst into the electrolyte. Simultaneously, the anodic reaction occurs on the anode side for the charge balance of the whole electrolyzer. The cathode and anode are usually separated by an ion-exchange membrane. (Figure 2).

### 3 ELECTROCATALYSTS OF ECR REACTION

The efficient ECR can be promoted via homogeneous and heterogeneous catalysis reactions. Homogeneous electrocatalysts are the microcyclic organics or metal-organic complexes possessing highly accessible metal active sites. Since the 1970s, homogeneous catalysis of ECR has been extensively studied. However, the high cost, toxicity, and intricate separation may hamper it from industrial applications. On the other hand, due to the low-cost and eco-friendly properties, heterogeneous electrocatalysis has received much attention in recent years. The methodologies of nano-catalyst synthesis in ECR are sophisticated referring to those of oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and HER. Thus, we will emphasize on the heterogeneous electrode materials in this section.

#### 3.1 Metallic electrocatalysts

The first step of ECR reaction on the surface of the metal catalysts is the generation of the CO\(_2\)•\(^-\) intermediate, followed by the possible electron/proton transfer steps. In general, to achieve high catalytic performance, stabilization of the intermediates on catalysts during the reduction is crucial, which determines the mechanisms and kinetics of the reactions.

The possible mechanisms of metal electrodes are summarized in Figure 3. According to different tendencies to bind intermediates, the polycrystalline metal electrodes can be divided into three groups. The metals from Group 1, including Hg, Pb, Bi, Sn, and In, prefer to bind *OCHO intermediate.
and benefit the formic acid/formate production.\textsuperscript{10} Au, Ag, Zn, and Pd, etc are classified in Group 2, which can bind the *COOH intermediate tightly after a protonation step from CO\textsubscript{2}•− intermediate and hence can eliminate H\textsubscript{2}O molecular to form *CO intermediate. However, the binding is not strong enough between these metals and the *CO intermediate and cannot facilitate further reduction, and thus releasing CO from the surface of the metal catalysts.\textsuperscript{22} Only Cu is categorized into Group 3, because it has strong binding energy to stabilize *CO. This is beneficial for further reduction of *CO and producing value-added products, such as hydrocarbons and alcohols.\textsuperscript{19} Other metals, like Pt, Ni, Fe, and Ti, are prone to bind hydrogen instead of carbon intermediates, incurring the preferential selectivity of HER and suppression of ECR reduction.\textsuperscript{10} Therefore, the binding energy of metals to intermediates is a dominated factor for high selectivity and effective ECR performances.\textsuperscript{23}

3.1.1 | Copper

Copper is the only metal that can reduce CO\textsubscript{2} to hydrocarbons and alcohols.\textsuperscript{24} These final products can store more energy through multi-electron (>2) reduction and are usually more valuable than formic acid or carbon monoxide. However, the large overpotentials render the unsatisfactory energy efficiency and the low selectivity of products on the surface of the polycrystalline Cu electrocatalyst.\textsuperscript{24} Many studies have uncovered the mechanisms of CO\textsubscript{2} reduction with Cu and provided various strategies to enhance the performance of the Cu catalyst, such as nano-sized and morphology design,\textsuperscript{25,26} alloying,\textsuperscript{14,27} and surface oxidation-reduction.\textsuperscript{28,29} These works have paved the way for the accessible application of Cu catalyst in ECR.

Cu was initially used in ECR in an aqueous system by Hori and his colleagues in the 1980s. They detected CH\textsubscript{4} after a galvanostatic electrolysis with a current density of 5 mA cm\textsuperscript{−2} under ambient conditions.\textsuperscript{30} Then, subsequent studies revealed that C\textsubscript{2}H\textsubscript{4} was also produced, and its faradaic efficiency increases with the enhanced temperature from 0 to 40°C, while the production of CH\textsubscript{4} was suppressed (Figure 4A).\textsuperscript{22} Besides, the electrolyte also affects the selectivity of Cu. As shown in Figure 4B, dilute KHCO\textsubscript{3} electrolyte is able to assist the formation of C\textsubscript{2+} compounds, whereas the concentrated solution prefers to the H\textsubscript{2} production. The authors explained that OH\textsuperscript{−} will generate with the proton transfer, and its release is much faster than neutralization with HCO\textsubscript{3}− buffer. This induces the elevated local pH around the electrode in a non-equilibrium situation, preventing hydrogen charge. Less HCO\textsubscript{3}− supplies in dilute electrolyte than concentrated one results in higher local pH, leading to the suppression of hydrogen and hence the higher faradaic efficiency of ECR. Figure 4C presents the relationship between onset potential and the selectivity of products. H\textsubscript{2}, HCOOH, and CO are preferentially produced at less-negative potentials, while CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{4} can be generated at more-negative potentials, a consequence of the distinctive reduction routines related to the intermediates.\textsuperscript{24}

**FIGURE 4** The pioneering works on polycrystalline Cu catalyst by Hori’s group. The relationships between (A) temperature, (B) concentration of the electrolyte, and (C) onset potential, and the Faradaic efficiency of products in ECR reaction. Reproduced with permission from Ref.22 (A) Copyright 1986 The authors and Ref.24 (B, C) Copyright 1989 The Royal Society of Chemistry Copyright
Local pH in an aqueous ECR reaction is a crucial factor that affects the selectivity of C₂ compounds on Cu. Yang et al. designed Cu mesoporous electrodes with different controlled widths (30 and 300 nm) and depth (40 and 70 nm, Figure 5A-D). They suggested that more narrowed width and increased depth result in higher selectivity of C₂ (Figure 5E). This is attributed to the elongated diffusion pathway of HCO⁻₃⁻ buffer without fast neutralization of OH⁻, and hence the higher local pH near the electrode material. They then analyzed the performances of Cu catalysis under a controlled convective flow. The rising speed of rotation caused the decrease of CO₂ conversion, a consequence of the shorten retention span of intermediates. Kas et al. also confirmed this principle. Figure 5F,G show the selectivity of reduction products with controlled electrolyte concentrations and pressures. As seen, low concentrations lead to the moderate buffer capacity of electrolyte, and thus the high local pH and high selectivity of C₂ species (ethylene). High pressure also benefits ethylene production. Although it can enhance the buffer capacity of electrolytes, the increase of CO surface coverage may be key to facilitate the C-C coupling.

The morphology and size of the Cu electrocatalyst are also the dominating factors to ECR performances. The nanoparticles (NPs) possess a large surface area and more active sites with low coordination numbers (surface planes, edges, and corners), enabling improved performances. Dispersed Cu nanoparticles with a diameter of ~7 nm exhibit a high Faradaic efficiency of 76% for methane at −1.35 V, compared to 44% for that of polycrystalline Cu. The partial current density of Cu-NPs is 4 times higher than that of Cu foil. Reske et al. have investigated particle size effect on size-controlled Cu-NPs ranged from 2 to 15 nm. They suggested that the smaller Cu-NP provides a larger total current density but inferior hydrocarbon selectivity. Lower coordination number sites of smaller particles around 2 nm and below are exposed, offering...
much stronger bonding of *CO and *H which may decrease the chance of C-C coupling to form hydrocarbons, and hence the higher possibility to form CO and H2.

Sargent’s group proposed that adding additives or coatings on catalyst surface can regulate the binding states of intermediates on Cu and control the selectivity of production.33,34 The CO-CO dimerization can be promoted by a N-C layer via reducing the energy barrier and enthalpy, which is confirmed by DFT calculations. They fabricated the N-C/Cu catalyst on polymer nanowires, and this catalyst can achieve 93% of C2+ FE with 300 mA cm−2 in a flow cell.35 Some recent works on Cu-related catalysts were summarized in Table 2. Many substantial efforts have been made on the promising Cu electrode, while some proposed hypotheses are still obscured or controversial. More studies will be done to understand both the catalysis mechanisms and the structure-function relationship.

Alloying metals with Cu can lower down the costs and, more importantly, the density of state (DOS) of Cu alloy can be shifted related to Fermi level by introducing other elements which can tune the binding strength toward the adsorbates.48-50 The catalytic processes of Cu alloys are fundamentally dependent on the metal-oxygen and hydrogen affinities of the second metal element. For instance, higher oxygen affinity but lower hydrogen affinity than Cu (Sn, In, and Pb, etc) cooperating with Cu causes the weak binding with the *COOH intermediate of the alloy, which is prone to produce HCOOH; the elements that have lower oxygen and hydrogen affinities than Cu (Zn, Ag, and Au, etc) have a stronger binding strength of *COOH than *CO, which are likely to generate CO via *CO desorption; other metals possess both higher O and H affinities than Cu (Co, Fe, Pt, and Ni, etc) help to favor HER rather than ECR.49

3.1.2 | Noble metals

Noble metals (Au, Ag, Pd, etc) often show good activity and low overpotentials.50-64 Hori and his co-workers found bulk Au electrode could convert CO2 into CO at a low overpotential, starting at −0.8 V vs NHE, and a high partial FE of 91% for CO at −1.10 V vs NHE with a partial current of 3.7 mA cm−2.53 Minimizing the particle size of Au can increase the ratio of low-coordinated active sites and change the binding strength of intermediate species. Zhu et al50 synthesized monodispersed Au-NPs from 4 to 10 nm (Figure 6A-C). Among them, 8 nm Au-NPs showed the highest CO FE of 90% at −0.67 V vs RHE. DFT results revealed that edge sites of Au-NPs are more active for CO formation, while corner sites are favorable for HER. 8 nm Au-NPs with 4 nm crystallite diameter provide a near-optimum high ratio of edge and corner sites, stabilizing *COOH and inhibiting HER reaction. Mistry et al54 also studied the size-controlled activity of Au-NPs. Notably, the decrease of particle size results in the increase of the total current density but inferior selectivity of carbon compounds, due to the increased ratio of the corner sites and hence the domination of HER. Au nanowires (NWs) with few corner sites exhibit a high FE of 94% at −0.35 V vs RHE for a duration of 6 hours without activity decay (Figure 6D,E). The good electrocatalysis performance of Au-NWs is attributed to the high ratio of edge sites (16%) and the moderate CO binding with these sites.51

In practice, silver is a good alternative metal catalyst due to its lower cost than Au and high selectivity in converting CO2 to CO.21 Hoshi and Hor et al studied the plane effects of single-crystal Ag for CO2RR. They proposed that the stepped Ag(111) is beneficial for CO product,35 a consequence of the stronger bind to *COOH intermediate.56,57 Thus, Peng et al57 synthesized preferentially oriented nanoparticles of Ag, exposing (111) and (100) facets orientation, which exhibits a high CO FE of 96.7% at −0.69 V vs RHE. Nanostructured Ag particles may show the enhanced activity and a different mechanism compared to the polycrystalline Ag, according to the Tafel slope (Figure 6F,G).52,58 The Tafel slopes of nanoparticles at c.a. 60 mV dec−1 indicate a fast electron transfer to CO2 prior to the rate-determining step. This is in sharp contrast to that of polycrystalline Ag (c.a. 120 mV dec−1) representing a rate-limiting step of the CO2− intermediate generation.52,58 Following that fast electron transfer of Ag-NPs, the rate-determining step may not be the protonation donated from HCO3− nor H2O, because HCO3− could donate greatly more hydrogen than H2O, but its concentration still showed a zero-order dependence on CO2RR activity.52,58 A possible rate-determining step, proposed by Lu et al,58 may be the migration of HCO3− from the electrolyte to the surface sites through the pores of nanostructured Ag.

Hori et al21 also attempted polycrystalline Pd foil electrode to reduce CO2, presenting the low FE of ~28% for CO and ~3% for formate in 0.1 mol/L KHCO3 under ~0.8 V vs RHE. As its counterparts, the activity of Pd is highly reliant on particle size.59-61 Gao et al59 synthesized 3.7 nm Pd-NPs, showing a high CO FE of 91.2% with greatly increased current density at −0.89 V. While CO is the major product at more-negative potentials (~0.45 to ~0.90 V vs RHE), formate is selectively produced on Pd-NPs surface at less-negative potentials (0.05 to ~0.25 V vs RHE), with a high FE of >90%. This is because the electrochemically formed PdHx surface at less-negative potentials promotes the hydrogenation of CO2 or even bicarbonate ions,62,63 but this surface is significantly occupied by *CO intermediate at more-negative potentials, recovering metallic Pd surface from PdHx surface.64

3.1.3 | Oxide(sulfide)-derived metals

In situ electro-reduction of thick metal oxide layers to oxide-derived (OD) metal NPs is an effective strategy to form the
| Catalysts                  | Products              | Potential (V vs RHE) | Current density (mA cm$^{-2}$) | FE (%) | Electrolyte                        | Ref. |
|---------------------------|-----------------------|----------------------|-------------------------------|--------|-----------------------------------|------|
| Cu-NPs                    | CH$_4$                | $-1.35$              | $-9$                          | 76     | NaHCO$_3$ (0.1)                   | 25   |
| CuPc                      | C$_2$H$_4$            | $-1.38$              | 2.8                           | 25     | KCl (0.5)                         | 36   |
| CuDAT-wire samples        | C$_2$H$_4$, C$_2$H$_5$OH | $-0.8$              | 90                            | 40% C$_2$H$_4$, 20% C$_2$H$_5$OH | KHCO$_3$ (1) | 37   |
| Cu-N-substituted aryldipyridinium | C$_2$H$_4$, C$_2$H$_5$OH | $-1.1$              | 1.02                          | 78.2 (C > 1) | 0.1 mol/L KHCO$_3$ + 10 mmol/L additive | 38   |
| Cu(II)-NU-1000            | Formate CO            | $-0.8$ to $-1.0$     | 1.2                           | 30     | NaClO$_4$ (0.1)                   | 39   |
| Cu/SnO$_2$                | CO                    | $-0.7$               | 4.6                           | 93     | KHCO$_3$ (0.5)                   | 40   |
| AuCu alloy nanoparticles  | CO                    | $-0.77$              | 1.39                          | 80     | KHCO$_3$ (0.1)                   | 27   |
| Cu dendrite               | C$_2$H$_4$, C$_2$H$_6$| $-0.8$               | 5.7                           | 55     | Na$_2$SO$_4$ (1)                 | 41   |
| N-C/Cu                    | C$_2$                | $-0.86$              | 300                           | 93     | KOH (1)                           | 42   |
| Oxygen-bearing Cu         | C$_2$H$_4$            | $-1.0$               | 44.7                          | 45     | KHCO$_3$ (0.5)                   | 43   |
| Sn-Cu/SnO$_x$             | Formate and CO        | $-0.7$               | 243                           | 98     | KOH (1)                           | 44   |
| Cu$_2$O@CuHHTP            | CH$_4$                | $-1.4$               | 11                            | 73     | KCl (0.1) KClO$_3$ (0.1)          | 45   |
| Cu$_2$S                   | HCOOH                 | $-0.9$               | 19                            | 87     | NaHCO$_3$ (0.1)                   | 46   |
| Cu$_2$O/Cu$_2$S           | HCOOH                 | $-0.9$               | 15.3                          | 67.6   | KHCO$_3$ (0.1)                   | 47   |
porous morphology of metal electrodes to enhance their activities. Kanan et al obtained OD-Cu and OD-Au nanoparticle films, exhibiting dramatically improved selectivity and durability and mitigated overpotentials. Then, Ma et al developed OD-Ag-NPs with a porous structure, which creates more active sites and generates a high local pH, showing a 20-fold higher FE to that of untreated polycrystalline Ag at the identical conditions (80% vs 4%). Other oxide-derived materials, like OD-Sn, Pb, and Bi, were also attempted, giving good activities.

The C2/C3 species can be obtained on OD-Cu electrodes, with a high selectivity of 50%-60% at moderate potentials, a consequence of the stronger surface binding to *CO intermediate than polycrystalline Cu. Verdaguer-Casadevall et al proposed that the surface sites of OD-Cu could bind CO more strongly than low-index and stepped Cu facets, which may arise from disordered surfaces at the grain boundary and defect terminations. Nilsson and co-workers used in situ ambient pressure X-ray photoelectron spectroscopy (APXPS) and quasi in situ electron-loss spectroscopy in the transmission electron microscope (EELS) to probe the active surface sites of OD-Cu electrode. They showed that the substantial amount of oxygen at the subsurface of OD-Cu leads to stronger CO binding, because of the minimized oxygen-induced σ-repulsion.

Kim and Hwang et al directly traced the ECR pathway on Cu beyond *CO by time-resolved attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS). C2+ path triggered by the CO dimerization to *OCCO was directly monitored, and results from ATR-SEIRAS suggested that the C-C coupling happens exclusively from CO dimerization while the *CHO would not participate. The *CHO intermediate is more likely to influence the CH4 formation. Qiu et al revealed the mechanism of the C-C coupling on OD-Cu. The Cu4O was generated upon ECR, and this active site can be stable even at −1 V vs RHE. After applying a certain bias potential on Cu4O, the energy barriers of *CO desorption and *CO dimerization were calculated to be 11.507 and 2.338 eV, respectively, indicating the much easier for C-C coupling in contrast to the CO releasing.

The participation of sulfur can also affect product selectivity. Luc et al studied the influence of the impurity of SO2 in CO2 flow on Cu, Ag, and Sn catalysts. Experimental results showed that only Cu is sensitive to SO2 impurity, that

![Figure 6](image-url)
is the S-modified Cu surface may form Cu$_2$S and enhance the conversion of CO$_2$ to formate. Furthermore, Cu$_2$S with a high density of grain boundaries can achieve high Faradaic efficiency of formate to be 87% at 0.9 V (vs RHE) and high activity. The change of the selectivity of Cu by introducing S can be attributed to the formation of positively charged Cu sites, which are prone to bind electronegative O rather than carbon of CO$_2$, and thus forming the *OCHO intermediate. These indicated the chemical environments of Cu can regulate the binding states of the intermediates, and the presence of Cu$^+$ may not be a sufficient condition for the C-C coupling.

3.2 | Carbon-based materials

Carbon electrocatalysts were also studied for ECR. Compared with the metallic materials, carbon materials hold distinctive superiority, including their high abundant resource, tailorable porous structures and large surface area, good electrical conductivity, inert properties to extreme conditions, and eco-friendliness. However, nonpolar pristine graphite materials, with sp$^2$-conjugated structure composed of neutral carbon atoms, can hardly interact with CO$_2$ by chemical adsorption, and hence the inferior capability of CO$_2$ activation. Introducing heteroatoms into carbon materials can effectively modify the electronic properties of the carbon surface and significantly boost the activity of carbon electrodes. This can be attributed to the changes in concentrations of charge carrier, local positive-negative charge states, the number of active sites, and the surface wettability. The heteroatoms, including B, N, S, F, etc, were doped into various carbon materials, which contain porous carbon, carbon nanotubes (CNTs), graphene, carbon nanofibers, etc, Figure 7. These materials showed comparable activity with those of metallic electrodes.

Nitrogen, the most frequent doping atom in carbon materials, has a similar radius but a larger electronegativity to carbon, giving an enhanced electrical conductivity as well as the extra active sites to carbon materials. N-doped graphene, CNTs, and carbon quantum dots, etc, have been utilized to reduce CO$_2$. Wang et al synthesized N-doped graphene via pyrolysis of graphene oxide and melamine. The obtained material with a N content of 5 atom% can trigger the conversion of CO$_2$ to formate with a small overpotential of 240 mV. Three types of N are doped in N-doped graphene, involving graphitic, pyridinic, and pyrrolic N (Figure 7A). Pyridinic N leads to more active sites and the positively charged adjacent oxidized carbon atoms, providing low free energy for activation and enhanced binding strength of intermediates, and thus low overpotential and high selectivity. For larger interfacial area and easy penetration of electrolyte, N-doped three-dimensional graphene foam was applied in CO$_2$RR. The electrode material was synthesized via a chemical vapor deposition (CVD) method and exhibited a small onset overpotential of −0.19 V for CO formation and a maximum FE...
of ~85% at −0.47 V. DFT calculation results also suggest pyridinic N is the most active sites to lower down the free energy barrier to form *COOH intermediate. In contrast to graphene, CNTs have higher curvatures that also affect the activity of CO₂RR. Chai and Guo investigated the catalyst behavior of graphene/carbon nanotubes by first-principle simulations, suggesting N-doping and curvature can significantly tune the product selectivity and activity. They concluded that the graphitic-N-doped edge sites effectively promote the CO₂RR activity due to the special electronic edge states; CNTs with a higher degree of curvature are favorable for CH₃OH and HCHO formation, while flat graphene prefers CO/HCOOH production. Besides, the curvature can also reduce the overpotentials for higher energy efficiency. N-doped CNTs were prepared by a liquid CVD method, showing a low overpotential of 0.26 V and a high selectivity of 80% to CO product (Figure 7B). The good electrochemical performance is assigned to the enhanced electrical conductivity, pyridinic N sites, strong binding energy of adsorbed *COOH, and high barrier for HER. Wen and Huang et al reported a Zn-MOF-74 derived N-doped carbon with large pore sizes as well as the high concentration of the active pyridinic and graphite N (68.31%). Due to the large pore sizes, a large amount of accessible N active sites was exposed, and the optimized catalyst offered a high FE of 98.4% at −0.55 V vs RHE which is the highest among the reported carbon materials. The FE CO values are highly related to the total content of the pyridinic and graphite N (Figure 7C-E), so these two N species were responded to the efficient CO₂-to-CO conversion.

C₂ species can also be produced on carbon materials in ECR. Song et al reported the N-doped mesoporous carbon in reducing CO₂ to ethanol. Nearly 100% selectivity and a high FE of 77% at −0.56 V vs RHE are achieved, indicative of preferential C-C coupling. Based on the experimental and DFT calculation results, pyridinic N sites, as well as the cylindrical channel structure, are able to promote dimerization of *CO to form OC- CO* intermediates.

Moreover, diamonds have been explored as a chemically stable electrocatalyst with good activity. Liu et al studied the N-doped nanodiamond/Si rod array for CO₂RR, which exhibits a high selectivity of acetate (~77%), fast-converting kinetics, and the inhibition of HER. In situ infrared spectra demonstrated that the pathway might be CO₂ → CO₂* → (COO)₂* → CH₃COO⁻. These are given by the N-induced defects and positively charged carbon atoms and the vertically aligned rod array structure. Subsequently, boron and nitrogen co-doped nanodiamonds showed an elevated selectivity of 93.2% (~1.0 V vs RHE) to ethanol, thanks to the synergistic effect of B, N co-doping.

Aside from these, single atomic catalysts (SACs) can effectively promote the CO₂RR. These complex materials have M-N-C (M is the metal ions) active sites, where the metal ions are anchored on the N defects in the carbon matrix by coordination bonds. The central ions, such as Fe⁺², Ni⁺², etc, and doped heteroatoms (N, S, B, etc) may synergistically affect the activity of these carbon electrocatalysts. Varela demonstrated that such metal-N-C catalysts are comparable with the polycrystalline gold benchmark, showing mitigated overpotentials and high selectivity of carbon products. Ju et al attempted Mn, Fe, Co, Ni, and Cu as the transition metal sites on the N-doped nanoporous carbon. Among them, Fe- and Ni-N sites are more active to reduce CO₂ to CO, while Co-N sites are prone to hydrogen evolution. Bi et al used a facile ion-adsorption approach to immobilize Ni⁺² on N-doped graphene. The optimal FE achieves 92% for CO formation at −0.68 V, with a current density of 10.2 mA cm⁻².

### 3.3 Theoretical calculations to guide the electrocatalyst design

Theoretical calculation on the ECR refers to the quantification of the energies and forces at the process of ECR. It can help the researchers to understand the mechanisms of ECR and guide them to find the more suitable electrocatalysts. As we discussed in Section 3.1, the adsorption/desorption states of the intermediates on the various electrode surfaces are the key factor for the selectivity of the products and the reaction kinetics. Based on the Sabatier principle, the binding strength between a suitable catalyst and the intermediates should be neither too strong nor too weak. This facilitates the intermediate adsorption and desorption, and thus the reaction rate of the ECR. The binding states of the adsorbates are influenced by not only the elements of the electrodes, but also the surface vacancies, exposed facets, corners, or edges, and the chemical additives on the catalysts, etc, and hence, the calculation is an effective strategy that unveils the structure-activity relationship of the surface-engineered electrodes. We here show some critical calculation studies for the pathway investigations on ECR.

#### 3.3.1 The pathway of ECR on the copper electrodes

Converting CO₂ into multi-carbon products is desirable but this process is more complicated and only the Cu electrodes exhibit considerable performance, so knowing the reaction pathway is of great significance. In 2010, Peterson et al revealed the mechanism of copper catalysis via the computing method. A computation hydrogen electrode (CHE) model coupled with density functional theory (DFT) was applied to calculate the reduction pathways of the products. Figure 8 depicts the formation pathways of (a) H₂, (b) HCOOH, (c)
CO, and (d) \( \text{CH}_4 \). The lowest energy pathway of \( \text{HCOOH} \) (Figure 8B) indicates that the adsorption of \( \text{CO}_2 \) and the electron/proton pair to the carboxyl (\( \cdot \text{COOH} \)) initiate the catalysis reaction, and this potential-limiting step requires \(-0.41 \) \( \text{V} \) by calculation. Then, the second electron/proton pair adds to the adsorbate to form \( \text{HCOOH} \). \( \cdot \text{CO} \) intermediate stems from \( \cdot \text{COOH} \) after electron/proton transfer and removal of water. Due to the weakly bind to the surface, \( \cdot \text{CO} \) is not only the intermediate of further reduction but also the emission gas product (Figure 8C). Subsequently, \( \cdot \text{CO} \) may convert to \( \cdot \text{CHO} \) by further hydrogenation, which is the key process of the formation of \( \text{CH}_4 \). This step starts at \(-0.74 \) \( \text{V} \) by calculation, more negative than that of \( \cdot \text{CO} \) formation, resulting in the more-negative potential range of \( \text{CH}_4 \) formation. The pathway can be described as \( \cdot \text{CO}_2 \rightarrow \cdot \text{COOH} \rightarrow \cdot \text{CO} \rightarrow \cdot \text{CHO} \rightarrow \cdot \text{CH}_2 \text{O} \rightarrow \cdot \text{CH}_3 \text{O} \rightarrow \text{CH}_4 \). Thus, the stabilization of \( \cdot \text{CHO} \) intermediate is crucial for mitigating the overpotential of \( \text{CH}_4 \) generation. Besides, with the decrease of \( \text{H}_2 \) production, CO and hydrocarbons are more preferable, because of the changes in surface coverages.

When the formation of CO becomes possible, the adsorbed carbon intermediates, instead of \( \cdot \text{H} \), will cover the surface sites of Cu, avoiding \( \text{H}_2 \) evolution. \( \text{C}_2\text{H}_4 \) is generated from \( \cdot \text{CHO} \) intermediate, the rate-limiting step, but CHE model is not suitable for calculating the non-electrochemical C-C coupling, and thus indistinguishable between various possible pathways.

Cheng et al\(^\text{93} \) have studied the mechanism of \( \text{CO}_2 \) to C1 species (CO and formate) on \( \text{Cu}(100) \) surface through quantum mechanics (QM) calculations. Taking into account the liquid/solid interface, they found greatly different pathways to form CO and formate. They suggested that forming \( \cdot \text{CO}_2 \delta^- \) intermediate from physisorbed \( \text{CO}_2 \) should overcome the free energy barrier of \( 0.43 \) \( \text{eV} \). However, this intermediate can be stabilized by the water solvent hydrogen bond (HB) network, without returning to physisorbed \( \text{CO}_2 \) in a 20 ps simulation. Upon Cu catalysis, the \( \text{HCOO}^- \) and CO formations are competing reactions. By calculation, only CO is reduced via \( \cdot \text{CO}_2 \delta^- \) electron/proton transfer, while the generation of \( \text{HCOO}^- \) is a consequence of the interaction between
surface $H^*$ and physisorbed $CO_2$. This conflicted with the previous hypothesis which describes formate is derived from $^{*}CO_2\delta-$ intermediate.

Insight into C-C coupling mechanism is significant to achieve high selectivity of C$_2^+$ species. Kuhl et al$^{94}$ have detected 16 different reduction species, involving 12 species of C$_2^+$. They explained that the wide variety of C$_2$/C$_3$ species might be attributed to the successive dihydroxylation of enol-like surface species. Schouten et al$^{95}$ proposed that C-C bond of C$_2$H$_4$ might generate from CO dimerization, two $^{*}CO$ intermediates coupling. Montoya et al$^{96}$ provided first-principle calculation results, demonstrating that it is kinetically more favorable for the generation of C-C bonds from the coupling of hydrogenated carbon intermediates, such as $^{*}CHO$ and $^{*}CH_2O$, than $^{*}CO$ dimerization. $^{*}CO$ may firstly be protonated and then couple to other C1 intermediates, which will overcome a lower energy barrier than direct $^{*}CO$ dimerization. However, based on Kim’s recent work using ATR-SEIRAS, C-C coupling occurs without the participant of $^{*}CHO$.$^{70}$ Thus, the possible pathway of the formation of C1 and C2+ on Cu catalyst surface was described by Etzold et al$^{97}$ (Figure 9).

Jiang et al$^{99}$ initially used DFT to calculate the facet dependence of the first C-C coupling steps on Cu catalyst. Calculation results indicate that Cu(100) and stepped (211) facets should be favorable for C$_2^+$ formation. To confirm this hypothesis, Cu-NPs with abundant Cu(100) facets were successfully synthesized, presenting C$_2^+$ Faradaic efficiency of $>60\%$ and a partial current density over 40 mA cm$^{-2}$.

We have discussed that the OD-Cu catalysts can provide excellent performances to produce multi-carbon products. Although it is commonly believed that the Cu(I) species facilitate the C$_2^+$ production, the real active sites and the mechanism are still obscure. Xiao et al$^{100}$ used the quantum mechanics methods and revealed that the Cu$^+$ sites alone actually deteriorate the efficiency, while the borders of oxidized and metallic Cu regions (Cu$^+$/Cu$^0$) will improve the performance. This is given by the synergetic effect of Cu$^+$-Cu$^0$ that enhances both CO dimerization and CO$_2$ activation. Very recently, Gong et al$^{101}$ further explained the respective role of the Cu$^+$ and Cu$^0$, according to the DFT results. They suggested that the metallic Cu is responsible for the CO$_2$ activation and facilitating the electron transfer and the oxidized Cu could strengthen the adsorption of $^{*}CO$ intermediate to boost C-C coupling.

### 3.3.2 Formate formation on the metal electrodes

The p-block metals, such as Sn, In, Bi, and Pd, and their derivatives generally show the high selectivity for formate/formic acid production.$^{102}$ These metal elements have strong oxygen
affinity and are more likely to generate HCOO* rather than *COOH and *CO, and hence the formate formation.

Jaramillo’s group studied ECR mechanism on various metal electrodes including Ni, Pt, Zn, Au, Cu, and Sn. They depicted a volcano-type curve of the HCOO* binding energy and the partial current density of HCOOH. Sn is at the top of the volcano curve meaning the optimized HCOO* binding energy of Sn and hence the highest formate selectivity. Interestingly, the metallic Sn is less active than oxidized Sn, and several reports performed the DFT studies to calculate the role of the oxidized Sn layer. Ge et al. found the dissociation of H2O to form a hydroxylated Sn layer is a crucial step in ECR. Their calculated free energy diagrams demonstrated that once the hydroxyls are generated, the CO2 molecule can insert into the OH* species to form bicarbonate species, which can be further reduced to HCOO* for formate production. Gong et al. also proposed the significant role of the surface hydroxyls on Sn. Based on the DFT results, H2CO3 molecules can be stabilized on SnO + H(101) surface via a hydrogen bond, and transform to HCOO*. Gong’s group also discussed the effect of oxygen vacancies on partial reduced SnOx for the ECR performance. A moderate content of O vacancies (Ov) of SnO/SnO2(110) can offer the most active surface and suppress the HER, which influences the binding strength between HCOO* and SnOx.

Bismuth (Bi) is another promising element for ECR to produce formate. The layer crystal structure of Bi makes it possible to be exfoliated to a 2D structure that can expose more under-coordinated active Bi sites. When Bi layers are stacked, the potential active sites are located at the terrace and edge. DFT analysis revealed that the edge sites provide the lower thermodynamic barrier for formate production and are more active than terrace sites. In addition, the curvature of Bi also affected the adsorption of the intermediates. The Bi nanotubes with the increasing curvature (monolayer slab, (20, 0) tube, (14, 0) tube) show reduced free energy for HCOO* adsorption and, meanwhile, the enhanced selectivity of formate. Constructing of Bi-Sn interfaces is also an efficient method. The addition of Bi to Sn upshifts the electron states of Sn away from Fermi level, which is favorable to HCOO* to absorb and formate generation.

The porphyrin-like M-Nx moieties are the main active sites, so the center metals and the coordination number are the critical factors to influence CO production. For example, the unsaturated Ni-Nx (x < 3) showed better CO selectivity than the well-defined Ni-N4 on NiPc. Based on DFT calculations, the free energy of the *COOH intermediate was lower on the unsaturated Ni-Nx sites than Ni-N4 sites. This trend can also be noticed on Co-Nx SACs. Two-N-atom coordinated Co (Co-N2) showed a better CO production than Co NPs and Co-N4. The lower required energy of CO2− formation on Co-N2 than Co-N4 leads to the higher CO2-to-CO activity, and the lower H* adsorption energy of Co-N2 is beneficial to prohibit the HER. The lower d-band center of Co-N2 (−0.81 eV) than Co-N4 (−1.06 eV) results in the stronger CO2− binding. Moreover, Geng and Zeng et al. compared Fe-N4 and Fe-Nx moieties for CO2-to-CO reaction, and found the Fe–N4 species has lower free energy to form *COOH, and the C on *COOH displays higher electron density on Fe–N5 than on Fe–N6, ensuring the better performance of Fe–N5. Apart from the coordination number, the coordinated N ligands can also affect the ECR. Pyrrolic N in Ni SACs offered lower energy for the generation of *COOH in contrast to the pyridinic N. In the Fe SAC, pyrrolic N can stabilize the Fe 3+ at −0.4 V vs RHE while pyridinic N does not stably support the Fe 3+ center.

### 4 | EFFECT OF REACTION CONDITIONS

Generally, ECR is conducted in the typical H-type electrolyzer, where the reduction and oxidation happen in the cathode and anode, respectively. The active species of carbon dioxide are the dissolved CO2(aq) and H2CO3, but the solubility of CO2 in an aqueous system is relatively low at the room temperature (33 mmol/L, 25°C, and 1 atm) which obstacles the mass transfer and coverage of active species on electrode upon ECR and hence limits the kinetics. Commonly, to accelerate the reaction rates, increasing the temperature can overcome the energy barrier and enhance the mass transfer, and increasing the concentrations of active species can enhance the coverage of CO2 on the electrode. However, elevating temperature renders a rapid decrease of the concentration of dissolved CO2 species and also facilitated competitive HER. Some researchers thus focused on high-pressure systems of CO2 or even supercritical environments. Dai’s group studied the electrochemical behavior of the Cu2O/Cu electrode in high-pressure CO2 environments. This electrode can provide 98% of FE for formate formation under over 45 atm which is greatly better than that at 1 atm, indicating the obviously suppressed HER and boosted ECR kinetics.
The electrolytes also affect the ECR performance. The solvated alkali metal cations at the outer Helmholtz plane can electrostatically interact with adsorbed species and influence the distribution of products.\textsuperscript{125-128} For Ag and Sn, increasing the radius of cations in the electrolyte can enhance the rate of CO and formate formation, but zero-related to HER; for Cu (100) and (111), the current densities of HCOO\textsuperscript{−}, C\textsubscript{2}H\textsubscript{4}, and C\textsubscript{2}H\textsubscript{5}OH increase as the radius of cation increased. Zhong et al\textsuperscript{128} also discussed the concentration effects on ECR performance. The increase of K\textsuperscript{+} concentration will cover up the electrode because of the electropositivity, and then block the adsorption of CO\textsubscript{2}, but the decrease of cation concentrations will lower down the ion conductivity, thus 0.1 mol L\textsuperscript{−1} KHCO\textsubscript{3} is relatively suitable for Cu-catalyzed ECR in H-cells. Beyond the aqueous system, other solvents (such as methanol, acetonitrile, dimethyl-sulfoxide, ionic liquids, etc)\textsuperscript{129-132} have been widely studied aiming at suppression of parasitic HER and dissolving higher concentration of CO\textsubscript{2}, but the costs and the viscosity are the challenges that should be considered.

Moreover, applying pulse current could be a subtle strategy to improve the ECR performance.\textsuperscript{48,133} Pulse current facilitates desorption of protons from the electrode surface and accumulation of carbonate/CO\textsubscript{ad} during the anodic pulsing, which can efficiently suppress HER and enhance the mass transfer of active CO\textsubscript{2} species. In particular, Cu electrode can get many benefits from pulse currents with periodic anodic currents due to the regeneration of electropositive Cu\textsuperscript{5+}, and the concurrence of Cu\textsuperscript{5+} and Cu\textsuperscript{0} leads to CO dimerization via formation of C\textsuperscript{5+}-C\textsuperscript{d−}.\textsuperscript{48}

5 | DESIGN OF CONCURRENT ELECTROLYSIS SYSTEMS

Most studies investigated the special catalysts on the cathode to reduce CO\textsubscript{2} in the three-electrode system (Figure 10A). However, the overall voltage of the electrolyzer relies on both the cathodic and anodic half-reactions, $E_{\text{overall}} = E_{\text{anode}} - E_{\text{cathode}}$; that means the anodic half-reaction inevitably affects the energy efficiency and practical applications of the complete cell. As we discussed, OER generally occurs at the anode side in the aqueous electrolyte. Its large overpotential and low product value are the intrinsic weaknesses of this reaction. Instead of applying appropriate catalysts to promote OER, alternative strategies have been proposed in replacing it with other oxidation reactions, mitigating overpotentials, and producing value-added chemicals.\textsuperscript{134-138} Bevilacqua et al\textsuperscript{137} combined CO\textsubscript{2} reduction and ethanol oxidation to acetate at cathode and anode (Figure 10B), respectively, providing a low working potential and hence a reduced energy consumption in contrast to the cell with OER, from 130 to 77 kWh. Llorente et al\textsuperscript{138} developed the anodic reaction in condensation of syringaldehyde.

\textbf{FIGURE 10}  Schematic illustrations of (A) the typical H-type electrolyzer; the modified electrolyzer of CO\textsubscript{2}RR (Reproduced with permission from Ref.128 Copyright 2017 The Electrochemical Society) and (B) alcohol oxidation (Reproduced with permission from Ref.137 Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim) and (C) Pairing ECR with methanol electrooxidation reaction to concurrently produce formate (Reproduced with permission from Ref.136 Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim); (D) the general design of continuous-flow device and (E) the process flow diagram of ECR in a continuous reactor. (Reproduced with permission from Ref.140 Copyright the Authors. Published by Elsevier Ltd.)
and o-phenyl-enediamine to more valuable 2-(3,5-dimethoxy-4-hydroxyphenyl)-benzimidazole (Figure 10C). More recently, Shi’s group coupled ECR and methanol electrooxidation to concurrent produce single production of formate with hundreds of milli-volt decrease of the onset voltage in contrast to coupling ECR and OER. Another study accomplished by Choi et al coupling ECR and anodic 5-hydroxymethylfurfural (5-HMF) electrooxidation to 2,5-furandicarboxylic acid (FDCA) under near-neutral conditions to overcome the pH gradient and thus high internal resistance of membrane.

6 | DEVICES

The cathode and anode are separated by membranes in H-type cells and flow cells, which is necessary for avoiding crossover between the anodic and cathodic products and permitting the transportation of certain types of ion for electrocompensation. The commonly used membranes are proton exchange membrane (PEM) and anion exchange membrane (PEM). But recently, Sargent’s group proved a concept that using a bipolar membrane to in situ generate H⁺ which can react with carbonate to produce active species, CO₂. Traditional H-type cell of ECR electrolyzer is strongly limited by the reactant mass transport and the batch mode. Aiming at sustainable applications with high energy efficiency, plenty of efforts have been made on the continuous-flow devices of ECR with low resistance of mass and electron transfer (Figure 10E). A universal architecture was depicted by Endrödi et al in Figure 10D, consisting of two flow channels separated by an ion-exchange membrane and surrounded by gas diffusion layers (GDL). This type of cell can significantly decrease the resistance between cathode and anode, and the GDL with porous structure provides high surface area for triple-phase interaction, which can offer high current densities at several hundreds of milli-ampere/cm². Zhang et al applied 2 mol/L KCl electrolyte with a simple Cu catalyst which can exhibit 150 mA cm⁻² with 80% C₂⁺ FE. Sargent’s group using an ionomer bulk heterojunction structure of Cu catalyst to achieve as high as 1 A cm⁻² of partial FE to produce multi-carbons, which has already been at industrial levels. However, this type of electrolyzer also meets the high-cost problem of GDL for large-scale applications.

7 | CONCLUSIONS AND PERSPECTIVES

Researchers have investigated ECR for several decades; however, the practical significance was recognized only in recent years due to the drastic climate change and energy crisis. But for practical use, there is still some distance from the state-of-the-art level to the target level. For practical applications, the selectivity of products should at nearly 90% with a current density above 300 mA cm⁻² and stability over 1000 hours. This calls for efficient and stable electrocatalysis systems. From the perspective of physical chemistry, we concluded that the ECR can be further developed from four dimensions (Figure 11): (1) thermodynamic of the cathode, (2) kinetic of the cathode, (3) thermodynamic of the anode, and (4) kinetic of the anode.

1. Thermodynamic of the cathode

Choosing a suitable goal product of the ECR process is the first step. We have introduced the standard electrode potentials of various half-reactions for C₁ and C₂ production (Table 1). Although CO and formate were produced at more-negative potentials (−0.106 V and −0.250 V vs RHE, respectively) than those of methanol (0.09 V), CH₄ (0.016 V), and...
C$_2$H$_4$, the formation of these two products is much easier with high selectivity due to their two-electron transfer pathways, and thus the separation cost can be reduced. According to the economic analysis based on the market prices of various products, the revenue per mole electron of CO and HCOOH was 0.9 and 1.5 × 10$^{-3}$ $\$/mol e^-$, respectively. In contrast, despite the market price of C$_2$H$_4$ is high (1.04 $\$/kg), it needs a high electricity cost owing to the 12-electron transfer pathway, so the reported revenue of C$_2$H$_4$ is only 0.2 × 10$^{-3}$ $\$/mol e^-$. Therefore, ECR to CO and formate might be the pioneers to achieve mass production in the industry. Considering the separation process, the liquid HCOOH requires a high cost of ~60 $/t$, which is sixfolds larger than that of CO separation. However, the storage and transportation of CO are more complex and expensive than liquid products. CO stream from ECR can participate in the Fischer-Tropsch process for chemical synthesis. On the other hand, the formate stream from ECR can be directly used in the emerging metal-CO$_2$ reduction. However, the storage and transportation of CO are more complex and expensive than liquid products. CO stream from ECR can participate in the Fischer-Tropsch process for chemical synthesis. On the other hand, the formate stream from ECR can be directly used in the emerging metal-CO$_2$ reduction. Therefore, when selecting the target cathodic reaction, the cost, profit, market demand, and potential applications of the products should be completely considered.

2. Kinetic of the cathode

Thermodynamic properties only determined the theoretical energy input of ECR and thus the equilibrium potentials, but the total energy consumption in practical electrolysis comes from the energy cost of thermodynamic, resistance (iR), and the exceeding energy to overcome the reaction energy barrier (overpotentials). Thus, the kinetics of ECR at the given potential could be influenced by the physical chemistry parameters of the ECR systems beyond the theoretical thermodynamic factor.

The dominant factor is the electrocatalysts because suitable electrode material can naturally reduce the activation energy barrier and enhance the selectivity of the target product. By subtle design of the electrode materials, the adsorption/desorption energy of intermediates can be tuned. On atomic scale, the coordination of the active sites can be regulated by exposing the specific facet, edge, terrace, corner, or curved surface; moreover, doping heterogenous atoms is able to influence the electron states and optimize the intermediate binding strength. Beyond the material, structure of the electrode can also affect the rate of ECR. Porous electrode using metal skeletons or foams can enlarge the geometric surface area to achieve high current densities, and the porous structure also influences the mass transfer and hence the tunable local pH and the selectivity of the products.

The low solubility of CO$_2$ gas in aqueous electrolyte limits the gas diffusion and the current density. Using the GDE can provide a three-phase interface and shorten the diffusion path of gaseous CO$_2$ to the catalysts. Inspiringly, Sargent’s group recently offers a simple but highly efficient electrolysis system, using an ionomer bulk heterojunction catalyst on GDE to tune the mass and electron transfer, which can achieve as high as above 1 A cm$^{-2}$ with 45% cathodic energy efficiency. This makes it possible for practical applications on high value-added chemical production by ECR. Pressuring CO$_2$ is another way to increase the concentrations of dissolved CO$_2$ in ECR. The solubility of CO$_2$ can be improved from 0.033 to 1.50 mol/L when the pressure changes from 0.1 to 6 MPa. This can not only enhance the current density of ECR, but also inhibit the HER due to the higher coverage of CO on the electrode, and widen the potential window of the ECR process.

Organic aprotic solvents, such as methanol, acetonitrile, etc, have a better ability to dissolve CO$_2$ than water. For example, the solubility of CO$_2$ in methanol is nearly four times higher than that of water. Besides, ionic liquids are also promising with high CO$_2$ solubility, wide electrochemical window, good conductivity, and low vapor pressure, but most of them are expensive with the slow rate of CO$_2$ mass transport.

3. Thermodynamic of the anode

In general, anodic OER takes place for the electron compensation when pairing with ECR, but the theoretical potential is as high as 1.23 V vs RHE. The economic analysis on ECR electrolysis showed that over 90% of energy consumption can be stemmed from the OER at the anode, but the obtained O$_2$ is rather cheap, and the potential formed reactive oxygen species may deteriorate the cell membrane. The concept of replacing the OER with some other oxidation reactions is emerging. These anodic reactions should possess lower potentials to reduce the total cell voltage and a greater value than the OER.

Methanol oxidation reaction (MOR) is a desirable candidate because the product formate ($\$1300$ per ton) is more valuable than methanol ($\$350$ per ton), and the partial oxidation of methanol to formate only requires 0.103 V. Shi et al. developed a concurrent system combining ECR and MOR for electro-synthesis of formic acid. This system enables the high utilization of the electrons for both sides of the electrolyzer, and the reduced cell voltage. Beyond the MOR, various reductive substances such as urea, N$_2$H$_4$, glycerol, glucose, and chitin were used for anodic reactions to substitute the OER, but most of them were coupled with HER, and pairing the ECR with the chemical-assisted anodic reactions will be a promising field for both of the fundamental study and the industrial applications.

4. Kinetics of the anode

As the cathodic ECR proceeds, the electrocatalysts of both OER and the alternatives are the most significant
factor toward the performance of anodic reactions. For the OER, the four-electron transfer mechanism renders it sluggish kinetics and thus the large overpotentials. On the other hand, although the standard electrode potentials of the chemical oxidation reactions are much lower than that of OER, the inevitable adsorption of oxygen species (-O or -OH) on the electrode still needs higher potentials, causing large overpotentials. Ni-based electrocatalysts can promote urea and alcohol oxidation reactions, but the active sites are identified as the Ni(OH)$_2$/NiOOH redox species, which requires >1.3 V vs RHE to launch the oxidation.\textsuperscript{148-152}

The alkaline environment is more favorable for the anodic reactions due to the high concentrations of OH$^-$. For instance, the first deprotonation step of the oxidation reactions of alcohols or glycerol is base-catalyzed, so the pH of the electrolyte can greatly influence the reaction rates.\textsuperscript{153} While if the alkaline anodic reaction is paired with the pH-neutral ECR, the pH gradient occurs, and thus the high internal resistance, and the exploration on anodic systems at near-neutral pH might be needed.

In conclusion, the electrocatalysts, reaction conditions, and devices for ECR have been widely explored and understood, and remarkable progress on this has been made in the last decades. Investigating better electrochemical systems is always the priority for researchers. GDL electrodes usually exhibited higher current densities but are more costly than traditional electrodes in H-cells, but current densities in H-cells can hardly reach hundreds of milliamperes per cm$^2$. Thus, to realize the large-scale application, more studies should be done from the lab-to-industrial scale and translated into actual profits.

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