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Catalyst–electrolyte interface chemistry for electrochemical CO₂ reduction†

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The electrochemical reduction of CO₂ stores intermittent renewable energy in valuable raw materials, such as chemicals and transportation fuels, while minimizing carbon emissions and promoting carbon-neutral cycles. Recent technoeconomic reports suggested economically feasible target products of CO₂ electroreduction and the relative influence of key performance parameters such as faradaic efficiency (FE), current density, and overpotential in the practical industrial-scale applications. Furthermore, fundamental factors, such as available reaction pathways, shared intermediates, competing hydrogen evolution reaction, scaling relations of the intermediate binding energies, and CO₂ mass transport limitations, should be considered in relation to the electrochemical CO₂ reduction performance. Intensive research efforts have been devoted to designing and developing advanced electrocatalysts and improving mechanistic understanding. More recently, the research focus was extended to the catalyst environment, because the interfacial region can delicately modulate the catalytic activity and provide effective solutions to challenges that were not fully addressed in the material development studies. Herein, we discuss the importance of catalyst–electrolyte interfaces in improving key operational parameters based on kinetic equations. Furthermore, we extensively review previous studies on controlling organic modulators, electrolyte ions, electrode structures, as well as the three-phase boundary at the catalyst–electrolyte interface. The interfacial region modulates the electrocatalytic properties via electronic modification, intermediate stabilization, proton delivery regulation, catalyst structure modification, reactant concentration control, and mass transport regulation. We discuss the current understanding of the catalyst–electrolyte interface and its effect on the CO₂ electroreduction activity.

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1. Introduction

Combustion of fossil fuels releases significant amounts of greenhouse gases into the atmosphere, resulting in the continuous accumulation of CO₂, and consequently, an imbalance in the carbon cycle. The global atmospheric CO₂ concentration was 410 ppm in 2018, accelerating at a rate of 2.87 ppm per year, which is ~100 times higher than the rate at the end of the

last ice age.¹ In response to climate change-related issues, including global warming,² ocean acidification,³ and ecosystem destruction⁴ caused by greenhouse gas emissions, 196 states signed the Paris Agreement on climate change in 2016. This agreement states that the global average temperatures should be maintained well below 1.5 °C, above pre-industrial levels.⁵ The primary sources of carbon emissions are automobiles, factories, and electricity generation plants.⁶ To adequately mitigate carbon emissions and promote a sustainable carbon cycle, carbon capture and utilization (CCU) technologies have to be incorporated with renewable wind, solar or hydropower electricity sources, which also extend the usage of renewable energy resources. Specifically, the electrochemical CO₂ reduction enables the storage of the intermittent renewable electricity in chemical forms under ambient conditions, producing various raw chemicals for use in production processes and transportation fuels.^{7–9}

In recent decades, studies on the electrochemical CO₂ reduction at the fundamental level have been intensified to understand the reaction pathways and catalytic properties. Furthermore, research efforts are focused on industry-scale

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applications and parameter optimization for improving the economic feasibility of the CO₂ electroreduction technology. Therefore, the research scope on the electrochemical CO₂ reduction encompasses electrokinetic analyses, *in situ* spectroscopic analyses, labelling experiments, mechanistic studies, density functional theory (DFT) calculations, catalyst material design, electrode structure modification, product evaluations, and electrolytic device engineering and optimization. The initial investigations into the electrocatalytic activities of polycrystalline single metal electrodes, combined with theoretical studies on key intermediates and the binding affinity, contributed to the understanding of the electrochemical CO₂ conversion process to target products.^{10–12} However, polycrystalline

single metal electrodes exhibit low activity and/or product selectivity. Furthermore, the scaling relations of the binding energies of various intermediates make it difficult to control the catalytic activity selectively.¹³ These limitations incentivized the modulation of active sites, including open-packed facets and grain boundaries, along with edge and corner sites,^{10,14–19} *via* nanostructuring, as well as the development of new active sites through alloying and interfacial structuring.^{20,21} In addition, electrokinetic, *in situ*, and isotopic analyses provided more direct experimental evidence for the reaction mechanisms of CO₂ reduction reaction (CO₂RR).^{22–24} In addition, theoretical studies have been conducted to support molecular insights into the catalytic process.²⁵ Recent studies have focused more on the



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system components, including electrolytic cells, electrolytes, and gas-diffusion-layer (GDL) electrodes, to ensure high catalytic performance in terms of the current density and faradaic efficiency (FE) for practical implementation.^{26–29} As the research on CO₂ electroreduction progresses, increasingly complex components are developed to increase the efficiency. Since each component creates an interface, which influences the overall activity, the catalyst–electrolyte interface should be adequately understood. An in-depth understanding of the catalyst–electrolyte interface, regarding the reaction intermediates, ionic distribution, arrangement of catalyst surface atoms, and transport behaviour, would facilitate the identification of the main factors influencing the CO₂RR activity. The importance of such an interfacial science is further rationalized by the inherent limitations of the catalyst such as unstable surface states, as well as the extrinsic fine control of the electrocatalytic process.

Herein, we review the current understanding of the catalyst–electrolyte interface and its impact on the CO₂RR performance, including FE, overpotential, and current density, as well as strategies for controlling the interface. First, based on previous technoeconomic analysis reports, the economic feasibility of the CO₂ electroreduction technology is evaluated. The technoeconomic results help to determine the key operational parameters that should be prioritized for practical implementation, such as the FE, operation potential, overpotential, and current density (*i.e.* production rate) depending on the CO₂ electroreduction condition. Subsequently, we introduce the fundamentals and challenges associated with the electrochemical CO₂RR. To address the issues, the kinetic equations of the CO₂RR are provided as a starting point. The mathematical expressions help to understand the factors that regulate the catalytic performance and identify the important challenges related to the catalyst–electrolyte interface. In the following chapter, beginning with the impact of the catalyst material on the activity/selectivity, we discuss, in detail, the strategies to control the catalyst–electrolyte interface *via* ligand chemistry,

electrolyte engineering, mass transport kinetics, three-phase boundary, and gas-phase conversion. The review articles published in recent years on the electrochemical reduction of CO₂ primarily focus on the catalyst (Table S1, ESI†), while about 10% of the currently emerging review articles focus on the catalyst–electrolyte interface. We believe that this review, based on technoeconomic perspectives and catalyst–surface modulation chemistry, can provide further insights into the catalyst–electrolyte interface.

2. Technoeconomic perspectives of electrochemical CO₂RR

The electrochemical reduction of CO₂ can produce hydrocarbons and oxygenates, which can serve as essential commodity fuels and chemicals.³⁰ However, achieving an economical CO₂RR is challenging because the target products (*e.g.* CO, olefin, paraffin, alcohols, *etc.*) are usually produced on a massive scale in the petrochemical industry. To secure the economic feasibility of CO₂RR processes, several studies have presented performance guidelines related to the current density, FE, conversion, and catalyst durability.

Early studies focused on the relationship between the minimum energy requirements and the economic feasibility of the CO₂ reduction process. These studies provided a quick screening method, which involved major cost contributors (*e.g.* electricity cost). Lu and Jiao estimated the CO₂RR costs with minimum overpotentials to identify economically feasible products.³¹ Among the major CO₂ reduction products, CO, formic acid, formaldehyde, and propanol were proposed to be economically feasible. They assumed that electricity cost (\$0.07 kW per h) accounted for a significant proportion. When other costs, including the capital and operational costs, and raw material prices are considered further, more rigorous results would be obtained. Meanwhile, Palmer *et al.* analyzed a CO₂RR using sunlight,³² and



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classified formic acid, acetaldehyde, and allyl alcohols as economically feasible CO₂RR products, while methane, ethylene, methanol, ethanol, propanol, and formaldehyde could not meet the lower boundary requirement for economic feasibility. To simplify the analysis, they assumed that electrochemical cell operates under an equilibrium voltage, determined by the Nernst equation, which provides positive results, but does not reflect the actual catalytic performance. When considering the overpotential of the CO₂RR, the boundary requirement for economic feasibility will become more stringent.

The economic feasibility analysis based on minimum energy requirements can serve as a quick method for identifying feasible CO₂RR products; however, more rigorous models considering electrochemical cell performance parameters (*e.g.* current density, overpotential, FE, and durability) were also developed to identify the minimum cell performance targets and realistic economic potentials. Verma *et al.* presented a CO₂RR performance target through a gross margin-based technoeconomic analysis.³³ Using their model, the effects of the current density, operating cell potential, FE, as well as the catalyst durability, can be evaluated. The gross margin model predicted that CO and formic acid are the only economically viable products when the CO₂ capture costs are considered. For CO production, the maximum operating cell potential responsible for the economic viability of the CO₂RR process decreases linearly as the FE of CO production decreases. Thus, syngas production can be another attractive option. The minimum current density of 465 mA cm⁻², which guarantees a zero gross margin, was determined with the cell potential of 1.6 V. Interestingly, they also presented a target catalyst durability relative to the current density. The minimum current density dramatically increases when the catalyst durability decreases below 2000 h. Bushuyev *et al.* determined the electricity costs, energy conversion, and FE targets for CO, formic acid, ethylene, propanol, methanol, ethanol, and ethylene glycol using a simplified technoeconomic analysis.³⁰ They claimed that the levelized costs of these compounds are lower than current market prices with achievable FEs and current densities. The cost evaluations for their analysis are based on the following: electricity cost, 2 cents per kW per h; electrolyzer cost, \$500 per kW; 60% energy conversion efficiency; and 90% FE. Luna *et al.* carried out a similar analysis for CO, ethanol, and ethylene production and described the production costs in terms of the electrolyzer energy conversion efficiency and electricity.³⁴ For their analysis, they employed a 90% FE, a current density of 500 mA cm⁻², and an electrolyzer cost of \$300 per kW. The sensitivity analysis in their study showed that the prices of all products compete with current market prices when the electricity cost falls below 4 cents per kW per h, with an energy efficiency of at least 60%.

More recently, the technoeconomic analysis of the electrochemical CO₂ reduction process was carried out on a more comprehensive level to account for not only the cell performance but also auxiliary operations, such as separation, recycling, and transportation processes. Jouny *et al.* presented a comprehensive technoeconomic study that considered the

CO₂ capture process, product-specific separation processes, and the electrolyte recyclability, along with the electrochemical CO₂ reduction system.³⁵ They presented a parametric sensitivity analysis that reflected the worst, base, and best-case scenarios. Consistent with other studies, CO and formic acid are proposed as the only profitable products under the base-case condition (*i.e.* electricity cost, \$0.03 kW per h; FE, 90%; current density, 300 mA cm⁻²; energy conversion, 40%; CO₂ capture cost, \$40 per ton). Conversely, *n*-propanol might also be a promising product under the optimistic case scenario (*i.e.* electricity cost, \$0.02 kW per h; FE, 100%; current density, 500 mA cm⁻²; energy conversion, 70%; negligible CO₂ capture cost). Chae *et al.* developed a monolithic device for CO₂RR by integrating photovoltaic and electrochemical cells, and they carried out a comprehensive technoeconomic analysis based on the device performance.³⁶ They concluded that the levelized cost of CO is about 10 times higher than the current market price due to the high electrolyzer cost. Thus, they recommended a relatively high current density and CO₂ conversion to secure the technoeconomic feasibility of the photo-electrochemical CO production process. Spurgeon and Kumar analysed CO₂ reaction pathways leading to liquid products, using a net present value-based technoeconomic analysis.³⁷ The CO₂ reaction pathway included the hybrid reaction of electrochemical CO₂ reduction to CO, the Fischer–Tropsch reaction, direct and cascade electrolysis for ethanol production, and electrochemical formic acid production. They reported that the costs of current state-of-the-art CO₂ reduction technologies cannot compete with present fuel production costs; however, formic acid production can be competitive with its commercial bulk production cost and the optimistic scenario of \$0.03 kW per h for electricity, 96% FE, 200 mA cm⁻² current density, 75% conversion, and 3.2 V cell potential. Herron *et al.* proposed a generalized framework for accessing the energy cost of a solar driven fuel system.³⁸ The framework considered CO₂ capture and transportation options, product-specific separation systems, and the recyclability of unreacted raw materials. The methanol production process from CO₂ was presented as a case study, and the market price of methanol was achievable at a single-pass conversion of 38% or higher and 40% selectivity. Rumayor *et al.* presented a comprehensive technoeconomic CO₂RR evaluation for formic acid production.³⁹ They considered catalyst durabilities of 2.5 and 4.45 years in their process model and assumed a cell potential and FE of 4.3 V and 42.3%, respectively. The result of this study indicated that even the formic acid production process is not yet profitable under the current conditions, considering the formic acid commercial process as a benchmark. Na *et al.* carried out general technoeconomic analyses of 16 possible CO₂RR products and demonstrated that weak economic feasibility is achieved if the current density is less than 2 A cm⁻², when a complete process, including product separation and recycling, is considered.⁴⁰ They, however, demonstrated that electrochemical coproduction (*i.e.* CO₂RR at the cathode and organic oxidation at the anode) has a recognizable economic potential and may compete in the current market with available technologies.

Meanwhile, recent progress demonstrated electrochemical CO₂RR performances. Specifically, Arquer *et al.* achieved a high current density of 1.3 A cm⁻² for the electrochemical CO₂RR experimentally by introducing a catalyst-ionomer bulk heterojunction. This study brightens the prospect that the CO₂RR technology can economically replace fossil-fuel-based chemical production technologies and that the catalytic activity improvement, achieved by adjusting the interface, plays an important role in ensuring economic feasibility.⁴¹

The economic feasibility of CO₂ reduction systems is a controversial issue. However, a comprehensive techno-economic analysis can provide insight into the catalytic requirements and research priorities. For a CO₂RR to be economically feasible, substantial improvement of the key performance parameters is required (*e.g.* FE, overpotential, and current density). The performance parameters can be classified into linear and nonlinear parameters. The overpotential is a linear parameter because it is linearly correlated to the electricity consumption and the corresponding operating cost. In contrast, an increase in the FE and current density corresponds to an exponentially decrease in the production costs. For example, the electrolyzer cost can be as high as 80% of the total equipment cost when the current density is lower than 100 mA cm⁻², and it rapidly decreases as the current density increases due to the inverse proportional relationship between the equipment cost and the current density.³⁶ FE also exhibits similar characteristics, although the current density may exert a significant influence because the electrolyzer is more expensive than conventional separation systems when both the FE and current density are low.⁴⁰ In general, the production cost is lowered when the key performance parameters are improved in the order of the current density, FE, and overpotential (*i.e.* when the current density and FE are low). In contrast, the overpotential can be the most influential parameter under a high current density and FE condition. Thus, catalytic activity research should focus primarily on improving the current density at the early stage (*e.g.* low FE and current density) and lowering the overpotential when optimum current density and FE are achieved.

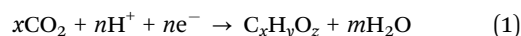
As we will discuss later, the early stage of the CO₂RR catalyst studies has been mostly performed in H-cell type electrolyzers, where CO₂ gas is bubbled through the electrolyte, resulting in a low partial current density for CO₂RR due to the limitation of the CO₂ solubility and diffusion. Considering the limited partial current density for the CO₂RR, FE improvement has been a high research priority, and the intrinsic/extrinsic catalytic activities are controlled by modifying the catalyst and catalyst-electrolyte interface to suppress the competitive hydrogen evolution reaction (HER) occurring in the aqueous electrolyte. Meanwhile, the CO₂RR current density could be increased by more than a hundred times, and a current density of over 1 A cm⁻² can be achieved by applying GDL-based electrolyzers. As the GDL-based electrolyzer creates new types of interfaces as a high flux of CO₂ gas is directly fed to the catalyst surface, the electrolyzer design and non-catalytic operating parameters affect the transport behavior of CO₂ molecules and protons at the catalyst-electrolyte interface as well as the intrinsic activity

of the catalytic active sites, and thus are deemed crucial for the FE and overpotential, particularly when C₂₊ chemicals are targeted as products of the CO₂RR. Therefore, engineering directions suitable for these new interfaces should be developed to improve the FE and overpotential. To understand the importance of the catalyst interface on the molecular level, the fundamentals of the CO₂RR and the effect of the interface engineering are discussed in the following sections.

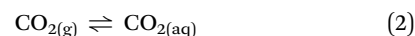
3. Fundamentals of electrochemical CO₂ reduction

3.1. A schematic of the conventional H-type cell system

Electrochemical CO₂RRs produce C_xH_yO_z chemicals by multiple electron and proton transfers to CO₂, as expressed by eqn (1) below:

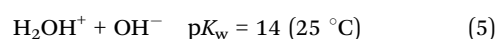
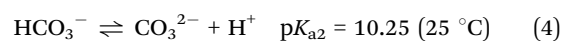
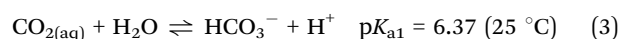


In the H-type cell (Fig. 1a), gaseous CO₂ is continuously supplied to the catholyte to dissolve and saturate CO₂ in the aqueous electrolyte by the chemical equilibrium between the gas and liquid phases (eqn (2)).⁴² The concentration of the dissolved CO₂ (*c*_{CO₂}) is given by Henry's law:⁴²



The aqueous CO_{2(aq)}, dissolved in the bulk electrolyte, can be transported to the cathode surface by convection and diffusion, where it finally undergoes proton-electron transfer. Normally, CO_{2(aq)} is considered a carbon source, while protons have different sources included in the electrolyte, such as bicarbonate, water, hydronium ions, and carbonic acid.^{43,44} Through isotopic experiments, it was established that CO₂-H₂O-HCO₃⁻ complex molecules act as a carbon source.⁴⁵

CO₂ molecules have complex acid-base equilibria in aqueous electrolytes. When gaseous CO_{2(g)} is dissolved, most of the CO₂ remains as solvated molecular CO_{2(aq)}, while only a small portion (~1/1000) of dissolved CO₂ is hydrated to carbonic acid (H₂CO₃).⁴² These CO₂ species participate in acid dissociation reactions to form HCO₃⁻ and H⁺, as shown in eqn (3). Conventionally, the solvated molecular CO₂ and carbonic acid are expressed with a single term "CO_{2(aq)}" in the equation.²⁵ Furthermore, the dissociation of HCO₃⁻ and the self-ionization of water are involved in the chemical equilibria (eqn (4) and (5)). CO₂-saturated 0.1 M KHCO₃ and 0.5 M KHCO₃ are popular electrolytes for CO₂RRs in conventional H-type cells, and the bulk pH values under the CO₂ partial pressure of 1 atm are 6.8 and 7.2, respectively; the bulk concentration of CO_{2(aq)} is approximately 33 mM (Fig. 1b).⁴²



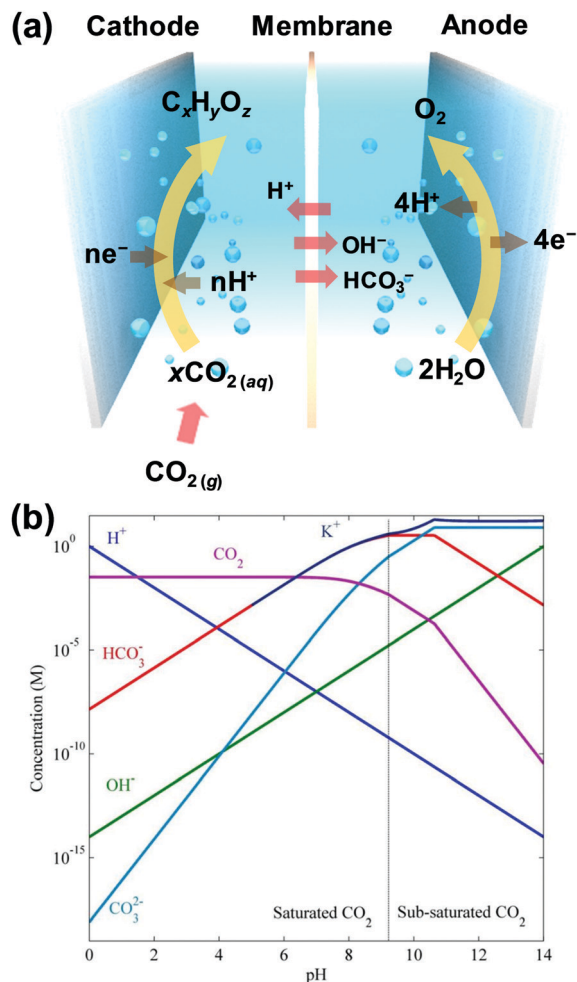


Fig. 1 (a) A schematic of the H-type reaction cell for the electrochemical reduction of CO_2 . The cell system is composed of a cathode, membrane, anode, and electrolyte. At the cathode, the aqueous CO_2 molecules are reduced to $\text{C}_x\text{H}_y\text{O}_z$ products *via* multiple transfers of the electrons and protons. At the anode, typically, the oxygen evolution reaction proceeds from water oxidation. The membrane separates the products and transports cations or anions selectively to complete the charge flow. (b) Concentration profiles of CO_2 , H^+ , OH^- , HCO_3^- , CO_3^{2-} , and K^+ ions as a function of the bulk pH of the potassium bicarbonate/carbonate electrolyte at 25°C and a total pressure of 1 atm. Adapted with permission from ref. 42. Copyright 2015, Royal Society of Chemistry.

Alkali metal cations (M^+) such as Li^+ , Na^+ , K^+ , and Cs^+ are used as supporting electrolyte cations. Various ionic species in the electrolyte, including M^+ , H^+ , HCO_3^- , OH^- , and CO_3^{2-} , facilitate ionic conduction. The membrane inserted between the catholyte and anolyte aids the mobility of ions, while inhibiting the crossover of gaseous products. Nafion membranes selectively transport cations and additionally inhibit the crossover of anionic liquid products, including formate and acetate. However, anion-exchange membranes are preferred to reduce the polarization losses induced by the membrane, because the exiting anions are major charge carriers.⁴² At the anode, the oxygen evolution reaction (OER) proceeds normally with water oxidation and functions as a counter half-reaction for CO_2RR to complete the electrochemical circuit.

3.2. Challenges of CO_2RR s

Electrochemical CO_2RR s can be categorized by the type of products formed, as listed in Table 1, such as HCOOH ,^{8,46–49} CO ,^{50,51} CH_4 ,^{52–54} CH_3OH ,⁵⁵ C_2H_4 ,^{56–61} $\text{C}_2\text{H}_5\text{OH}$,^{62–64} CH_3COOH ,^{65,66} $\text{C}_3\text{H}_7\text{OH}$,^{67–70} $\text{C}_3\text{H}_4\text{O}_2$,⁷¹ $\text{C}_4\text{H}_4\text{O}_3$,⁷¹ and graphitic carbon.⁷² As the products are formed *via* the activation of stable CO_2 molecules and a series of electron–proton transfer steps, the thermodynamic equilibrium potential for full reaction equations does not reflect the energetic advantages of the CO_2RR . The energetics of each reaction step determine the actual onset potentials. Previously, various reaction pathways and intermediates were proposed based on experimental observations and theoretical calculations. These are still debating points due to the highly complex and multiple reaction steps. A comprehensive summary can be found in recent review articles.^{26,73–75} Here, we briefly address a specific reaction pathway for each product to explain the key challenges associated with the CO_2RR (Table 1).^{55,66,70–73,76–81}

One of the challenges is that intermediates participating in a specific reaction pathway have similar binding affinity to the surface. For example, for CO production, $^*\text{COOH}$ and $^*\text{CO}$ are involved *via* the carbon atom. $^*\text{COOH}$ needs to be stabilized to decrease the reaction overpotential, while a low $^*\text{CO}$ binding energy is required for easy desorption from the catalyst surface. However, it is difficult to control the binding affinities individually on single metal electrodes because of their linear scaling relation. Similarly, in CH_4 production, the binding affinities of the intermediates are correlated,^{76,77,82,83} which prevents selective electrocatalytic reduction.

Furthermore, various reaction pathways have common intermediates that can branch out into different intermediates or products. $^*\text{CO}$ is the shared key intermediate not only in CO production but also in the production of most hydrocarbons, including CH_4 , C_2H_4 , CH_3OH , and $\text{C}_2\text{H}_5\text{OH}$. In another example, the CH_4 and CH_3OH pathways have $^*\text{CHO}$ as a common intermediate but proceed with different intermediates ($^*\text{CHOH}$ or $^*\text{OCH}_2$) after $^*\text{CHO}$, according to the binding affinity of the respective catalysts.^{55,84} The C_2H_4 , $\text{C}_2\text{H}_5\text{OH}$, and CH_3COOH pathways have $^*\text{CO-CO}$ or its protonated species as common intermediates, although the final product can vary substantially depending on the subsequent steps.^{66,76} Due to these features, obtaining a single product with a high FE (*e.g.* control of product selectivity) is very challenging especially when the products are targeted to C_{2+} chemicals.

More importantly, the undesirable HER can competitively occur because proton donors are also required for CO_2RR . As the binding affinity of adsorbed H ($^*\text{H}$) is correlated with those of C-binding intermediates according to theoretical studies,⁷⁴ selectively suppressing the HER over CO_2RR becomes another major issue to be addressed, especially when the catalyst–electrolyte surface has an overwhelming approach of proton donors including water molecules.

Besides the product selectivity and overpotential issues, to achieve high CO_2RR production rates (*i.e.* partial current density), the reactant concentrations at the catalyst surface should be sufficiently high. However, in the conventional H-type cell, CO_2

Table 1 Products, reaction equations, and equilibrium potentials for the electrochemical reduction reactions of CO₂. The reaction pathways and involved intermediates for each product are referenced from the previous reports. The black (►) and white (▷) triangles indicate coupled electron–proton transfer and C–C coupling steps, respectively. The arrows (⇒) indicate water incorporation step. The star symbol (*) means an active site. For C₂₊ products, the reaction steps before C–C coupling steps are omitted for simplicity

Product	Reaction	E^0 (V _{RHE})	Reaction pathway	Ref.
Formic acid	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}_{(\text{aq})}$	−0.12	* + CO ₂ ► *OCHO ► *HCOOH	73
Carbon monoxide	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO}_{(\text{g})} + \text{H}_2\text{O}$	−0.10	* + CO ₂ ► *COOH ► *CO	77
Methane	$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_{4(\text{g})} + 2\text{H}_2\text{O}$	0.17	* + CO ₂ ► *COOH ► *CO + H ₂ O ► *CHO ► *CHOH ► *CH + H ₂ O ► *CH ₂ ► *CH ₃ ► *CH ₄	80
Methanol	$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH}_{(\text{aq})} + \text{H}_2\text{O}$	0.03	* + CO ₂ ► *CO + *OH ► *CO + H ₂ O ► *CO ► *CHO ► *OCH ₂ ► *OCH ₃ ► *CH ₃ OH	55
Ethylene	$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_{4(\text{g})} + 4\text{H}_2\text{O}$	0.08	*CO + *CO ▷ *CO–CO ► *CO–COH ► *COH–COH ► *C–COH + H ₂ O ► *CH–COH ► *CH–C + H ₂ O ► *CH ₂ –C ► *CH ₂ –CH ► *C ₂ H ₄	76
Ethane	$2\text{CO}_2 + 14\text{H}^+ + 14\text{e}^- \rightarrow \text{C}_2\text{H}_{6(\text{g})} + 4\text{H}_2\text{O}$	0.14	*C ₂ H ₄ ► *C ₂ H ₅ ► *C ₂ H ₆	78
Ethanol	$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH}_{(\text{aq})} + 3\text{H}_2\text{O}$	0.09	*CH ₃ + *CH ₃ ▷ *C ₂ H ₆ *CO + *CO ▷ *CO–CO ► *CO–COH ► *C–CO + H ₂ O ► *CH–CO ► *CH–CHO ► *CH ₂ –CHO ► *CH ₃ –CHO ► *CH ₃ –CH ₂ O ► *C ₂ H ₅ OH	79
Acetic acid	$2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_3\text{COOH}_{(\text{aq})} + 2\text{H}_2\text{O}$	0.11	*CO + *CO ▷ *CO–CO ► *CO–COH ► *C–CO + H ₂ O ► *CH–CO ► *CH ₂ CO ⇒ CH ₃ COOH	80
Propanol	$3\text{CO}_2 + 18\text{H}^+ + 18\text{e}^- \rightarrow \text{C}_3\text{H}_7\text{OH}_{(\text{aq})} + 5\text{H}_2\text{O}$	0.10	*CO + *CO–COH ▷ *CO–CO–COH ► ... ► *C ₃ H ₇ OH	81
Methylglyoxal	$3\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_3\text{H}_4\text{O}_{2(\text{aq})} + 4\text{H}_2\text{O}$	0.02		66
2,3-Furandiol	$4\text{CO}_2 + 14\text{H}^+ + 14\text{e}^- \rightarrow \text{C}_4\text{H}_4\text{O}_{3(\text{aq})} + 5\text{H}_2\text{O}$	0.01		70
Graphite	$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{C}_{(\text{s})} + 2\text{H}_2\text{O}$	0.21		71
Hydrogen	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})}$	0	* ► *H ► *H ₂	72

molecules are dissolved and supplied in the liquid electrolyte, and the CO₂ concentration is depleted at the catalyst surface due to the low CO₂ solubility and inadequate mass transport from the bulk electrolyte, in contrast to the scenario where the high CO₂RR rate is achieved. A simple modelling study reported that the local CO₂ concentration (at the catalyst surface) is close to ~0 mM at a current density of 25 mA cm^{−2}, when 0.1 M KHCO₃ aqueous electrolyte was used.⁸⁵

3.3. Kinetic equations and key factors for CO₂RRs

The thermodynamics, kinetics, and reaction mechanisms of the CO₂RR can address the major challenges associated with the CO₂RR, such as the product selectivity, overpotential, and current density. In this section, several equations on the rates

of CO production and HER are introduced (Table 2). The reaction mechanisms are referred from previous reports, where the acid reaction mechanism is assumed.^{77,84,86} Such mathematical expressions indicate which factors affect the CO₂RR and provide systematic insights for improving the CO₂RR performance.

From the equations, assuming that the c1 step is rate-limiting in the CO production, it can be identified that lowering the free energy of reaction (ΔG_{c1}^0) would lead to an increase in the forward rate constant and reaction rate of step c1. As ΔG_{c1}^0 is a function of the *COOH binding energy ($E_{\text{b}}(\text{COOH})$) with the same directionality,⁸⁷ strengthening the *COOH binding affinity is expected to improve the CO production. If we assume that the c3 step is rate-limiting, *e.g.* strong CO binding,

Table 2 The elementary reaction steps and corresponding rate equations of CO production and H₂ evolution reactions referred from the previous reports.^{77,84,86} The net reaction rates of each step (r_{ci} and r_{hi}) are expressed as a function of the rate constants (k_{ci} , k_{ci}' , k_{hi} and k_{hi}'), surface coverages (θ_* , $\theta_{\text{COOH}*}$, $\theta_{\text{CO}*}$ and $\theta_{\text{H}*}$), and partial pressures (p_{CO_2} , p_{CO} and p_{H_2}). ΔG_{ci}^0 and ΔG_{hi}^0 are the free energy of the reaction at 0 V vs. RHE. $\Delta G_{\text{ci}}^\#(U_{\text{ci}}^0)$ and $\Delta G_{\text{hi}}^\#(U_{\text{hi}}^0)$ are the free energy of the activation at the reversible potential. $E_{\text{b}}(\text{CO})$ is the CO binding energy. U is the potential vs. RHE

	CO production	H ₂ evolution
Reaction step	* + CO ₂ (g) + H ⁺ + e [−] ⇌ COOH* (c1) COOH* + H ⁺ (aq) + e [−] ⇌ CO* + H ₂ O(l) (c2) CO* ⇌ CO(g) + * (c3)	* + H ⁺ (aq) + e [−] ⇌ H* (h1) H* + H ⁺ (aq) + e [−] ⇌ H ₂ (g) + * (h2)
Rate equation	$r_{\text{c1}} = k_{\text{c1}}\theta_*p_{\text{CO}_2} - k_{\text{c1}}'\theta_{\text{COOH}*}$ $r_{\text{c2}} = k_{\text{c2}}\theta_{\text{COOH}*} - k_{\text{c2}}'\theta_{\text{CO}*}$ $r_{\text{c3}} = k_{\text{c3}}\theta_{\text{CO}*} - k_{\text{c3}}'\theta_*p_{\text{CO}}$	$r_{\text{h1}} = k_{\text{h1}}\theta_*[\text{H}^+] - k_{\text{h1}}'\theta_{\text{H}*}$ $r_{\text{h2}} = k_{\text{h2}}\theta_{\text{H}*}[\text{H}^+] - k_{\text{h2}}'\theta_*p_{\text{H}_2}$
Forward rate constant	$k_{\text{ci}} = A_{\text{ci}} \exp \left[-\frac{\Delta G_{\text{ci}}^\#(U_{\text{ci}}^0) + \beta_{\text{ci}}(eU + \Delta G_{\text{ci}}^0)}{k_{\text{B}}T} \right] \quad (i = 1, 2)$ $k_{\text{ci}} = \nu_{\text{CO}} \exp \left[-\frac{E_{\text{b}}(\text{CO})}{k_{\text{B}}T} \right] \quad (i = 3)$	$k_{\text{hi}} = A_{\text{hi}} \exp \left[-\frac{\Delta G_{\text{hi}}^\#(U_{\text{hi}}^0) + \beta_{\text{hi}}(eU + \Delta G_{\text{hi}}^0)}{k_{\text{B}}T} \right] \quad (i = 1, 2)$

lowering the CO binding energy will increase the CO desorption and CO production rates. Given that the intermediate binding energies depend on the catalyst materials as well as the binding sites,^{10,87–90} developing catalysts that can stabilize *COOH and destabilize *CO with a broken scaling relation becomes one of the important strategies for enhancing the CO production rate at low overpotentials.

Note that the free energy of reaction and intermediate binding energies can also be influenced by components of the reaction environment, such as the electrolyte ions and coadsorbates present at the catalyst–electrolyte interface.^{10,91–97} These chemical species not only change the electronic property of the catalysts but also impose adsorbate–intermediate interactions, which affect the intermediate binding energies and the free energy of reaction. Furthermore, one can observe that the rate equation of CO production is correlated with the CO₂ partial pressure, *i.e.* the reactant concentration (Table 2). This implies that a high CO₂ concentration corresponds to increased CO production rates. As described in the previous section, the CO₂ concentration at the catalyst surface can be depleted, limiting the reaction rate as dissolved CO₂ is fed to the catalyst surface through a long pathway. Utilizing a GDL electrode with short pathways allows for a much higher CO₂ concentration at the catalyst surface,⁸¹ inducing several orders of magnitude higher current density. Na *et al.* reported that many CO₂RR products (*e.g.* CO, formic acid, *n*-propanol, acetaldehyde, acetone, acetic acid, ethylene glycol, *etc.*) have relatively low production costs compared to current market prices when the current density exceeds 2 A cm^{−2}, even if the complete product separation and recycling costs are considered.⁴⁰ Accordingly, the engineering of the catalyst–electrolyte interfaces allows for the control of the catalytic activity beyond just combining and engineering the materials. Additionally, we can consider the contribution of the free energy of activation. The rate constant includes the free energy of activation at the reversible potential ($\Delta G_{ci}^\ddagger(U_{ci}^0)$), where the free energies of the initial and final states involved in the reaction pathway are the same.⁷⁷ This term depends on the electrocatalyst materials, as well as the electrolyte environment.^{84,98–100}

Furthermore, similar approaches for suppressing the HER to enhance the FE of the CO₂RR are available. Increasing the free energy of reaction of the h1 step by destabilizing *H for the catalysts with a low *H binding affinity can lower the rate constants (Table 2). In contrast, for catalysts with a high *H binding affinity, stabilizing *H can elevate the free energy of reaction and the forward rate constant of the h2 step. Therefore, modifying the *H binding affinity using catalysts, ions, and adsorbates can be an effective strategy for suppressing the HER. In addition, the high local pH formed at the electrode surface during the CO₂ electroreduction can be increased by the low electrolyte buffer strength and the slow diffusion of proton donors from the bulk electrolyte region, which can retard the HER rate (*e.g.* local pH effect),^{44,101,102} thereby enhancing the CO₂RR product selectivity.

Using the parameters included in the kinetic equations, advanced catalysts can be designed, and the focus needs to be extended to the interfacial area of the catalyst and electrolyte to address the problematic issues. Engineering the catalyst–electrolyte interface can provide useful solutions for breaking the scaling relations imposed on the intermediate binding energies, and for controlling the coadsorbates, electrolyte ions and concentration of chemical species.

4. Design of interfaces between the catalyst and the surface modulator

4.1. The impact of catalysts on CO₂RRs

The relative binding energy between the catalyst surface atom and the reaction intermediates is the key factor influencing the CO₂RR activity and selectivity. The binding properties were revealed to be closely related to the type and structure of the catalysts. Here, we briefly introduce experimental results and theoretical insights on single metal electrodes, as an example, to understand the effect of the catalyst on the CO₂RR performance. First, the type of metal primarily determines the type of major products formed, as shown in the representative FE data for various single metal electrodes (Fig. 2a).¹¹ Single metals can

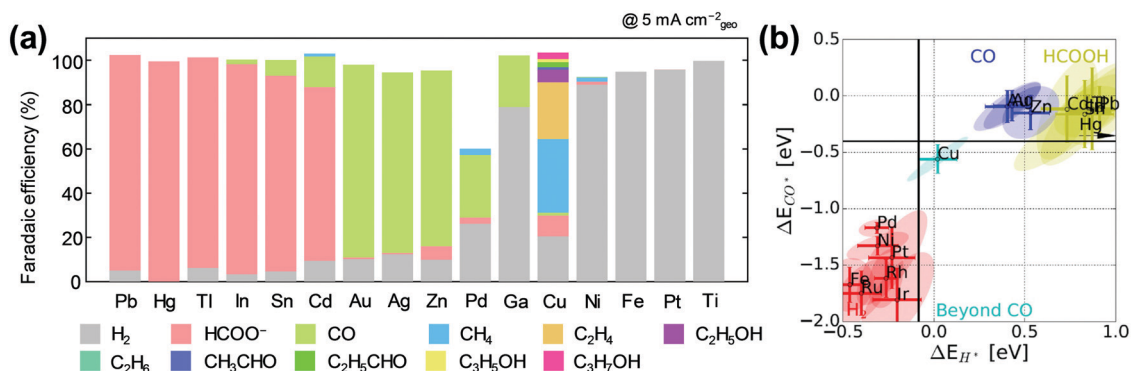


Fig. 2 (a) Faradaic efficiencies (FEs) of various reaction products measured by Hori *et al.* after constant current electrolysis in 0.1 M KHCO₃ on single metal electrodes. The electrolysis was conducted at the same 5.0 mA cm_{geo}^{−2} except for the Hg electrode measured at 0.5 mA cm_{geo}^{−2}. Adapted with permission from ref. 11. Copyright 1994, Elsevier. (b) The plot of binding energies of *CO and *H intermediates on various single metals. The horizontal and vertical black lines represent energy values corresponding to ΔG_{CO} = 0 and ΔG_H = 0, respectively. Adapted with permission from ref. 12. Copyright 2017, Wiley-VCH.

be categorized based on the by major products: HCOO^- , CO , and H_2 . Cu metal is specially classified because it can produce a variety of hydrocarbons and alcohols, ranging from C_1 to C_3 chemicals. Such a different electrocatalytic trend can be explained by the selective binding affinity of metals to certain reaction intermediates (Fig. 2b). The horizontal and vertical black lines indicate energy values corresponding to $\Delta G_{\text{CO}} = 0$ and $\Delta G_{\text{H}} = 0$, respectively. The HCOO^- group metals, such as Cd, Pb, and Sn, possess poor binding energies for $^*\text{H}$, $^*\text{COOH}$, and $^*\text{CO}$, which are intermediates in the H_2 and CO evolution pathways; however, they relatively favour the binding of $^*\text{OCHO}$, which is a key intermediate in the production of HCOOH .^{12,74,75,103}

In contrast, H_2 group metals, such as Ni, Pt, and Rh, have strong binding affinities for $^*\text{CO}$, while their $^*\text{H}$ binding affinities are appropriate for the HER, approaching the line of $\Delta G_{\text{H}} = 0$ (Fig. 2b).^{10,104} Accordingly, H_2 becomes the dominant product, while $^*\text{CO}$ is poisoned at the metal surface. Cu and CO group metals, including Au, Ag, and Zn, commonly have medium binding affinities for $^*\text{H}$ with $\Delta G_{\text{H}} > 0$ (Fig. 2b). However, there is a difference in their $^*\text{CO}$ binding energies ($\Delta G_{\text{CO}} > 0$ for CO group metals and $\Delta G_{\text{CO}} < 0$ for Cu). Considering that CO can be adsorbed on the Cu surface, $^*\text{CO}$ can undergo further electron-proton transfers to produce hydrocarbons and alcohols.⁸² Conversely, $^*\text{CO}$ can be desorbed from CO group metals due to the positive free energy of adsorption.

However, it should be noted that the major product of CO_2RR depends on the applied potentials even on the same electrode. It has been reported that the selectivity of a certain product basically forms a parabolic curve as a function of the potential with optimum selectivity.⁴⁷ Furthermore, Pd nanoparticles (NPs) produce HCOO^- selectively at low overpotentials, while CO evolves as a dominant product at high overpotentials.¹⁰⁵ On Cu-based electrodes, the major product changes from HCOO^- or CO to C_2H_4 to CH_4 depending on the applied potential.¹⁰⁶ These phenomena are related to the change in the complex

factors, including the reaction kinetics, preferential reaction pathways, binding sites, adsorbate coverages, number of active sites, defects of the catalyst surface, and local concentration of reactants, with the potential difference.²⁵

More quantitative information on the overpotential and product selectivity of CO_2RR can be obtained using the concept of limiting potential (U_{L}), which is an effective mean of the theoretical onset potential.⁸² In addition, comparing the limiting potentials of CO_2RR and HER can provide information on the ability of electrocatalysts to drive the CO_2RR selectively and suppress the HER.^{10,98}

The reported limiting potentials on (211) metal surfaces as a function of $^*\text{CO}$ binding energy, where the adsorbate-adsorbate interactions by CO adsorption are considered under 0.5 ML $^*\text{CO}$ coverage, are shown in Fig. 3.¹⁰ The black and red lines represent the dependence of U_{L} on the $^*\text{CO}$ binding energy for the elementary steps of the CO_2RR and HER. The H_2 group metals (Pt, Rh, Pd, and Ni) are positioned at the top of the volcano plot for the HER, showing $U_{\text{L,HER}}$ values close to 0 V (vs. RHE). In contrast, $U_{\text{L,CO}_2\text{RR}}$ is much more negative than $U_{\text{L,HER}}$ with $^*\text{CO} \rightarrow ^*\text{CHO}$ as the potential-determining step (PDS), due to their high $^*\text{CO}$ binding energies. This can explain why the H_2 group metals predominantly produce H_2 . For CO group metals such as Au and Ag, $\text{CO}_2 \rightarrow ^*\text{COOH}$ is the PDS due to the low $^*\text{CO}$ binding energy, and $^*\text{CO}$ can be desorbed from the surface, while the $|U_{\text{L,CO}_2\text{RR}} - U_{\text{L,HER}}|$ values are as small as 0.40 and 0.46 V. Consequently, Au and Ag metals are CO-selective with low HER activities. The Cu metal is near the centre of the volcano plot composed of $\text{CO}_2 \rightarrow ^*\text{COOH}$ and $^*\text{CO} \rightarrow ^*\text{CHO}$ lines. The moderate $^*\text{CO}$ binding allows for the easiest $^*\text{CO}$ hydrogenation among single metals to produce various hydrocarbon products, including CH_4 .

Furthermore, engineering the material factors of single metal electrocatalysts, such as the particle size, exposed facet, grain boundary, vacancy, edge, and corner sites, has been reported to significantly influence the overpotential and product selectivity because the intermediate binding energies are highly

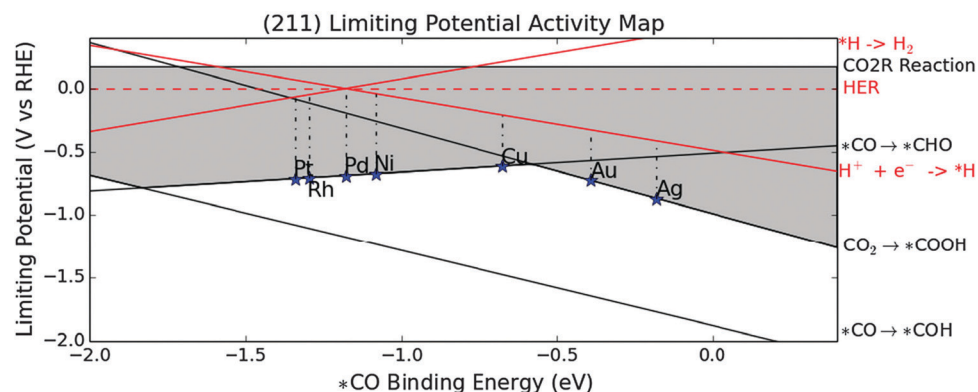


Fig. 3 Limiting potentials of the single metal(211) surfaces as a function of $^*\text{CO}$ binding energy for CO_2RR and HER. The limiting potentials are defined as the potential where all elementary reaction steps become exergonic. The black and red lines show the dependence of limiting potentials on $^*\text{CO}$ binding energy. The $\text{CO}_2 \rightarrow ^*\text{COOH}$ is potential-determining on Au and Ag with weak $^*\text{CO}$ binding affinity while $^*\text{CO} \rightarrow ^*\text{CHO}$ for Pt, Rh, Pd and Ni due to their strong $^*\text{CO}$ affinity. Cu is near the top of volcano plot constituted of the $\text{CO}_2 \rightarrow ^*\text{COOH}$ and $^*\text{CO} \rightarrow ^*\text{CHO}$ lines. Adapted with permission from ref. 10. Copyright 2014, Royal Society of Chemistry.

sensitive to the atomic arrangement of active sites.^{14,107} For example, in comparison with Au(111), the overpotentials of CO production on the (211) facet, edge, corner, and grain boundary sites decrease by 0.40, 0.42, 0.50, and 0.48 V, respectively, varying with the intermediate binding energy.^{10,88,89,108} Moreover, the value of $U_{\text{L,CO}_2\text{RR}} - U_{\text{L,HER}}$ decreases, indicating the relative suppression of the HER. Such under-coordinated sites with high surface energies are known to contribute to the modification of the binding energy. Similarly, anisotropic nanomaterials and nanostructured catalysts with rough and curved surfaces have been applied to maximize the surface catalytically active sites.^{109,110}

The chemical identity of electrocatalysts and their surface geometric arrangements have helped in broadening the spectrum of materials from monometallic to bimetallic catalysts of various combinations of transition metals. Attempts to develop catalysts can be found in other review articles involving doping, alloying, mixing patterns, and supported structures, *etc.*^{20,21,111} Bimetallic materials have effective tunability in controlling heteroatomic binding sites, surface strains, d-band centres, and interface creation, leading to the change in the intermediate binding strength. The movement of the key intermediate across the separate active sites is also proposed with bimetallic or multicomponent catalysts in the concept of tandem catalysts. Furthermore, bimetallic candidates with defined structural information can be found using DFT calculations combined with machine learning.¹¹² It is highly anticipated that a variety of

high-performance multimetallic catalysts with proper binding affinities will be developed shortly.

Besides catalyst development, the surface molecular approach has emerged in recent years, because it is a straightforward and simple method for tuning the activity and reaction pathways at the catalyst interfaces. The following sections focus on design strategies for modifying catalyst interfaces using surface modulators. The interface conditions have attracted significant interest as the chemical properties of a heterogeneous catalyst surface can vary extensively and distinctively based on the interaction with diverse surface molecules. In addition, as the catalyst size approaches the nanoscale region, additional surfaces are exposed, which allow for more effective interfacial engineering. The interaction between the catalyst and the organic molecules (or polymers) on the surface can exert four possible catalytic synergistic effects on the current density, FE, and overpotential (Fig. 4): (i) the electronic modification of catalytic materials, (ii) stabilization of reaction intermediates, (iii) regulation of proton delivery, and (iv) structural transformation. In the following subsections, we review the recent studies where activity and selectivity enhancements were achieved using surface modulators, as summarized in Table 3. The promotional effect is divided into four categories, and for each category, the catalytic materials, surface modulators, responsible functional groups of the modulators, and proposed chemistry are described.

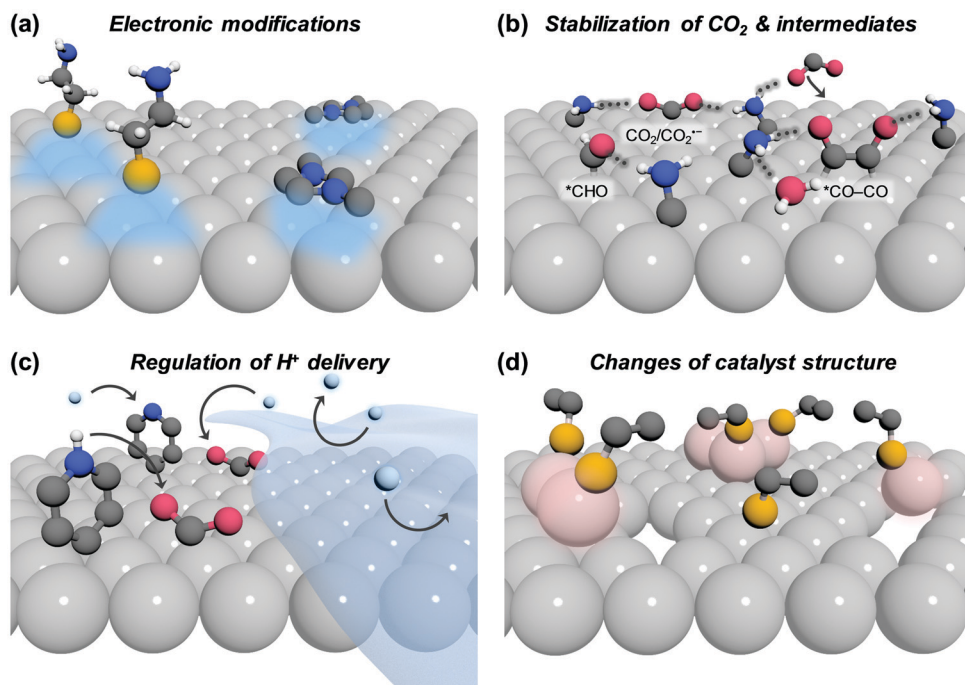


Fig. 4 Schematic illustration of the chemistry at the interface between the catalyst and surface modulators and the potential roles of the modifiers tuning the activity and selectivity for the electrochemical CO₂RRs: (a) electronic modifications, (b) stabilization of the reaction intermediates and CO₂, (c) regulation of proton delivery, and (d) changes in catalyst structure. Dark grey, white, yellow, blue, red balls indicate C, H, S, N, and O atoms, respectively. For better visibility, some molecules are drawn without H atoms. The simplest NHC molecules are displayed in (a) C–NH₂ represents the surface modulator and in (b) providing H-bonding network. In (c), blue blurred sphere and blue layer indicate proton and hydrophobic polymer, respectively. Pink sphere represents restructured surface atoms by surface modulators in (d).

Table 3 Summary of the combinations of the catalysts and surface organic modulators classified by the major promotion effect. The products with the increased selectivity, responsible functional groups, and proposed role of them are also summarized

Ref.	Category	Additive	Catalyst	Enhancement	Responsible moiety	Proposed main function
96	Electronic modification	Cysteamine	Ag NPs	• CO FE $\times 4$ • $E_{\text{onset}} -0.3$ V shift (vs. Ag foil) • CO and H₂	Ag-S interaction	Localization of unpaired electron
97		Thiols	Ag NPs		Ag-S interaction	Electronic stabilization of both *H and *COOH
97		Amines	Ag NPs	• Max. CO FE 29% $\uparrow$ (vs. thiol-Ag NPs)	Ag-N interaction	Electronic stabilization of *COOH and destabilization of *H
116		NHC ^a	Au NPs	• CO FE 30% $\uparrow$ • Specific $j_{\text{CO}} \times 7.6$ (vs. OA-Au NPs)	Carbene (electronic effect)	Strong electron donation to Au NPs
117		NHC	Pd foil	• C₁ FE 63% $\uparrow$	Carbene (electronic effect)	Stabilization of *COOH intermediate
118	Polyfluoroethylene-based binders	Nafion	Au ₂₅ cluster	• Specific $j_{\text{C1}} \times 32$ (vs. bare Pd foil) • CO FE $\sim 25\%$ $\uparrow$ (vs. PVDF-Au₂₅) • CO FE $\sim 50\%$ $\uparrow$ (vs. Nafion-Au NPs) • CO FE $\sim 10\%$ $\uparrow$ (vs. PAA-Au NPs)	Au-SO ₃ ⁻ interface	Change in adsorption energy of *CO
119		Polyfluoroethylene-based binders	Au NPs		-CF ₂	Destabilization of *H adsorption
120	Stabilization of reaction intermediates and CO ₂	Polyethylenimine	N-Doped CNT	• Formate FE 26% $\uparrow$ (vs. bare N-CNT)	-NH ₂	Stabilization of *CO ₂ * ⁻ radical by hydrogen bonding
121		Cysteamine	Ag NPs	• CO FE 83% $\uparrow$ • TOF $\times 53$ (vs. bare Ag NPs)	-NH ₂	Enhanced CO ₂ chemisorption by hydrogen bonding
122		Amino acids	Cu-Based electrodes	• Hydrocarbons $\uparrow$ (-1.3 to 1.9 V_{RHE})	-NH ₃ ⁺	Stabilization of CHO* intermediate by hydrogen bonding
123		Methyl carbamate	Cu foil	• CH₄ FE 34% $\uparrow$ (vs. bare Cu foil) • (-1.6 to 2.2 V_{RHE})	-NH ₃ ⁺	Stabilization of CHO* intermediate by hydrogen bonding
124		Poly(acrylamide)	Cu foam	• C₂H₄ FE $\times 2$ (-0.96 V_{RHE})	-NH ₂	Stabilization of CO-CO dimer by hydrogen bonding and increased CO coverage
125	Regulation of proton delivery	Porphyrin	Au NPs	• $E_{\text{onset}} -0.29$ V shift • Specific $j_{\text{CO}} \times 110$ (vs. OA-Au NPs)	Tetradentate	Stabilization of *COOH
133		2-MPA ^b	Au foil	• $\sim 100\%$ H₂ FE (> -0.8 V_{RHE})	COOH	Reaction pathway governed by proton donation ability (pK_a)
133		4-PEM ^c	Au foil	• $j_{\text{formate}} \times 3$ (vs. bare Au foil)	Pyridine	
133		Cysteamine	Au foil	• Similar FE	NH ₂	
124		Poly(allylamine)	Cu foam	• $j_{\text{formate}}, j_{\text{CO}} \times 2$ (vs. bare Au foil)	N atoms	Proton delivery
134	Hydrophobic polymers	Hydrophobic polymers	OD-Cu ^d	• $\sim 100\%$ H₂ FE (-0.96 V_{RHE}) • CO FE $\uparrow$ (vs. bare OD-Cu) • (-0.7 V_{RHE})	Hydrophobicity	Hydrophilic surface slightly facilitating H adsorption $\rightarrow$ HCO ₂ intermediate
134		Hydrophilic polymers	OD-Cu	• Formate FE $\uparrow$ (vs. bare OD-Cu) • (-0.7 V_{RHE})	Hydrophilicity	Hydrophobic surface inhibiting H adsorption for direct adsorption of CO ₂
135	Change of catalyst structures	Poly(4-vinyl pyridine)	Cu foil	• Max. formate FE 27% $\uparrow$ (vs. bare Cu foil) (-1.3 V_{Ag/AgCl})	Pyridine	<i>In situ</i> formation of active Cu-pyridyl complex
136		2-Phenylethanethiol	Au foil	• j_{CO} and CO FE $\times 2$ (vs. bare Au foil)	Au-S interaction	Creation of active defect sites by surface reorganization
137		Substituted N-pyridinium cations	Cu foil	• C₂H₄/CH₄ ratio $\times 130-830$ (vs. bare Cu foil) (-1.1 V_{RHE})	Pyridine	Poisoning specific Cu sites for C ₁ and H ₂ production
138		N,N'-Ethylene-phenanthroline dibromide	Cu foil	• C₂H₄ FE 30% $\uparrow$ (vs. bare Cu foil) (-1.1 V_{RHE})	Br ⁻ & organic cation	Evolution of cube-like morphology by Br ⁻ & stabilization of this morphology by the organic cation
57		Cysteamine	Cu ₂ O NCs ^e	• C₂H₄ FE 30% $\uparrow$ after 6 h (vs. initial NCs) (-1.1 V_{RHE})	N/A	Fragmenting Cu ₂ O NCs to smaller Cu ₂ O nanocrystals with many crystal domains

^a N-heterocyclic carbene. ^b 2-Mercaptopropionic acid. ^c 4-Pyridylethylmercaptan. ^d Oxide-derived Cu. ^e Nanocubes.

4.2. Electronic modification

The adsorption strength between the catalysts and reaction intermediates determines the overall catalytic activity, where optimum binding strength is required to achieve the best activity. In addition, the relative binding energy with different intermediate species governs the thermodynamically favoured reaction pathways, which suggests that designed CO₂ reduction catalysts should prefer the adsorption of carbon-containing species over hydrogen adsorption for high selectivity. The adsorption energetics of CO₂ reduction electrocatalysts are mainly regulated by their electronic structures (*i.e.* the d-band position). Therefore, the modulation of electronic structures is one of the most effective methods for designing catalytic materials. In the case of CO production by CO₂RR, balancing the *H, *CO, and *COOH adsorption abilities of the catalytic materials is crucial for obtaining high activity and selectivity.⁸² Ag and Au have the highest activities for CO generation, attributed to their optimum electronic structures for *CO and *COOH binding energetics. High binding energy of *COOH, the intermediate species involved in the rate determining step, is preferable to decrease the overpotential, while high binding energy of *CO slow down the CO desorption from the catalyst surface. However, the improvement of their activities is challenged by the linear scaling relation of the *CO and *COOH binding energies, where the correlation line is slightly offset from the theoretical apex. Kim *et al.* suggested a strategy to break this intrinsic correlation of d-band metals and to boost the activity of Ag-based catalysts.¹¹³ It was first proposed computationally that p-band elements can induce a partial covalency to metal catalysts and modulate the electronic structures. Among various p-band elements, S and As were expected

to be highly effective in enhancing the CO₂ reduction performance of Ag-based catalysts. Later, this concept was realized experimentally.⁹⁶ Ag NPs were colloiddally synthesized in the presence of cysteamine molecules, which acted as both an anchoring agent and S-containing surface modulator. A maximum CO FE of 84.4% was achieved with 5 nm Ag NPs at −0.75 V (*vs.* RHE), while an Ag foil showed a maximum efficiency of 70.5% at a 400 mV higher overpotential. The improvement was attributed to the unpaired electron localization due to cysteamine, which broke the scaling relation and improved *CO and *COOH binding energies toward the vertex (Fig. 5a and b).⁹⁶

Since cysteamine molecules contain both thiol (S) and amine (N) functional groups, the respective role of each group should be investigated. Hwang and co-workers prepared thiol- and amine-capped Ag NPs.⁹⁷ Oleylamine-capped Ag NPs exhibited a maximum CO FE of 94.2% at −0.75 V (*vs.* RHE) and maintained a high selectivity of >80% over a wide potential range. In contrast, an FE of 65.5% was obtained with dodecanethiol-capped Ag NPs. DFT calculations showed that the amino group destabilizes only *H binding, thereby maintaining the *COOH energetics, while the thiol group improves both *H and *COOH binding strengths toward the volcano apex, increasing the effectiveness of the Ag–amine interaction for CO₂ reduction.⁹⁷

The promotional effect of surface amine molecules significantly depends on their molecular structure, surface coverage, and anchoring sites. Wallace and co-workers investigated the structural effect of surface amines to improve the CO₂RR activity of Au NPs.¹¹⁴ The authors found that linear amines generally promoted CO₂RR, while branched amines resulted in a decrease in activity. Among the linear amines, long-chain amines were more effective than short-chain ones, which is

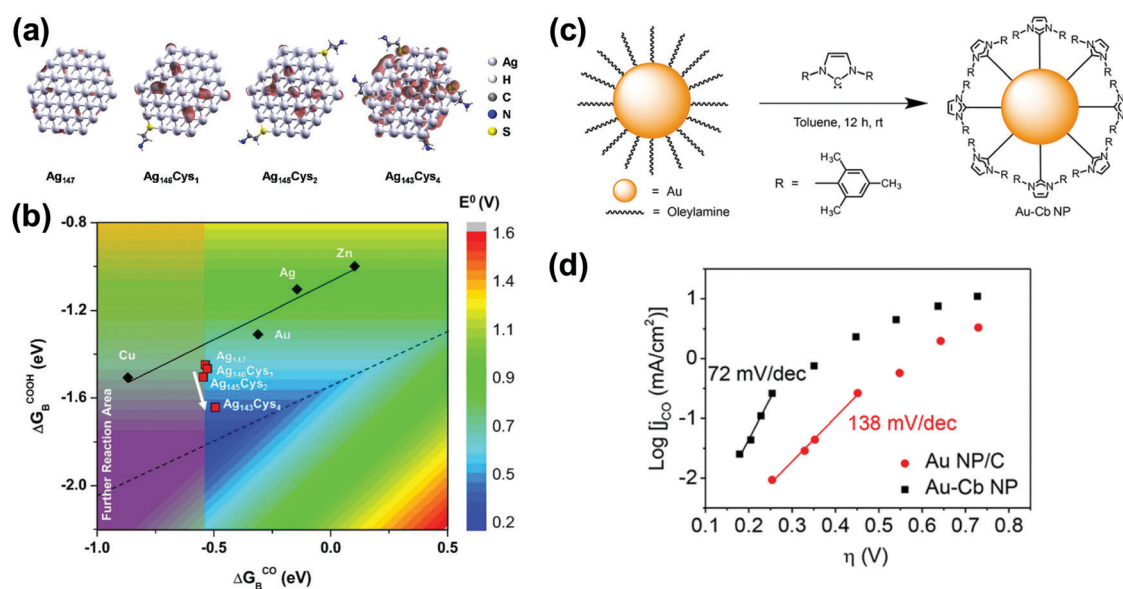


Fig. 5 (a) Models for the cysteamine-anchored Ag nanoparticles, Ag_(147−n)Cys_n (*n* = 0, 1, 2, and 4). (b) DFT-calculated *CO and *COOH binding free energies for the Ag_(147−n)Cys_n models. Reprinted with permission from ref. 96. Copyright 2015, American Chemical Society. (c) Schematic illustration of functionalization process of Au NPs with NHC molecules and (d) Tafel plots of parental Au NPs and functionalized Au NPs for CO production measured in CO₂-saturated 0.1 M KHCO₃. Reprinted with permission from ref. 116. Copyright 2016, American Chemical Society.

related to the optimal coverage achieved with long-chain amine molecules. The activity improvement by amines was only noticeable with small Au NPs, implying the existence of synergistic effects between the amine group and the undercoordinated Au sites.¹¹⁴

The electron donating and withdrawing abilities of surface molecules play a significant role in tuning the electronic structure of the catalytic centre. This strategy is analogous to the method by which the activity of molecular catalysts is improved.¹¹⁵ Chang's group successfully enhanced the activity of Au NPs using electron-rich N-heterocyclic carbene (NHC).¹¹⁶ The NHC molecules were spontaneously adsorbed on the Au NPs, replacing the parent surfactant due to the strong interaction with the Au NPs (Fig. 5c). NHC-functionalized Au NPs showed a 7.6 times higher CO production rate with a high FE of 83% compared to those of oleylamine-capped Au NPs (FE = 53%). Tafel analysis suggested that the surface NHC molecules strongly donated σ -electrons to Au NPs, thereby facilitating the first electron transfer step from Au to CO₂, which is thought to be the general rate-determining step (RDS) of CO₂RR (Fig. 5d).¹¹⁶ The same group later extended the NHC functionalization approach to Pd foils to enhance the production of C1 chemicals (*i.e.* formate and CO) by 32-fold.¹¹⁷ The activity and selectivity changes were considered sensitive to the structure of the surface NHC derivatives, suggesting the potential of fine-tuning the performance through surface modulation.

Regarding the electrocatalyst applications, the performance of powder-type catalytic materials is typically tested by dispersing them in a solvent (*i.e.* an alcohol/H₂O mixture) and depositing them on a working electrode substrate. To prevent the mechanical detachment of the catalyst during the reaction (specifically during gas-evolving reactions), a polymer binder was used. Nafion, a specialized polymer for proton conduction, was predominantly used in the preparation of the catalyst electrode. Despite the significant Nafion amounts in the catalyst layer (*i.e.* 1 mg of the catalyst and 10 μ L of a 5 wt% Nafion solution result in a catalyst to Nafion mass ratio of 1: ~0.5), its role in electrocatalysis has barely been investigated. Flake *et al.* investigated the role of Nafion and polyvinylidene fluoride (PVDF) on the surface of an Au₂₅ cluster and 5 nm Au NPs.¹¹⁸ The main structural difference between both polymers was the presence of sulfonate groups in Nafion. The authors found that Nafion-containing catalysts exhibited considerably higher CO FE than PVDF-containing ones and the bare Au foil. X-ray photoelectron spectroscopy (XPS) measurements revealed that the Nafion-containing Au showed significant shifts in the Au 4f binding energy. This indicated that the sulfonate group altered the electronic state of Au and optimized the adsorption energy of the key reaction intermediates.¹¹⁸ Furthermore, Chen and co-workers systematically investigated the effect of polymer binder types.¹¹⁹ Five types of polymers were selected, including Nafion, polyfluoroethylenes, poly(vinyl alcohol), and poly(acrylic acid). The electrocatalytic performance of the Au NPs supported on carbon black indicated that F-containing polymers (including Nafion) promoted the selective

CO₂RR to CO. DFT calculations suggested a strong HER-suppression effect of C–F functional groups, which led to a high CO selectivity. These results opened the possibility of utilizing polymers with these groups, other than Nafion, as alternatives for CO₂ reduction, and highlighted out the importance of polymer binders as catalytic activity modulators.¹¹⁹

4.3. Stabilization of reaction intermediates and CO₂

The adsorption mode and geometry are other important factors influencing the activity and selectivity of catalytic processes. The surface structure has direct relevance to the adsorption properties; therefore, surface molecules affect the binding energies of intermediates. Catalytic materials have a limited number of possible surface configurations due to their crystal structures and surface energies. Combining core catalysts with surface modulators that interact with the reactant (CO₂) and reaction intermediates can create intriguing synergies to lower the activation energy, thereby stabilizing the reactants and intermediates. Meyer *et al.* investigated the synergy between N-doped carbon nanotube (NCNT) catalysts and polyethyleneimine (PEI).¹²⁰ PEI-coated NCNT exhibited a maximum formate FE of 87% and a three-fold higher intrinsic activity compared to those of NCNT. PEI-NCNT and NCNT have a common RDS, *i.e.* the first electron transfer to CO₂, as indicated by their similar Tafel slopes. The authors assumed that the promotional effect of the PEI layer was attributed to the stabilization of the CO₂^{•−} intermediate radical by the hydrogen bonding network of PEI and the increase in the local CO₂ concentration.¹²⁰ Other than the Meyer group's report, almost all organic modifier studies utilized Ag, Au, and Cu as platform materials. Since synergistic catalytic effects between carbon nanomaterials and surface modulators have rarely been reported, intensive investigations should be conducted in the future.

Hydrogen bonding at the catalyst surface enormously benefits the CO₂ electrocatalysis. Regarding the above-mentioned Ag-cysteamine system (Section 4.2), the Goddard group assumed that cysteamine could have a stabilizing as well as an electronic effect on CO₂ and conducted detailed quantum mechanics calculations.¹²¹ It was revealed that cysteamine not only exerted an effect on the electronic structure, but also stabilized the chemisorption of CO₂ molecules with the support of the opposite NH₂ group using hydrogen bonding networks (Fig. 6a). Experimentally, they showed that the modification of Ag NPs with C₁₁ analogue of cysteamine (C₂) only moderately decreased the overpotential.¹²¹

Wang *et al.* successfully doubled the hydrocarbon production by coating Cu(OH)₂ nanowires with amino acids (Fig. 6b).¹²² The promotional effect was general for various types of amino acids and several Cu-based electrodes, including Cu nanowires, Cu foil, and annealed Cu. The authors attempted to reveal the origin of the activity enhancement by investigating the role of each functional group in amino acid (*i.e.* amine and carboxyl groups). Other groups, such as carboxyl, nitro, and quinone, lowered the production rate of hydrocarbons, indicating that the activity improvement was attributed to the amine group. DFT calculations explained that the NH₃⁺ group (protonated amine under

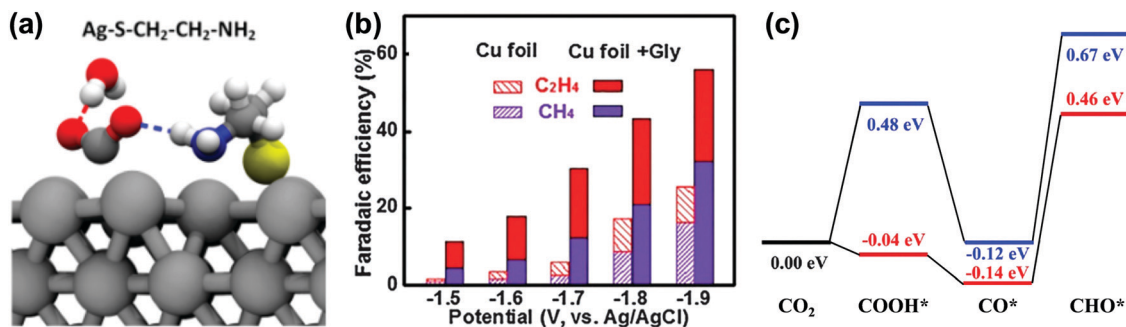


Fig. 6 (a) Schematic illustration of the hydrogen bonding interaction between CO₂ and a cysteamine molecule stabilizing the CO₂ chemisorption on Ag. Reprinted with permission from ref. 121. Copyright 2018, American Chemical Society. (b) Faradaic efficiency of a bare Cu foil and glycine-attached Cu foil toward CH₄ and C₂H₄ as a function of applied potentials measured in CO₂-saturated 0.1 M KHCO₃. (c) DFT calculated free energy diagram of CO₂ reduction to *CHO on Cu surface with (red line) and without (blue line) a glycine molecule. Adapted with permission from ref. 122. Copyright 2016, Royal Society of Chemistry.

experimental conditions) could form a hydrogen-bond with *COOH and *CHO intermediates, where the latter is an important intermediate for hydrocarbon production (Fig. 6c).¹²² Similar results were obtained by Zhang *et al.*, where methyl carbamate containing amine groups on Cu foil could enhance CH₄ formation up to 81.6% at −2.13 V (vs. RHE).¹²³ They suggested that the protonated amine (−NH₃⁺) could stabilize *CHO intermediates by hydrogen bonding and partial charge transfer from Cu to C. The *CHO intermediates are important for CH₄ production rather than CO dimerization.

The reports on the promotional effects of surface modulators occasionally contradict one another. Andreoli *et al.* prepared Cu foams modified with poly(acrylamide), poly(acrylic acid), and poly(allylamine).¹²⁴ Only the poly(acrylamide)-modified electrode exhibited a remarkable two-fold activity improvement for C₂H₄ production at −0.96 V (vs. RHE), while the poly(acrylic acid)-modified one showed only a slight increase. The poly(allylamine)-based Cu foams showed a HER selectivity of almost 100%, which is rather contradictory to previous work that proposed the promotional role of the amine group.¹²² DFT calculations revealed that the acrylamide oligomers on Cu surfaces are beneficial because they (i) increase the local CO coverage and (ii) stabilize the CO–CO dimers, which are important intermediates for C₂₊ chemical production. It is assumed that amine groups may elevate the CO₂RR rate cooperatively with other groups on Cu surfaces.¹²⁴

Liu *et al.* demonstrated the possibility of utilizing porphyrin molecules as surface promoters.¹²⁵ Typically, surface modulators partially block catalytic sites; however, owing to the open structure of such a tetradentate ligand, reactants could access almost the entire surface of the functionalized porphyrin–Au hybrid. The functionalized Au NPs exhibited a 300 mV lower overpotential, higher CO FE, and much better long-term stability (72 h) compared to the oleylamine-coated Au NPs. The enhancement by the porphyrin molecule was explained by the fast electron transfer and stabilization of the *COOH intermediate.¹²⁵

4.4. Regulation of proton delivery

The CO₂RR selectivity for each product is affected by the relative reaction kinetics of the competitive and/or shared

intermediates. In particular, the chemical species involved in the RDS are important in determining the activity and selectivity. As CO₂RR proceeds *via* multiple reaction steps involving electrons and/or protons, the products have different pH-dependences according to the involvement of the proton in the RDS. The CO₂RR also competes with HER; therefore, the pH of the electrolyte can change the product selectivity of the CO₂RR and H₂ production. This change is not limited by the pH of the bulk electrolyte and is sensitively affected by the local pH gradient near the catalyst–electrolyte interface. For example, CH₄ formation is proposed to involve a proton-transfer RDS, which forms *CHO, implying that a high pH is not favourable.^{126–128} The proton reduction (*i.e.* the HER), in most cases, also depends on the electrolyte pH as the major chemical species of the proton donor vary (*i.e.* proton, water, bicarbonate, or other protonated chemical species) and, thus, affect the reaction pathway. Typically, a large overpotential is required in an alkaline electrolyte,¹²⁹ and at a low pH, the reactions with the proton-transfer RDS would dominate. In contrast, the production rates of C₂H₄ and C₂H₅OH from CO₂RR on the Cu electrode are proposed to be independent of pH since the rate-determining C–C bond formation step is considered not to involve proton transfers.¹³⁰ Therefore, a high local pH is generally pursued for the selective generation of C₂ products and well suppress the H₂ and CH₄ formations. However, a bulk alkaline electrolyte is not suitable for a typical H-type cell, where dissolved CO₂ molecules are fed through the aqueous electrolyte, due to the rapid equilibration of CO₂ with OH[−] to generate bicarbonate/carbonate, leading to the absence of usable CO_{2(aq)}.

Therefore, the pH is one of the crucial factors in controlling the selectivity of targeted products from the CO₂RR. In the H-type cell, neutral electrolytes are widely used for the CO₂RR.⁴² Even under neutral conditions, the advantage of a high pH in the CO₂RR can be exploited by roughening the electrode surface or introducing a porous structure, so that a local pH gradient can be created near the catalyst surface due to the insufficient mass transfer under the CO₂RR conditions. This aspect will be discussed in Section 5. Another approach involves the direct feeding of gaseous CO₂ to the catalyst surface through the reactor design, enabling the use of the alkaline

electrolyte on one side of the catalyst layer (also discussed in Section 5).

The addition of surface organic molecules that have different affinities to proton and water (water is also a proton source) can elaborately control the local proton transfer at the catalyst-electrolyte interface and the reaction selectivity. Earlier works carried out by Bocarsly *et al.* showed the possibility of tuning the reaction pathways of CO₂ electroreduction, using proton-mediating molecules. The authors demonstrated the generation of a six-electron product (CH₃OH) on hydrogenated Pd and Pt electrodes in a pyridine-containing aqueous solution.^{131,132} These results are impressive because these metals cannot independently produce CH₃OH in aqueous solutions, which highlights the proton-mediating role of pyridine.

To systematically study the proton delivery capability of surface modulators, Flake *et al.* prepared three molecules; 2-mercaptopropionic acid (MPA), 4-pyridylethylmercaptan (PEM), and cysteamine, with different pK_a values of each functional group, and attached them onto an Au foil.¹³³ The thiol group at one end formed a strong Au-S covalent bond, and the group at the other end induced functionality at the Au-modulator interface. The Au-MPA electrode showed almost 100% HER selectivity, which indicated that the facile proton donating ability of the carboxyl group (pK_a = 3.7) promoted the HER. For Au-PEM, a three-fold increase in formate production was observed (Fig. 7a). This result was attributed to the moderate pK_a value (5.2), resulting in an appropriate amount of adsorbed H and inhibiting the first electron transfer to CO₂ to form

*COOH, the reaction intermediate for CO (Fig. 7b). The adequate *H coverage supported the formation of the *OCHO intermediate and subsequently the formate. The cysteamine-modified Au showed similar FEs for the products compared to the bare Au foil, while the current densities were doubled.¹³³

Recently, Toma *et al.* presented new insights into the catalytic performance of Cu-polymer composites.¹³⁴ The authors prepared oxide-derived (OD) Cu foils and 10 types of polymers. The polymer-coated OD-Cu was tested for CO₂ reduction at -0.7 V (vs. RHE), where hydrocarbon products are barely produced. Protic polymers enhance the HER activity as the protic groups facilitate proton delivery to the electrode. Interestingly, there was a distinct correlation between their hydrophobicity (contact angle) and the formic acid/CO product ratio (Fig. 7c). Using reactive molecular dynamics simulations, the water density surrounding the modified OD-Cu surface was calculated. The hydrophilicity and hydrophobicity influenced the nanoscale water structure in the vicinity of the electrode, which, in turn, impacted the hydrogen binding energy and product selectivity (Fig. 7d).¹³⁴

4.5. Change in catalyst structures

Another key aspect involves studying the dynamic changes in the catalyst and/or surface organic molecules to understand the promotional roles of surface modulators. A strong interaction between the catalyst and surface molecules can induce structural modifications that may lead to activity and selectivity changes. For instance, Chernyshova *et al.* investigated Cu foils coated with poly(4-vinyl pyridine).¹³⁵ The modified Cu electrode

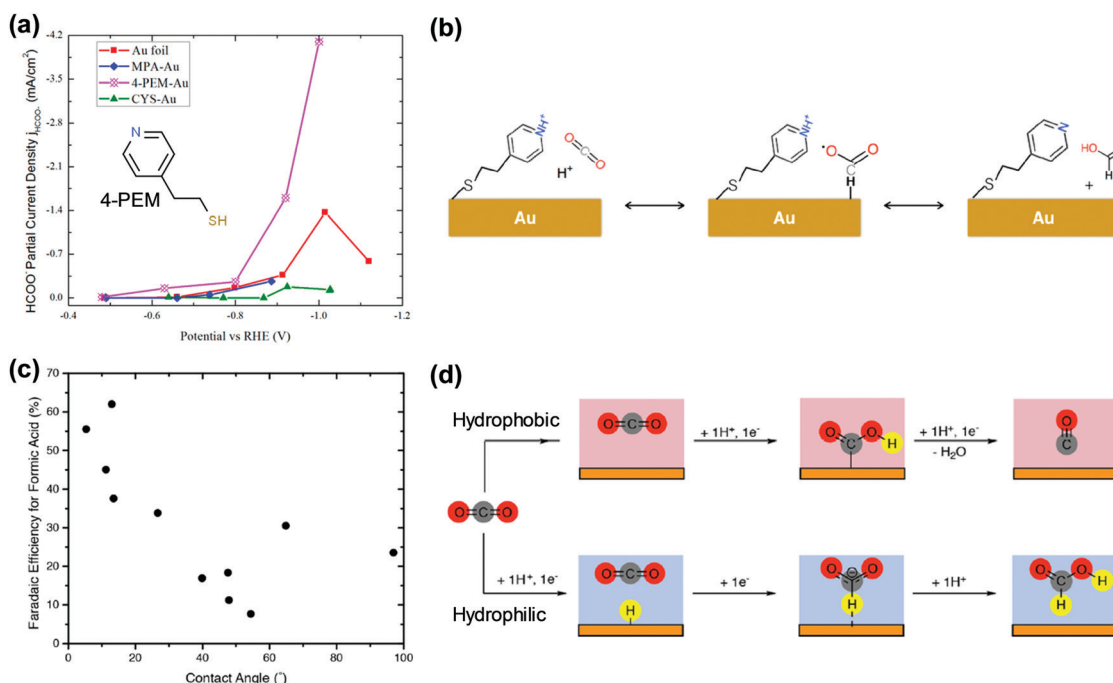


Fig. 7 (a) Formate FE of Au foils modified by three organic molecules with different pK_a values measured in CO₂-saturated 0.1 M KHCO₃. (b) Proposed reaction mechanism of the formate production at 4-PEM and Au interfaces. Adapted with permission from ref. 133. Copyright 2017, American Chemical Society. (c) Relation of formate FE and contact angle of modified Cu foil by polymers with various hydrophilicity. (d) Proposed reaction mechanism for CO and formic acid production when the catalyst surface is hydrophobic or hydrophilic. Reprinted with permission from ref. 134. Copyright 2018, American Chemical Society.

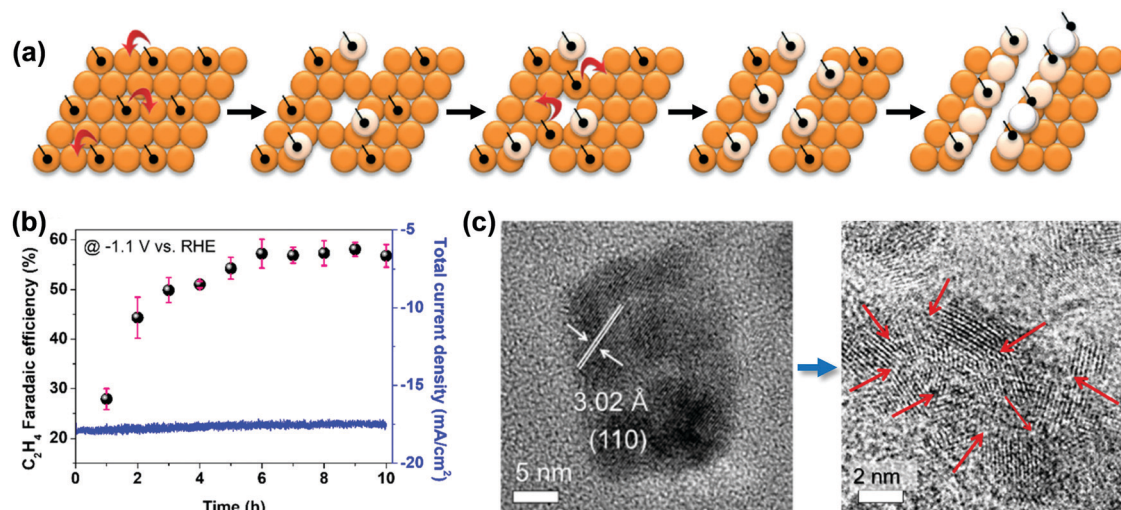


Fig. 8 (a) Schematic illustration of the surface reconstruction process induced by strong interaction between Au surface and ligands (indicated by tailed dots), which pulls out the lattice atoms. Reprinted with permission from ref. 136. Copyright 2019, Royal Society of Chemistry. (b) C_2H_4 faradaic efficiency and total current density of cysteamine-coated Cu_2O nanocubes (NCs) measured over time. (c) Transmission electron microscope images of the initial Cu_2O NCs and fragmented Cu_2O nanocrystals with multi-domains after the electrochemical measurement. Reprinted with permission from ref. 57. Copyright 2019, American Chemical Society.

exhibited a maximum FE of 40% toward formate production in a 0.1 M $KHCO_3$ solution at -1.3 V (vs. Ag/AgCl). XPS and Raman analyses revealed the formation of a pyridyl- Cu^{II} complex (Cu^{II} -N bond) during the electrolysis and showed that this structure was stable for 30 h of operation. This phenomenon was attributed to the *in situ* dissolution of Cu atoms and their subsequent complexation by the pyridyl group of the polymer.¹³⁵ Xu *et al.* examined Au-thiol interface systems.¹³⁶ The formation of strong covalent Au-S bonds can withdraw the surface Au atoms, thus creating many defect sites that are favourable for CO_2 RR (Fig. 8a). The defect sites result in a two-fold enhancement in both the CO FE and current density.¹³⁶ The restructuring of the Au surface was also predicted using DFT calculations when NHC was supported on Au.¹¹⁶ The Au atoms could be pulled from the lattice by strong interactions with two carbene molecules.

Some organic molecules increased the CO_2 reduction product selectivity by blocking specific active sites. The Agapie group demonstrated the promoted C_{2+} chemical production on polycrystalline Cu using *N*-substituted pyridinium and phenanthroline additives in the electrolyte (10 mM).^{137,138} The authors achieved a total FE of ~ 70 – 80% for C_{2+} products at -1.1 V (vs. RHE) in the presence of *N*-tolylpyridinium chloride¹³⁷ and *N,N'*-ethylene-phenanthroline dibromide.¹³⁸ Such a high selectivity was ascribed to the efficient suppression of CH_4 and the H_2 formation. The *N*-arylpyridinium additives induced the highest C_{2+} selectivity. The authors assumed that the improvement by the pyridinium additives was attributed to the selective poisoning of the Cu active sites for CH_4 and H_2 production and the increased local pH near the electrode.¹³⁷ For phenanthroline bromide, the morphology of the Cu surface was transformed to cube-like nanostructures with (100) Cu facets, which are known to be efficient for C-C coupling.¹³⁸

The site-blocking strategy could specifically be beneficial if the active site for the HER can be selectively inhibited. Jaramillo *et al.* showed that aqueous 1-ethyl-3-methylimidazolium solutions (0.1 M) can suppress the HER activities of Cu, Ag, and Fe metals by up to 75%.¹³⁹ However, it should be cautioned that the inhibition effect was not observed at high pH values and the molecule was susceptible to both reductive and oxidative potentials which could induce its breakdown.¹³⁹

Some combinations of electrocatalysts and surface organic molecules could remarkably promote structural changes that induce significant activity improvement. Hwang *et al.* prepared cysteamine-capped Cu_2O nanocubes (NCs) *via* one-pot polyol reductions.⁵⁷ Interestingly, chronoamperometric measurement revealed that within 6 h, the C_2H_4 FE increased from 27% to 57.3% (Fig. 8b). High-resolution transmission electron microscopy (HR-TEM) analysis indicated that the initial ~ 20 nm-sized Cu_2O NCs were fragmented into fine Cu_2O nanocrystals with a domain size of 2–4 nm, implying a close packing with numerous domain boundaries (Fig. 8c).⁵⁷ In preceding studies, Cu-based CO_2 reduction electrocatalysts generally suffer from severe aggregation and deformation of their initial morphologies, resulting from an *in situ* dissolution–redeposition process under applied negative potentials.^{140–142} In this regard, the electrochemical fragmentation phenomena were attributed to the presence of surface cysteamine molecules.

4.6. Comparison of activity improvement by surface modulators

To summarize this section, the molecular functionalization of the catalyst surface has been recently proven to be a simple and straightforward approach for the extrinsic modification of the CO_2 RR activity and selectivity. This method changes the catalyst–electrolyte interface, which can lead to optimization of

the catalyst structure and the binding mode, consequently stabilizing the reaction intermediates, and modification of the transport behaviour of protons and water. These surface additives provide an opportunity to fine-tune the catalyst-electrolyte interface, which cannot be fully achieved only with catalyst design and electrolyte engineering. The electrocatalytic activities of reported catalysts before and after the addition of a surface promoter are summarized to show the extent of improvement. Fig. 9 displays the maximum CO₂-to-CO FEs and CO partial current densities of Ag- and Au-based catalysts. Bare Ag foil exhibits mediocre maximum CO FEs ranging from 70 to 80%, only at highly negative potentials (< -1.1 V vs. RHE). The activity increase is remarkable when Ag-based NPs are surface-functionalized, as evidenced by the 300–600 mV decrease in the overpotential at the maximum CO FE, as well as the increase in the maximum CO FEs to over 90% (Fig. 9a). For Au-based catalysts, the significant increase in the maximum FE from $\sim 30\%$ to $\sim 100\%$ is noticeable, while the decrease in the overpotential at the maximum CO FE is also significant (100–400 mV) (Fig. 9b). Similar trends in the activity improvement are observed in terms of the CO partial current density, where the overpotential is reduced by up to 600 mV to obtain the same current density (Fig. 9c and d). Notably, the surface

functionalization strategy combined with nanostructure leads to a similar degree of activity enhancement that has been accomplished by the catalyst design. For instance, the generation of abundant grain boundaries in polycrystalline Au electrodes led to the overpotential decrease of ~ 200 mV and an increase in the CO FE by 20%, which can be achieved by tuning the interfaces with the same catalysts (Fig. 9b and d).⁵⁰ Furthermore, we note that particle-type Au catalysts exhibited significant improvement than the Au foil with surface modulators (Fig. 9d). This implies that the interface tuning effect can be maximized with high-surface-area catalysts, and the surface structure can affect the interaction between the surface atoms and promoter molecules.

The CO₂RR performance was also summarized for Cu-based catalysts (Fig. 10). Among many chemicals made from Cu-based catalysts, the activity for only C₂H₄ is shown as it is a special multicarbon product that is the most attractive and intensively studied. The surface promoters at Cu interfaces can induce an increase in the C₂H₄ selectivity by ~ 10 –50%, while bare Cu foils exhibit low C₂H₄ FEs of 5–20%. Although quantitative discussions on the other products are not presented here due to the lack of numerical data, Table 3 shows that the surface modulators facilitate varying selectivity between CO and formate

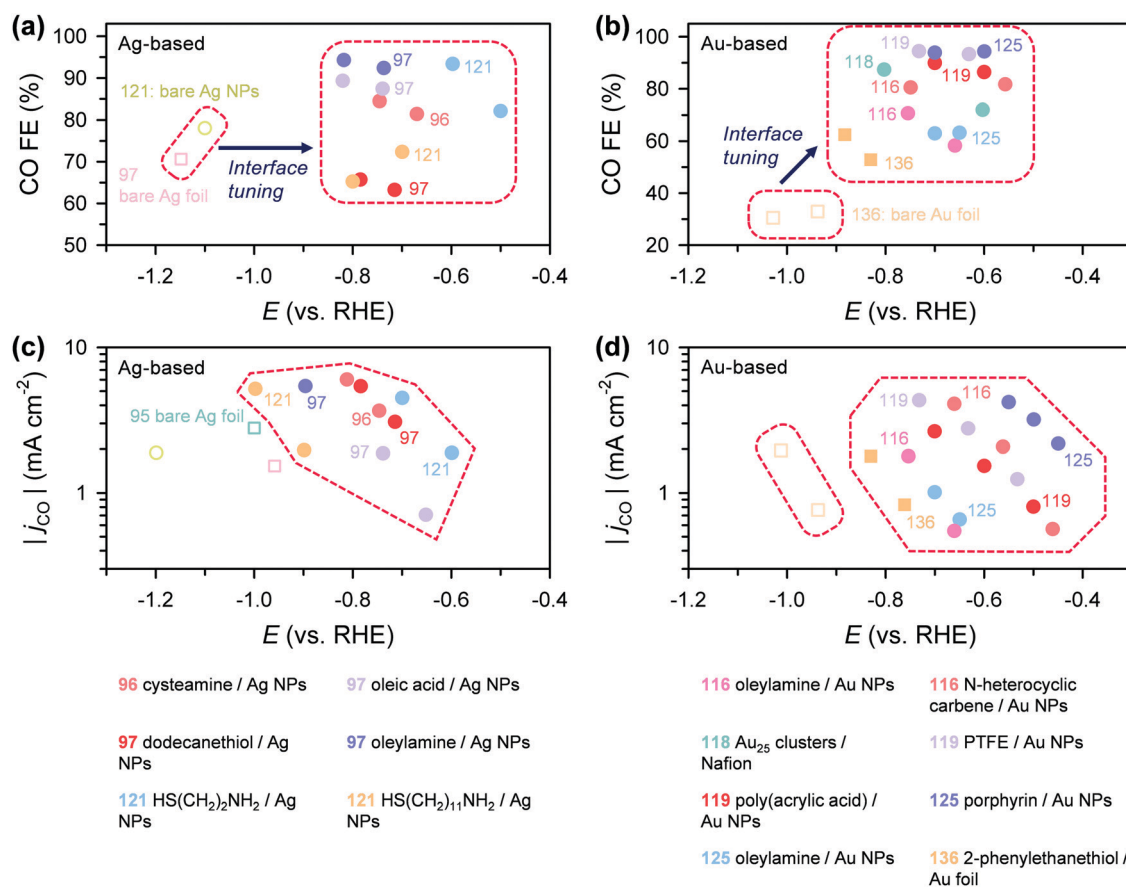


Fig. 9 Summary of the maximum CO FEs of reported (a) Ag-based catalysts and (b) Au-based catalysts, and the CO partial current densities of reported (c) Ag-based catalysts and (d) Au-based catalysts with and without the surface modulators. The numerical data were carefully extracted using a plot digitizer software. The numbers denote the reference numbers.

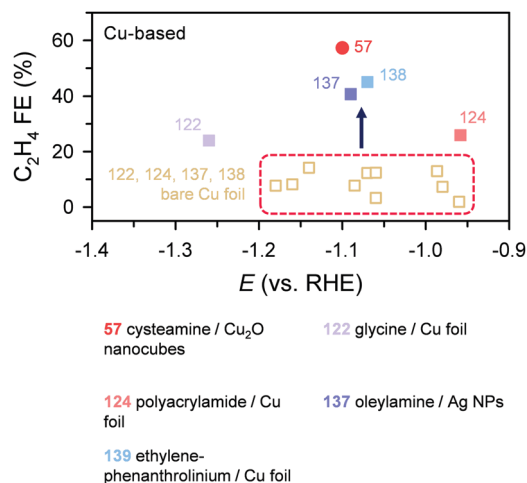


Fig. 10 Summary of the reported maximum C_2H_4 FEs of interface-modified Cu-based catalysts and bare Cu foils as a function of applied potential. The numerical data were carefully extracted using a plot digitizer software. The numbers denote the reference numbers.

at low overpotentials, C_2H_4 and C_2H_5OH at intermediate overpotentials, and CH_4 at high overpotentials. We envisioned that the design of appropriate molecules can break the trend of potential dependence in Cu-based catalysts for efficient CO_2 RRs to produce hydrocarbons.

4.7. Future guidelines for surface modulation research

Many organic modulators possess multiple functional groups in a single molecule, which play different roles in electrocatalysis at the interfaces. In some cases, the effect of a certain functional group may dominate that of another group. If the functional groups have similar catalytic effects at the interfaces, we could measure their average properties or an unexpected new result from their cooperative interaction. Therefore, it is necessary to identify the role of each group to clearly understand the chemistry through systematic investigation.

We note that the surface modulator covers the catalyst or sometimes changes the surface arrangement of the catalyst. These phenomena can impair the activity comparison of modified catalysts with unmodified ones. Therefore, researchers are encouraged to measure the electrochemically active surface area (ECSA) and discuss the ECSA-normalized CO_2 reduction activity. Among various reported methodologies, the double layer capacitance measurement is the simplest and, thus, the most popular method for estimating the ECSA.^{143,144} However, extreme care must be taken in both the measurement and interpretation because organic modulators are expected to exhibit double layer capacitance. The underpotential deposition method is preferred to this method because probe atoms (mostly Pb) are selectively deposited on the metal catalyst.¹⁴⁵

Another consideration is that the surface density of the modulator can critically affect the electrocatalytic performance as shown in Wallace *et al.*¹¹⁴ and Wang *et al.*¹²² These studies commonly suggest that low or excessive amounts of surface modulators are rather detrimental to the activity. Therefore, it

is recommended to specify the used amount and to quantify the surface coverage and surface contents of the modulators to acquire consistent results in future studies.

Even the molecules that bind strongly with catalysts can electrochemically detach at CO_2 RR potentials. Flake and Xu *et al.* revealed, using attenuated total reflectance infrared (ATR-IR) spectroscopy before and after electrochemical tests, that a significant number of surface-bound thiols were lost after the operation.¹³⁶ This result necessitates the estimation of the binding stability of modulators on catalyst surfaces under negative potentials in future studies, as well as the confirmation whether or not the enhancement is attributed to the surface molecules.

Until now, most surface modulator studies have been carried out in aqueous H-type electrolysis cells for fundamental investigation. The catalyst–electrolyte interface is an important factor that must be considered also in other types of CO_2 electrolysis cells utilizing gas-diffusion electrodes (GDEs), which have recently emerged to obtain commercially relevant current densities. The surface functionalization also provides a great opportunity to modify the catalyst–electrolyte– CO_2 three-phase interface, as demonstrated by Sargent group for the improved production of C_2 chemicals in both microfluidic and membrane electrode assembly cells, which are discussed in detail in Section 5.^{146,147} We envision that the surface modulator strategies for activity enhancement will be an interesting research area, regardless of the reactor type.

Finally, it was found that most of the studies focused on the effect of N-containing compounds, with a few cases of S- and F-groups. There is still an extensive research scope for research to improve the catalyst performance and study new electrochemical, catalytic phenomena, as well as the underlying chemistry. Future studies are encouraged to further investigate other organic promoters with a variety of functional groups.

5. Understanding catalyst–electrolyte interfaces

The electrocatalytic activity of CO_2 reduction catalysts is typically measured using an electrochemical system, where CO_2 and the proton source are mediated by an aqueous electrolyte. When an electrode is immersed in the electrolyte, an electric double layer is constructed at the electrode–electrolyte interface, where covalently bonded species and reaction intermediates are present in the inner Helmholtz plane (IHP), and hydrated ions are situated in the outer Helmholtz plane (OHP), held by electrostatic forces (Fig. 11a). In addition, there are several dynamic equilibria involving CO_2 and H_2O , which can potentially vary the local ion distribution and pH at the interface as the CO_2 RR proceeds (Section 3.1). Therefore, the electrolyte is the other important component that can control the CO_2 RR activity at the catalyst interface.

Concerning the ion types and applied electrode potential, the ionic distribution at the electric double layer is determined, which strongly affects many factors for the CO_2 RR, as schematically

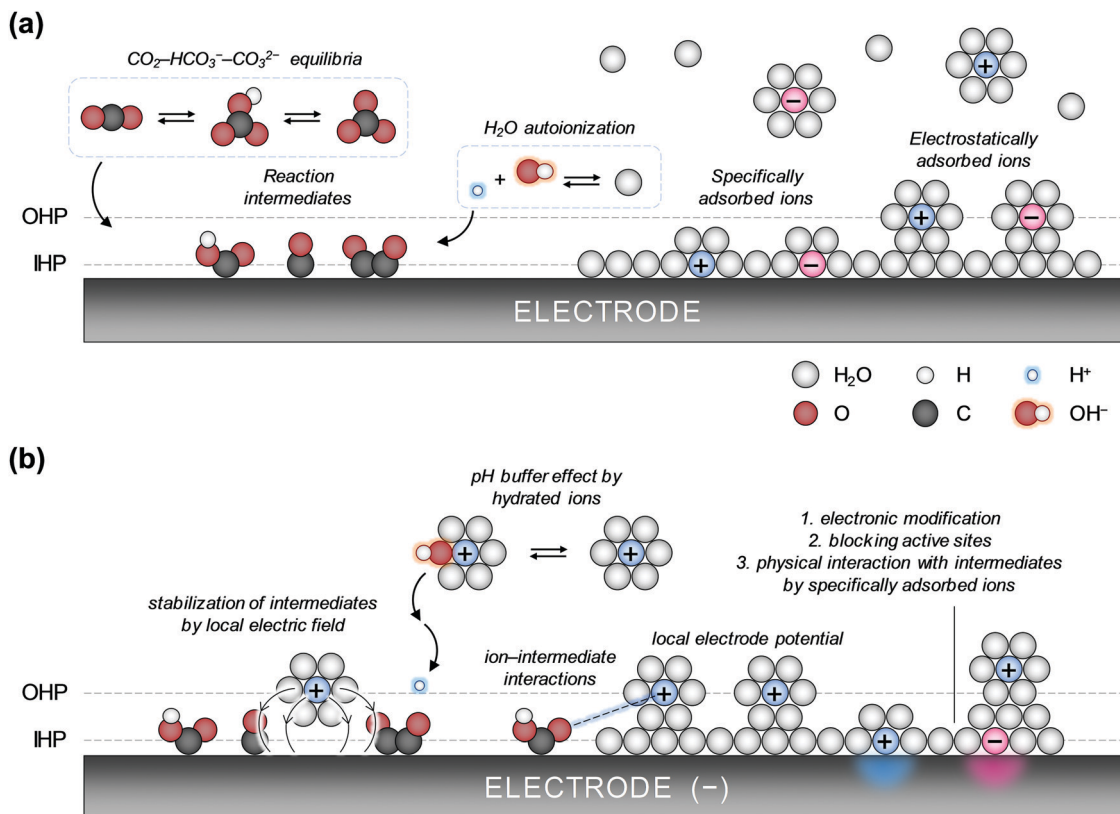


Fig. 11 (a) Simplified schematic illustration of the electric double layer composed of the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP) with chemical equilibria involved. (b) Schematic illustration of possible effects of the interfacial ions on the catalyst surface or the electrocatalytic process under the CO_2RR conditions with the negative potential applied.

illustrated in Fig. 11b. At the potentials where the CO_2RR occurs, the electrode is negatively polarized. This situation results in the attraction of the hydrated cations to the electrode owing to Coulomb interactions and, subsequently, the increase in the population of cations at the OHP. The cations at the OHP elevate the local electrode potential, which can change the charge transfer kinetics. The cations also generate a local electric field, which improves the stability of the covalently adsorbed intermediates at the IHP. Conversely, they may rather directly interact with the polar intermediates by Coulomb interactions. In addition, the hydrated cations act as pH-buffering agents, which determine the local pH, pH-dependent reaction mechanism, and proton transport. Meanwhile, specifically adsorbed ions at the IHP can have multiple roles: they can alter the electronic structure of the surface catalyst atoms, block the active sites, and interact with the intermediates *via* van der Waals forces. These catalytic effects are greatly influenced by the type and concentration of the electrolyte. Despite the importance of the electrolyte-dependent electric double layer structure on the electrocatalytic process, its contribution has been less understood compared to the impact of heterogeneous catalysts. This is mainly because the characterization of electrolytes or their interaction with the catalyst surface during CO_2RR is not well-established yet. The role of electrolytes is typically proposed based on experimental CO_2RR activity trends and simulation results. Mass diffusion and the chemical balance of the

individual chemical species in the electrolyte must be considered to understand the role of the electrolyte.

5.1. Effect of the electrolyte type on the interface

Bicarbonate (or carbonate) is a popular electrolyte for CO_2RR as it provides near-neutral pH, and the dissolved CO_2 concentration is relatively high.^{148–152} The role of the bicarbonate has been a subject of controversy; however, recent studies have attempted to characterize the catalyst surface using *in situ* spectroscopy for clarification. Xu *et al.* attempted to identify the role of the bicarbonate anion in the CO_2RR on CO-selective metal electrodes using *in situ* attenuated total reflectance-surface enhanced infrared absorption spectroscopy (ATR-SEIRAS).⁴⁵ With ^{13}C isotope labelling and electrokinetic experiments, it was revealed that surface bicarbonate anions rapidly equilibrated with aqueous CO_2 rather than the dissolved CO_2 used for the reduction reaction. Shao and co-workers arrived at a similar conclusion using a Cu electrode. In addition, the authors proposed that even the dissolved CO_2 required pre-equilibration with bicarbonate, which is more easily attracted to the surface cations than CO_2 .¹⁵¹

Bicarbonate is a general electrolyte for CO_2RR ; however, its corresponding alkali metal cations appear to have a significant effect on the CO_2RR activity and selectivity, owing to the relatively high population of the cations at the OHP. Numerous previous papers have shown that large alkali cations enhance

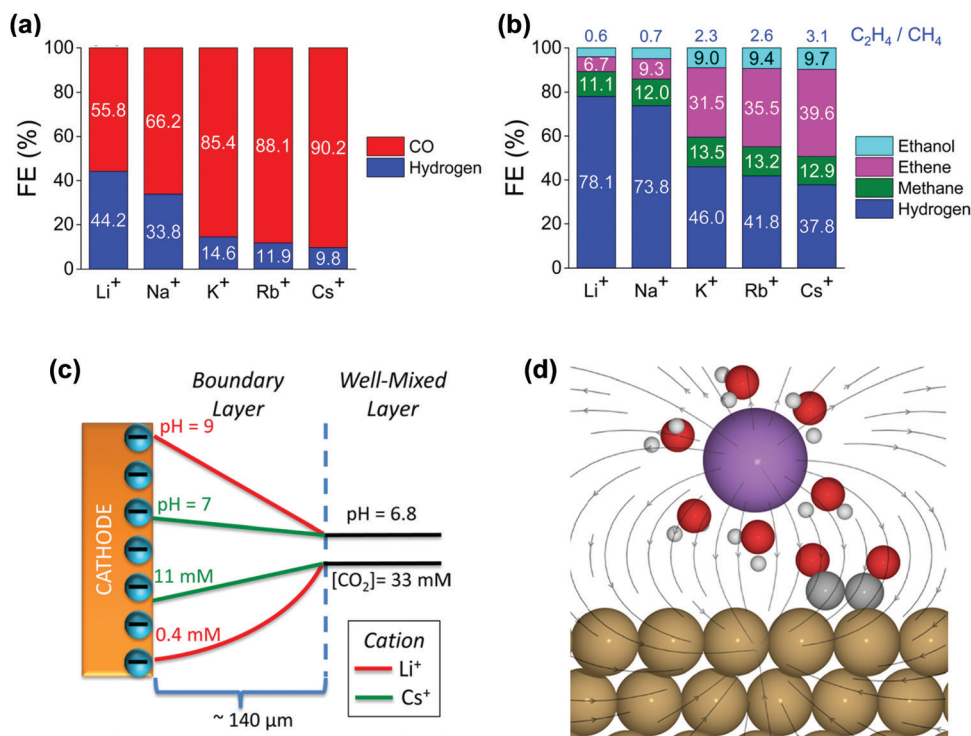


Fig. 12 CO₂RR product distribution of (a) Ag foil and (b) Cu foil as a function of the cation type measured at -1.0 V (vs. RHE) in CO₂-saturated 0.1 M bicarbonate electrolyte. (c) CO₂ concentration and pH profiles as a result of cation-dependent hydrolysis constant. Reprinted with permission from ref. 156. Copyright 2016, American Chemical Society. (d) Schematic illustration of the local electric field created by cation at the catalyst interface and stabilized OCCO intermediate. Reprinted with permission from ref. 95. Copyright 2017, American Chemical Society.

the FE toward C₂ products on Cu and C₁ products on Ag and Sn.^{153–155} In an earlier work, Hori *et al.* explained that large cations are specifically adsorbed more easily than small ones due to the relatively small hydration numbers.¹⁵³ Many specifically adsorbed cations could elevate the potential at the OHP and decrease the local proton concentration, thereby suppressing the HER. The Bell group explained cation-size-dependent CO₂RR activity trends with the interfacial pH (Fig. 12a and b).¹⁵⁶ It was claimed that the cation size significantly affects the hydrolysis constant of the hydrated cation. Consequently, the pK_a value of Li⁺ was calculated to be three times higher than that of Cs⁺. The hydrated Cs⁺ acted like a buffer, maintaining the low pH near the electrode and increasing the local CO₂ concentration compared to Li⁺ by 28 times (Fig. 12c).¹⁵¹ This cation-dependent pH at the electrode–electrolyte interface was experimentally demonstrated by Cuesta *et al.* using *in situ* ATR-SEIRAS. The authors utilized the ratio between the interfacial CO₂ and HCO₃[−] concentrations, which is related to the pH.¹⁵⁷

The Bell group provided new insights regarding the cationic promotion effect, particularly at relatively low overpotentials, where the local pH is marginally built.¹⁵⁸ They found that the HER and CH₄ partial currents remained steady, while formate, C₂H₄, and C₂H₅OH formations proceeded using large alkali cations. DFT calculations revealed that the high density of the large cations at the OHP increased the interfacial dipole field compared to the case with small ones, which improved the stability of key reaction intermediates with high dipole

moments (*e.g.* *CO₂, *CO, and *OCCO). The cation-size independent production of H₂ and CH₄ was attributed to the zero dipole moment of *H and *CHO, which are the reaction intermediates of these products (Fig. 12d).⁹⁵ It was suggested that the interfacial field effect could be maximized using high-valence cations with small radii.^{27,158} However, transition metal ions (Fe²⁺, Zn²⁺, *etc.*) significantly deactivate the metal electrode by electrodeposition, even in trace amounts.^{159–161}

The electrocatalytic process of CO₂RR is largely affected by the cation type due to the high population of cations under negative reaction potentials. In addition to the contributions of cations, anions contribute significantly to control the electrocatalytic trends by modifying the interface. First, the buffering capability of an anion can affect the product distribution.¹³⁰ For Cu-based electrodes, non-buffering anions, such as SO₄^{2−} and ClO₄[−], increase C₂H₄ and C₂H₅OH selectivity with a high C₂/C₁ ratio, while phosphate dominantly increases the H₂ selectivity at a low overpotential and CH₄ at a high overpotential. Bicarbonate produced both C₂ and C₁ with a mediocre C₂/C₁ ratio. In a non-buffering electrolyte, the locally elevated OH[−] concentration at the interface can even suppress the formation of H₂ and CH₄, whose RDSSs involve proton transfers. In contrast, the buffering anion can mitigate the pH changes by acting as a proton donor, where its donating power depends on the pK_a of the anion, and thus increase the H₂ and CH₄ selectivity. The production rates of the other products (CO, formate, C₂H₄, and C₂H₅OH), independent of the proton transfer,

are constant across the entire pH range.¹³⁰ The second effect of anions involves a more direct modification of the interface, including catalyst structure change and interaction with the reaction intermediates, enabled by specifically adsorbed anions that have strong affinity to the catalyst surface in the IHP. Halides have been most actively investigated as promoting anions for the CO₂RR, particularly for C₂ production on Cu-based electrodes.¹⁶² Ogura and co-workers achieved very high C₂H₄ FE using a CuBr-modified Cu mesh in the presence of 3 M KBr.^{163,164} The high efficiency was attributed to the stabilization of methylene intermediate radicals by CuBr.^{163,164} Recent works provided activity trends on Cu-based electrodes based on halide-containing electrolytes, where the CO₂ reduction current density increased in the order of Cl[−] < Br[−] < I[−] (Fig. 13a and b).^{165–168} However, there were inconsistencies in the product distributions. Strasser *et al.* achieved improved CH₄ production in the presence of halides.¹⁶⁵ Cuenya *et al.* reported that C₂H₄, CH₄, and formate productions were promoted,¹⁶⁶ and Yeo *et al.* were able to increase the C₂H₄ and C₂H₅OH selectivity using halide anions.¹⁶⁷ It is assumed that these research groups have their independent protocols for preparing the Cu foil electrodes, leading to different local surface structures. This, in turn, could affect the adsorption of halide anions, which is facet dependent.¹⁶⁹

However, it is consistently suggested that electrochemical cycling or electroreduction conditions induces surface

reconstruction, which increases the roughness (effective surface area) and/or *in situ* exposure of the Cu(100) surface, thus favouring the C–C coupling process (Fig. 13c and d).^{165–168,170} Another explanation of the boosting effect of halide is the change of electronic structure of the Cu surface. It was suggested that halide can suppress the complete reduction of Cu and stabilize Cu⁺ (or Cu₂O) species under the highly reductive conditions, which has been demonstrated to be effective for C–C bond formation (Fig. 13e).^{166,171} Interestingly, the presence of iodide in the electrolyte enhanced the long-term stability as well as the activity; however, more detailed research is required.¹⁶⁸

Halides can also affect the CO₂RR activity of other metals, such as Ag and Zn, selectively producing CO.^{172–177} For Zn, however, different trends were observed for OD-Zn catalysts and reported by Hwang *et al.*, where the CO production activity increased in the order of I[−] < Br[−] < Cl[−]. The presence of halide ions during the preparation of OD-Zn catalysts can modulate the surface roughness as well.¹⁷³ Zhao *et al.* showed that the presence of Cl[−] led to the formation of surface Zn–Cl bonds, which could suppress the HER more effectively and promote reductive CO₂ adsorption from electron-rich Cl species.¹⁷⁷ The adsorption of a halide anion on the catalyst surface has been proposed to modulate the binding energies of the intermediates. The interaction between the anion and the catalyst is also proposed to modulate the electronic states of the

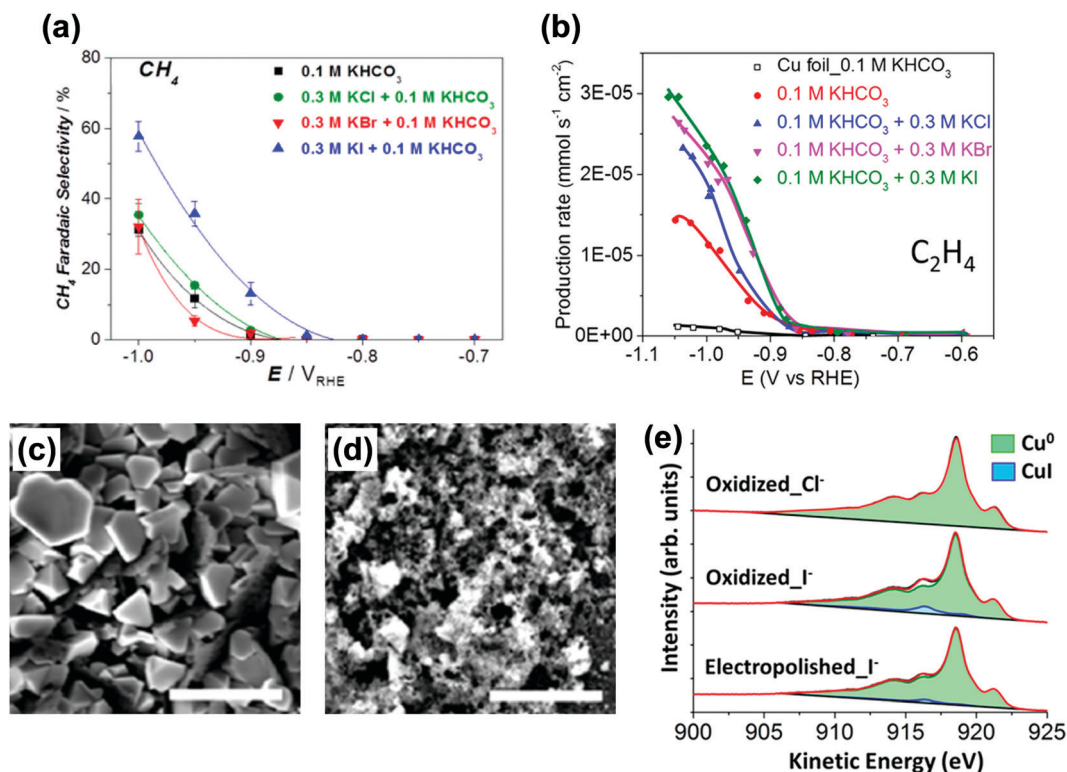


Fig. 13 (a) CH₄ faradaic efficiency of Cu foil as a function of potentials in CO₂-saturated 0.1 M KHCO₃ in the presence or absence of 0.3 M KX (X = Cl, Br, I). Reprinted with permission from ref. 165. Copyright 2016, American Chemical Society. (b) C₂H₄ production rate of Cu foil as a function of potentials in CO₂-saturated 0.1 M KHCO₃ in the presence or absence of 0.3 M KX. Scanning electron microscopy images of Cu foil (c) after immersed in 0.1 M KHCO₃ + 0.3 M KI solution (d) after CO₂ electrolysis. (e) Cu Auger LMM X-ray photoelectron spectra of treated Cu foils after CO₂ reduction reaction at −1.0 V (vs. RHE) for 1 h. Reprinted with permission from ref. 166. Copyright 2017, American Chemical Society.

catalyst and affect the activity as well. The proposed origin of the halide effect is not general for the CO₂RR but varies depending on the electrode materials. It is assumed that the electronic effect appears dominant for Ag- and Zn-based catalysts because no dramatic structural deformation occurs. For Cu-based catalysts, however, the promotional effect of halides is attributed to the combination of structural and electronic effects. These effects presumably synergize because *in situ* roughening increases the density of specifically adsorbed halides, and the *in situ* generation of Cu(100) can promote halide adsorption, owing to relatively strong adsorption energy on the facet.¹⁶⁹ Determining the effect of each factor will be a challenging task due to the great difficulty associated with decoupling these effects. One aspect that is worth considering to explain the anion-dependent activity is the interfacial electric field created by specifically adsorbed anions, revealed to be critical for the cation.¹⁶⁹

Oh *et al.* investigated the effect of CN[−] and Cl[−] anions on Au surfaces.¹⁷⁸ Such specifically adsorbed anionic species can directly interact with the electrocatalyst and/or adsorbed reaction intermediates. CN[−] and Cl[−]-adsorbed Au surfaces exhibited a higher current density of CO FE than bare Au. DFT calculations suggested that the adsorbed CN[−] and Cl[−] could stabilize the *COOH intermediate mainly *via* van der Waals interactions. Although such anions have been considered as catalyst poisons, they can be utilized as promoters in the CO₂RR, providing interface tuning of the adsorbed anions. However, most of the specifically adsorbed anions were unstable and easily detached under the respective operating conditions.¹⁷⁸

The electrolyte effect on non-metallic electrocatalysts has rarely been documented. Doped carbon nanomaterials have attracted immense attention as potential catalysts for selective CO or formate production.¹⁷⁹ Due to their substantially different catalyst surface properties (and presumably electric double layer structure), diverse electrocatalytic trends are expected with this electrolyte type, necessitating the study on carbon-based electrodes. Einaga's group investigated the influence of the electrolyte type on the CO₂ reduction activity of boron-doped diamond (BDD) electrodes.^{180–182} In hydroxide-HCl-based solutions, BDD produced formate rather than CO, regardless of the cation type.¹⁸⁰ The highest FE of 71% was obtained with Rb⁺-based electrolytes. Interestingly, the formate selectivity was higher at low concentrations of large cations and high concentrations of small ones. Subsequently, the same group systematically examined the influence of the electrolyte composition using various types of alkali metal-based halide solutions.¹⁸¹ Regardless of the halide type, the formate selectivity was relatively high when large cations were present in the electrolyte. However, two different trends were noticeable compared with the cases in previous studies using metal electrodes: (i) comparable or higher FE for formate was obtained in Rb⁺-based (not Cs⁺-based) electrolytes, particularly in RbBr solutions (FE = 95%); and (ii) the current density was larger with small cations. In addition, the authors found that halides (Cl[−], Br[−], and I[−]), as well as sulfate anions, could efficiently produce formate through their specific adsorptions. Regarding the anions, improved

selectivity was obtained with small anions. Recent work by the same group showed a higher formate selectivity for BDD in KCl solution than in KClO₄ solution.¹⁸² They assumed that the adsorption of CO₂•[−] radical intermediates occurs preferentially in the KCl solution.

5.2. Regulation of mass diffusion near the catalyst interface

In CO₂RR, the mass diffusion of the reactants (*i.e.* CO₂, H⁺, and H₂O) is another important parameter that controls the catalytic activity beyond the intrinsic activity of the catalyst. The mass diffusion of CO₂ limits the catalytic activity at a current density of several tens of mA cm^{−2} due to the low aqueous CO₂ solubility of 33 mM under ambient conditions (*i.e.* room temperature, 1 atm, and neutral pH).^{42,183} The temperature and pressure dependences of the gas solubility, described by Henry's law, have widely been applied by researchers to improve the low solubility.^{184–186} However, because the reaction proceeds at a low temperature and high pressure, it is difficult to achieve a perfect solution due to the limited ion mobility at low temperatures and the instability of the reactor operation at high pressures. Therefore, the mass diffusion control of reactants (*i.e.* CO₂, H⁺, and H₂O) near the electrode surface is important. In addition, the mass diffusion of the proton sources affects the catalytic activity, both in liquid electrolytes and in GDE type cells. In this section, we describe two categories of results obtained by the mass diffusion control of CO₂, H⁺, and OH[−]: (i) the local pH effect and (ii) the application of a three-phase interface by modifying the catalyst structure.

5.2.1. Mass diffusion control through proton supply: local pH gradient. To increase the CO₂RR selectivity, the activity can be improved by increasing the local CO₂ concentration at the catalyst–electrolyte interface. The HER activity can be suppressed by modulating the local proton concentration. With regards to the mass diffusion control, due to the low CO₂ solubility in water, inhibiting the HER was more effective for increasing CO₂RR selectivity. Gupta *et al.* proposed that OH[−] ions are accumulated in near-neutral KHCO₃ electrolytes, as the CO₂RR proceeds at a high reaction rate due to the unbalanced supply and consumption of protons, resulting in an increase in the pH at the interfacial boundary layer of the electrode compared to that in the bulk electrolyte.¹⁸⁷ Such a local pH gradient can be an important parameter for controlling the CO₂RR product selectivity,^{188–190} because the competitive electrochemical CO₂RR and HER occur at different pH values.

For instance, when Hall *et al.* introduced an inverse opal structure of Au that could generate large pH gradients within the pores, the CO₂RR partial current density did not significantly change; however, the HER partial current density was inhibited by 10-fold (Fig. 14a).¹⁰¹ They proposed that the increased local surface basicity selectively retarded the HER activity as the thickness of the inverse opal structure increased. Subsequently, Dunwell *et al.* observed pH changes near the Au electrode–electrolyte interface by *in situ* analysing the difference in the concentrations of HCO₃[−] and CO₃[−] ions using ATR-SEIRAS.¹⁹¹ As the concentration of the OH[−] ions increased near the catalyst–electrolyte interface, the concentration overpotential

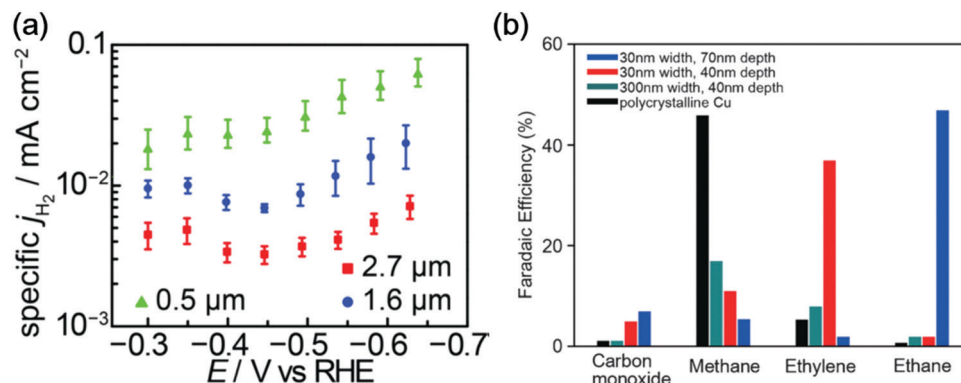


Fig. 14 (a) H_2 production current density of thickness-controlled Au inverse opal (Au-IO) samples in CO_2 -saturated 0.1 M KHCO_3 electrolyte. Reprinted with permission from ref. 101. Copyright 2015, American Chemical Society. (b) Comparison of FE for hydrocarbons with pore diameter and depth of Cu electrode measured at -1.7 V (vs. normal hydrogen electrode; NHE). Reprinted with permission from ref. 196. Copyright 2017, Wiley-VCH.

of the HER increased also. The CO_2 concentration at the electrode surface was not low, despite the high pH gradients. This is because the hydration kinetics of CO_2 are slow, and the effective CO_2 concentration is almost maintained.¹⁹² Similarly improved CO FEs have been demonstrated with Ag or Zn catalysts, whose morphologies were controlled to induce local pH differences.^{25,193} To explain the local pH effect, recent fluid dynamic calculations suggested that the consumption rate of the proton is much higher than that of CO_2 in a spatially confined catalyst surface, which contributed to effective suppression of the HER.¹⁹⁴

In addition, local pH gradients not only limit the HER but also effectively control the $\text{CH}_4/\text{C}_2\text{H}_4$ ratio at Cu electrodes. This is because CH_4 production prevails at low pH values and decreases with increasing pH, while C_2H_4 production is more or less constant, having a pH-independent activity.¹⁹⁵ In particular, Yang *et al.* observed that CO_2RR products (CH_4 , C_2H_4 , and C_2H_6) could be adjusted according to the pore size and depth on Cu electrodes (Fig. 14b),¹⁹⁶ They intentionally utilized the local pH effect, which was reproducibly confirmed by other studies, showing similar trends with Cu electrodes.^{197–199} The design of the morphology and dimensions at the catalyst-electrolyte interface strongly affects the mass diffusion of reactants and, thus, the catalytic selectivity. These are the widely used strategies in CO_2RR s compared to other electrocatalytic reactions, such as water electrolysis.

5.2.2. Mass diffusion control through CO_2 supply: a three-phase interface achieved by modifying the catalyst structure. To improve the CO_2RR activity, increasing the gaseous CO_2 supply to the catalyst surface can be a more active and direct approach than suppressing the HER. Therefore, new electrode designs deviating from traditional electrolyzer configurations have been proposed to overcome the CO_2 diffusion limitations. Yano *et al.* introduced a gas-liquid-solid three-phase interface by supplying CO_2 gas directly from the acidic electrolyte to the electrode and reported a high CO_2RR performance with Ag and Cu electrodes.^{163,200} This report, however, lacked a detailed description of the electrode configuration that allowed a stable three-phase interface. Subsequently, it was reported that a 15 nm ultrathin metal layer catalyst was produced from an Sn

catalyst for formate formation and coated with graphene to control the catalyst surface.²⁰¹ In this study, the graphene-coated ultrathin Sn catalyst showed a current density of 21.1 mA cm^{-2} and FE of 89% at -1.8 V (vs. saturated calomel electrode; SCE), while the bulk Sn showed 1.6 mA cm^{-2} and 44.5%, respectively. The improvement highlights the facilitated electrolyte diffusion between the graphene layers introduced at the Sn catalyst interface. The graphene layer improves the CO_2 adsorption and reduces the mass diffusion limitations of the common catalysts (Fig. 15a).²⁰¹ This study demonstrated that the changes in the catalyst structures can also control the reaction interface to increase the CO_2 supply, which results in relatively high CO_2 reduction rates.

Recently, Li *et al.* developed a new type of electrode configuration by depositing Au on a polyethylene polymer nanotemplate, after which they rolled and sealed the electrode to directly inject CO_2 gas to perform a CO_2RR .²⁰² In this electrode structure, gaseous CO_2 was successfully supplied directly to the catalyst, and a three-phase interface, catalyst (solid)-electrolyte (liquid)- CO_2 (gas) was maintained (Fig. 15b).²⁰² This eliminated the CO_2 solubility limit in the electrolyte and resulted in a very high CO current density of 25.5 mA cm^{-2} , while the flat Au electrode exhibited a CO partial current density of $\sim 2 \text{ mA cm}^{-2}$ at -0.6 V (vs. RHE).

Warkerley *et al.* fabricated a hydrophobic Cu dendrite catalyst surface by coating the surface with a 2.5 nm thick layer of 1-octadecanethiol to exploit the “plastron effect.”²⁰³ The catalyst was able to separate CO_2 from the electrolyte layer and trap it on its surface, much like a spider traps gas under hydrophobic hairs in water (Fig. 15c).²⁰³ By introducing a three-phase interface in this completely separated catalyst-electrolyte-gas system, the CO_2RR only participates in the CO_2 gas diffusion near the three-phase boundary. In this system, the contact area between the catalyst and the electrolyte is significantly reduced, which results in a low HER FE below 10%, but induces very high C_{2+} product selectivity of 56% (C_2H_4) and 17% ($\text{C}_2\text{H}_5\text{OH}$).

5.2.3. Summary of mass diffusion control. In these electrochemical CO_2RR studies, mass diffusion experiments focus on

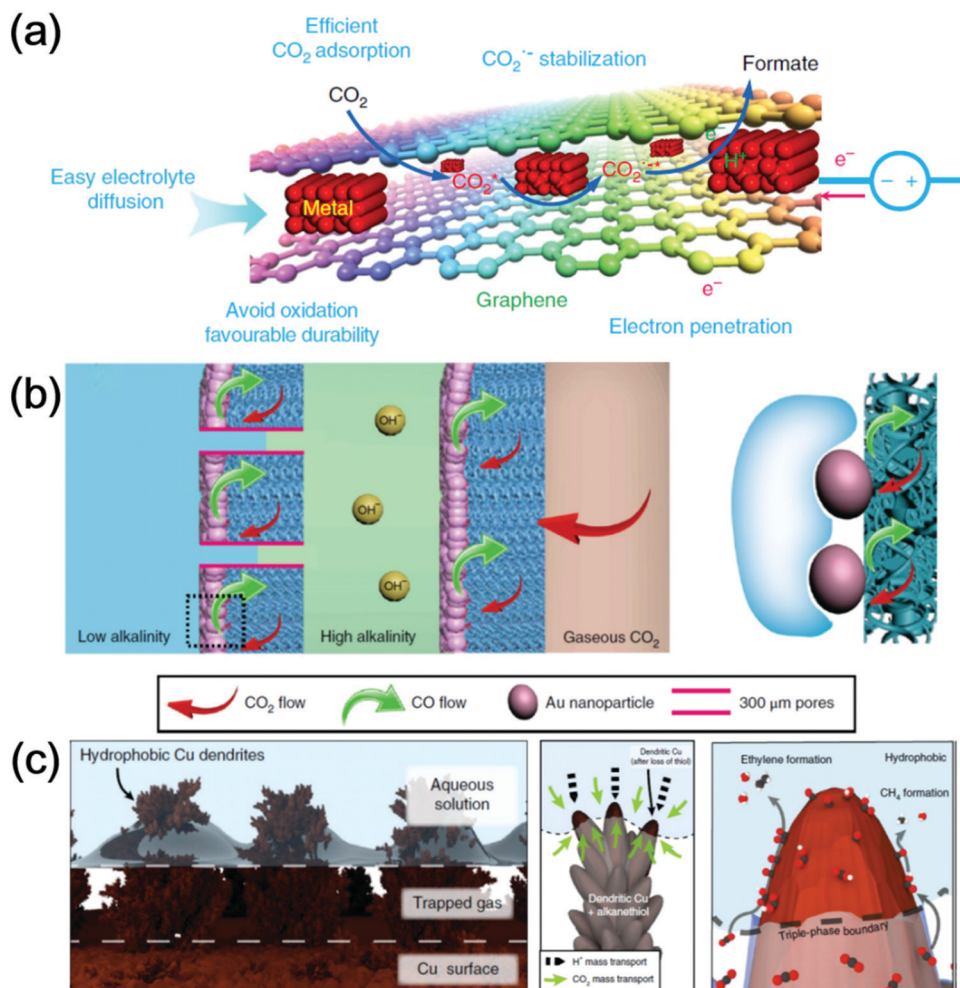


Fig. 15 (a) Schematic illustration depicts the advantages of ultrathin metal layer confined in graphene for electrochemical CO₂ reduction. Reprinted with permission from ref. 201. Copyright 2016, Nature Publishing Group. (b) Illustration of gas flow and three phase interfaces in CO₂RR of Au nanoparticle electrode on polyethylene template. Reprinted with permission from ref. 202. Copyright 2018, Nature Publishing Group. (c) Illustration of the electrochemical CO₂RR at the interface with the three-phase interface structure formed by the plastron effect in the hydrophobic Cu dendrites electrode. Reprinted with permission from ref. 203. Copyright 2019, Nature Publishing Group.

the interfacial environment of aqueous reaction electrodes (*i.e.* CO₂ aqueous solubility, local pH, *etc.*). Either the proton supply or CO₂ supply is controlled to overcome the limitation of the mass transfer from the bulk to the catalyst–electrolyte interface. The interfacial environment of the CO₂ aqueous reactions was successfully controlled to suppress the hydrogen-producing reactions and to increase the selectivity of the CO₂RR. To increase the CO₂RR current density, different methodologies have been applied to modify the conventional electrode configurations and introduce a solid–liquid–gas three-phase system, even with aqueous electrolytes. Attempts have been made to create three-phase interfaces by injecting CO₂ gas directly into the electrode surface. The CO₂ mass transfer limitations were removed by changing the electrode configuration or by introducing a hydrophobic material on the electrode surface to increase the CO₂ capture capacity. Recently, CO₂ electrolyzers using GDEs were developed to utilize the three-phase interface and to demonstrate

the scaling potential of this process, which will be discussed in the next section.

5.3. Design of CO₂ electrolyzers using GDEs

The research on improving the CO₂ mass transfer by changing the catalyst structure has been successful to some extent; however, exceeding the CO₂RR current density of $\sim 30 \text{ mA cm}^{-2}$ is still difficult even with a high overpotential in the aqueous H-cell.²⁰⁴ There is a technical mismatch with the oxidation current density in CO₂ electrolyzers because the current density for the OER increases significantly as the overpotential increases, while the CO₂RR current density rather decreases due to the extensive HER activity. To achieve a high CO₂ reduction current density at a practical level, it is desirable to feed CO₂ gas directly to the catalyst layer of the GDE instead of dissolving CO₂ in the aqueous electrolyte. These CO₂ gas-phase electrolyzers can achieve current densities of hundreds of mA cm^{-2} for CO₂ conversion.^{61,205–208} In this section, (i) the

characteristics of CO₂ electrolyzers using GDEs and (ii) the importance of interface control in this system are discussed.

5.3.1. CO₂ electrolyzer type and properties. Both membrane reactors and microfluidic (flow cell) reactors have shown significant progress as CO₂ electrolyzers (Fig. 16).²⁰⁹ Membrane reactors have previously been used in water electrolysis or fuel cell systems, and liquid electrolytes or gaseous reactants flow at each electrode separated by a membrane.^{209,210} CO₂ can reach the cathode in a dissolved state in liquid electrolytes or directly in the gaseous phase, although the latter is more beneficial for facile CO₂ transport, which increases the current density.^{205,211} The basic configuration with the GDL centres the membrane and stacks the GDL on each side of the cathode and anode, resulting in a membrane electrode assembly (MEA, Fig. 16a).²⁰⁹ The GDL acts both as a catalyst support and gas transport channel at the backside, where humidified CO₂ gas is directly delivered to the catalyst layer. This design allows the direct feeding of gaseous CO₂, and the porous GDL structure increases the effective contact between the CO₂ molecule and the catalyst layer, leading to an improvement in the current density. In MEA, the CO₂RR occurs at the boundary where the CO₂ gas, catalyst surface, and membrane (electrolyte) adjoin; moreover, the balanced flux of the CO₂ molecule, proton source, and electron/ion transfers are required at the interface.^{212–215} Therefore, in addition to designing an active electrocatalyst, the MEA configuration, operations (*e.g.* CO₂ gas feeding), types of membrane, flow channel design, *etc.* are

other critical factors to consider in managing the catalyst–electrolyte interface.

Another successful CO₂ electrolyzer using the GDE is the microfluidic cell system, demonstrated by Kenis's group for the CO₂RR. This cell typically consists of a thin channel of less than 1 mm, where the cathode and anode are separated and the electrolyte flows between them; some reactors can even function without a membrane (Fig. 16b).^{209,216,217} Unlike the case of the MEA system, the supplied CO₂ gas diffuses through the porous GDL to naturally form a three-phase interface of electrolyte–catalyst–gas even when water vapour is not supplied. The advantage is that the CO₂RR product and the oxidation product are separated and diffused into the respective regions without the separation membrane in some cases. This reactor can achieve high current densities because the CO₂RR can proceed at the junction of the catalyst and liquid catholyte, which is less sensitive to the ion transfer rate, particularly through the membrane.^{59,218} For the liquid chemical producing catalysts such as Cu, a membrane has to be introduced between the electrolyte channels to separate the liquid products and to avoid re-oxidation of the liquid product at the anode side.²¹⁹ The performance of the flow cells has been significantly improved over the past few years. Although the relationship between the activity of the catalyst and the H-cell and flow cell cases is yet to be clearly understood, high-performing catalysts are shared. In both cases, the catalyst surface contacts the liquid aqueous electrolyte; however, the direction of CO₂ supply in the flow cell

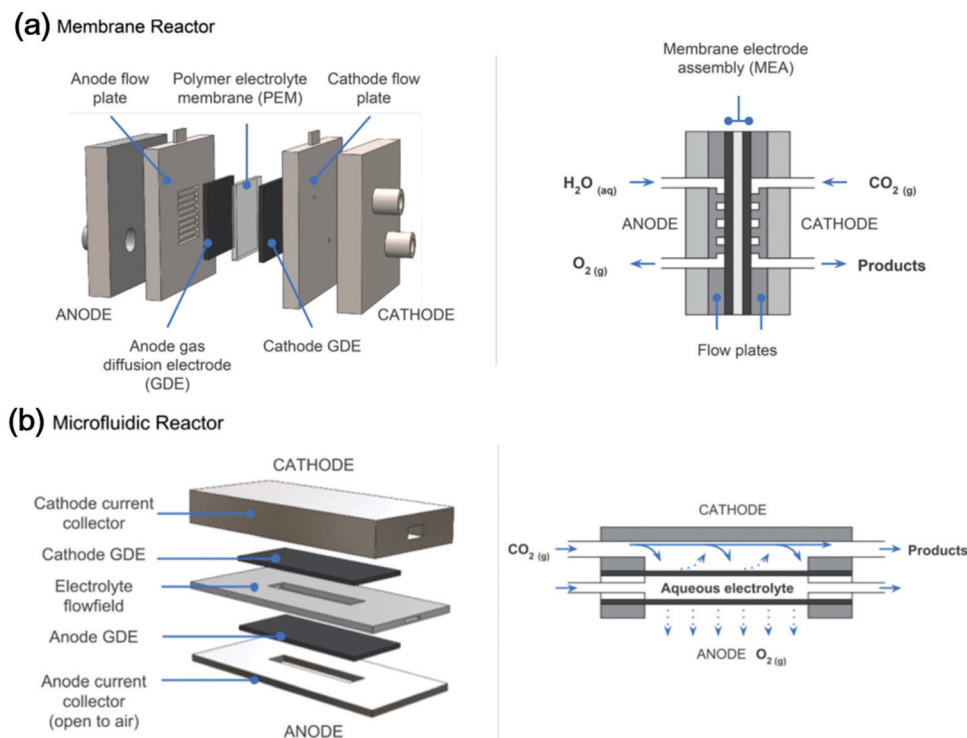


Fig. 16 Structure diagram of common flow cells for electrochemical CO₂RR. (a) Membrane-based reactor that include a membrane electrode assembly (MEA) and use gas diffusion electrodes (GDEs) for the anode and cathode. (b) Microfluidic reactor with channel through which electrolyte flows between the anode and cathode consisting of GDE. Reprinted with permission from ref. 209. Copyright 2018, American Chemical Society.

differs in that it is separated from the liquid flow. In addition, the alkaline electrolyte can be applied in the flow cell, while the buffered bicarbonate neutral electrolyte is popular in the H-cell due to the low proportion of CO₂ gas in the alkaline electrolyte according to the equilibrium. Therefore, it is expected that some of the strategies developed in the H-cell would be valid in the flow cell, although new approaches suitable for the flow cell must be developed considering the different environments. The CO₂RR performance in the flow cell indicated the dependence of the deposition method on the catalyst electrode layer, the added layer on the catalyst materials, composition of the GDL, and pH control of the electrolyte, all implying that the control of the catalyst–electrolyte interface is important.^{220,221}

5.3.2. Importance of interface control in CO₂ electrolyzers using GDE. High current densities and CO₂RR product selectivity have been reported for microfluidic cell systems; however, the configuration of this system is more challenging compared to the MEA system because of the difficulty in managing the flow in small channels and multiple stacked cells. Both the microfluidic cells and MEA systems are actively developed for CO₂RR applications, with the individual components and operational conditions optimized to achieve high efficiency; however, more studies are required to understand the control of the interface in these systems.^{59,61,218} As studied in the H-cell, increasing the porosity of the catalyst has a significant positive effect on the activity as it can affect the intrinsic activity as well as the extrinsic activity related to the mass transport.²²² Similarly to the case in conventional H-cells, the catalyst–electrolyte interface of the GDE-based electrolyzers determines the CO₂RR performance; however, additional care must be taken to control the hydrophilicity under the consideration of proton/ion transfer *versus* flooding the catalyst surface. The active sites of the catalyst surface should not be completely covered with liquid water to ensure the direct supply of gaseous CO₂ molecules to the catalyst.

For the microfluidic cell systems, the catalytic performance and durability are sensitive to the hydrophobicity of the GDL due to the continuous contact between the electrolyte and the GDL. A decrease in the hydrophobicity of the electrode surface can cause flooding of the electrolyte, which breaks down the three-phase interface formed in the catalyst layer. When this three-phase interface collapses, the gaseous CO₂ mass transport in the catalyst layer is interrupted, and the current density for CO₂RR decreases significantly, while HER current density increases. Overall, the cell showed reduced performance, as well as poor stability when the electrolyte contact area was increased.^{223–227}

Dinh *et al.* applied PTFE membranes as GDLs in CO₂RR electrolyzers, where a Cu catalyst layer was deposited instead of carbon-based ones to utilize the hydrophobic property of PTFE.⁵⁹ The introduction of additional carbon materials on the electrode extended the production stability from a few hours to 150 h and successfully secured the stability of the three-phase interface (Fig. 17a).⁵⁹ This study emphasizes that the durability of the three-phase interface significantly affects the durability of the CO₂RR in gas-type reactors. Modifying the

contact between the catalyst and the electrolyte led to a breakthrough in high-performing CO₂ electrolyzers. Kenis's group reported that the performance of the microfluidic cell also depends on electrolyte conditions, such as the pH, the anionic type of the salt, and the ionic liquid, because the three-phase boundary formed in the catalyst layer is in contact with the electrolyte.^{220,221}

In the MEA system, CO₂ gas can be supplied to the catalyst surface without contacting the aqueous electrolyte, which makes the flooding issue more manageable and reduces the performance degradation attacked by the aqueous electrolyte. Even in the MEA system, the mass transfer of CO₂ gas to the catalyst surface is still an important factor in determining the CO₂RR activity, according to the results that the CO₂RR current density and the product distribution highly depend on the CO₂ flow rate, the partial pressure of CO₂, and the catalyst thickness of the Cu catalyst layer.²²⁸ Although a low CO₂ flow rate can have a high single-pass CO₂ conversion rate, a flow rate higher than 10 sccm is desirable to obtain optimal C₂₊ products at a current density of 100–150 mA cm^{−2}. The optimum partial pressure of CO₂ is observed for the selective C₂H₄ production over CO production, and a 250 nm thick Cu layer showed higher C₂H₄ selectivity than a 50 nm thick layer, implying that sharp thickness control enhanced the C–C coupling activity. More studies are required to understand the flow of the chemical species, including CO₂, intermediates, liquid products, and ions, through each interface, including the porous catalyst layer and particularly across the membrane. The systems feeding humidified CO₂ were recently reported to show enhanced performance with a stability duration of over 100 h; however, the CO₂RR performance is yet to be improved compared to the case with the microfluidic cells.^{147,228,229} Depending on the specifics of the system, the CO₂RR can differ significantly. Studying the interface of each reaction system in detail and controlling the reaction variables is of importance for future applications.

As mentioned earlier, chemical mediators have been applied to modulate the catalyst–electrolyte interface and improve the CO₂RR performance in H-cell systems. Similar attempts to control the interface by introducing chemical mediators in the flow cell systems have been reported. A Co phthalocyanine (CoPc) catalyst was applied to the flow cell system, introducing functional groups, such as phenol or trimethyl-ammonium, which can induce local pH buffer effects, resulting in a high current density (>150 mA cm^{−2}), turnover frequency (TOF), and FE (Fig. 17b and c).^{230,231} In addition, when *N*-aryl-dihydropyridine-based oligomers were added to the Cu catalyst, C₂₊ chemicals were preferably produced. The oligomer could reduce the activation barrier for the formation of C₂ intermediates by modifying the dimerization step of 2CO_{bridge} into the CO_{bridge} + CO_{atop} step (Fig. 17d).¹⁴⁷ The reports suggest that the introduction of various functional groups on the catalyst surface enables the control of the CO₂RR performance by changing the environment of the catalyst interface, even in CO₂ electrolyzers using the GDE.

5.3.3. Summary of CO₂ electrolyzers using GDEs. Although a high current density (>1 A cm^{−2}) is reported for microfluidic

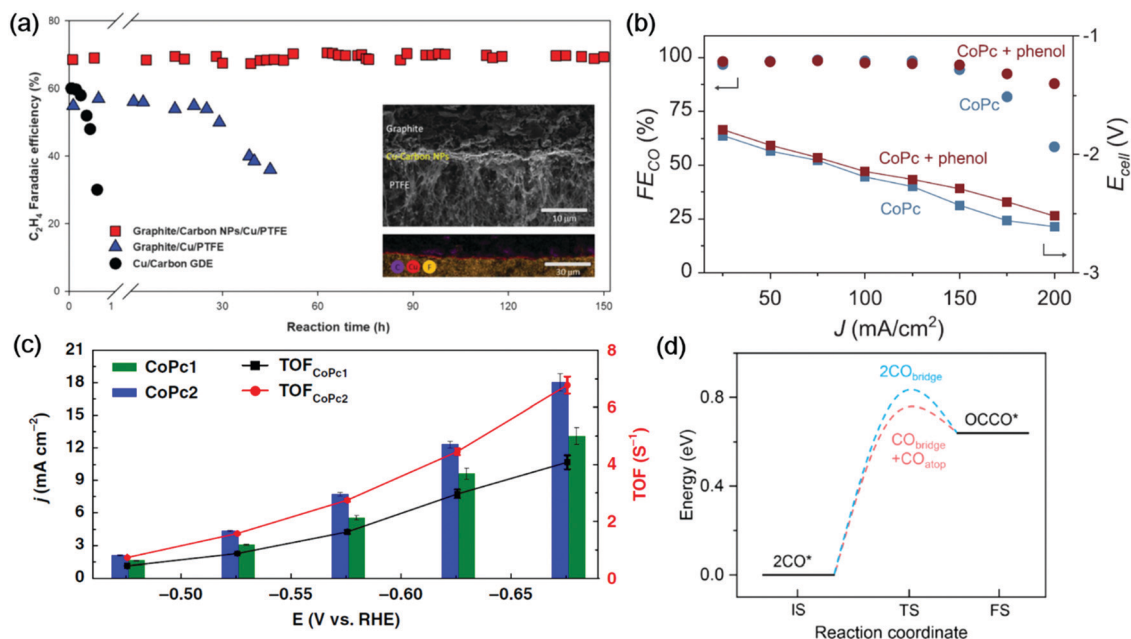


Fig. 17 (a) Results of stability test in microfluidic reactor according to GDL composition at 7 M KOH condition. Graphite/carbon NPs/Cu/PTFE electrode stably produced ethylene for 150 hours, while carbon NPs were missing from the electrode configuration, showing 30 hours of stability. In the case of carbon GDE, the performance decreased very quickly. Reprinted with permission from ref. 59. Copyright 2018, American Association for the Advancement of Science. (b) The application of phenol functional group to Co phthalocyanine (CoPc) catalyst maintained CO FE in the high current density range ($>150 \text{ mA cm}^{-2}$) and lowered the flow cell operate potential. Reprinted with permission from ref. 230. Copyright 2019, American Association for the Advancement of Science. (c) CoPc2 catalysts, incorporating trimethyl-ammonium functional groups and three *tert*-butyl functional groups, increased current density and turnover frequency. Reprinted with permission from ref. 231. Copyright 2019, Nature Publishing Group. (d) Introduction of *N*-aryl-dihydropyridine-based oligomers into Cu catalysts could improve performance by lowering the activation energy of the C2 intermediate formation step. Reprinted with permission from ref. 147. Copyright 2019, Nature Publishing Group.

systems, the long-term durability of the GDL is an important factor which can be challenging under a highly alkaline electrolyte condition. The flooding or degradation of the GDL sharply decreases the activity, and overwhelming HER performance is achieved. Therefore, it is important to carefully control the interface between the catalyst layer and the GDL electrolyte. The hydrophobicity of the GDL is an important factor in maintaining the three-phase interface of the electrode, and the CO_2RR performance varies depending on whether the hydrophobicity is maintained or not. In contrast, the MEA system is less affected by the GDL degradation issues, although the ion transfer characteristics of the membrane have a great influence on the performance, which can be modulated by the interface control with chemical species. Aside from the system approach, attempts have recently been made to improve the properties between the catalyst and the reaction interface by introducing various functional groups. Further developments can be expected in the future following these directions.

6. Conclusions and perspectives

Modulating the catalyst–electrolyte interface has emerged as a promising strategy for increasing the efficiency of the electrochemical CO_2RR . This strategy can provide additional direction to overcome the limitations of the catalyst design, such as

scaling relations and Sabatier volcano-like relations, that have been observed in simple metal catalyst surfaces. Indeed, the interface tuning significantly improved the FE and partial current density at relatively low overpotentials, which, thus far, has been accomplished by the design of catalyst structures and compositions (Fig. 9 and 10). The modification of the catalyst–electrolyte interfaces includes adding foreign molecules (or polymers), changing the electrolyte compositions and concentrations, and designing novel reactors and electrode structures, as well as the combination of these methods. These modification strategies of the catalyst–electrolyte interfaces significantly affect both the intrinsic and extrinsic catalytic activities.

The surface organic modulators adsorbed on the catalyst surface impact the interfacial chemistry by interacting with catalysts, reactants, and intermediates, which primarily affect the intrinsic activity of the active sites. Meanwhile, the organic additives on the catalyst surface also influence the extrinsic catalytic activities by modifying the mass transport of the protons or CO_2 molecules through the catalyst layer *via* chemical interactions. In the conventional and fundamental H-cell systems, as well as the CO_2 gas-fed electrolyzers, it was established that the surface treatment can effectively improve the current density and FE activity toward more practical levels. The review of recent studies provides insights into the possible functions of the surface additives, divided into four categories

with respect to the interfacial chemistry (Fig. 4). Although the effectiveness of the molecular tuning strategy has been well demonstrated, the promoted electrocatalysis is yet to be fully understood. Therefore, more fundamental studies are required to exploit the effect of surface modulators further. However, there are great challenges associated with identifying the role of the surface modulators, because activity improvement originates from a complicated interplay of multiple factors (*e.g.* cysteamine can both change the electronic structure of the catalyst and provide a hydrogen bonding network), which are generally difficult to decouple. The elaborate design of molecules and advanced (*operando*) surface-sensitive spectroscopies will address the respective roles. Fortunately, there are many organic molecules available from databases. Using computational studies, researchers could conduct screening tests to identify the best organic modulator or elucidate the core factors by experimentally changing the atoms and functional groups of the organic modulators, which provides new research directions for optimizing the catalytic performance.

Interestingly, nature already utilizes this concept in many enzymes to effectively catalyse biological reactions. These enzymes are composed of an active metal centre (or cluster) and surrounding peptides. The organic components around the active centres support enzymatic reactions by binding reactants and facilitating the transfer of protons and electrons. For example, cytochrome *c* oxidase, a biological oxygen reduction catalyst in the respiratory chain, comprises a haem-Cu binuclear centre and an adjacent tyrosine moiety.²³³ The binuclear centre cooperatively adsorbs O₂ molecules while tyrosine plays a key role as a proton and electron transfer agent.²³⁴ The natural oxygen-evolving complex in photosystem II is composed of a Mn₄CaO₅ cluster and its surrounding amino acids.²³⁵ The amino acids facilitate the delivery of protons and electrons and the formation of hydrogen bonding networks with H₂O molecules.²³⁶ We envision that lessons from nature could aid the design of interfaces between heterogeneous catalysts and surface organic modulators by providing a more fundamental understanding of the synergistic processes.

The electrolyte compositions and concentrations are also highly crucial for determining the CO₂RR activity by tuning the electric double layer. The electric double layer structure affects not only the reaction environments (pH and CO₂ concentration) but also the adsorption strength and charge transfer kinetics. Despite extensive efforts to reveal the cation effect using computational methodologies, the function of anions (particularly for specifically adsorbed anions) remains elusive. In addition, the distribution of charged species is purported to be sensitive to the electronic structure of catalysts and applied potentials. A material-dependent study will provide profound insights into the electrolyte and double layer effects. However, due to the difficulty in identifying the double layer structure, experimental and computational breakthroughs are strongly pursued to characterize and describe the structure of the electric double layer, which will, in turn, afford further guidelines.

Since many dynamic equilibria, ion movements, and consumptions of H⁺ and CO₂ are involved at the interfaces during

the CO₂RR, the *in situ* mass transport of reactants (CO₂, H⁺, H₂O) and ions is critical for improving the activity and selectivity. The regulation of the mass transport through meso-macroscopic structuring has particularly shown effectiveness in improving the selectivity and overpotential by generating local pH and boosting the local CO₂ mass transport. However, these strategies led to only a marginal increase in the current density of a few tens of mA cm⁻², which does not meet the requirement for practical applications. The fundamental limitation of the CO₂ supply through the slow CO₂ diffusion and low CO₂ concentration in the aqueous media has been successfully circumvented in the novel reactor design, where a distinct catalyst (solid)–electrolyte (liquid)–CO₂ (gas) three-phase interface is created compared to that of a conventional H-cell configuration. The application of a flow cell and MEA CO₂RR reactor could considerably increase the current density to commercially relevant levels (>1 A cm⁻²) by interface modifications.⁴¹

The control of the three-phase interface is the most important criterion for achieving the maximum activity in flow cell/MEA systems. This is because the proton (or H₂O in alkaline solution) and H₂O (as a steam in MEA) transports become significant as gaseous CO₂ is provided at a sufficient rate. Therefore, the performance of those devices is critically determined by extrinsic factors, such as the electrode thickness, hydrophobicity, and binder contents. In particular, controlling the hydrophobicity of the electrode in the CO₂ gas-fed electrolyzer is crucial which affects the gas–electrolyte–catalyst boundaries. More importantly, it is closely relevant to the flooding of the device, which causes the destruction of the three-phase boundary and a sudden decrease in performance. The balanced CO₂ flow and water control are other key factors involved in the three-phase boundary generation and destruction.

Since high current densities had been achieved with the CO₂ gas-fed electrolyzers, intensive technoeconomic analyses were conducted. The technoeconomic feasibility of CO₂RR is still a controversial issue because different results can be derived, depending on the assumptions, such as the electricity costs, electrocatalytic performance, and target chemicals. In general, low-level economic analyses considering electrolyzers and simplified models show more promising results than detailed process models, which include separation and recycling processes. Importantly, the technoeconomic analyses suggest the necessity for substantial improvement of the electrocatalytic performance (FE, current density, and overpotential) and the relative importance of each performance criterion: the current density has the greatest impact on improving the economic feasibility at the early stage. The FE and overpotential, which determine the separation and electricity costs, respectively, are the secondary major factors, which become more influential as the current density increases, suggesting the future research direction for practical application of CO₂RR technologies.

A catalyst–electrolyte interface development map in Fig. 18 displays the CO₂RR current density as a function of the overpotential.^{41,57,59,61,96,147,202,205,221,222,230,232} Regardless of the electrochemical reactor system, the modification of the catalyst–electrode interface has successfully increased the

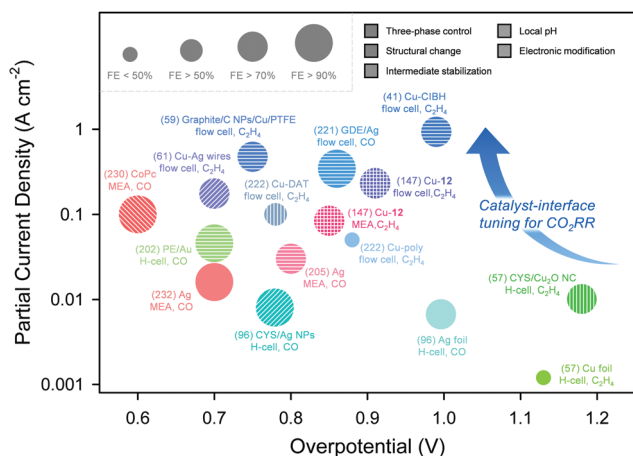


Fig. 18 The development map of the catalyst–electrolyte interface showing for the electrochemical CO₂RR. The numbers in the parentheses indicate the reference numbers. The size of the circle corresponds to FE for the product denoted. CIBH: catalyst–ionomer bulk heterojunction. DAT: 3,5-diamino-1,2,4-triazole. PE: polyethylene. CYS: cysteamine. NC: nanocube.

CO₂RR current density at relatively low overpotentials. The most remarkable improvement is achieved when the CO₂RR current density is increased by ~100-fold, attributed to the adjustment of the three-phase boundary for any type of electrocatalyst. The technoeconomic analyses highlight that the FE has a high impact on the economic feasibility at a high current density. This correlation suggests the next goal in CO₂RR research: a huge improvement in the target product selectivity in CO₂ electrolyzers to reduce the separation costs. For these purposes, the catalyst–electrolyte interface requires systematic studies, which have been rarely conducted due to the complicated involvement of various interfacial factors. The surface modulators in the H-cells and the recent study on the effect of molecular additives in CO₂ electrolyzer suggest important perspectives and guidelines for enhancing the CO₂RR performance.¹⁴⁷

As shown in Fig. 18, despite the significant differences in the method of CO₂ supply and the electrode structure in the H-cells and CO₂ gas-fed electrolyzers, the high FEs of the reported catalysts demonstrated in H-cells have been well translated to the GDE reactors by interface tuning. It is highly probable that the interfacial chemistry knowledge gained from the H-cell studies, to some extent, can be also applied in the CO₂ gas-fed electrolyzers. In addition, the recent activity and selectivity enhancements in high-current reactors, achieved by a molecular functionalization strategy,¹⁴⁷ also suggest the presence of common interfacial chemistries in the H-cell and CO₂ gas-fed electrolyzers. Therefore, although the research on high-current reactors has practical importance, the importance of the H-cell study should not be undervalued as it can still provide a well-established foundation for the interface research. Furthermore, the difference in the interfacial processes between H-cells and GDE reactors needs to be clarified.

Lastly, in the CO₂ gas-fed electrolyzer research, Cu-based electrodes received significant research attention compared to

CO₂-to-CO conversion catalysts because many valuable chemicals can be produced on Cu surfaces, although the product selectivity and overpotentials require further improvement. Several studies have demonstrated that CO₂-to-CO conversion catalysts, such as Ag or single-atom catalysts can produce CO with a high FE over 95% selectivity. However, the faradaic efficiency for single C₂₊ chemicals (*i.e.* C₂H₄ or C₂H₅OH) is below 80%, and high overpotentials are required for C–C coupling reactions on Cu-based electrodes. The generation of multiple products originates from the involvement of various reaction intermediates and mechanisms, such as C–C coupling, tautomerization, and isomerization. These surface processes can be tuned by the interfacial species to produce minor but economically feasible chemicals, such as acetaldehyde, acetone, acetic acid, and ethylene glycol, which have been identified as valuable targets over C₂H₄ or C₂H₅OH according to the technoeconomic analysis. This also provides the possibility of increasing the C₃₊ multicarbon selectivity by the interface modification, for instance, toward *n*-propanol, the most profitable product expected. Therefore, the study of the interface in commercially relevant reactors is encouraged to the increase FE or decrease overpotential for practical CO₂RR applications.

Conflicts of interest

There are no conflicts to declare.

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