

Advances in electrocatalytic carbon dioxide reduction reactors, electrolytes and catalysts

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Abstract. With the advance of The Times, people's demand for fossil energy has greatly increased, and it is the main energy for people to develop economy and science and technology. However, the large-scale exploitation of fossil energy has led to environmental pollution and energy crisis, and the concentration of CO₂ in the air continues to rise, and the greenhouse effect is becoming more and more serious. Therefore, the conversion of CO₂ into the high value-added fuels and chemicals we need will be a major measure to solve environmental problems. So, converting CO₂ into fuels or high value-added chemicals using CO₂ electrocatalytic reduction (CO₂RR) technology is an effective way to alleviate the current problems of energy and environment. In this paper, we summarize the research progress in reaction systems, electrolyte effects, and catalyst development in CO₂RR experiments, focusing on the electrocatalytic aspects of CO₂. Finally, we provide an outlook on the CO₂ electrocatalysis industry.

Keywords: Electrocatalytic, CO₂ reduction reaction, catalyst, electrolyte, reactor.

1. Introduction

Since the industrial revolution, the demand for fossil energy has increased dramatically and it is the main source of energy for economic and technological development. Fossil energy sources mainly include oil, gas and natural gas. However, the extensive extraction and use of fossil fuels has led to a steady increase in the concentration of CO₂ in the air. CO₂ can be penetrated by visible light from the sun and strongly absorbs infrared rays from terrestrial radiation, which increases the temperature of the earth's surface and produces the greenhouse effect. This is a serious threat to the environment on which mankind depends for its survival.

The Chinese government formally proposed a dual carbon target at the UN General Assembly on 22 September 2020, committing that by 2030, China's CO₂ emissions will peak, and by 2060, China will achieve carbon neutrality. How to improve the utilisation of CO₂ will be a major problem for China and the world [1]. CO₂ is an extremely stable linear molecule, and the bonding energy of the carbon-oxygen double bond is 750kJ/mol kilojoules per mole [2]. To break the carbon-oxygen double bond, a strong external driving force is required. There are several means of converting CO₂ into chemicals with added value: thermochemical conversion, electrocatalysis, photocatalysis and bioconversion. Among these conversion methods, the electrocatalytic CO₂ reduction method has a number of outstanding advantages: 1. the reaction process can be regulated; 2. the reaction conditions are mild; 3. there is a wide variety of reaction products such as C₁ (CO, HCOOH, CH₄, and CH₃OH), C₂ (C₂H₄, C₂H₅OH, and CH₃COOH); 4. the electricity required for the reaction can be obtained from a number of renewable energy sources, such as solar energy, wind energy, etc. During the reaction process, the power used in the reaction can be generated from a variety of sources. The power required for the reaction can come from some renewable energy sources such as solar wind energy, and only water and CO₂ gas are used in the reaction process, which does not produce pollutants and meets the requirements of green chemistry. However, CO₂ electrocatalysis also has some problems that need to be solved: low solubility of CO₂ in water, which leads to limited mass transfer, difficulty in controlling the single selectivity of the reaction products, and the existence of the hydrogen reduction reaction (HER) side reaction competition in the reaction process.

2. Mechanisms of CO₂ Electrocatalytic Reduction

The electrochemical CO₂ reduction reaction involves multiple proton and electron transfer steps ($2e^-$, $4e^-$, $6e^-$, $8e^-$ and $12e^-$), and the products generated are not the same for different electron transfer steps, and even if the number of electrons transferred is the same, the conditions of the reaction, the acidity or alkalinity of the electrolyte, the type of catalyst, and the surface bonding strengths and interactions affect the generation of different substances from CO₂. Among the reaction products of $2e^-$ electron transfer are formic acid and carbon monoxide, $4e^-$ electron transfer reaction products are formaldehyde and ethanol, etc., $8e^-$ electron transfer products are methane and ethane, etc., while $12e^-$ electron transfer products are ethylene. In general, the more electrons in the transfer path, the more difficult the CO₂ reduction reaction. The whole reaction process can be divided into three steps:

(1) CO₂ molecules are adsorbed and activated by active sites on the catalyst surface to form *CO intermediates; and

(2) *CO gets a proton and an electron and turns into the active intermediate *COOH;

(3) The active intermediate *COOH continues to get an electron and a proton, and is further reduced to the target product. The final target product structure is rearranged and desorbed from the catalyst surface, completing the CO₂RR process.

Currently, it is widely believed that there are four CO₂ activation reaction mechanisms, as shown in Figure 1 [3].

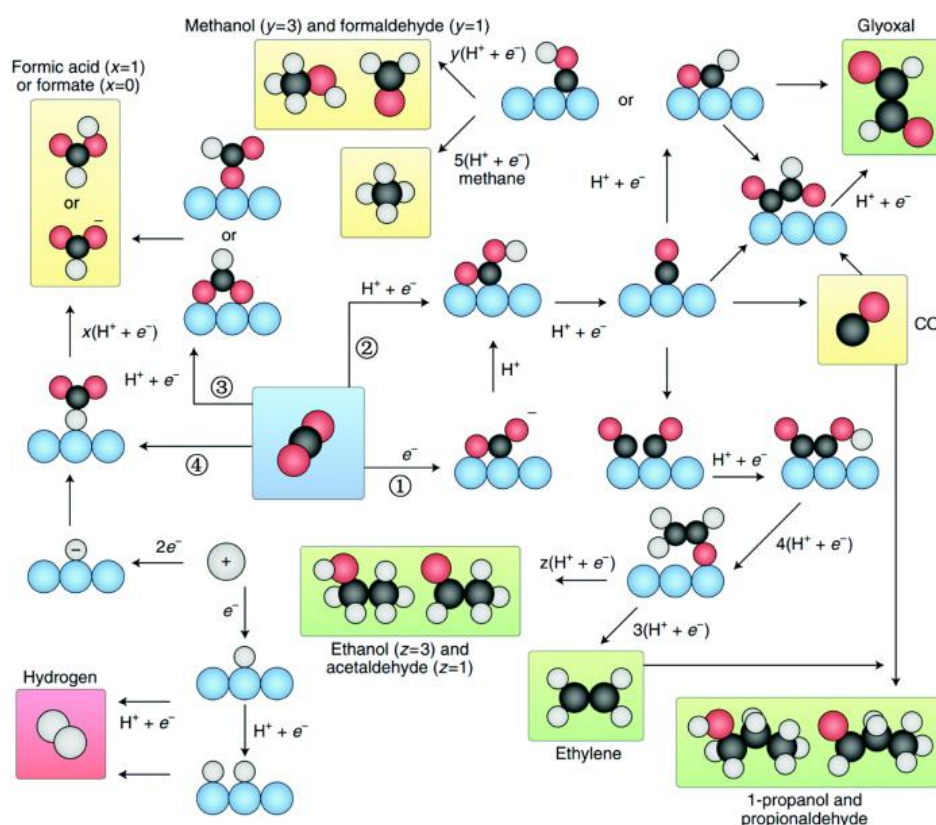


Figure 1. Four routes for the reduction of CO₂ to different products [3]

The reaction path for the generation of CO and formic acid by $2e^-$ electron transfer occurs as shown in Fig. 1. Firstly, CO₂ needs to be activated to form CO₂* radicals, and CO₂ radicals, as the key intermediates of the reaction, have different configurations on the surface of the catalyst that determine different reaction paths, and different reaction paths result in different reduction products, which ultimately produce CO or formic acid. If the protonation of CO₂ radical on the catalyst surface tends to produce *COOH radical, the reduction path is the carboxylation pathway, and *COOH will combine with a proton and an electron to produce *CO, and finally *CO will be desorbed from the catalyst surface to form CO; if the CO₂ radical on the catalyst surface tends to combine with a proton and an electron, the reduction pathway is the acylation pathway, and will produce *OCHO⁻, which will finally

desorb from the catalyst surface to form formic acid. In addition to formic acid and CO, the C₁ products include methanol, and we can get the reaction path $\text{CO}_2 \rightarrow \text{COOH}^* \rightarrow \text{CO}^* \rightarrow \text{COH}^* \rightarrow \text{CHOH}^* \rightarrow \text{CH}_2\text{OH}^* \rightarrow \text{CH}_3\text{OH}$ for methanol production from the diagram [3].

In addition to C₁ products, CO₂ molecules can also be reduced to C₂ products through dimerization between two *CO or C-C coupling of intermediates such as *CO and *CH, and subsequent hydrogenation and oxygenation processes, with ethylene and ethanol being the more common C₂ products. The catalytic mechanism for the reduction of CO₂ to ethylene is controversial and requires further study. At present, it is generally believed that CO₂ is first reduced to CO*, and then CO* is adsorbed by Cu, and hydrogenated at higher negative potentials to generate adsorbed CH*, which is then coupled to ethylene. SANTATIWONGCHAI team simulated the process of electrocatalytic reduction of CO₂ to generate the product C₂H₄ on the Cu(100) crystal surface, and the results showed that CO₂ is reduced to CO, and then C-C coupling occurs, but coupling is not possible. C-C coupling, but the coupling mode is different, there are *CO*CO, *CO*CHO or *CO*COH coupling and other forms, after which the key intermediate *CCH will be formed, and finally desorbed from the electrode surface to form ethylene [4].

Schouten et al. postulated a mechanism for the reduction of CO₂ to ethylene on the Cu (111) crystalline surface: after forming CO in its adsorbed state, CO₂ is first hydrogenated, then coupled and deoxygenated to form C₂H₄ [5]. On the other hand, on the Cu (100) crystalline surface, CO₂ first forms the key intermediate CO, then forms a CO dimer, which is bonded to an alkylene glycol or a complex metallocyclic compound, and finally deoxygenated to selectively form ethylene compounds, and finally the removal of oxygen selectively generates C₂H₄ [6]. For CO₂RR, most of the studies suggest that C₁ intermediates such as *COOH, *CO, *CHO, and *COH are also involved in the reaction pathway of the C₂ product, which is shown in Fig. 1, where the coupling of CO/*CO intermediates to *C₂O₂ is regarded as a rate-controlling step. In addition, the reaction of the intermediate HOCCH* via the dihydroxylation pathway (Route 1) or the hydrogenation pathway (Route 2) determines the selectivity to ethylene and ethanol. The product selectivity is determined by the different structures and oxidation states of the catalysts [7-8].

Yang et al. used P-doped graphene aerogel as a catalyst for the electroreduction of CO₂ to ethanol. The results of in situ Raman spectroscopy showed that adsorbed *CO intermediates were essential for the formation of ethanol. In addition, DFT calculations illustrated that the zigzag edge configuration of graphene with P-active sites could enhance the binding energy of *CO and increase the coverage of *CO on the catalyst surface, thus promoting the formation of *COCHO by C-C coupling, which was conducive to the generation of EtOH [9].

3. Progress in CO₂RR Reactor Research

The electrolytic cell required for CO₂ electrocatalysis consists of four main parts: anode and cathode electrodes, electrolyte for transporting protons, and ion exchange membrane for separating the cathode anode. At present, the reaction vessel can be mainly classified into H-type electrolytic cell, microfluidic flow electrolytic cell, and membrane electrode electrolytic cell. Their reaction device diagrams are shown in Fig. 2a, 2b, 2c.

3.1. H-type electrolytic cell reactor

A complete H-type electrolytic cell for electrocatalytic CO₂ reduction reaction was first established by Lee et al. in 2001 [10]. The H-type electrolytic cell apparatus is divided into an anode chamber and a cathode chamber separated by an ion exchange membrane. In the anode chamber, the anode electrode generally consists of graphite and metallic platinum, which is mainly used to transfer protons through the electrolysis of water in the CO₂RR; the cathode chamber consists of a working electrode and a reference electrode, in which the working electrode's main function is to convert the CO₂ gas into the target product, while the reference electrode is used to correct the error in the measurement system. The H-type electrolysis cell can be used to test the activity and performance of the catalyst in a very

intuitive way, and can be quickly evaluated and screened. The H-cell is very intuitive to test the activity and performance of catalysts and can be used for rapid evaluation and screening of catalysts, and it is easy to assemble with low manufacturing cost. Therefore, it is still widely used for performance testing of electrocatalytic CO₂ reduction [11-12]. However, the H-type electrolytic cell itself has great limitations in practical industrial production. Firstly, the solubility of CO₂ is very small (less than 0.034 mol/L), which results in only a small amount of CO₂ reacting with the working electrode to form products; secondly, the high resistance of the device results in the mass transfer process being limited, which leads to the very low reaction current density (less than 100 mA cm⁻²) [13-17]. Thirdly, the hydroxide ions in the alkaline electrolyte reacted easily with the dissolved CO₂, losing the input CO₂ to some extent.

3.2. Flow electrolysis cell

In order to solve the problems of the H-type electrolysis cell mentioned above, in 2010, KENIS et al. proposed a novel device, the microfluidic reactor [18]. The CO₂ diffusion path in the flow cell is only ~50 nm compared to the conventional H-type cell (~50 μm) (Fig. 2d).

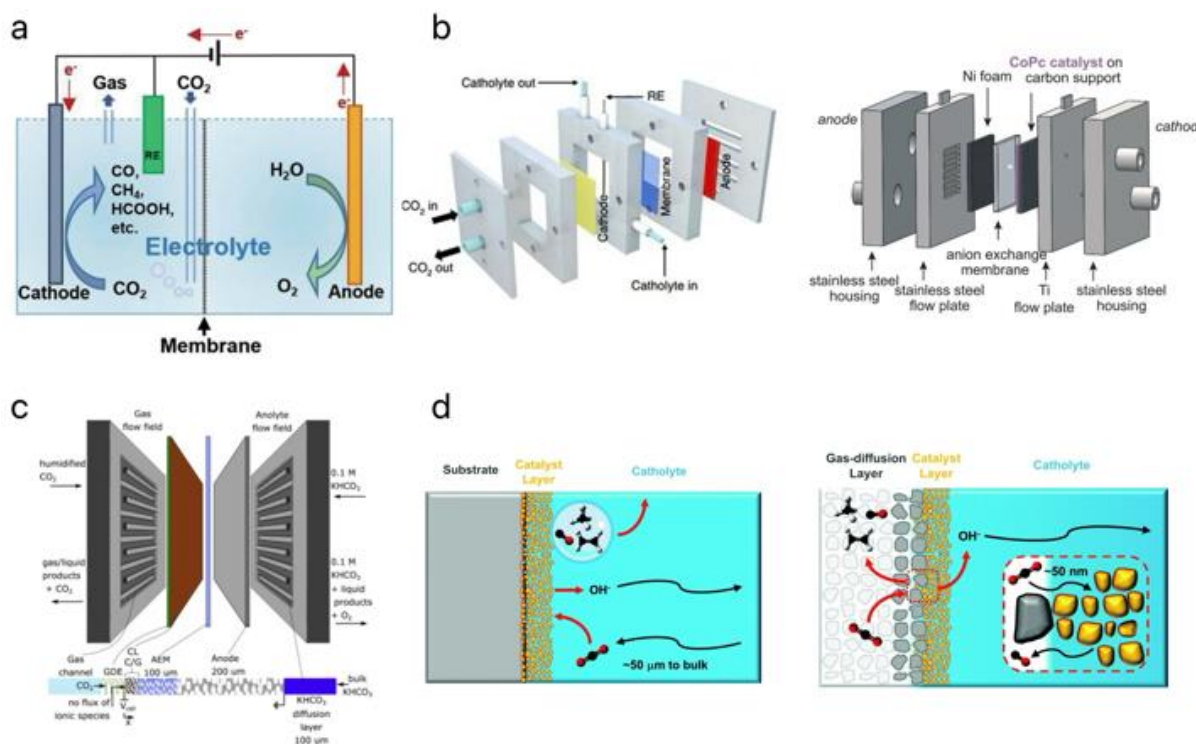


Figure 2. (a) Schematic diagram of the H-type electrolytic cell setup [19] (b) Schematic diagram of a typical flow-through electrolytic cell setup [20-21] (c) Schematic diagram of the membrane electrode electrolytic cell setup (d) Comparison of CO₂ gas transport paths in the H-type electrolytic cell (left) and the flow-through cell (right) [22]

The main reaction device of the flow cell consists of five main components: support plate, flow field plate, cathode gas diffusion electrode (GDE), ion exchange membrane and electrolyte [23]. The support plate, flow field plate and gas diffusion electrode are innovative components of the flow cell compared to the H-type cell.

The support plate is the outermost part of the flow cell system, so it must be flat and sealed and corrosion-resistant to prevent interference from the outside environment and leakage of the internal feedstock products, creating an independent environment for the reaction inside the flow cell. The ends of the flow field plate are connected to gas conduits to balance the CO₂ gas and to facilitate the flow of electrolytes. Since different orifice shapes, numbers and other parameters in the flow field plate affect the pressure balance of the system, there are many designs of flow field plate orifices. This paper summarises several of the more common types of flow field plates. The pin-type flow field plate has

a relatively simple shape, and the structure shown in Fig. 4a is one of the most common flow field structures with multiple channels and low pressure drop, where the pins are usually arranged in a grid-like distribution over the whole plate. It is this structure that leads to the presence of uneven flow and stagnation regions in many areas of its channels, making the reactant transport efficiency reduced.

The structure of the parallel flow field plate is shown in Fig. 3b. This type of flow field plate can effectively reduce the pressure drop [23], however, its flow channels are easily blocked by electrolyte and carbonate crystals, and the CO₂ diffusion will be hindered, and may even bypass the catalyst active region [24]. The serpentine flow field is the most common flow field plate used in current applications. Its structure is shown in Fig. 3c, which has only one flow channel throughout the plate from gas inlet to outlet [25]. This structure is designed to discharge the electrolyte quickly without blocking the channel, but the excessively long flow channel leads to a large internal voltage drop and uneven current density distribution [26].

Considering the structural advantages of serpentine and parallel flow field plates, the researchers proposed the spiral flow field plate, which combines the advantages of serpentine and parallel flow field plates [27]. Through 3D modelling of three typical cooling flow field plates, it was found that the spiral flow field plate had the best heat transfer performance and the serpentine flow field plate had the largest pressure drop, and the results are shown in Fig. 3 (e). The staggered flow field plate, as shown in Fig. 3d, can greatly increase the battery energy density, and a very obvious feature of this flow field plate is that the liquid can completely pass through the diffusion layer. Compared with the serpentine flow field, the staggered flow field has better water removal capability, lower pressure drops, excellent transport capability, and more uniform current distribution [28]. However, due to the high resistance of the diffusion layer and the high pressure drop of the liquid, it is easy to destroy the catalyst attached to the electrodes, leading to the instability of the electrolysis system.

In addition, there are many new types of flow field plates, such as waveform flow field plates [29], tubular flow field plates [30] and so on. Different flow field length, shape, material and other parameters will affect the pressure balance, electric field distribution and gradient fluctuation of the system, which in turn affects the performance of the whole flow cell [31].

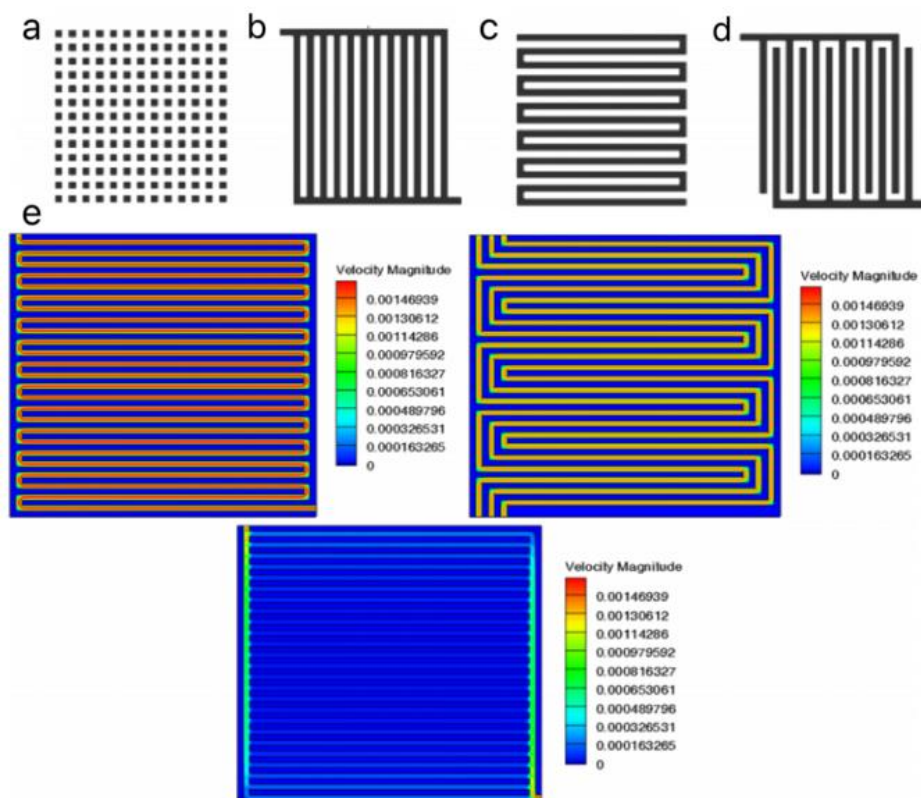


Figure 3. (a) Grid flow field (b) Parallel flow field (c) Spiral flow field (d) Fractal flow field (e) Flow velocity in the three flow fields [32].

The gas diffusion electrode (GDE) is the core component in the flow electrolytic cell, which is a special porous hydrophobic membrane electrode that can transport a large number of gases such as CO₂ to reach the inside of the electrode and connect with the overall solution (electrolyte) outside the electrode to form a stable three-phase (solid, liquid and gas) interface, thus improving the performance of CO₂RR. The GDE mainly consists of a gas diffusion layer (GDL), a collector (CC) and a catalyst layer (CL) [33-34]. The GDL generally consists of a porous material with electrical conductivity, which provides an attachment layer for the catalyst, while hydrophobic porous channels within the layer transport the gas and exclude water as a reaction product. An ideal gas diffusion layer should meet the three conditions of good drainage, good permeability and good conductivity; the collector can effectively maintain a good electron transport rate and reduce the internal resistance loss of the system; the catalyst layer is the catalytic layer where the electrochemical reaction occurs in the electrode. The gas transported from the gas diffusion layer in this layer with the catalyst and electrolyte in the layer together to form an electrochemical reaction activation point. The reaction gas is then reduced. Therefore, it is the key junction for the formation of "gas-liquid-solid", which is often called the "three-phase reaction zone". The rational design of these three components is conducive to the smooth and efficient operation of the entire flow cell plant.

Compared with the H-shaped electrolysis cell, this structure allows the CO₂ gas to diffuse directly to the catalyst through the gas diffusion electrodes, and the shorter gas diffusion path increases the reaction current by one to two orders of magnitude, thus accelerating the rate of CO₂ mass transfer. In addition, the catalytic product can be generated directly between the electrolyte and the gas diffusion electrode, which is conducive to stabilizing the local reaction environment. However, there is a pressure difference before the CO₂ gas and liquid flow channels, and the gas diffusion electrode is easily penetrated by the electrolyte, resulting in clogging of the electrode holes, which seriously affects the stability and high efficiency of the system. To address this type of problem, in 2018, the Sargent team sputtered Cu catalyst on a gas-diffusion layer of polytetrafluoroethylene (PTFE) and sprayed carbon black nanoparticles to allow it to react as a gas-diffusion electrode in the flow cell [35]. The method uniformly dispersed the catalyst. The results showed that the Faraday efficiency (FE) of the C₂ product generated at the electrode surface exceeded 70% and the electrolysis unit could be operated for more than 150 h. In 2021, sargent's team significantly extended the application of hybrid liquid-phase flow batteries by adding electrolytes to the cathode and anode chambers. sargent et al. utilised hybrid liquid-phase flow batteries to efficiently modulate the cathode / anode chamber environment (1 M H₃PO₄ and 3 M KCl as the cathode electrolyte and 0.5 M H₂SO₄ as the anode electrolyte), achieving over 50% C₂ selectivity at 1.2 a cm × 2 [36].

In addition to this, an improved microfluidic flow electrolytic cell was proposed by Park et al. in 2018, who used a gas-phase flow cell (membrane electrode assembly (MEA)) to achieve highly efficient electrocatalytic CO₂RR. Compared to the microfluidic flow electrolytic cell, the membrane electrode electrolytic cell (MEA) does not require a cathodic electrolyte. The anode and cathode catalysts are directly loaded on both sides of the membrane or gas diffusion layer [37]. This prevents the gas diffusion electrodes from being immersed in water and clogging the pores with carbonate crystals. And this configuration reduces the internal resistance of the device and increases the current density. However, the membrane electrode electrolysis cell is not suitable for CO₂RR that generates liquid products, because the generated liquid products will be retained at the cathode and may penetrate the gas diffusion electrode and flood the gas holes for transporting CO₂. In 2019, Sargent, when confronted with this problem with membrane electrode assemblies, he used a pump to continuously separate the products from the cathode electrolysis chamber, which effectively improved the stability and lifetime of the membrane electrode assemblies [38].

4. Effect of electrolyte on CO₂RR

Electrolytes play a very important role in CO₂RR by forming a closed loop in the electrocatalytic system, conducting ions to the cathode and anode, and influencing the stability of the intermediate

products of the CO₂RR conversion process. Most CO₂RR reactions are carried out in aqueous electrolytes, and the most common electrolyte at present is the bicarbonate solution of alkali metals. At this stage, the research on electrolyte is mainly in three aspects: pH, cation effect and anion effect.

4.1. The effect of electrolyte pH on CO₂RR

Since CO₂ dissolves in water to form carbonate and bicarbonate, the electrolyte for CO₂RR is generally neutral or acidic. If the pH is too low, there will be a high concentration of hydrogen protons in the reaction, which will promote the occurrence of HER to a certain extent, and HER and CO₂RR react at the same time in the cathode, which is in competition with CO₂RR, so the promotion of HER will inhibit CO₂RR. If the pH is too high, the dissolved CO₂ may react with OH⁻ to form carbonate and bicarbonate crystals, which will increase the electrical resistance of electrolytic system, and there will be a large amount of salt. resistance of the electrolytic system, and there will be a large accumulation of salt, which tends to clog the gas diffusion electrodes in flow cell installations. Electrolyte pH does not only determine the concentration of hydrogen ions, it also affects the concentration of CO₂. Since there is a chemical equilibrium between CO₂, carbonate, bicarbonate and water, pH also affects the distribution of these substances in the electrolytic system. The concentration of CO₂, CO₃²⁻, HCO₃⁻, H⁺, and OH⁻ in K⁺ as a KHCO₃/K₂CO₃ electrolyte as a function of pH is shown in Figure 4a [39]. The results in the figure show that the CO₂ concentration is more stable when the pH of the electrolyte is less than 8, and the CO₂ concentration starts to decrease when the pH is >8. When the pH is >9, the CO₂ concentration decreases sharply, and it turns to carbonate and bicarbonate, and the bicarbonate becomes the main substance in the electrolyte. And there is also related literature that the most suitable pH for CO₂RR electrolyte is 9-10 [40].

4.2. Cation effect

Cations in the electrolyte also affect CO₂RR, especially alkali metal ions. As the radius of metal ions tends to decrease (Cs⁺ (170 pm) > Rb⁺ (149 pm) > K⁺ (138 pm) > Na⁺ (102 pm) > Li⁺ (69 pm)), the intensity and rate of CO₂RR reaction decreases. This is because the larger the radius of the metal ion, its water binding energy will decrease. And the metal ions will combine with water molecules, which are oriented on the catalyst surface under the mutual force of the electrodes, forming the Helmholtz outer potential at the electrode-electrolyte interface. Thus, the weak hydration capacity of metal ions will affect the outer Helmholtz potential and give it a greater specific adsorption capacity [41]. Resasco et al. found that hydrated alkali metal cations near the electrode can generate a dipole field in the outer Helmholtz plane (Fig. 4b), which stabilises intermediates (e.g., *CO₂, *CO), and that such a field reduces the energy of adsorption of *CO₂, thereby promoting the formation of two-electron products and C- and C-containing products. thereby promoting the generation of two-electron products and C-C coupling products [42]. Although the activity of HER is also affected by metal ions, the trend is different from that of CO₂ RR, which is Li⁺ > Na⁺ > Cs⁺ > K⁺ in 0.1 mol·L⁻¹ MHCO₃ (M = Li⁺, Na⁺, K⁺, Cs⁺) aqueous solution. Koper's team has further investigated the effect of a large number of univalent and multivalent metal cations (Li⁺, Cs⁺, Be²⁺, Mg²⁺, Ca²⁺, Ba²⁺, Al³⁺, Nd³⁺, and Ce³⁺) on the CO₂RR reaction and the HER. They chose an electrolyte with a pH of 3 and found that acidic cations with moderate hydration radii (e.g., Nd³⁺, Ce³⁺) promoted CO formation at low overpotentials, whereas the CO fraction of current density at increased in the order Ca²⁺ < Li⁺ < Ba²⁺ < Cs⁺ at high potentials (Fig. 4c), which was mainly due to the promotion of water reduction by acidic cations [43]. Recently, Choi et al. proposed a CO₂RR mechanism based on cation-coupled electron transfer to determine the role of cations in regulating the activity and selectivity of CO, CH₄, and C₂H₄ formation during the CO₂RR process, and they showed again that the cation effect is caused by the cation-associated surface charge densities of the electrodes, through kinetic studies [44].

4.3. Anion effect

Since CO₂RR occurs at the cathode and the cathode adsorbs cations, the anionic effect can be easily overlooked. Hori et al. first investigated anions in electrolytes and demonstrated that CO₂RR is more

likely to produce ethylene and ethanol in KCl, KCl, and KPC electrolytes [45], while dipotassium phosphate (dipotassium phosphate) is more favorable for the production of HER and methane, compared to the use of HCl as the electrolyte, and H_2PO_4^- has a buffering capacity and can neutralize with the OH^- produced to inhibit the pH rise of the electrolyte, thus favoring HER. H_2PO_4^- has a buffering capacity, which can neutralise the OH^- produced and inhibit the increase in electrolyte pH, thus favoring HER. Recent studies have shown that HCO_3^- produces a certain amount of OH^- compared to H_2PO_4^- [46]. Moreover, HCO_3^- is also considered to be a more suitable anion for CO_2RR , which neither promotes the competitive reaction HER nor converts CO_2 to carbonate or bicarbonate, avoiding the reduction of CO_2 concentration and CO_2RR activity. Some researchers believe that HCO_3^- can increase the concentration of dissolved CO_2 near the electrode surface, thus accelerating the CO_2RR rate. In addition to this, halides also affect the CO_2RR process. Kunya et al. observed that halide ions reconfigure the nanostructures on the CuO surface and effectively reduce the overpotential of CO_2RR in the order of $\text{Cl}^- < \text{Br}^- < \text{I}^-$ (Fig. 4d) without affecting the selectivity [47]. The halide ions adsorbed on the copper oxide surface can provide charge to the CO_2 molecule, contributing to the formation and stabilization of the $^*\text{COOH}$ intermediate. Halide ions can be selectively adsorbed on the surface of the Cu catalyst, leading to enhanced selectivity of the C_2^+ product. According to DFT calculations, it was shown that in ECO_2RR , halide ions have an effect on the reaction energies of Cu (111), Cu (100) and Cu (211), for example, by weakening the CO^* , CHO^* and COH^* intermediates to adjust the binding strength of ERCO_2 . Furthermore, DFT has shown that halide elements can accelerate the hydrogenation of CO^* to CHO^* , thereby contributing to enhanced C_2^+ selectivity through CHO^* coupling. Therefore, understanding the effect of halide ions on copper surface activity and selectivity is crucial for the future design of ERCO_2 electrocatalysts [48].

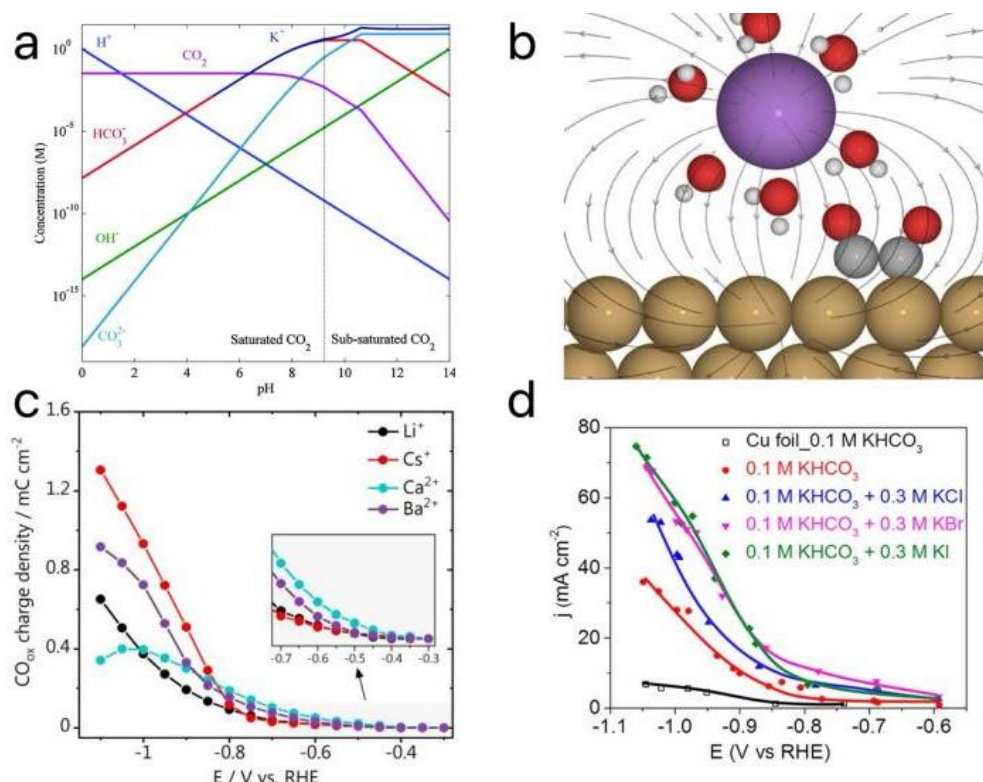


Figure 4. (a) Concentration of dissolved carbon-containing substances in a potassium bicarbonate/carbonate electrolyte as a function of pH at a temperature of 25°C and a total pressure of 1 atm. (b) Hydrated alkali metal cations in the vicinity of the electrode produce a dipole field in the outer Helmholtz plane (c) CO partial current density increases at high potentials in the order $\text{Ca}^{2+} < \text{Li}^+ < \text{Ba}^{2+} < \text{Cs}^+$ (d) Halide ions in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$ Effective reduction of overpotential of CO_2RR

5. Progress in CO₂RR catalyst research

In order to improve the reaction rate, selectivity to specific products and total conversion of CO₂RR, researchers need to study various metal catalysts extensively.

In the 20th century, Hori et al. conducted electrocatalytic experiments on CO₂ at different metal electrodes, and he classified metal electrodes into four categories based on the reduction products: 1. Metal materials whose main product of reduction is HCOO⁻ (Pb, Hg, In, Sn, Cd, Ti) 2. Materials whose main product of reduction is CO (Cu, AuAg, Zn, Pd, Ga, Ni, Pt) 3. H₂ material: Ni, Fe, Pd, Pt, Ti, etc.; 4. The only material whose main product is hydrocarbon is Cu. Nowadays, as many scientists are further researching in the field of CO₂RR, they also classify the catalysts according to the reduction products. The synthesis of C₁ products from CO₂ is an efficient way to use CO₂ and a way to achieve sustainable development. Researchers have studied several related catalysts, for example, one researcher extracted Pb from waste lead-acid batteries as a catalyst and developed a new proton exchange membrane system for electrolysis of CO₂RR, which can reduce CO₂ to formic acid with a formic acid production efficiency of more than 93% [49]; in addition to Pb, Cu-based catalysts can be used to reduce CO₂ to formic acid. In addition to Pb, Cu-based catalysts are also capable of producing C₁ products. Han et al. prepared a novel layered coordination polymer (CuPEDOT) as a catalyst for the selective reduction of CO₂ to CH₄ with a Faraday efficiency of 62.7% in a flow cell at a current density of 354 mA/cm²[50]. Different catalysts have different selectivities for the products. For C₂ products, such as ethylene and ethanol, most of the main catalysts are copper-based. In this paper, we will briefly analyse the relationship between the structure and performance of copper-based catalysts.

5.1. Crystal surface modulation

In 2003, Hori et al. carried out CO₂RR experiments with a current of 5 mA/cm² using single-crystal copper as catalyst, and found that the selectivity of the products was related to the crystallographic facets [51]: CO₂ predominantly produces C₂H₄ on the Cu (100) facets, whereas CH₄ is formed predominantly on the Cu (110) and Cu (111) facets. Norskov simulated the *CO dimerization process of CO₂ on the Cu (111) and Cu (100) crystal faces by the *CO dimerization process [52]. They found that the energy barrier for *CO dimerization on Cu (100) was only 0.33 eV compared to 0.68 eV on Cu (111), which implies that *CO is more readily produced on Cu (111), and for the next hydrogenation step, the energy barrier on the surface of Cu (100) is lower than that on Cu (111). These results suggest that the different crystalline surfaces of Cu affect the reaction paths and hence the product selectivity. Similarly, Koper used theoretical calculations to explain the reaction mechanism for the formation of some C₂ products (C₂H₄, EtOH and MeCHO) on Cu (100) [53]. They similarly found that the *CO dimerization process preferred to occur on Cu(100). Sargent et al. found that the adsorption capacity of the reaction intermediates varied between the different crystal faces of the Cu group during CO₂RR [54]. They calculated the adsorption strengths of CO₂*, COOH*, CO*, and H*, and by their adsorption energies found that the CO₂RR intermediates tended to be adsorbed on Cu(100), while the adsorption of H* (HER-related intermediates) was strongest on Cu(211), and the results are shown in Fig. 5a. Therefore, the adsorption of CO₂RR intermediates can be promoted by modulating the exposure of different crystalline facets. In addition, the simultaneous presence of multiple crystalline facets can form high refractive index crystalline surfaces and exhibit excellent CO₂ electroreduction activity [55-57]. Choi et al. chemically synthesized Cu nanowires enriched with Cu (100) crystalline facets, and found that Cu (511) assembled from 3 (100) and (111) exhibited high selectivity towards C₂H₄, and the proportion of the present Cu (100) crystalline facets was maintained at the same level for 200 h. The results are shown in Fig. 5a. facets were maintained at 45.40% ± 5.62%, showing good stability[58]. Hori et al. prepared a variety of Cu-based high-index facets by introducing step atoms to low-index facets at a constant current density of 5 mA/cm². They used electrodes of Cu (S)-[n(110) × (111)], Cu(S)-[n(111) × (110)], Cu (S)-[n(111)×(111)], Cu(S)-[n(100)×(110)] and Cu(S)-[n(110)×(100)], and the results are shown in Fig. 5b, where the values of C₂H₄/CH₄ on the (711) and (911) crystallites are around 10, whereas the selectivity of the (100) low-exponential crystallite is only 1.3%. It can be seen from the results that the high index crystal faces

such as (711), (810), and (911) are more favorable for the production of C_2 products compared to the low index crystal faces [59]. Although the high-index crystalline surface has higher catalytic activity relative to the low-index crystalline surface, it also has higher surface energy, which makes it difficult to stabilise the existence of nanocrystals during the growth process, and it is easily converted into low-index crystalline surface, so how to stabilise the existence of the high-index crystalline surface is also a need for further research in the future.

In summary, the CO_2RR product selectivity as well as the catalyst activity can be improved by performing crystal surface modulation of metal catalysts, i.e., the target product can be selectively produced by regulating the exposed crystal surface.

5.2. Size effect

In electrochemical CO_2RR , the size of the catalyst greatly affects the activity as well as the selectivity of the catalyst. Generally, when the size of a metal catalyst decreases, its specific surface area becomes larger, and it is able to chemisorb more CO_2 , CO , H atoms, etc. during the CO_2RR process, thus increasing the reaction rate. Chorkendorf et al. investigated the size effect of platinum nanoparticles, and they found in their experiments that the number of low-coordinated atoms on the surface of the metal base increased with the decreasing of the platinum nanosize, which is due to the fact that the platinum size is increasing at the same time as the size of the platinum nanoparticles is decreased [60-61]. The reason is that the specific surface area of platinum is increasing while decreasing the size of platinum, favouring adsorption of more feedstock. To further investigate the relationship between size and performance of metal catalysts, Resk's team prepared copper-based catalysts with an average size of 2-15 nm [62]. They also found that when the size of the nanoparticles was less than 5 nm, CO_2 was preferred to generate CO rather than hydrocarbons such as C_2H_4 , CH_4 , and the results were shown in Fig. 5(c,d). In Fig. 5, the reaction product was mainly CO in 1-5 nm, and when the size was gradually larger than 10 nm, the product was mainly hydrocarbons such as C_2H_4 , CH_4 and the Faraday efficiency became larger with the size.

Therefore, when choosing the appropriate size of catalyst, we should not pursue the small size of catalyst particles, and we should precisely control the size of catalyst according to the desired products, otherwise it will often cause counterproductive effects.

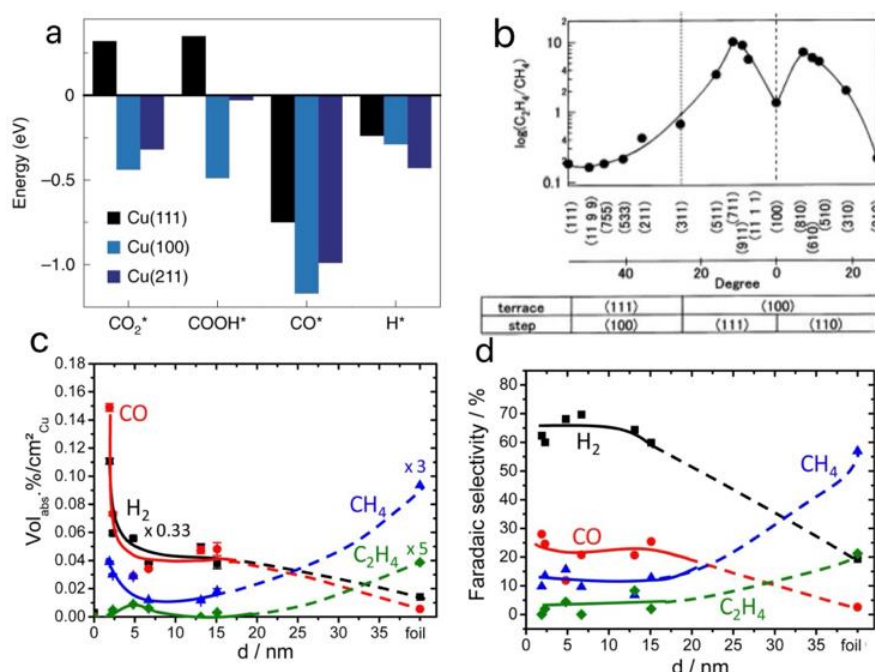


Figure 5. (a) Adsorption energies of four intermediates on three crystalline surfaces of Cu (b) C_2H_4/CH_4 values of different index crystalline surfaces of Cu-based (c) Different Cu particle sizes versus composition of the gas reaction products (d) Faraday efficiencies of the gas compositions over Cu nanocatalysts

5.3. Defect structure

At this stage, many studies have proved that the defects can effectively condition the physical and chemical properties of the catalyst surface, and the common defects are vacancies and heteroatom doping. Li et al. introduced Cu vacancies into Cu sulphide (Fig. 6a), and the experimental results found that the Faraday efficiency of CO was greatly improved and the concentration of Cu vacancies could regulate the CO selectivity. According to the DFT calculations, the reason can be obtained: Cu vacancies change the electronic structure of S, greatly increasing the Gibbs free energy of H^* , and Cu vacancies weaken the adsorption between polymetallic interactions, the intermediate *COOH is easier to form [63]. In this aspect of doping, some researchers Designed F-doped Cu catalysts (e.g., Fig. 6b, c) with current densities exceeding 400 mA/cm^2 in a flow cell, and $FE_{C_2^+}$ could reach 70.4% at 0.97 V in a 1 mol/L KOH solution (e.g., Fig. 6d) [64]. This catalyst (F-Cu) can generate CO at a lower potential and has a strong adsorption capacity for it, and CO can be stabilised on its surface rather than escaping as gaseous CO, which is more conducive to C-C coupling. Meanwhile, the F element optimises the hydrophobicity of the catalyst to a certain extent and slightly inhibits the occurrence of HER side reactions. Recently, some researchers successfully doped copper into Au nanoclusters and synthesized a new catalyst ($[Au_{15}Cu_4(DPPM)_6C_{14}(C\equiv CR)_1]_2^+$) of AuCu alloy nanoclusters (e.g., Fig. 6e), which has a Faraday efficiency of up to 90% in electrocatalytic CO_2 to CO in a membrane electrode assembly cell and also has a good stability (Fig. 6fgh) [65]. Han et al. doped P into a copper catalyst by using in situ electrodeposition and achieved a Faraday efficiency of 80.2% in an H-type electrolytic cell, and the stability of this catalyst reached 12 h [66]. DFT studies have shown that P has a strong ability to transport protons, which reduces the free energy of the hydrogenation process and thus enhances the adsorption of intermediates of the catalyst for the CO_2RR reaction. In conclusion, crystal defects such as vacancies and doped heteroatoms can modulate the electronic structure of metal catalysts, thus altering the adsorption capacity of the catalysts for a variety of substances as well as the reaction energy barriers for CO_2RR .

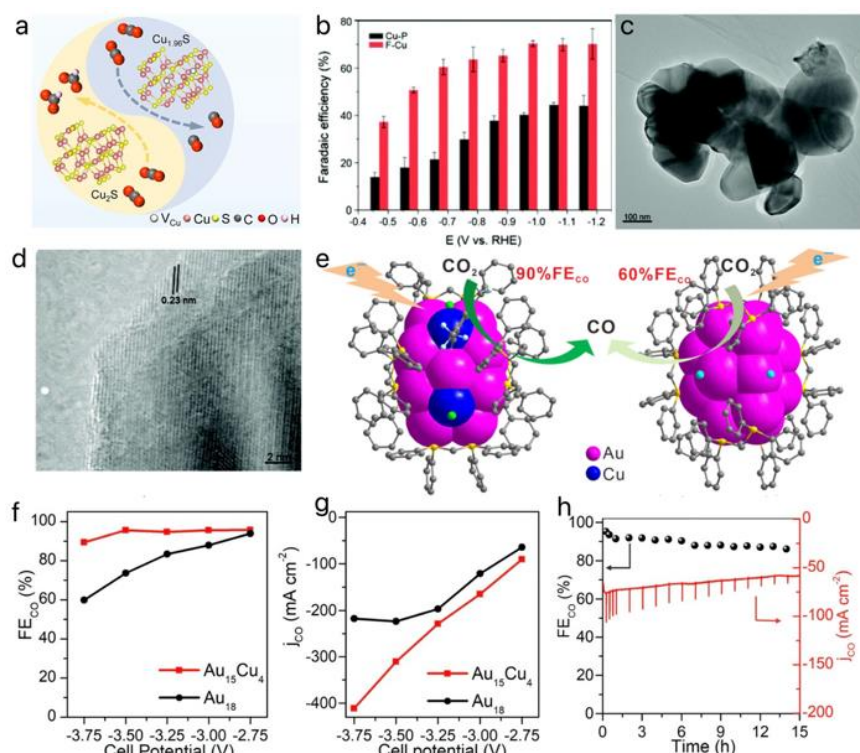


Figure 6. (a) Schematic representation of Cu vacancies introduced in copper sulphide (b) Faraday efficiencies of C_2^+ products of Cu-P and F-Cu catalysts at various potentials. (c)-(d) TEM and HRTEM images of F-Cu [64] (e) Schematic of AuCu alloy nanoclusters. (f-g) FECO and j_{CO} of $Au_{15}Cu_4/C$ and Au_{18}/C at various potentials in MEA electrolytic cell. (h) Stability test of $Au_{15}Cu_4/C$ at -2.80 V potential in MEA electrolytic cell [65].

In addition to vacancies, doping and these defects, grain boundary (GB) is also one of the defects in crystals. A grain boundary can improve the physical and chemical properties of catalytic materials because it has a relatively unique crystal and spatial structure, so it can promote the adsorption of the reaction intermediate $^*\text{CO}$ by Cu-based catalysts and improve the selectivity of C_2^+ products in CO_2RR [67-68]. Gong et al. A grain boundary-rich copper catalyst (GB-Cu) (Fig. 7a) was prepared by additive-controlled electrodeposition (with PVP as additive), and the experimental selectivity for ethylene and ethanol was as high as 70%. Based on in situ ATR-SEIRAS characterization, they found that the grain boundaries promoted the adsorption of Cu on $^*\text{CO}$. As shown in Fig. 7 (b and c), $\Sigma 3$ twin grain boundaries were chosen to simulate grain boundary-rich Cu nanoparticles [69]. Calculations based on the CO binding energies at different positions showed that the grain boundaries enhanced the CO binding energies of the atoms around them, thus promoting C-C coupling. In addition to this, Wang et al. synthesised $\text{Cu}_2\text{CO}_3(\text{OH})_2$ precursors with smooth surface nanoribbon structure using hydrothermal reduction method, where copper nanoribbons were formed by stacking tiny nanoparticles and exposed Cu (111), Cu (200), and Cu (220) facets, which yielded abundant grain boundaries [70]. CO_2RR experiments using this catalyst showed that the abundant grain boundaries could promote CO_2 activation, and the grain boundaries could promote the adsorption of $^*\text{CO}$ on Cu, thus facilitating the C-C coupling to form $^*\text{OCCO}$ and $^*\text{OCCOH}$ intermediates, and improving the selectivity to C_2 products (Fig. 7d). In order to demonstrate the effect of crystal boundaries on the catalytic activity, they also investigated the reaction of three c-catalyst samples with different crystal structures (ED-Cu, OD-Cu, and TR-Cu) in CO_2RR , and according to the in situ Raman spectra (Fig. 7e), it can be seen that the intensity of the $\text{CO}_{2\text{ad}}$ Raman peak becomes stronger with the increase of cathodic potential, especially for ED-Cu, whose $\text{CO}_{2\text{ad}}$ Raman peak intensity is much stronger than that of OD-Cu and TR-Cu, which indicates that ED-Cu has the strongest CO_2 adsorption and activation ability compared to the other two catalysts. From the above results, both defects, doping and crystal boundaries, can effectively improve the CO_2RR product selectivity, so we can also consider combining the two to improve the CO_2RR process together. For example, Zhu et al. used grain boundary and doping engineering to design a multi-boundary catalyst of R-Sn-Cu for CO_2RR . Through the dual modulation of Sn doping and polycrystalline boundaries, the catalyst was able to achieve a CO Faraday efficiency of 99% at -0.8V. From this, it can be reacted that the polycrystalline boundary and Sn dopant can synergistically improve the catalytic performance of Cu [71].

Although much has been achieved in the design of Cu-based catalysts, it is still a challenge to produce efficient and economical catalysts. In order to meet the requirements of practical applications, the structural design and preparation of catalysts should also be considered more from the economic point of view.

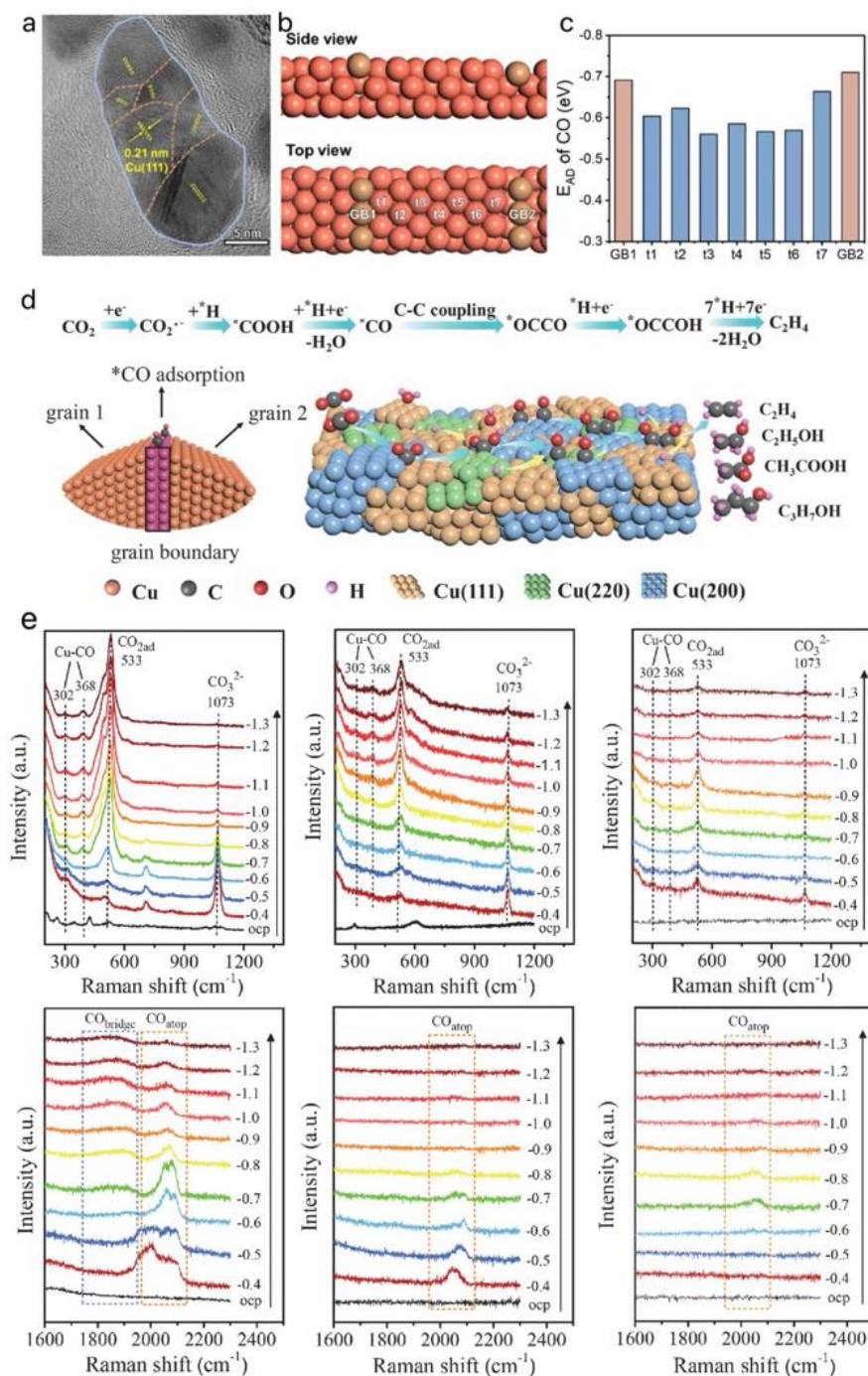


Figure 7. (a) Crystal boundaries of copper catalysts with different dot orientation regions delineated by orange dashed lines [70]. (b) Different binding sites on the atomic structure of GB-Cu [70]. (c) $^*\text{CO}$ binding energies at different positions in the structure of GB-Cu [70]. (d) Schematic diagram of the catalytic mechanism of copper nanocatalyst (ED-Cu). (e) In situ Raman spectra of ED-Cu, OD-Cu and TR-Cu in CO_2RR in the 200-1400 and 1600-2500 cm^{-1} regions [71].

6. Summary and Outlook

China's research on CO_2RR started in the 1980s and has developed rapidly in the last decade, triggering the interest of many scientific researchers. CO_2RR is a clean, green and sustainable technology. This review summarises the reaction mechanism of CO_2RR , the types of flow devices and their respective advantages and disadvantages, the effect of electrolyte on the reaction, and in terms of the crystalline surface of the catalyst, its dimensions, and defects. Strategies to improve catalyst performance are discussed. Currently CO_2RR still faces the great challenge of obtaining products with

practical applications in low-cost and high-efficiency electrolysis units. Therefore, the future industrialization and industrialization of CO₂RR should be carried out in the following aspects:

1. Selection and development of electrolysis devices.

A crucial issue for the industrialization of CO₂RR is the design of suitable large-area reactors and reactors. The development of the reactor needs to address the issue of long-term stability of the device, in particular, the catalyst tends to fall off from the electrodes during prolonged electrolysis in a flow cell, so a new type of adhesive with good durability and high bonding properties needs to be developed. The electrolysis device generates heat during the reaction process, which also affects the long-term stability of the device and the activity of the catalyst, so for the design of the reaction device, it is necessary to take into account the problem of heat dissipation, and it is necessary to balance the relationship between heat dissipation and sealing. As for the flow field plate in the flow electrolysis cell, it is also necessary to consider the gas inhomogeneity caused by its pressure drop and other problems, and there should be further innovation and development for the existing flow field plate.

2. the choice of electrolyte solution.

In different electrolytes, the current density and product selectivity of CO₂RR reaction are different, and it is difficult to inhibit HER in acidic electrolyte, while it is difficult to solve the problem of CO₂ loss in alkaline electrolyte. Therefore, it is important for pH regulation and the use of anionic and cationic effects to change the performance of electrolytes. At this stage, the electrolyte solution is mainly carbonate, but in the future, we still need to develop a new type of electrolyte to solve the problem of CO₂ dissolution and inhibition of HER, and the liquid electrolyte in the CO₂RR liquid product is also difficult to separate the problem, so the development of solid-state electrolyte system is also a future direction of application.

3. Selection and development of high-performance catalysts.

The research on CO₂ reduction to various products over Cu-based catalysts has made great progress in recent years, but there are still many challenges in practical production. New Cu-based materials are further explored by using more advanced synthesis and characterisation methods and combining theoretical calculations with experimental studies. The electronic structure and surface morphology of Cu-based can be reconstructed, and the Cu-based catalysts can be doped or alloyed to expose more low-coordination active sites or change the local electronic structure, among other methods. Of course, while designing and producing catalysts, it is important to consider whether the production process will generate pollution, whether the subsequent process of large-scale industrial production is industrial safe and whether the production cost is appropriate.

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