

Review

Electroreduction of CO₂ toward High Current Density

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Abstract: Carbon dioxide (CO₂) electroreduction offers an attractive pathway for converting CO₂ to valuable fuels and chemicals. Despite the existence of some excellent electrocatalysts with superior selectivity for specific products, these reactions are conducted at low current densities ranging from several mA cm⁻² to tens of mA cm⁻², which are far from commercially desirable values. To extend the applications of CO₂ electroreduction technology to an industrial scale, long-term operations under high current densities (over 200 mA cm⁻²) are desirable. In this paper, we review recent major advances toward higher current density in CO₂ reduction, including: (1) innovations in electrocatalysts (engineering the morphology, modulating the electronic structure, increasing the active sites, etc.); (2) the design of electrolyzers (membrane electrode assemblies, flow cells, microchannel reactors, high-pressure cells, etc.); and (3) the influence of electrolytes (concentration, pH, anion and cation effects). Finally, we discuss the current challenges and perspectives for future development toward high current densities.

Keywords: CO₂ electroreduction; electrocatalysts; electrolyzers; high current densities; electrolytes; long-term operations; challenges and perspectives



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1. Introduction

Electrochemical reduction of carbon dioxide (CO₂) to chemicals is considered to be a sustainable strategy in preventing our planet from global warming while keeping the growth of our economy. So far, commercially available CO₂ electroreduction reaction (CO₂ER) technologies are almost nonexistent [1]. A cost-competitive CO₂ electrolysis requires a high current density (>200 mA·cm⁻²), a high selectivity, a low overpotential (<1 V), and a long-term operation (>8000 h or 1 year) [2,3]. Among these factors, the current density is a key indicator for evaluating the catalytic performance, because a higher current density represents a higher reaction rate. Therefore, technical developments regarding electrocatalyst, electrolyzer, electrolyte, and operational condition are greatly demanded in order to realize high current density.

CO₂ electroreduction involves different numbers of electrons and protons to produce specific products. Elemental metallic catalysts can be classified into the following three categories according to their major products: (1) Au, Ag, Pd, and Zn to produce CO [4–6]; (2) Pb, Bi, Sn, In, and Hg to produce formic acid/formate [7–9]; (3) Cu to produce various hydrocarbons [10–12]. Although the above catalysts have demonstrated remarkable selectivity towards different products, they are still far away from industrial application, especially regarding the aspect of the current density. However, in order to have a sustainable impact on the environment and climate, industrially relevant research is urgently required [13].

Therefore, the integration of catalyst innovations and reactor designs is desirable. Traditional CO₂ERs are conducted in an H-type cell, which is limited to relatively low current densities due to the limited solubility of CO₂ in aqueous solution. To meet the

requirements for industrialization, various reactor configurations such as the GDE-based flow cell, microchannel reactor, membrane electrode assembly, and high-pressure cell have been developed. Although perovskite catalysts in solid oxide electrolyzer cells (SOECs) can electrolyze CO₂ at the gas–solid interface with a high current density [14–16], they are not discussed within the scope of this article, due to their restricted operational conditions and products. In an economically practicable electrolyzer, variables related to electrodes, electrolytes, and operations should also be taken into account.

In this review, we give a comprehensive summary of catalysts for various products under high current densities. The developments of advanced CO₂ER technologies, including the electrolyzer design, electrode structure, electrolyte effect, and operating conditions are also discussed. We ultimately provide an overview of the development towards high current density by considering three aspects: the design of electrocatalysts, electrolyzers, and appropriate anode reaction coupling.

2. Mechanisms of CO₂ER

CO₂ electrochemical reduction can proceed through reduction pathways involving two to eighteen electrons to produce various products including formic acid (HCOOH)/formate (HCOO[−]), carbon monoxide (CO), methane (CH₄), methanol (CH₃OH), acetic acid (CH₃COOH), ethanal (CH₃CHO), ethanol (CH₃CH₂OH), ethylene (CH₂CH₂), and others. The most commonly reported reactions are listed below in Table 1.

Table 1. Electrochemical reactions and their equilibrium potentials.

Reaction	E ⁰ /(V vs. RHE)
2H ⁺ + 2e [−] → H ₂	0.00
CO ₂ + 2H ⁺ + 2e [−] → CO + H ₂ O	−0.10
CO ₂ + 2H ⁺ + 2e [−] → HCOOH	−0.12
CO ₂ + 6H ⁺ + 6e [−] → CH ₃ OH + H ₂ O	+0.03
CO ₂ + 8H ⁺ + 8e [−] → CH ₄ + 2H ₂ O	+0.17
2CO ₂ + 8H ⁺ + 8e [−] → CH ₃ COOH + 2H ₂ O	+0.11
2CO ₂ + 10H ⁺ + 10e [−] → CH ₃ CHO + 3H ₂ O	+0.06
2CO ₂ + 12H ⁺ + 12e [−] → CH ₃ CH ₂ OH + 3H ₂ O	+0.09
2CO ₂ + 12H ⁺ + 12e [−] → C ₂ H ₄ + 4H ₂ O	+0.08
3CO ₂ + 18H ⁺ + 18e [−] → CH ₃ CH ₂ CH ₂ OH + 5H ₂ O	+0.10

During CO₂ER, a CO₂ molecule is first adsorbed onto a vacant catalyst site, electron transfer is carried out to form various intermediates [17], and then the corresponding products are obtained [18]. Figure 1 shows the proposed reaction mechanisms for various CO₂ER products. The generally accepted first step in CO₂ER is the protonation process of the CO₂ molecule on different atoms (C or O atom) to form *OCHO or *COOH. In order to produce HCOOH, a further proton and electron transfer is needed. The production of CO requires the formation of *COOH in the first step, followed by H⁺/e[−] transfer to the hydroxyl group and then the loss of H₂O [19]. The weak bond of *CO with the surface of a metal catalyst such as Au or Ag promotes the desorption of CO. In order to obtain C₂₊ products, either *CO dimerization [20] or *CHO formation [21] is required. The generation of *CHO is thought to be the potential-determining step for generating methane and ethylene [22]. However, the rate-determining steps for methane and ethylene are distinct, with the first e[−] transfer for ethylene, and the second e[−] transfer for methane [23].

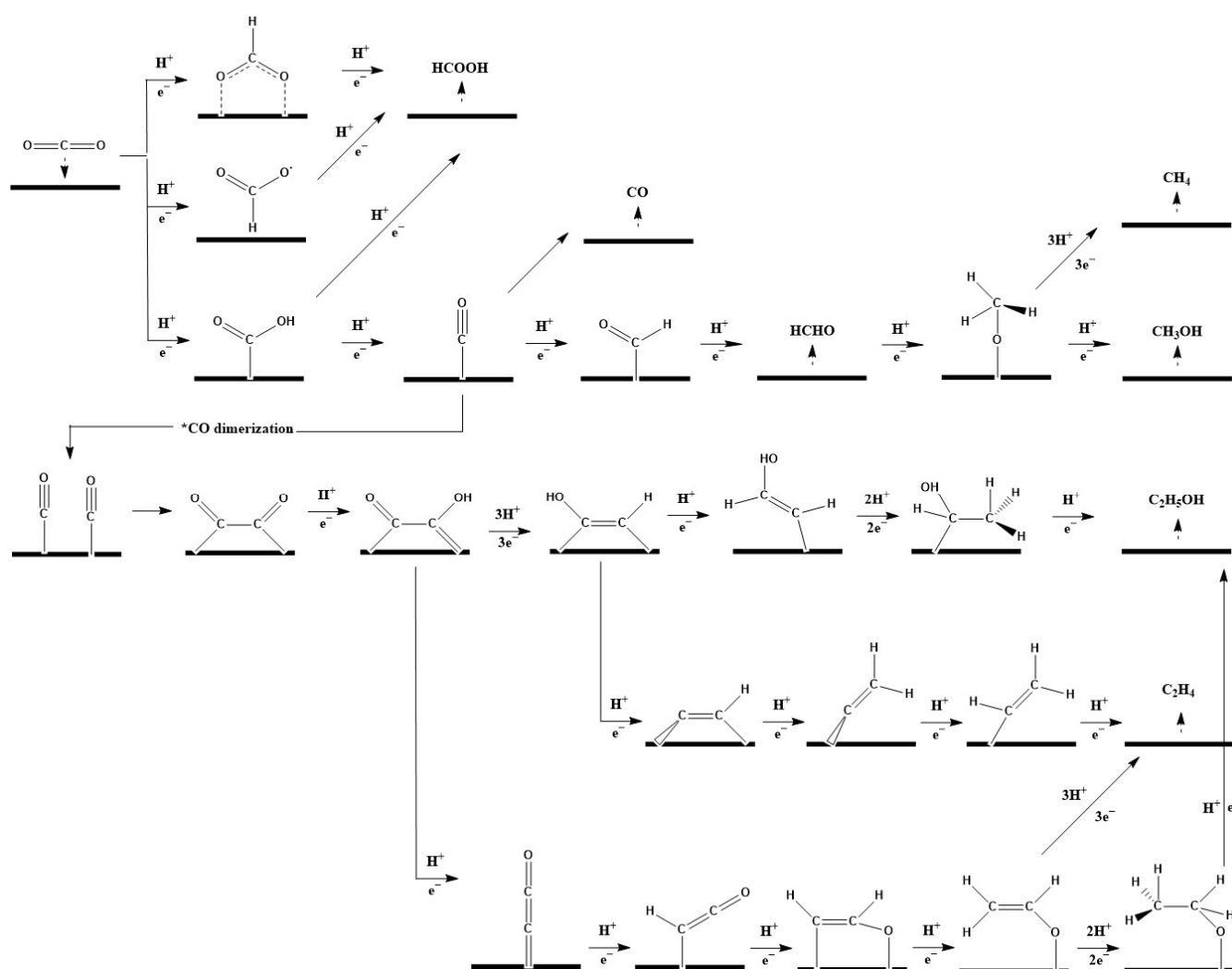


Figure 1. Proposed reaction routes for CO₂ electroreduction to various products such as CO, HCOOH, CH₄, CH₃OH, C₂H₄, and C₂H₅OH [18,24–28].

3. Electrocatalysts for CO₂ Electroreduction

Elemental metallic catalysts for CO₂ electroreduction are traditionally classified into four distinct groups depending on their major products, according to experimental data produced by Hori et al. [29] (Figure 2). In aqueous electrolytes, Au, Ag, and Zn catalysts mainly produce CO, whereas Cd, In, Sn, Hg, Tl, Pb, and Bi [30] catalysts favor the production of HCOOH. Cu is unique, and only Cu-based catalysts are able to yield large amounts of hydrocarbons, as they facilitate the formation of C–C bonds [31,32].

Ti	Fe	Co	Ni	Cu	Zn	Ga
99.7 %	94.8 %		88.9 %	67.5 %	79.4 %	79.0 %
			Pd	Ag	Cd	In
			28.3 %			
			26.2 %	81.5 %	78.4 %	94.9 %
						88.4 %
			Pt	Au	Hg	Tl
			95.7 %	87.1 %	99.5 %	95.1 %
						97.4 %
						Bi

Figure 2. Periodic table and Faradaic efficiencies of various metals depending on the major products in CO₂ electroreduction: CO (blue); HCOOH (yellow); mixed hydrocarbons (red); H₂ (green).

3.1. Metal-Based Catalysts

3.1.1. Noble Metals

(I) Au

Currently, noble metal catalysts such as gold (Au) and silver (Ag) show good performance for the electroreduction of CO₂ to CO [33]. Among these, Au-based catalysts have been investigated extensively for their high CO selectivity at low overpotential, which is owing to the moderate adsorption of *COOH and *CO on the Au surface [34,35]. However, Au is confined to industrial applications with high costs. These costs can be mitigated by reducing the loading on the electrodes and modifying the surface morphologies.

The use of microporous or mesoporous supports with high surface areas represents a promising method of achieving lower precious metal loadings. Jhong et al. [36] reported that Au nanoparticles supported on poly(2,2'-(2,6-pyridine)-5,5'-bibenzimidazole) polymer (PyPBI) multiwall carbon nanotubes (MWNTs) on gas diffusion electrodes in microfluidic electrolysis cells can attain a partial current density for CO (j_{CO}) of 160 mA cm⁻² at −1.17 V (vs. RHE; all potentials correspond to this reference electrode unless otherwise specified). It is emphasized that the loading of Au nanoparticles was 0.17 mg cm⁻². Verma et al. [37] further improved the synthesis method to reduce the Au loading from ~50% by weight to ~15% on PyPBI/MWNTs supports, and the synthesized Au nanoparticles in an alkaline flow electrolyzer led to a high j_{CO} of 158 mA cm⁻² at a cell overpotential (η_{cell}) of 0.94 V.

Alternatively, surface modification with polymer composites on metal could manipulate the electronic and geometric structures of the metal surface to promote CO₂ adsorption, stabilize intermediates, or weaken the product binding energy. Ma et al. [38] reported polyvinyl alcohol (PVA)-modified Au NPs, which achieved a j_{CO} of 98.6 mA cm⁻² and 90% FE_{CO} in a two-component cell. Tafel analysis indicated that the improvement in the performance of PVA-modified Au NPs might be attributed to the hydrogen-bond network at the metal–polymer interface stabilizing the intermediate (*COOH).

(II) Ag

As a precious metal, Ag can electrochemically convert CO₂ to CO with high selectivity. The performance of noble metal catalysts in CO₂ electroreduction has a size-dependent effect. To be specific, before the optimal size is reached, the catalytic activity dramatically increases with reducing nanoparticle size; however, when the diameter of the nanoparticles continues to drop, the activity reduces [34,39,40]. Density functional theory (DFT) calculations indicate that these trends are associated with the fact that the numbers of low-coordinated sites such as edges and corners increase for small nanoparticles [40]. Such low-coordinated sites can result in the reactants or intermediate products binding more strongly. For Ag nanoparticles, for example, the edges, which facilitate CO₂ adsorption and stabilize the intermediate COOH*, serve as active sites for CO₂ER leading to CO, and the corner sites of Ag serve as active sites for HER [41]. Thus, by controlling the sizes of the Ag particles, the ratio between edge and corner sites can be increased to promote CO production. Ma et al. [42] compared the activities of Ag nanoparticles supported on titanium dioxide (Ag/TiO₂, 40 wt%) and on carbon black (Ag/C, 40 wt%). The j_{CO} of the former catalyst reached 101 mA cm⁻² in a flow cell, which was twice as high as the latter catalyst. Through structural characterization, the authors found that Ag particles with the optimal size were dispersed uniformly on the TiO₂ carrier. Wang et al. [43] reported a layer-by-layer (LBL) growth and MOF-mediated approach for coating a Ag coordination polymer on a porous carbon-based microporous layer (MPL) to control the Ag loading. The obtained Ag gas diffusion electrodes (GDEs) displayed a peak j_{CO} of 385 mA cm⁻² in a gas-fed zero-gap flow electrolyzer.

As well as stabilizing and dispersing precious metal catalyst particles, support materials can also have a tremendous influence on electron conduction and mass transport. Carbon-based supports can enhance the intrinsic electrical properties through the synergetic effect of heteroatom (e.g., sulfur, boron, etc.) dopants. Chen et al. [44] reported Ag-decorated sulfur-doped graphitic carbon nitride/carbon nanotube nanocomposites (Ag-

S-C₃N₄/CNT) for efficient CO₂ER to CO, demonstrating a notable j_{CO} of 303 mA cm⁻² in a flow cell configuration. The experimental results benefited from the selective adsorption of CO₂ and the complex oxygenated intermediates (e.g., *COOH, *CO) of graphitic carbon nitride (g-C₃N₄), and the improvement in the conductivity of S-CNT.

The above Ag nanoparticles were deposited on substrates or gas diffusion layers (GDL) for reduction. Few studies used support materials directly as co-catalysts to improve the performance of metal nanoparticle catalysts. Ma et al. [45] integrated MWCNTs with Ag in a “layered” or “mixed” structure, using an easy one-step method (Figure 3). In the former structure, the MWCNTs layer is covered with a Ag catalyst layer, and in the latter, the Ag nanoparticles and MWCNTs are merged homogeneously. The “mixed” structures attained a best j_{CO} of 350 mA cm⁻² in a flow reactor. These observed results may be due to the lower charge transfer resistance in the “mixed” structures.

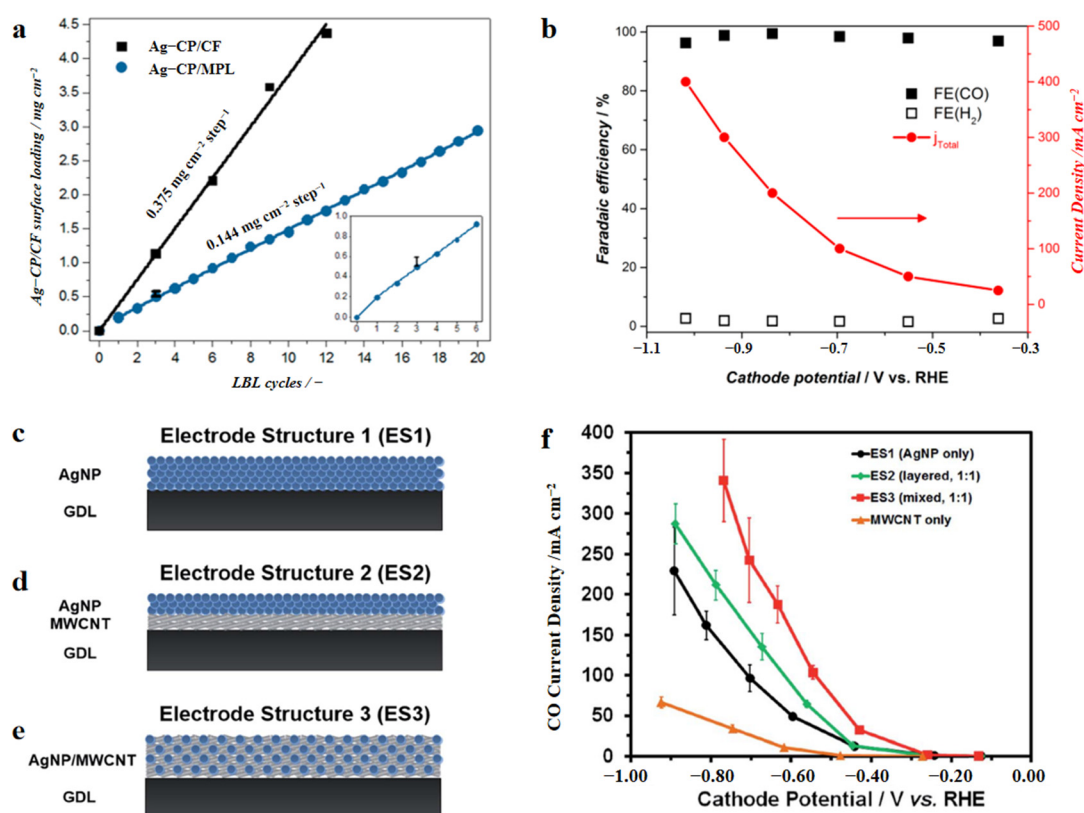


Figure 3. (a) Surface loading of Ag coordination polymer vs. cycles of layer-by-layer deposition method. (b) FE_{CO}, FE_{H₂}, and total current density of Ag coordination polymer (3 cycles) on MPL vs. cathode potential in a gas-fed zero-gap flow electrolyzer. Reproduced with permission from Ref. [43]. Copyright 2019 American Chemical Society. The schematic diagram of three electrode structures: (c) AgNPs deposited on a GDL (ES1); (d) MWCNT layer deposited on a GDL and covered with an AgNP layer (ES2); (e) AgNPs and MWCNTs mixed uniformly and deposited on a GDL (ES3). (f) Values of j_{CO} of ES1, ES2, ES3 vs. cathode potential in a flow cell. Reproduced with permission from Ref. [45]. Copyright 2016 the Royal Society of Chemistry.

(III) Pd

Palladium (Pd)-based materials have been studied as potential catalysts for selectively reducing CO₂ to CO and formate [46,47]. Zhu et al. [48] controlled the shape of Pd to investigate the effect of the crystalline facets on CO₂ conversion. They synthesized Pd cubes (100) and Pd octahedra (111). The Pd octahedra (111) exhibited a high j_{CO} of 220 mA cm⁻², which was higher than that of the Pd cubes (100).

Pd shows different electrochemical performance at various overpotentials. In an electrolyte solution with a pH near 7, a Pd electrocatalyst mainly produces HCOOH at low overpotentials, while CO is the major product at high overpotentials. Theoretically, a weak CO binding energy over the electrocatalyst surface is beneficial for producing CO in CO₂ER. Hence, reducing the CO binding energy over the surface of a Pd catalyst is an effective strategy for enhancing the selectivity for CO at low overpotentials. Molecular tuning by inducing functionalized organic molecules can be helpful in weakening the CO binding energy on the surface of Pd catalysts. Xia et al. [49] fabricated a polydiallyldimethyl ammonium (PDDA)-modified Pd catalyst, exhibiting a j_{CO} of $\sim 279 \text{ mA cm}^{-2}$ at -0.65 V .

CO₂ electroreduction performances of noble metal catalysts are summarized in Table 2.

Table 2. CO₂ electroreduction performances of noble metal catalysts.

Catalyst	$j_{\text{main product}} / \text{mA cm}^{-2}$	Main Product	Electrolyzer	Reference
Au/PyPBI/MWNTs	160	CO	Microfluidic cell	[36]
Au/PyPBI/MWNTs	158	CO	Flow cell	[37]
PVA-Au/C	98.6	CO	Two-component cell	[38]
Ag/TiO ₂	101	CO	Flow cell	[42]
Ag-CP/MPL-nC	385	CO	Zero-gap flow cell	[43]
Ag-S-C ₃ N ₄ /CNT	303	CO	Flow cell	[44]
Mixed AgNP/MWCNT	350	CO	Flow cell	[45]
Pd octahedra (111)	220	CO	Flow cell	[48]
Pd/C-PDDA	~ 279	CO	Microfluidic flow cell	[49]

3.1.2. Non-Noble Metals

(I) Cu

To date, copper (Cu) is the only metal catalyst that can reduce CO₂ to multicarbon (C₂₊) and hydrocarbon products. C₂₊ products such as ethylene (C₂H₄), ethanol (EtOH), and n-propanol (n-PrOH) are attractive in spite of the multistep and multielectron transfer reactions that make the design of the catalysts challenging. In order to promote C₂₊ production, effective strategies have been developed for manipulating the structures of Cu-based catalysts, such as modulating the nanostructure, controlling the facets, and promoting oxide-derived states.

Exploring appropriate synthesis methods to design the nanostructure of Cu with abundant active sites enables C₂₊ production. Metal–organic frameworks (MOF) and their derivatives are ideal platforms for increasing the catalyst's active sites. Zhu et al. [50] synthesized a three-dimensional Cu dendrites electrocatalyst (d-Cu-1) derived from hollow Cu-MOF, which achieved a high j_{HCOOH} of 100.3 mA cm^{-2} in a traditional H-cell. Yang et al. [51] presented porous cupric oxide nanowires (OD-Cu), derived from MOF using a controllable annealing method. These polycrystalline nanocatalysts demonstrated a $j_{\text{C}_2\text{H}_4}$ of 141 mA cm^{-2} in a flow cell (Figure 4a,b). Yao et al. [52] also presented a Cu-MOF-derived Cu@Cu_xO core@shell structure, in which Cu⁺ can be formed rapidly and then Cu²⁺ can be transformed to Cu⁰ slowly (Figure 4c,d). The interfaces between Cu⁺ and Cu⁰ promote CO dimerization, leading to a $j_{\text{C}_2\text{H}_4}$ of 150 mA cm^{-2} in a flow cell. Wang et al. [53] examined the activities of different shapes of Cu nanoparticles and found that Cu nanocubes with Cu(100) facets performed better than Cu nanospheres. The Cu nanocubes achieved a $j_{\text{C}_2\text{H}_4}$ of 144 mA cm^{-2} in a flow cell (Figure 4e,f).

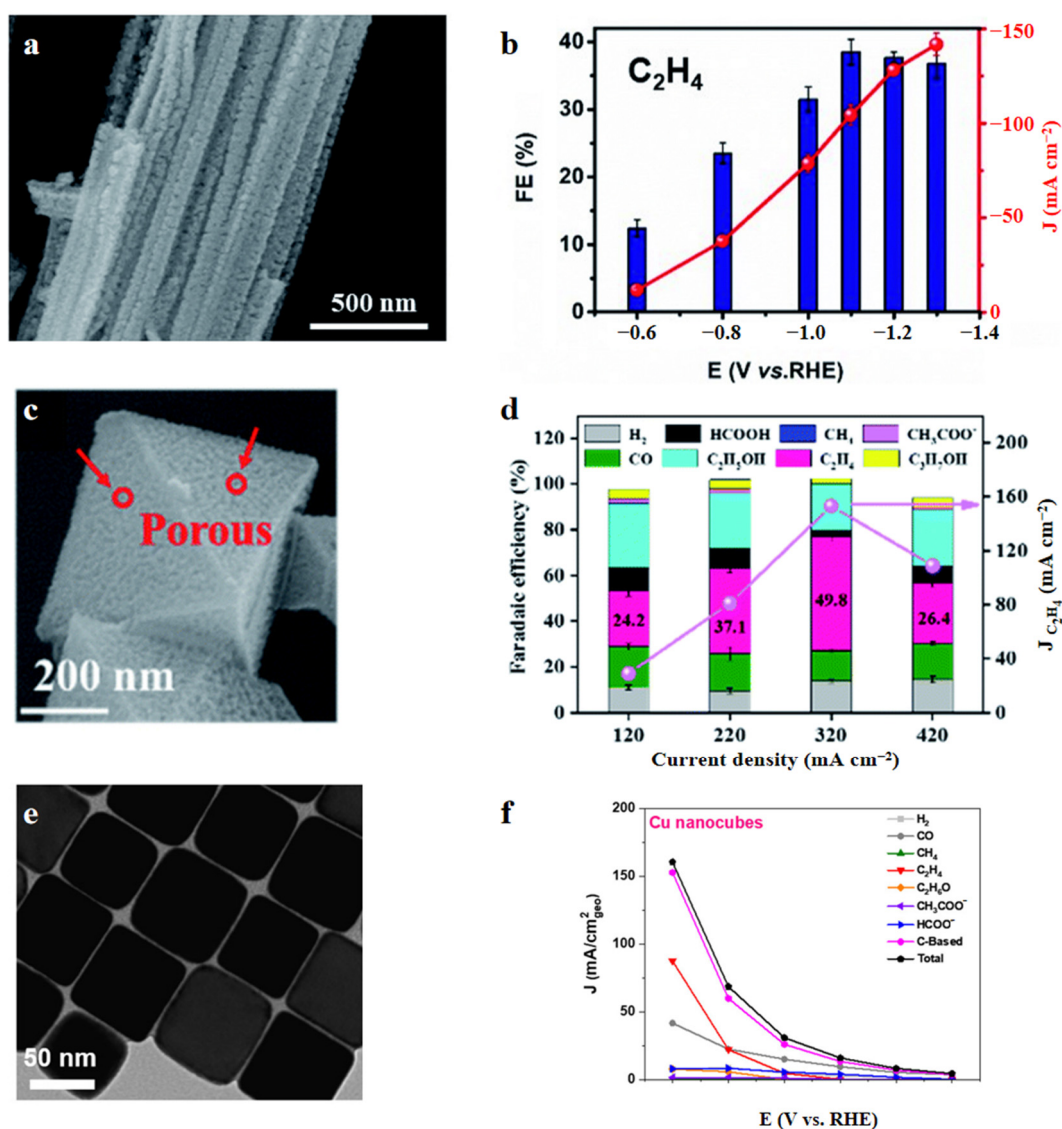


Figure 4. (a) SEM image of CuO nanowires; (b) FE and $j_{C_2H_4}$ of OD-Cu in a flow cell. Reproduced with permission from Ref. [51]. Copyright 2020 The Royal Society of Chemistry. (c) SEM image of a single octahedral particle; (d) FE_{product} and $j_{C_2H_4}$ vs. total current density in a flow cell. Reproduced with permission from Ref. [52]. Copyright 2020 The Royal Society of Chemistry. (e) TEM image of Cu nanocubes; (f) $j_{product}$ vs. potential for Cu nanocubes in a flow cell. Reproduced with permission from Ref. [53]. Copyright 2019 American Chemical Society.

In order to produce cost-effective catalysts, modifying metals in the form of homogeneous alloys or heterogeneous composites should be a promising approach. Recently, several studies have paid close attention to synergistic geometric and electronic effects in bimetallic catalysts to boost CO₂ electrocatalysis by improving CO₂ adsorption and C=O activation. Since Sn electrodes have the advantages of high catalytic activity, low cost, and low toxicity [54], alloying Sn with Cu is effective for selective CO₂ reduction. Ju et al. [55] developed a Sn-decorated Cu-coated electrospun polyvinylidene fluoride (Sn/Cu-PVDF) nanofibers GDE, acting as a well-performing catalyst to attain a high j_{CO} of above 100 mA cm⁻². Xiang et al. [56] applied an in situ electrochemical spontaneous precipitation (ESP) method to synthesize Cu–In electrocatalysts with a GDE, and the optimum nanoscale “core–shell” structure of the Cu–In catalyst achieved a high j_{CO} of ~173 mA cm⁻² in a flow cell.

Nonetheless, due to the oxyphilic properties of metal in air and to the poor electrical conductivity of most metal oxides, controlling the surface structure of catalysts is a great challenge [57]. Preparing core-shell structured catalysts with a highly conductive metal core and a thin metal oxide shell is a feasible approach to solving the above problems. Ye et al. [58] reported a SnO_x shell and Sn-Cu core for CO_2 ER, and the optimal $\text{Sn}_{2.7}\text{Cu}$ catalyst achieved a j_{C1} of $\sim 397.88 \text{ mA cm}^{-2}$. DFT calculations indicated that the interfaces of the reconstructed Sn and SnO_x favored the formation of HCOOH via optimizing the binding of the HCOO^* intermediate.

Alloying can not only promote CO_2 adsorption and activation but also change the reduction pathway. Electrochemical reduction of CO_2 to C_2H_4 or $\text{C}_2\text{H}_5\text{OH}$ usually requires the same $^*\text{C}_2\text{H}_3\text{O}$ intermediate. Thus, in order to obtain ethanol rather than ethylene, it is crucial to stabilize and hydrogenate this intermediate to promote alcohol production. Li et al. [59] introduced Ag to a Cu catalyst ($\text{Ag}_{0.14}/\text{Cu}_{0.86}$) to destabilize the C_2H_4 intermediates, thereby promoting $\text{C}_2\text{H}_5\text{OH}$ production. A very high $j_{\text{C}_2\text{H}_5\text{OH}}$ of 102.5 mA cm^{-2} was obtained in a flow cell.

Further studies have concentrated on modifying Cu catalysts with other non-metal materials (e.g., N, F), especially at high current densities. Ma et al. [60] reported a F-modified Cu catalyst (F-Cu) with an extremely high j_{C_2+} of 1.28 A cm^{-2} (mainly C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$) in a flow cell. Lee et al. [61] manufactured a self-formed tandem carbon nanofibers catalyst doped with N and Cu (Cu/N-CNF), using an oxygen-partial-pressure-controlled calcination method, exhibiting a $j_{\text{C}_2\text{H}_4}$ of 372 mA cm^{-2} . Chen et al. [62] discovered that N-doped graphene quantum dots (NGQ) on CuO-derived Cu nanorods (NGQ/Cu-nr) could achieve a $j_{\text{C}_2+\text{alcohols}}$ of 147.8 mA cm^{-2} .

Controlling the grain boundaries and microstrains formed in oxide-derived Cu, which can be proposed as catalytic sites, contributes to better catalytic performance. However, the annealing of GB-containing Cu catalysts could reduce the density of GBs [63]. Indeed, different cooling rates can result in different physical properties in microcrystalline materials. Yang et al. [64] tuned the grain boundaries and microstrains in CuO electrocatalysts by fast cooling with liquid nitrogen. Compared to samples with slower cooling rates, the fast-cooled CuO (CuO-FC) exhibited a high j_{C_2} of 231 mA cm^{-2} (mainly $\text{C}_2\text{H}_5\text{OH}$).

The CO_2 reduction reaction pathway is highly sensitive to the surface structure of Cu. Cu(110) favors the production of oxygenated hydrocarbons such as $\text{C}_2\text{H}_5\text{OH}$ and CH_3COOH [65,66]. Cu(100) and step facets such as Cu(211) preferentially produce C_2+ products, due to the activity for CO dimerization [67,68]. In addition, Cu(111) is more selective toward CH_4 as the major hydrocarbon product, while the Cu(100) facet is more favorable for C_2H_4 [69]. Wang et al. [70] proposed a method based on in situ electrodeposition of Cu (Cu- CO_2), which could increase the ratio of Cu(100)/total facets by 70%, thus promoting the formation of C_2+ products. They reported a j_{C_2+} of 520 mA cm^{-2} in a flow cell.

Furthermore, Zhang et al. designed segmented gas diffusion electrodes (Cu/Fe-N-C s-GDE) to integrate the CO_2 -to-CO and CO-to- C_2+ steps on two sites, achieving an FE_{C_2+} of 90% and a j_{C_2+} of over 1 A cm^{-2} [71].

CO_2 electroreduction performances of Cu-based catalysts are summarized in Table 3.

(II) Zn

Zn, as an earth-abundant metal, can also reduce CO_2 to CO with relatively low cost compared with noble metal catalysts such as Au and Ag. However, bulk Zn catalysts suffer from low activity and CO selectivity. Nanostructured Zn catalysts have been synthesized to overcome these limitations.

Luo et al. [72] developed a facile electrodeposition method to fabricate porous-structured Zn electrodes to efficiently reduce CO_2 to CO in a GDE. The j_{CO} could be boosted to 168 mA cm^{-2} in a flow cell, which can be attributed to the enhanced surface area and the local pH effect. In previous work, the surface area of the electrocatalyst could be significantly increased by introducing Cu^{2+} at the time of electrodeposition of Zn, whereas the introduction of Cu^{2+} compromises the FE_{CO} [73]. Inspired by this, Lamaison et al. [74]

introduced Ag^+ during the electrodeposition of Zn to obtain an Ag–Zn alloy catalyst with a high surface area, with a j_{CO} of 286 mA cm^{-2} at elevated pressure.

Table 3. CO_2 electroreduction performances of Cu-based catalysts.

Catalyst	$j_{\text{main product}} / \text{mA cm}^{-2}$	Main Product	Electrolyzer	Reference
d-Cu-1	100.3	HCOOH	H-cell	[50]
OD-Cu	141	C_2H_4	Flow cell	[51]
$\text{Cu@Cu}_x\text{O}$	150	C_2H_4	Flow cell	[52]
Cu nanocube	144	C_2H_4	Flow cell	[53]
Sn/Cu-PVDF	>100	CO	Flow cell	[55]
Cu–In/GDE	~173	CO	Flow cell	[56]
$\text{Sn}_{2.7}\text{Cu}$	397.88	CO + HCOOH	Flow cell	[58]
$\text{Ag}_{0.14}/\text{Cu}_{0.86}$	102.5	$\text{C}_2\text{H}_5\text{OH}$	Flow cell	[59]
F–Cu	1280	mainly C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$	Flow cell	[60]
Cu/N–CNF	372	C_2H_4	Flow cell	[61]
NGQ/Cu–nr	147.8	$\text{C}_2 + \text{C}_2\text{H}_5\text{OH}$	Flow cell	[62]
CuO–FC	231	C_2 (mainly $\text{C}_2\text{H}_5\text{OH}$)	Flow cell	[64]
Cu– CO_2	520	C_{2+} (mainly C_2H_4)	Flow cell	[70]
Cu/Fe–N–C s–GDE	>1000	C_{2+}	MEA	[71]

(III) Cd

The current density in CO_2 electroreduction can be considerably increased by increasing the local electric field at the tips of sharp metal nanostructures [35,75]. Since electrostatic repulsion exists, free electrons will migrate to the zones with sharpest curvature, so that the local electrostatic field in metal nanoneedles will be enhanced by an order of magnitude over that of conventional nanorods and nanoparticles. Gao et al. [76] reported a cadmium sulfide (CdS) nanoneedle (CdS needle) with high curvature, exhibiting a j_{CO} of 212 mA cm^{-2} in a flow cell. This current density can be attributed to the enriched K^+ concentration at the regions of high curvature of the CdS needles, caused by electric fields, as K^+ can stabilize CO_2 through noncovalent interaction.

(IV) Sn

Formate, as an important liquid product of CO_2 reduction, can be regarded as an ideal hydrogen carrier or liquid fuel for low-temperature fuel cells [77]. However, the formation of HCOOH is limited by the inert CO_2 molecule, and effective catalysts are needed to activate the reaction process, such as some main-group metals (e.g., Sn, Pb, In, Tl) and transition metals (Cd, Hg) with a d10 electronic configuration. Sn is low in price, high in selectivity, and without toxicity compared with noble metals such as Pd and Au or toxic metals such as In.

Among the Sn-derived catalysts, Sn oxides (SnO , SnO_2 , and SnO_x) are attractive, due to their appropriate orbital energy and electronic configuration; however, because of the relatively low intrinsic electrical conductivity, Sn oxides are not active enough for the formation of formate [78]. Löwe et al. [79] fabricated a SnO_2 -based GDE, achieving a j_{formate} of 800 mA cm^{-2} at 50°C in a semi-batch cell, which can be attributed to optimization of both the catalyst particle size and the dispersion, together with the impact of temperature on the solubility and diffusion coefficients of CO_2 in the electrolyte. Xiang et al. [80] fabricated a carbon-black-supported SnO_2 catalyst and found that the optimum SnO_2/C mass ratio achieved a maximum j_{formate} of $\sim 211 \text{ mA cm}^{-2}$ in a flow cell.

Introducing other metals to form Sn-based bimetallic materials is an alternative strategy for improving electrochemical performance. Cu foams have a large surface area and high conductivity, and thus can be an alternative catalyst carrier [81]. Wang et al. [82] deposited Sn on a Cu foam to form heterostructured $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$ (CuSn–C). A j_{formate} of 148 mA cm^{-2} was achieved in a flow cell. In the interface between the Cu_6Sn_5 and

Cu₃Sn intermetallics, the adsorption of the intermediate tended to favor HCOO* rather than COOH*, so that CO₂ was selectively converted to HCOOH.

(V) Bi

In addition to the previously mentioned transition metals with a d10 electronic configuration, Bi, which shows intrinsic inertness toward HER, is also considered to be an advanced electrocatalyst for CO₂ conversion to formate. Díaz-Sainz et al. [83] studied Bi-GDEs working in a continuous mode in a filter press reactor to reduce CO₂ to formate, and found a j_{formate} of up to 210 mA cm⁻². Deng et al. [84] reported the preparation of carbon-nanorods-encapsulated bismuth oxides (Bi₂O₃@C) prepared by a facile spatially confined pyrolysis method and exhibiting a j_{formate} of above 200 mA cm⁻² in a flow cell. These outstanding performances were attributed to the effects of the high formate selectivity of Bi₂O₃ and the ability of the carbon matrix to improve the current density. Xia et al. [85] developed an ultrathin two-dimensional Bi (2D-Bi) catalyst with abundant undercoordinated active Bi sites in solid electrolytes, with a maximum j_{formate} of over 172.2 mA cm⁻² in a flow cell. Yang et al. [86] proposed leafy Bi-MOF-derived bismuth nanosheets (Bi NSs) electrocatalysts. The j_{HCOOH} could exceed 374 mA cm⁻² in the flow cell configuration.

Most of the reported Bi-based electrocatalysts show poor conductivity and limited exposure of active sites; however, metallene, a new 2D material with a thickness of a few layers and abundant defective and unsaturated sites, is currently emerging. Cao et al. [87] developed atomically thin bismuthene (Bi-ene), which can deliver a j_{HCOOH} of ~200 mA cm⁻².

CO₂ electroreduction performances of other non-noble catalysts are summarized in Table 4.

Table 4. CO₂ electroreduction performances of other non-noble catalysts.

Catalyst	$j_{\text{main product}}$ /mA cm ⁻²	Main Product	Electrolyzer	Reference
P-Zn	168	CO	Flow cell	[72]
Ag-Zn	286	CO	High-pressure cell	[74]
CdS needle	212	CO	Flow cell	[76]
SnO ₂ -GDE	800	Formate	Semi-batch cell	[79]
SnO ₂ /C	~211	Formate	Flow cell	[80]
CuSn-C	148	Formate	Flow cell	[82]
Bi-GDEs	210	Formate	Filter press reactor	[83]
Bi ₂ O ₃ @C	>200	Formate	Flow cell	[84]
2D-Bi	172.2	Formate	Flow cell	[85]
Bi NSs	374	HCOOH	Flow cell	[86]
Bi-ene	~200	HCOOH	Flow cell	[87]

3.2. Metal-Free Carbon Catalysts

Carbon-based electrocatalysts without any metal content have gained attention for CO₂ reduction, due to their high abundance, low cost, large available surface area, and resistance to poisoning [88]. Different heteroatoms such as N, P, or other chalcogens with carbon can modulate the charge redistribution among carbon atoms to add active sites for catalysis and lower the free energy barrier for CO₂ER [89].

Yang et al. [90] developed N and S co-doped, hierarchically porous carbon membranes (NSHCF) to achieve a j_{CO} of 96.82 mA cm⁻² in an H-cell. This performance can be ascribed not only to the co-doping of pyridinic N and carbon-bonded S atoms, which can significantly reduce the free energy barrier for the binding of the *COOH intermediate, but also to the well-developed hierarchically porous structures of NSHCF, providing sufficient channels. Chen et al. [91] fabricated a novel electrocatalyst involving N, P co-doped carbon aerogels (NPCA), achieving a j_{CO} of 143.6 mA cm⁻² in an H-type cell. The excellent results can be attributed to the pyridinic N and co-doped P, which were selective for CO and inhibited HER.

CO₂ electroreduction performances of metal-free carbon catalysts are summarized in Table 5.

Table 5. CO₂ electroreduction performances of metal-free carbon catalysts.

Catalyst	$j_{\text{main product}} / \text{mA cm}^{-2}$	Main Product	Electrolyzer	Reference
NSHCF	96.82	CO	H-cell	[90]
NPCA	143.6	CO	H-cell	[91]

3.3. Single-Atom Catalysts

Single-atom catalysts (SAC) have been widely investigated for their high atomic efficiency, superior activity, and selectivity. However, the low loading of 1–2 wt% limits the industrial application of single-atom metals [92]. Approaches to anchoring single atoms onto high-surface-area supports can increase atomic dispersion and density, to achieve an industrial-level current density [93]. Yang et al. [94] designed a well-distributed Ni single-atom/porous carbon fiber membrane catalyst (NiSA/PCFM) with excellent mechanical strength via the electrospinning method, yielding a j_{CO} of 308.4 mA cm^{−2} in a flow cell. They also applied the same method for single-atom Co sited on a high-yield carbon nanofibers membrane (CoSA/HCNFs) with a continuous porous structure, which led to a j_{CO} of 211 mA cm^{−2} in a flow cell [95].

Recently, transition metal–nitrogen–carbon (M–N–C) catalysts have exhibited outstanding catalytic activity as electrocatalysts for CO₂ electroreduction. M–N–C refers to an N-coordinated single-atom transition metal (M–N_x) supported on a carbon matrix, such as a single atom anchored on an N-doped graphene matrix [96]. Note that different N species (such as graphitic N, pyrrolic N, and pyridinic N) can exist on carbon supports.

As metallic Fe nanoparticles in Fe–N–C materials could reduce the overpotential, Fe–N–C catalysts synthesized with different support materials and precursors have been investigated [97–100]. However, the experimental results demonstrated limited current density. Fe³⁺ shows faster CO₂ adsorption and weaker CO absorption than conventional Fe²⁺ sites. Gu et al. [101] reported a Fe³⁺–N–C catalyst for efficiently catalyzing CO₂ with a j_{CO} of 94 mA cm^{−2} in a flow cell.

Nevertheless, the Fe–N_x moiety may be poisoned by strong chemisorption of CO, compared to Ni–N–C, and thus the electrocatalytic performance of the former [102] is lower than that of the latter [103]. Zheng et al. [104] reported a Ni single-atom catalyst on commercial carbon black (Ni–NCB) employed in an anion membrane electrode assembly (MEA), giving a j_{CO} of 130 mA cm^{−2}. Jeong et al. [105] developed a Ni–SA–NCs catalyst using Si spheres as templates, yielding a j_{CO} of around 380 mA cm^{−2} in an MEA cell.

Restraining the aggregation of metal precursors on substrates at high temperature is crucial for M–N–C catalysts. Zeolitic imidazolate frameworks (ZIFs) are attractive because of their many pores, large surface areas and adjustable composition. Wang et al. [106] reported a variety of cyano-substituted Ni-phthalocyanines-derived SACs in ZIFs (Ni–SAC(Pc)), which exhibited a superior j_{CO} of 200 mA cm^{−2}. Guo et al. [107] fabricated an ellipsoidal hierarchical nanoporous Ni–N–C electrocatalyst (Ni₂₀–N–C) derived from a porphyrin-based porous Zr–MOF, that could achieve a very high j_{CO} of 645 mA cm^{−2}. The outstanding results can be attributed to micropores and interconnected mesopores leading to enhanced CO₂ mass transfer (Figure 5).

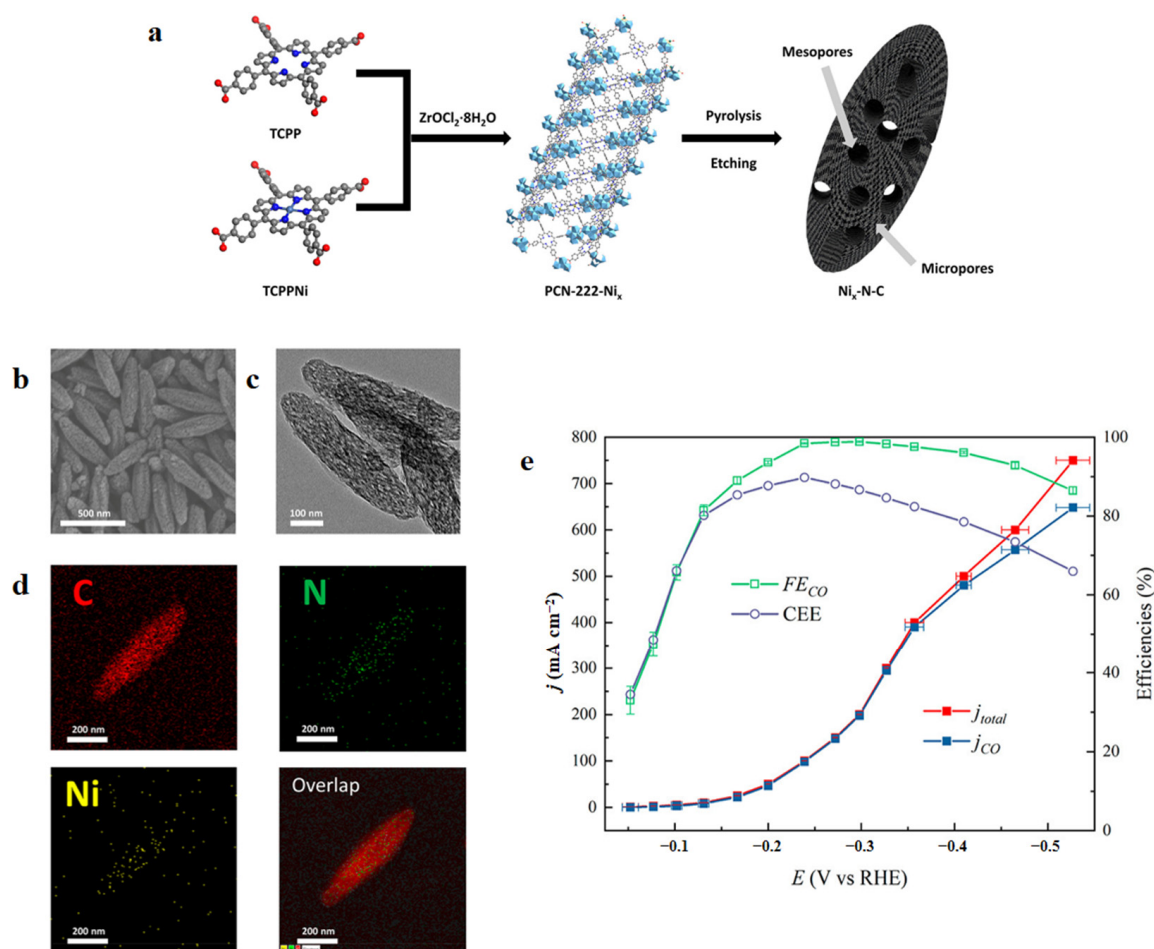


Figure 5. (a) Fabrication procedure for $\text{Ni}_x\text{-N-C}$ catalysts. SEM images of: (b) $\text{Ni}_{20}\text{-N-C}$; (c) $\text{Ni}_{100}\text{-N-C}$. (d) EDS mappings. (e) Electrocatalytic performance of $\text{Ni}_{20}\text{-N-C}$ in 6 M KOH. Reproduced with permission from Ref. [107]. Copyright 2020 American Chemical Society.

Zhang et al. [108] revealed that pyrolytic temperatures and oxygen-containing groups in the carbon substrate have an impact on the number of atomic metal active sites. With all factors optimized, Ni-N-C with the highest Ni loading of approximately 4.4 wt% exhibited a j_{CO} of 152 mA cm $^{-2}$ in a flow cell. Zhang et al. [109] engineered various pendant groups on phthalocyanine to form types of dispersed Ni phthalocyanine molecules supported on carbon nanotubes. The optimized catalyst with a methoxy group (NiPc-OMe MDE) could convert CO_2 to CO with a high j_{CO} of over 300 mA cm $^{-2}$.

In addition, Wen et al. [110] regulated the local electronic environments of Ni species (Ni(NC)-1) to activate catalytically inert sites into active sites, achieving a considerable j_{CO} of 158.4 mA cm $^{-2}$ in a flow cell.

CO_2 electroreduction performances of single-atom catalysts are summarized in Table 6.

Meanwhile, Co-N-C [111,112], Cu-N-C [113,114], Ce-N-C [113], and Pr-N-C [113], have the potential for current or selectivity improvements in CO_2 reduction to CO and should be further explored.

Table 6. CO₂ electroreduction performances of single-atom catalysts.

Catalyst	$j_{\text{main product}} / \text{mA cm}^{-2}$	Main Product	Electrolyzer	Reference
NiSA/PCFM	308.4	CO	Flow cell	[94]
CoSA/HCNFs	211	CO	Flow cell	[95]
Fe ³⁺ -N-C	94	CO	Flow cell	[101]
Ni-NCB	130	CO	MEA cell	[104]
Ni-SA-NCs	380	CO	MEA cell	[105]
Ni-SAC(Pc)	200	CO	Flow cell	[106]
Ni ₂₀ -N-C	645	CO	Flow cell	[107]
NiPc-OMe MDE	>300	CO	Flow cell	[109]
Ni(NC)-1	158.4	CO	Flow cell	[110]

3.4. Molecular Catalysts

Pyridine/pyridinium (py/pyH⁺) species have been revealed to be effective co-catalysts, not only for the aforementioned M-N-C catalysts but also for molecular catalysts. Molecular catalysts are highly selective to CO in CO₂ER as they have a more tunable ligand structure of the primary and secondary coordination spheres than solid state catalysts, improving catalytic efficiency. Ren et al. [115] developed a cobalt phthalocyanine (CoPc1) catalyst to convert CO₂ to CO, obtaining a j_{CO} of 175 mA cm⁻² in a zero-gap membrane flow reactor (Figure 6a). Cobalt phthalocyanine with a trimethyl ammonium group connecting up the phthalocyanine macrocycle (CoPc2) can show great durability at the highest j_{CO} of 165 mA cm⁻² in a flow cell [116], which may be attributed to the through-space reciprocities between the O atoms in CO₂ (partial negative charge) and the trimethyl ammonium substituent (positive charge). These through-space interactions can promote CO₂ molecule reduction coordinated with the Co metal center (Figure 6b,c).

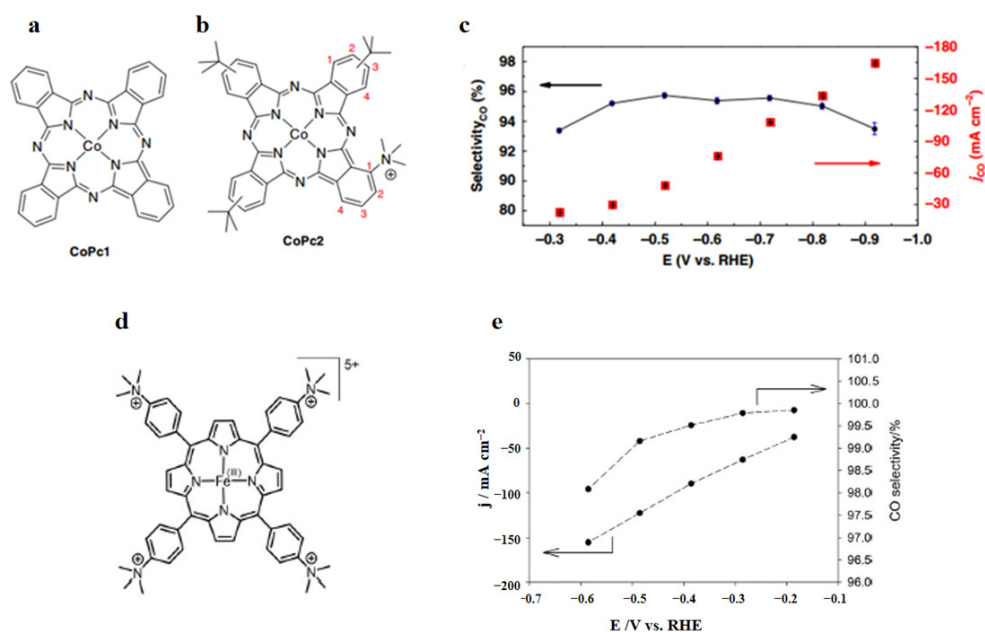


Figure 6. Structure of: (a) cobalt phthalocyanine catalyst CoPc1; (b) CoPc2. (c) FE_{CO} and j_{CO} of CoPc2 vs. potential. Reproduced with permission from Ref. [116]. Copyright 2019 Springer Nature Limited. (d) Structure of FeP; (e) j_{CO} and FE_{CO} of FeP vs. potential. Reproduced with permission from Ref. [117]. Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In addition, depositing a molecular catalyst onto carbon supports with many pores, such as carbon powder, carbon nanotubes, and graphene, can be a promising way to improve catalyst activity. Torbensen et al. [117] developed an Fe porphyrin (FeP) and

carbon black mixture loaded on carbon paper as a GDE in a flow cell, achieving a j_{CO} of 152 mA cm^{-2} (Figure 6d,e).

CO_2 electroreduction performances of molecular catalysts are summarized in Table 7.

Table 7. CO_2 electroreduction performances of molecular catalysts.

Catalyst	$j_{\text{main product}} / \text{mA cm}^{-2}$	Main Product	Electrolyzer	Reference
CoPc1	175	CO	Zero-gap membrane flow cell	[115]
CoPc2	165	CO	Flow cell	[116]
FeP	152	CO	Flow cell	[117]

In order to provide the reader with a comprehensive overview, we summarize the catalysts which can electrochemically reduce CO_2 to different products with high current densities in Figure 7. CO is the simplest product of CO_2ER , involving a two electron/proton process. As shown in Figure 7, the products of CO are closest to industrial application. Tests of different catalysts for reducing CO_2 to CO under various current densities have been explored, and the selectivities are generally around 90%. HCOOH is also a kinetically viable product of CO_2 electrolysis. The selectivity for HCOOH is high but at a relatively low current density. As the product molecules become more complex, the reaction selectivity drops dramatically at high current density, especially for $\text{C}_2\text{H}_5\text{OH}$ formation.

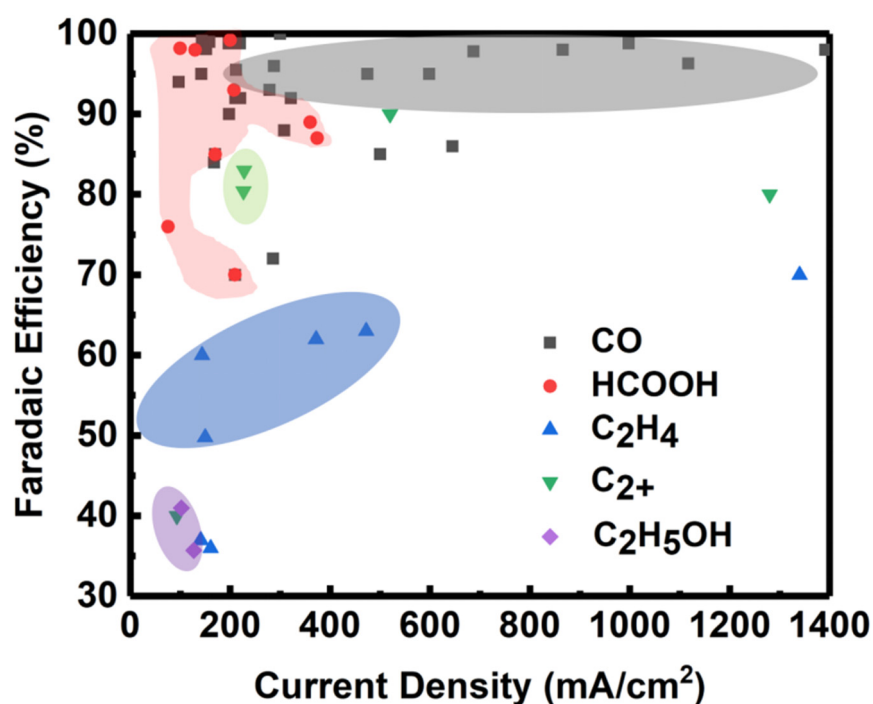


Figure 7. Faradaic efficiency and corresponding current density for different CO_2ER products. [43,48–53,59–61,63,64,70,72,74,76,79,83,84,86,87,90,91,94,95,103,107,110,115,118–134].

4. Electrolyzer Design

4.1. Electrolyzer Types

Five main architectures have emerged for CO_2 electrolyzers: H-type cells, microchannel reactors, liquid-phase electrolyzers, membrane electrode assemblies, and high-pressure cells (Figure 8). To date, H-type cells are still used for evaluating most of the catalysts for CO_2 electroreduction. The catalyst is completely submerged, and CO_2 is usually bubbled into the electrolyte in these H-type cells. Therefore, the low solubility of CO_2 in aqueous electrolyte sets a limit on the current density of CO_2 electroreduction and makes it difficult

to reach industrial scales ($>100 \text{ mA cm}^{-2}$). In order to surmount these barriers, a series of investigations has been conducted on electrochemical reactors [122].

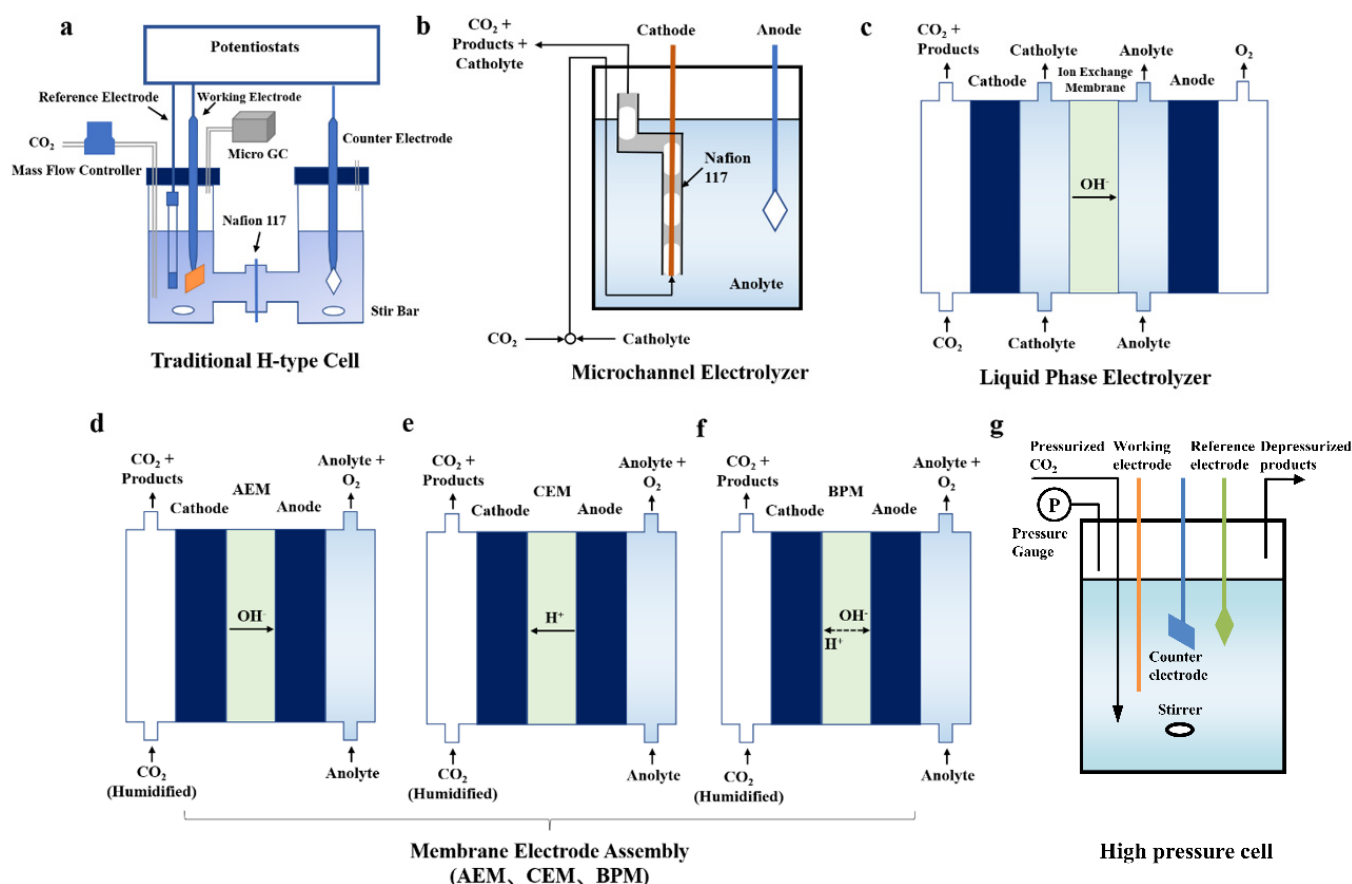


Figure 8. Illustrations of different electrolyzer types. (a) H-type cell. Reproduced with permission from Ref. [135]. Copyright 2017 The Royal Society of Chemistry. (b) Microchannel electrolyzer. Reproduced with permission from Ref. [136]. Copyright 2020 American Chemical Society. (c) Liquid-phase electrolyzer; (d–f) membrane electrode assembly (AEM, CEM, BPM) electrolyzers; (g) high-pressure cell. Reproduced with permission from Ref. [137]. Copyright 2019 Elsevier Inc.

4.1.1. H-Type Cell

The fundamental exploration of CO_2ER is commonly carried out in an H-type cell, which contains an anode and a cathode compartment. The two compartments are divided by an ion-exchange membrane (e.g., Nafion 117) to provide proton conductivity and mitigate the crossover of liquid-phase products from the working electrode to the counter electrode. In the cell, CO_2 gas is bubbled into and dissolved in the liquid electrolyte. The configuration of the H-type cell is simple; thus, investigations into reaction mechanisms of catalysts are usually carried out in this reactor. However, the cell suffers mass transfer limitations due to the low CO_2 solubility in liquid electrolyte, so the current density is usually below 30 mA cm^{-2} . Interestingly, Chen et al. [91] achieved a significant current density (143.6 mA cm^{-2}) in an H-type cell. The catalyst they used was N,P co-doped carbon aerogel carbonized at 900°C (NPCA900), and the electrolyte was $0.5 \text{ M [Bmim]PF}_6/\text{MeCN}$.

4.1.2. Microchannel Electrolyzer

Compared with conventional equipment, the interface area of the microchannel reactor is large. Due to the rapid rate of mixing, the discrete phase size in the microchannel is greatly reduced and the mass/heat transfer resistance is weakened [138–141]. Therefore, researchers who are focusing on CO₂ electroreduction have used the microreactor as an efficient electrolyzer for process intensification [142–145].

Due to the low CO₂ solubility in aqueous electrolyte, the electroreduction of CO₂ is limited by mass transfer at high current density. A cylindrical microchannel electrochemical reactor was built to enhance mass transfer. The reactor consists of a pre-mixing section (5 m circular microchannels with an inner diameter of 1 mm used to pre-saturate the electrolyte with CO₂) and a reaction section (cylindrical cation-exchange membrane tube, Nafion 117). The working electrode is located in the center of the Nafion 117 membrane tube (Figure 9) [136].

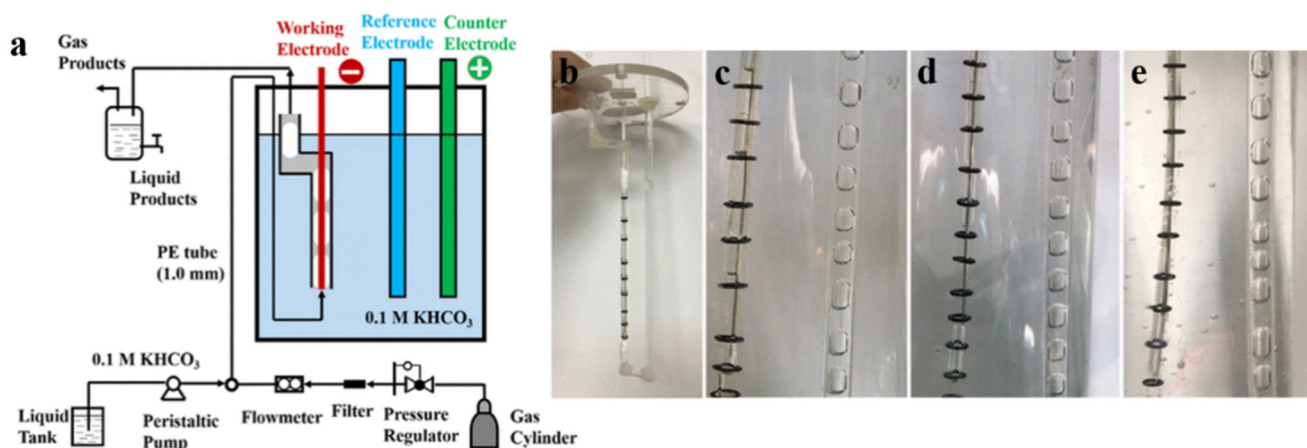


Figure 9. (a) Schematic diagram of the microchannel electrolyzer. (b–e) Optical images of cylindrical cation-exchange membrane tube. Reproduced with permission from Ref. [136]. Copyright 2020 American Chemical Society.

Increasing the microchannel number is one convenient and secure way to make it possible for the microreactor to achieve industrial scale-up [142,146]. Zhang et al. [136] developed a reactor with multiple microchannels in series to increase the CO₂ conversion (Figure 10a). When the number of microchannels in series increased from one to four, the conversion rate of CO₂ was correspondingly increased by four times. Compared with the traditional H-type cell, the CO₂ conversion rate in the microchannel showed an increase of 70.9%, due to the prolonged contact time between the gaseous CO₂ and the surface of the cathode (Figure 10b). The drawbacks of the GDE, such as the extremely low CO₂ conversion rate due to the radial flow, the complicated system setup, and carbonate salt formation and flooding, can be overcome by using a microchannel electrolyzer. Furthermore, Zhang et al. [136] also developed a reactor with multiple microchannels in parallel to enhance the yield in CO₂ electroreduction (Figure 10c). The CO FE values were all over 95.0%, regardless of the number of the microchannels, indicating that industrial-scale amplification of the microchannel reactor can easily be achieved by simply increasing the number of microchannels in parallel (Figure 10d).

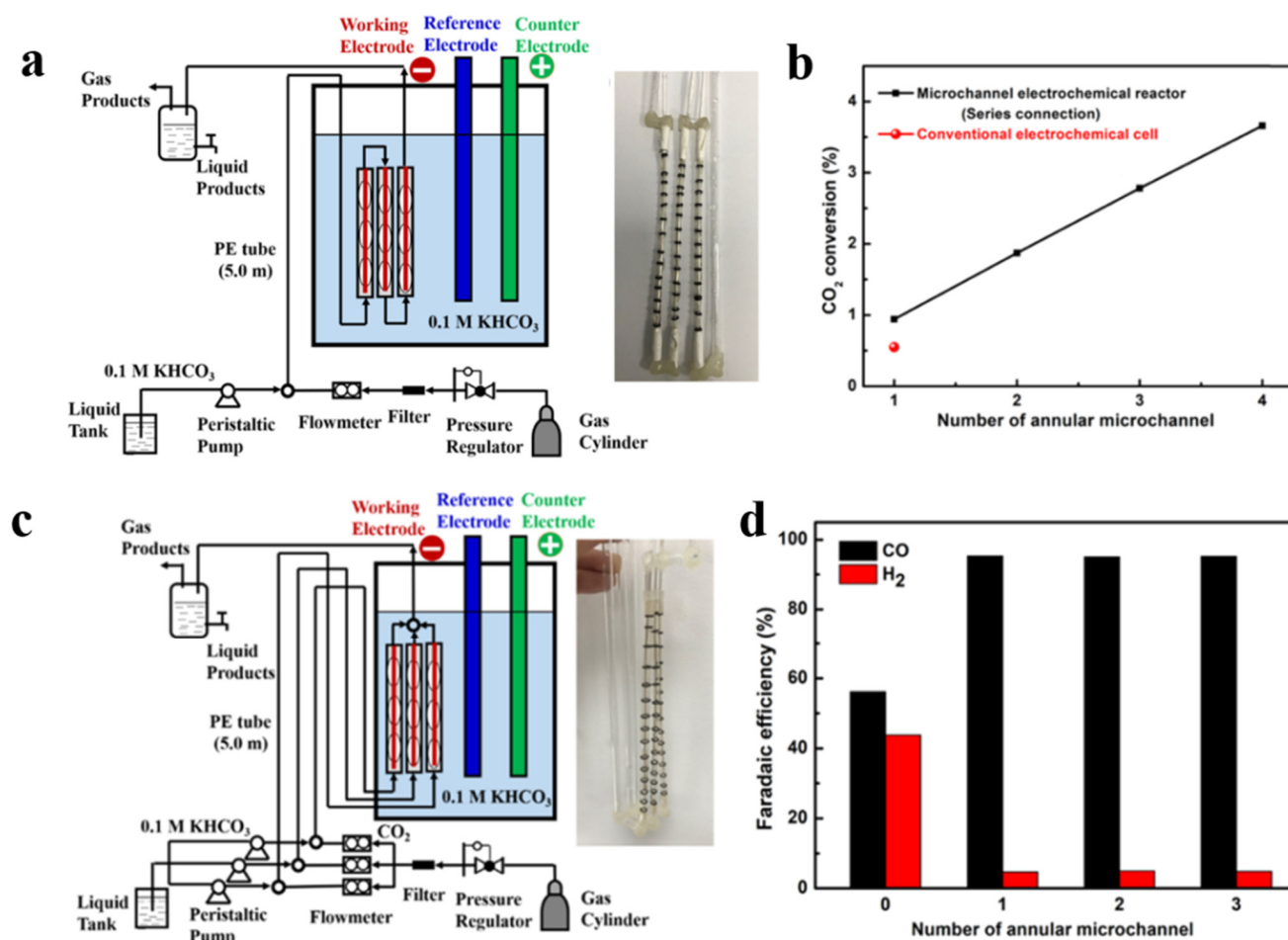


Figure 10. (a) Diagram of the microchannel reactor with three microchannels in series. (b) CO₂ conversion vs. number of annular microchannels. (c) Diagram of the microchannel reactor with three microchannels in parallel. (d) FE_{CO}, FE_{H₂} vs. number of annular microchannels. Reproduced with permission from Ref. [136]. Copyright 2020 American Chemical Society.

4.1.3. Liquid-Phase Electrolyzer

Liquid-phase electrolyzers have drawn significant attention worldwide due to their ability to be scaled up and achieve an industrially viable process. They are typically composed of three flow channels, which are used for the gaseous CO₂, catholyte, and anolyte, respectively. The gas and catholyte channels are separated by a GDE, while an ion-exchange membrane separates the catholyte and anolyte channels. In this liquid-phase configuration, the diffusion layer thickness of CO₂ is much less than in the H-type cell. Target products such as CO [44,56,76,95,107,110,116,117,123,147], formate [79,83,84], and multicarbon hydrocarbons/oxygenates [59,70,148] can be obtained at high rates (current densities). Most of the studies mentioned above were carried out in the liquid-phase configuration.

As well as lab-scale tests, pilot-scale CO₂ER is being developed using a GDE-based liquid-phase configuration. Evonik and Siemens [126] used a commercial Ag-based GDE in an industrial-scale chlorine–alkaline electrolyzer at a high current density of 300 mA cm^{−2}, with an operational duration of over 1200 h. The Kopernikus project P2X [149] conducted CO₂ER at a gas diffusion electrode with a 10 cm² cell size at 30 bar, at up to 300 mA cm^{−2}, achieving an FE_{CO} of above 90% over 1500 h. Furthermore, the first scaling step up to 300 cm² was accomplished, and the rated power of the cell was around 300 W.

4.1.4. Membrane Electrode Assembly (MEA)

An MEA is composed of a cathode and an anode separated by an ion-exchange membrane, including a cation-exchange membrane (CEM), an anion-exchange membrane (AEM) [48,55,104,105,115,128,132,150], and a bipolar membrane (BPM) [151]. To maintain the membrane hydration during operation, the inlet CO₂ gas must be humidified. There are three advantages of MEAs compared with their liquid-phase counterparts. Firstly, the MEA needs fewer electrolyte pumps, due to the removal of the catholyte, which eliminates multiple sources of instability such as electrolyte impurity deposition onto the catalysts, electrolyte flooding with GDE, and the formation of bicarbonate/carbonate salts. Secondly, it can be pressurized easily. Thirdly, it reduces ohmic losses. Larrazábal et al. [152] developed an MEA composed of a porous Ag membrane cathode and an IrO₂/C anode with a Sustainion AEM separating the two electrodes, achieving a high j_{CO} of around 200 mA cm⁻² at 3.3 V (applied potential). Lee et al. [128] reported a gas-fed MEA consisting of carbon-supported Pd and Ag catalysts as a GDE cathode, and AEM and Ti felt as the anode. This MEA achieved a j_{total} of above 200 mA cm⁻² with an FE_{CO} of over 95% at a cell potential of -3.0 V. Using carbon-supported noble metal catalysts can help to reduce the amount of noble metal required and promote long-term stability. Furthermore, increasing the flow rate can further boost the yield of CO.

Nevertheless, liquid products may accumulate in the GDE and hinder gas diffusion. To obtain the target concentrated liquid product stream and maintain stability, timely extraction of liquid products from the GDE is necessary. Furthermore, the reactions between K⁺ and OH⁻ result in the formation of potassium bicarbonate crystals on the cathode side, which can hinder the CO₂ flow and reduce the yield of the MEA [115]. The performance of the MEA can be recovered by washing off these crystals.

Another disadvantage is the significant CO₂ crossover through the AEM, mostly appearing in the form of CO₃²⁻ but partly appearing in the form of HCOO⁻, which can cause ineffective conversion of CO₂ and overestimated catalytic performance. Hence, it is necessary to treat membrane crossover as an important factor when evaluating the electrochemical performance of an MEA electrolyzer at high current densities, as well as the conventional activity and selectivity. Unlike typical alkaline liquid electrolytes (e.g., KHCO₃, KOH), a type of high-ionic-conductivity alkaline polymer electrolyte (APE) was applied in an MEA with a common Au/C catalyst, achieving 500 mA cm⁻² at 3 V (cell voltage) at an operational temperature of 60 °C (Figure 11d–f) [132].

To achieve highly effective electroreduction of CO₂ in a gas-fed MEA, an appropriate number of protons are needed, which usually originate from the H₂O molecules in the aqueous electrolyte. Supplying too few H₂O molecules will starve the cathode and make the CO₂ reduction reaction sluggish, while too much H₂O will reduce the ability of CO₂ to reach the surface of the catalyst (i.e., flooding) and reduce the energy efficiency and Faradaic efficiency of CO₂ER production. Reyes et al. [150] researched the effect of cathode flooding on electrocatalytic performance and found a 37% drop in j_{CO} and a 450 mV enhancement in cell voltage (E_{cell}). By coupling a hydrophobic cathode and a microporous thin film (≤ 40 μm), cathode flooding can be effectively alleviated, making it feasible to meet commercial requirements ($j_{\text{CO}} \geq 100$ mA cm⁻² and $E_{\text{cell}} < 3$ V).

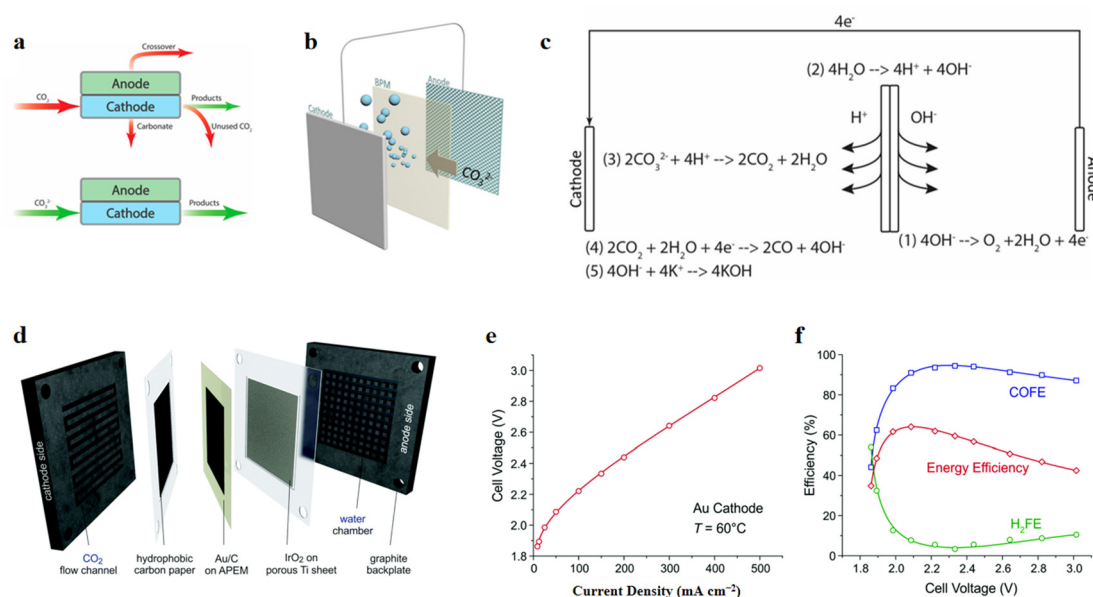


Figure 11. (a) Carbon loss mechanisms. (b) Diagram of CO₂ formation in the BPM through acid-base equilibrium reaction of H⁺ and CO₃²⁻. (c) Reaction mechanism using CO₃²⁻ as feed and BPM in electrolyzer. Reproduced with permission from Ref. [151]. Copyright 2019 American Chemical Society. (d) Schematic images of MEA using alkaline polymer electrolytes. (e) I–V curves for operation at 60 °C; (f) FEs of CO and H₂ production and energy efficiency. Reproduced with permission from Ref. [132]. Copyright 2019 The Royal Society of Chemistry.

4.1.5. High-Pressure Cell

In order to realize the industrialization of CO₂ electroreduction, the available amounts of CO₂ near the surface of the electrode urgently require enhancement. The supply of CO₂ to reaction sites in aqueous media is limited, due to poor solubility at ambient temperature and pressure. Thus, strategies for elevating the CO₂ partial pressure could be one of the most feasible methods of addressing this issue. According to Henry's law [153], the CO₂ gas dissolved in the aqueous solution is proportional to the pressure of CO₂. Significant efforts to explore optimal high-pressure cells have been made since the 1990s [154–156].

A typical high-pressure cell is a stainless-steel autoclave (Figure 8g), equipped with a pressurized CO₂ inlet and a depressurized product outlet. Before the process of electrolysis, CO₂ can be regulated to the operative pressure through a pressure gauge and a pressure relief valve, and then introduced into the electrolyte. The products are depressurized to 1 atm in preparation for further analysis. Recently, experiments have been conducted in a one-chamber high-pressure cell at relatively lower pressure, as shown in Table 8 [74,157–159].

Table 8. CO₂ electroreduction performances under high pressure.

Catalyst	$j_{\text{main product}}$ /mA cm ⁻²	Main Product	Pressure/Bar	Reference
Ag	123.22	CO	30	[154]
Pb	200.8	HCOOH	~60	[155]
Hg	201.8	HCOOH	~20	[155]
In	215.2	HCOOH	~60	[155]
Ag-alloyed Zn	286	CO	9.5	[74]
Zn@Ag-2PTFE	106.76	CO	9	[157]
Ag dendrites foam	288.68	CO	9.5	[158]
Ag-Pd	318	CO	9.5	[159]

In addition, the incorporation of GDEs into the flow cell systems and pressurization have been used to test the CO₂ reduction capability and ease the transportation for further downstream processing [125,160].

In order to provide the reader with a comprehensive overview of electrolyzers, we summarize CO₂ER conducted in various reactors at high current densities in Figure 12. Due to the mass transfer limitation of CO₂ in aqueous solution, the current density of the H-type cell is generally less than 30 mA cm⁻². Although Figure 12 shows several experimental results in H-cells where the partial current densities were over 100 mA cm⁻², the applied electrolytes were high-cost ionic liquids. The liquid-phase electrolyzer is one of the most widely studied reactors. As far as is known, CO₂ER processes with the highest current densities have been conducted in MEAs. Compared with their liquid-phase counterparts, MEAs need less electrolyte, eliminating electrolyte flooding and the formation of bicarbonate/carbonate salts. The selectivities of high-pressure reactors are relatively low.

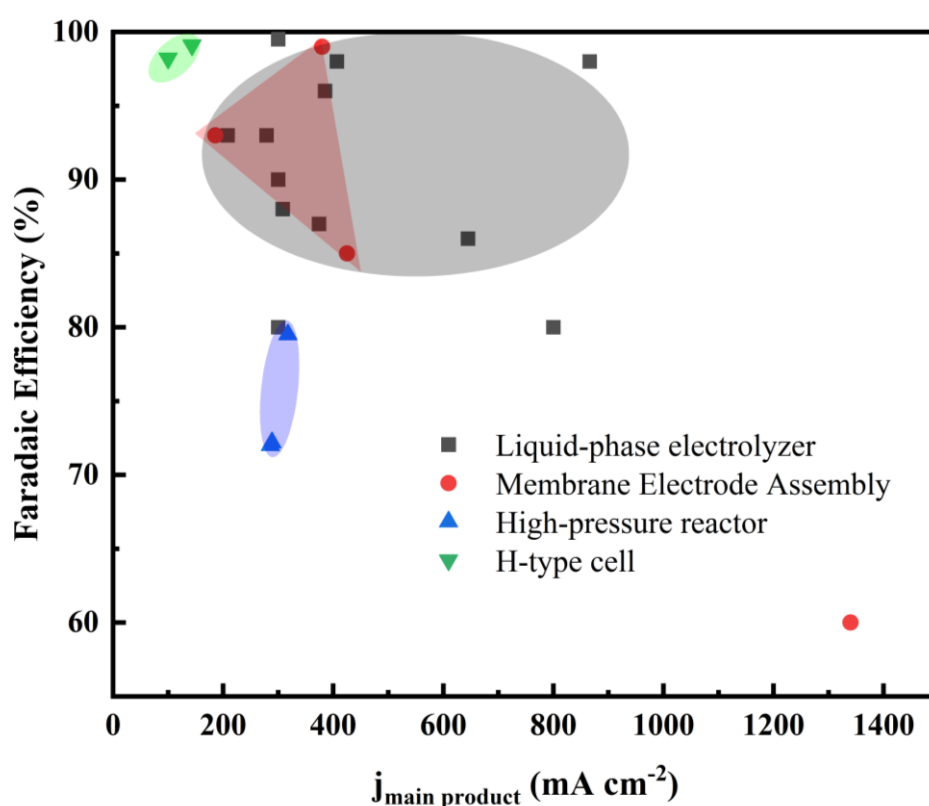


Figure 12. Faradaic efficiency and corresponding current density for CO₂ER in different reactors.

4.2. Gas Diffusion Electrodes (GDE)

4.2.1. Typical GDE

In recent years, GDE-based flow cells have attracted extensive attention, as they can reduce the CO₂ mass transfer limitation in aqueous electrolyte [133]. A typical GDE consists of a macroporous, a microporous, and a catalyst layer (Figure 13). CO₂ gas is directly delivered to the back side of the catalyst layer through the macroporous and microporous layers, which are both porous and hydrophobic. The front side of the catalyst layer is in close contact with the liquid electrolyte. The main function of the microporous layer is to provide a stable framework, which facilitates electronic contact and CO₂ gas passage. The microporous layer enhances further electronic contact between interfaces and effectively prevents flooding.

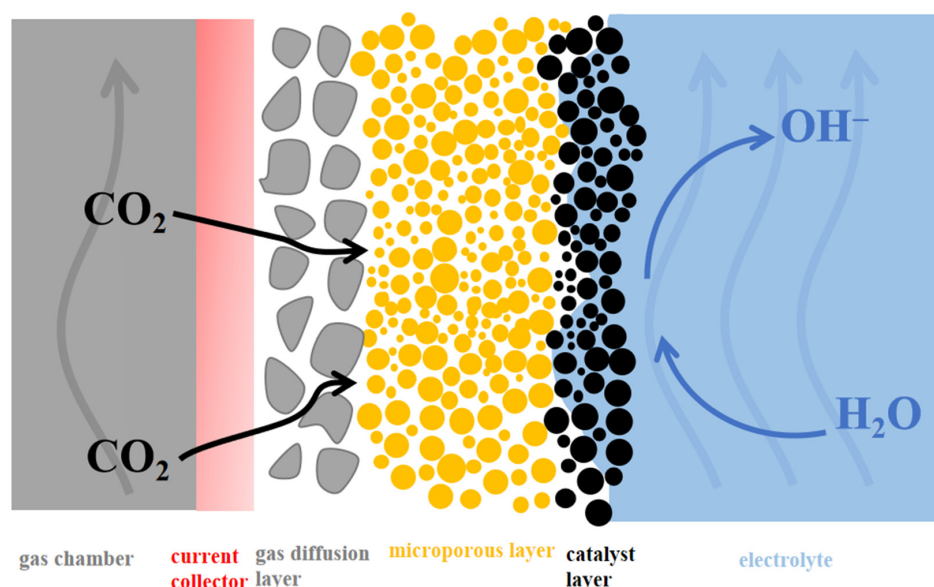


Figure 13. Illustration of catalyst layer on GDE.

Catalysts are usually applied to the GDL via electrochemical deposition, drop-casting [44], electromagnetic sputtering, or airbrushing. One major difference between the GDE and the H-cell is that the thickness of the CO_2 diffusion layer in the former (~ 50 nm) is less than 1/1000 of that of the latter (~ 50 μm). Hence, using a GDE can significantly improve current densities [161].

Recently, an inert material layer has been introduced on top of the catalyst layer, which functions as a current collector and protects the active catalyst from the deposition of electrolyte contaminants (e.g., Fe, Co, Ni, favoring H_2 production) as well as catalyst restructuring [162–164].

4.2.2. Integrated GDE

One drawback of the traditional GDE is that the link between the catalysts and the substrate is loose, which means that the catalysts split away easily. Therefore, the electrochemical performance and long-term durability of CO_2 electrocatalysis will be adversely affected. To avoid this problem, He et al. [94,95,114] developed an integrated strategy to fabricate GDE without adhesives (i.e., combining GDLs), forming a highly stable CO_2 –electrolyte–catalyst three-phase interface for CO_2 electrocatalysis under high current densities (Figure 14).

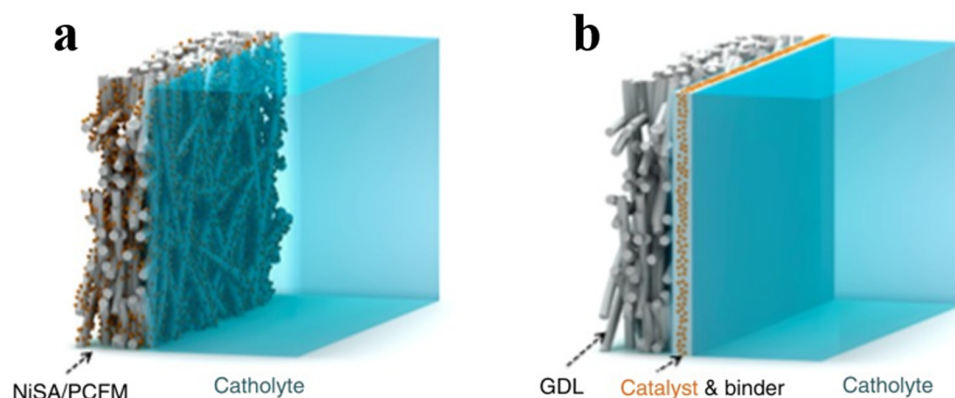


Figure 14. (a) Typical GDE loaded with catalyst via polymer binder. (b) Ni single-atom/porous carbon fiber membrane used as integrated GDE. Reproduced with permission from Ref. [94]. Copyright 2020 Springer Nature Limited.

Interestingly, there are two completely opposing views on whether CO₂ER is conducted at a three-phase interface (namely, the CO₂ gas–aqueous electrolyte–electrocatalyst interface) or at a two-phase interface (namely, the dissolved CO₂–electrocatalyst interface). The former is widely used to describe the mechanism of devices with a GDE. Burdyny et al. argued that the CO₂ in the GDL reacted in the liquid phase during electrocatalysis, rather than in the gas form, which can be evidenced by the interesting experimental phenomenon that stable CO₂ER could be maintained when the GDE was flooded. The results indicated that the three-phase interface does not exist [161,165].

4.3. Hydrophobic Electrode Design

Important advances in GDE-based electrolyzers have been made due to a breakthrough in the CO₂ mass transport limitation where the diffusion layer thickness cannot be reduced. However, the stability of GDLs remains a challenge in flow cells. One major reason is that the catalyst layer in GDLs is hydrophilic. After a long period of exposure to the electrolyte, a liquid film is formed surrounding the catalyst particles, which blocks CO₂ diffusion.

Recently, arrangements of the local environment of the gas/liquid/solid interface have gradually attracted widespread interest in CO₂ER. These methods include hydrophobic engineering of the surface of the catalyst, employed to trap more CO₂ to increase the local CO₂ concentration in proximity to the catalyst [166–169]. Niu et al. [168] reported a hydrophobic hierarchical Cu catalyst which mimicked the structure of the leaves of *Setaria*. This hydrophobic Cu structure exhibited a maximum $j_{\text{C}_2^+}$ of $255 \pm 5.7 \text{ mA cm}^{-2}$ in a flow cell. Xing et al. [167] showed that polytetrafluoroethylene (PTFE) added to commercial Cu led to the achievement of a partial current density of over 250 mA cm^{-2} . This improvement can be attributed to the enhancement of the CO₂ supply and the suppression of H⁺. DFT calculations showed that the local environment of the hydrophobic electrode could increase the energy barrier of H⁺ desorption, which depresses HER and facilitates CO₂ER [166].

4.4. Flow Pattern

To tackle the problem of the CO₂ mass transfer limitation, different flow patterns have been examined for comparison. Flow patterns can be divided into two configurations: “flow-through” and “flow-by” configurations. The distinction relates to the flow mode in the GDL, which is convective for “flow-through” and diffusive for “flow-by” configurations (Figure 15). The “flow-through” configuration can perform better at limited current densities than the “flow-by” reactor, for the same FE [123].

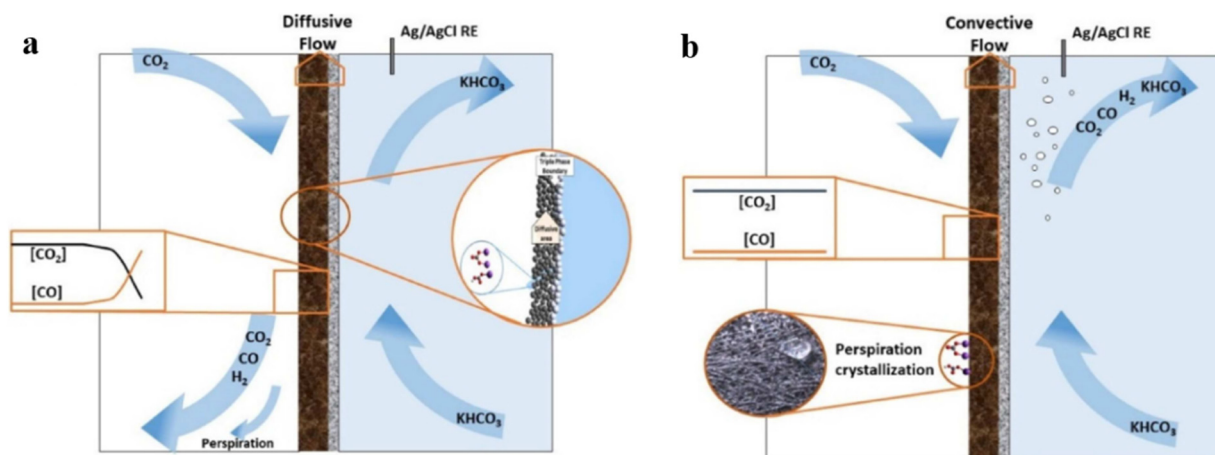


Figure 15. Illustration of two flow patterns: (a) flow-by pattern and (b) flow-through pattern. Reproduced with permission from Ref. [123]. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

In the “flow-through” configuration, the gaseous CO_2 is forced to pass through the pores of the GDE to reduce the thickness of the boundary layer between the GDE surface and the electrolyte, which accordingly alleviates the CO_2 mass transport limitation. Vedharathinam et al. [170] demonstrate a 73-fold increase in j_{CO} using a 3D porous “flow-through” electrode. However, the alkaline environment resulted in carbonate precipitation in the cathode flow channels, partly blocking the CO_2 flow in “flow-through” configurations [43]. Hence, “flow-by” configurations are more common for long-term operations.

Compared with the “flow-through” electrolyzer, CO_2 in a “flow-by” electrolyzer is not pushed through the pores but enters the gas compartment at the top of the cell. The CO_2 gas only accesses the pores by diffusion, and therefore there are no gas bubbles in the catholyte flow channel, and the resistance of the cell is reduced. Nevertheless, in this “flow-by” mode, a pressure difference exists between the two sides of the GDE. The electrolyte may penetrate [134] and ultimately block the pores, preventing CO_2 diffusion, which reduces the active area of the GDE. However, as the pressure difference increases to prevent perspiration, crystallized salt accumulation on the gas side is observed. So indeed, the phenomenon of perspiration has both positive and detrimental effects. The key points are to control the differential pressure across the GDE and manage the perspiration rate to avoid flooding. Jeanty et al. [165] controlled the pressure difference at the GDE by recirculation, to maintain an FE_{CO} of approximately 60% at 150 mA cm^{-2} for hundreds of hours.

5. Electrolyte

Combining catalyst materials modification with varying the local environment can notably reduce the energy barrier for CO_2 reduction processes [161]. Aqueous electrolytes (e.g., KHCO_3 and NaHCO_3) can facilitate H^+ transport and offer a good reaction environment, and therefore most CO_2 ER studies are conducted in aqueous solutions. However, the solubility of CO_2 in water is approximately 34 mM at ambient temperature and pressure. In order to enhance the CO_2 solubility, studies on liquid electrolytes with mixed components (e.g., ionic liquids [50,171]) have been undertaken in recent years. Ionic liquids are a promising absorbent for CO_2 . However, their high cost makes them unsuitable for industrial applications. In recent years, electrolyte design optimization has been widely investigated in terms of electrolyte concentration, pH, cation and anion composition, etc. In this section, we will focus on the above four important effects.

5.1. Concentration

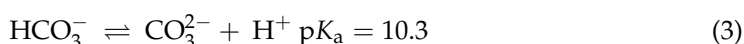
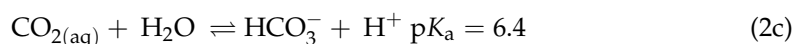
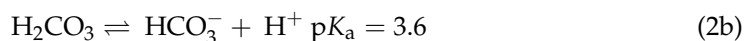
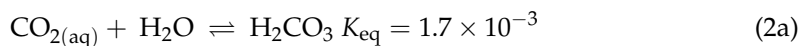
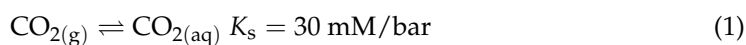
The effect of electrolyte concentration on the reaction rate mainly originates from OH^- , regardless of the type of cation [172]. Higher concentrations of electrolyte lead to a higher concentration of OH^- adsorbed on the catalyst surface, thereby decreasing the charge transfer resistance (R_{ct}) and the thickness of the electrical double layer (EDL) [119]. Verma et al. [172] found that when the electrolyte solution concentration increased from 0.5 M to 3.0 M, the j_{CO} improved by several times. In addition, HER can be significantly inhibited by improving the electrolyte concentration. It was shown that FE_{CO} could be increased by 22% when the KOH concentration changed from 0.1 to 0.5 M. Using a Ag catalyst, it was observed that the FE_{CO} increased linearly with KOH concentration, which is due to the increase in the concentration of K_2CO_3 produced by the capture [151].

However, the range of influence of the electrolyte concentration is narrow, due to the mass transport limitation [76]. Kenis et al. [117] found that when the KOH concentration exceeded 2 M, there was no major increase in j_{CO} , even though the concentration continued to increase. Therefore, from an industrial point of view, lower concentrations of aqueous electrolytes are more cost-efficient.

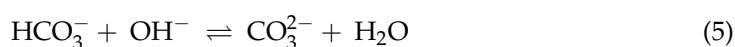
5.2. pH

The pH of the electrolyte plays a crucial part in its selectivity and overpotential. Since the local pH at the surface of the catalyst can increase as CO_2 electroreduction proceeds,

there may be a huge pH difference between the local cathode and the bulk solution [135]. The key equilibrium reactions of the CO₂/bicarbonate system are as follows [173–176]:



When pH > 7, the above can be written as:



The rates of deprotonation reactions (2b, 3, 5) are very high, so it can be assumed that CO₃^{2−} and HCO₃[−] are always in balance [175]. However, the rate of the CO₂ hydration reaction is very low, and thus the concentration of H₂CO₃ is extremely low [174,175]. In addition, the rate of the reaction between CO₂ and OH[−] (Reaction 4) is higher than that of Reaction 2 when pH > 10 [176].

CO₂ER products have high pH dependencies. Early studies showed that the production of C₂H₄ is largely unrelated to pH in H-type cells, unlike the pH-dependent production of CH₄ [177]. In recent years, higher C₂H₄ selectivity has been achieved with a high-pH alkaline electrolyte in flow cells [122]. Gabardo et al. [125] found that alkaline conditions can lead to reduced overpotentials and H₂ production, facilitating CO generation on the Ag catalyst in liquid-phase electrolyzers, while the selectivity for CO decreases as pH increases, which benefits HCOOH formation. A C–C coupling process occurs with high concentrations of OH[−] at the catalyst interface, with high energy input [133]. According to the above studies, we can draw the conclusion that higher pH values have kinetic benefits for CO₂ER and can effectively reduce overpotentials and inhibit the hydrogen evolution side reaction, to obtain higher selectivity in CO₂ electroreduction. However, the concentration of CO₂ will inevitably decline due to the high pH in an H-type cell, so it is challenging to find a balance between the reaction kinetics and mass transfer. For flow cells, this problem can be solved successfully by optimizing the GDE design and employing continuous electrolyte flow. In addition, CO₂ER in acidic media provides an alternative method of eliminating the formation of bicarbonate/carbonate salts. Sargent et al. [178] reported concentrating K⁺ near the active sites of the catalyst to promote CO₂ER on Cu in acid conditions (pH < 1). They achieved a single-pass CO₂ utilization of 77% at a j of 1.2 A cm^{−2}. The presence of K⁺ suppresses HER. With an increase in K⁺ concentration, the selectivity for CO₂ER increased, while the HER selectivity decreased.

5.3. Cation Effects

With regard to cation effects, cation identity is a critical factor for CO₂ER. The hydration tendency of an ion in aqueous solution has a negative correlation with its radius, i.e., the larger the ionic radius, the higher the electrode adsorption. Therefore, large ions such as Cs⁺ can repel H⁺ ions from the cathode [179]. Furthermore, small hydrated cations experience smaller repulsion near the electrode, facilitating CO₂ adsorption [178]. Thorson et al. [179] showed that a large-radius cation, specifically Cs⁺, in an electrochemical flow reactor, could achieve a partial current density of 72 mA cm^{−2} at a cathode potential of −1.4 V.

Saeki et al. [171] found that the cation of the supporting electrolyte played an important role in CO₂ER in tetrabutylammonium tetrafluoroborate (TBABF₄), performed at 200 mA cm^{−2} (20 °C) or 333 mA cm^{−2} (25 °C) under 40 atm, with a CO₂ and methanol

medium (the mole fraction of CO_2 was about 33%), yielding CO as the main product. The TBA ion promoted CO_2 reduction to $\text{CO}_2^{\bullet-}$, which may be stabilized by forming an ion pair, $\{\text{TBA}^+-\text{CO}_2^{\bullet-}\}$ and/or by being directly adsorbed on the catalyst as $\text{CO}_{2ad}^{\bullet-}$. Then, $\text{CO}_2^{\bullet-}$ reacted with CO_2 to produce CO. In addition, the TBA ion offered a hydrophobic environment around the catalyst, which can also benefit CO formation. Ma et al. [60] found that when the cation changed from Na^+ to K^+ , the formation rate of C_2H_4 on an F-modified Cu catalyst increased significantly from 428 to 721 $\mu\text{mol h}^{-1} \text{cm}^{-2}$, while the C_2H_4 formation rate decreased due to the increased production of HCOOH when the cation was changed to Cs^+ . This indicates that excessive H_2O activation capacity is not conducive to the generation of C_2H_4 but is conducive to the production of HCOOH on the F-modified Cu.

5.4. Anion Effects

Anions were found to have a major influence on decreasing the onset potential. Among the available anions, OH^- has outstanding benefits, as HER can be significantly suppressed in an alkaline environment. Moreover, a solution including OH^- , such as a KOH electrolyte can induce high conductivity, which reduces ohmic losses compared with KHCO_3 electrolytes [125]. However, extremely highly alkaline environments are harmful to product selectivity, though this can be offset by higher pressure. Edwards et al. [180] reported a pressurized alkaline electrolyzer with 50 bar of pressurization in 5 M KOH, which demonstrated a full cell EE of 67% at a current density of 200 mA cm^{-2} . As well as alkaline solutions, alkaline polymer electrolytes (APEs) without the addition of an alkaline solution were used as a high-performance CO_2 electrolyzer, achieving an excellent current density of 500 mA cm^{-2} at 3 V (cell voltage) at 60 °C, which can be explained by lower gas permeability leading to a minimized gap between the electrodes and a small ohmic loss [132].

It can be observed that j_{CO} is related to the anion in an aqueous solution, and the influence degree follows the order from the biggest to the smallest: OH^- , CO_3^{2-} , HCO_3^- , and Cl^- . Furthermore, FE_{CO} also changes significantly with the anion, following the sequence: $\text{OH}^- \geq \text{HCO}_3^- > \text{CO}_3^{2-} \approx \text{Cl}^-$ [119]. Specifically, the local environment and the reduction reaction influence each other. The local environment can directly affect the CO_2ER path and dynamics, while CO_2ER also highly affects the local environment [161]. Bhargave et al. [119] proposed that a high j_{CO} was more likely to be obtained under the conditions of a high-concentration CsOH electrolyte with a large flow rate. They performed CO_2 electroreduction on ordinary Ag nanoparticles, achieving a j_{CO} of 417 mA cm^{-2} and an FE_{CO} of 100% at -2.5 V (cell potential).

6. Conclusions and Outlook

This paper systematically summarized the major research conducted at relatively high current densities in order to meet the requirements of industrial applications of CO_2ER . Explorations of metal catalysts, especially the innovations of novel nanostructures and composite materials, are major fields for researchers to develop. In addition, the optimal design of reactors and the arrangement of the reaction microenvironment are also being investigated to improve the activity. Despite remarkable advances having been made in various aspects, long-term experiments at high current densities ($>1 \text{ A cm}^{-2}$) have not yet been carried out stably. On the basis of recent progress, we would like to emphasize four directions for future development:

- (1) The design of cost-efficient catalysts. Novel and cheap catalysts should be developed to replace or reduce the use of noble metals. Tailoring the morphology, crystal structure, and electronic distributions are three important strategies to optimize the usage of the active sites. By introducing heteroatoms (e.g., N, P, or other chalcogens), other metals, or specific functional groups, the lattice defects of metal catalysts such as vacancies and grain boundaries can be regulated.

- (2) Innovations in electrolyzers. Progress is also needed in the design of cheaper electrolyzers with higher efficiency. The facility should also be flexible enough to adapt to different CO₂ resources such as CO₂ captured from flue gas and biogas. At the same time, the use of a GDE (e.g., carbon matrix, PTFE) for stable and large-scale CO₂ conversion should be optimized. In the future, better GDEs with excellent conductivity, hydrophobicity, and appropriate ventilation will be an intriguing development direction.
- (3) Research into non-OER anode reactions. Although the anodic OER reaction is green, it does not yield economic benefits. Coupling CO₂ER with an anode oxidation reaction with more commercial value could be another industrially accessible approach. In this manner, CO₂ electrolyzers could be easily integrated into other industrial processes in which the main product is formed on the anode. The existing challenge is proper product separation.
- (4) The exploration of complicated mechanisms. The electroreduction of CO₂, especially to C₂₊ products, involves various electron transfer processes and the formation of intermediates. Theoretical calculations can provide new insights into the structure–property relationship and the rational design of catalysts. Remarkable effort has been dedicated to obtaining a better mechanistic understanding through DFT calculations and operando/in situ techniques. However, computational models are simplified and limited at present and require further development.

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