



Engineering Flow-Through Hollow Fiber Gas-Diffusion Electrodes for Unlocking High-Rate Gas-Phase Electrochemical Conversion

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Designing advanced electrodes with efficient contact with gas, electrolytes, and catalysts presents significant opportunities to enhance the accessibility of concentrated gas molecules to the catalytic sites while mitigating undesirable side reactions such as the hydrogen evolution reaction (HER), which advances the gas-phase electrochemical reduction toward industrial-scale applications. Traditional planar electrodes face challenges, including limited gas solubility and restricted mass transport. Although commercial flow-by gas-diffusion electrodes can reduce mass transfer resistance by enabling direct diffusion of gas molecules to active sites, the reliance on diffusive gas flow becomes insufficient to meet the rapid consumption demands of gas reactants at high current density. Flow-through hollow fiber gas-diffusion electrodes (HFGDEs) or hollow fiber gas penetration electrodes (HFGPEs) provide a promising solution by continuously delivering convective gas flow to active sites, resulting in enhanced mass transport and superior gas accessibility near the catalytic sites. Notably, HFGDEs have demonstrated the ability to achieve current densities exceeding multiple amperes per square centimeter in liquid electrolytes. This review provides a comprehensive overview of the design criteria, fabrication methods, and design strategies for porous metallic HFGDEs. It highlights the state-of-the-art advancements in HFGDEs composed of various metals (e.g., Cu, Ni, Ag, Bi, Ti, and Zn), with a particular focus on their utilization in the electrochemical conversion of CO₂. Finally, future research directions are discussed, underscoring the potential of porous metallic HFGDEs as a versatile and scalable electrode architecture for diverse electrochemical applications.

1. Introduction

Electrolysis of small gas molecules into high-value commodity products offers a promising strategy to reduce dependence on usage of non-renewable fuel, particularly when powered by renewable electricity.[1-6] For the industrial-scale application of these electrolysis processes, achieving a high current density exceeding 200 mA cm⁻² with a high selectivity (Faradaic efficiency (FE) > 80%) and long-term operation stability (>10,000 h) is essential to minimize capital expenditures.^[7] To approach this goal, several challenges must be addressed. Gas molecule reactants such as CO₂ and N₂ possess strong chemical bonds (C=O, 732 kJ mol⁻¹; N \equiv N, 945 kJ mol⁻¹), requiring multiple electron and proton transfer for their reduction.[8-12] Hydrogen evolution reaction (HER) is a major side reaction in gas-phase electrochemical reduction reactions (e.g., CO2RR), as both processes compete for protons and electrons at the same catalytic sites, with HER having a lower activation energy barrier. HER is particularly favored when the availability of the reactive gas at the electrode surface is limited, leading to an increased reaction rate.^[13,14] The gas reduction reactions

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Figure 1. a) A comparison diagram of the partial current density of CO (PCD_{CO}) for the state-of-the-art electrocatalyst coupling with non-gas-diffusion electrodes (Non-GDE), flow-by gas-diffusion electrodes (flow by-GDE), and flow-through hollow fiber gas-diffusion electrodes (flow through-HFGDE) for electrochemical conversion of CO₂ to CO. Schematic of gas diffusion of b) Non-GDE, c) flow by-GDE, and d) flow-through HFGDE. e) schematic of the HFGDE for gas-phase electrochemical reaction.

are further constrained to occur only at the triple-phase interface formed by gas, catalysts, and electrolytes. $^{[15-18]}$

Recent studies have made encouraging progress in developing highly efficient electrocatalysts, achieving excellent Faradaic efficiencies (FEs) under specific conditions.^[19–28] However, the majority of these electrocatalysts are deposited on conductive planar/porous electrodes and tested in a batch H-Cell setup, which inherently limits current density (**Figure 1**a). This is because the reactive gases are bubbled into the catholyte, and their low solubility results in significant mass transfer resistance of gas within the liquid phase (Figure 1b).^[9,13,14,29] Gas-diffusion electrodes (GDEs) can address these limitations by quickly diffusing reactive gas to active catalytic sites, thereby improving mass transfer and reaction kinetics (Figure 1c).^[13,29] When integrated into flow cells under alkaline conditions, GDEs have demonstrated industrially relevant current densities exceeding 200 mA cm⁻².^[6,3035] Compared to planar or porous electrodes (Figure 1a), the improved mass transfer in GDE configuration delivers an

order-of-magnitude enhancement in current density (Figure 1a).^[30–35] Despite these advancements, the availability of reactive gas becomes insufficient with diffusive gas flow alone at ampere-level current densities, where the rapid consumption of gas reactants exacerbates mass transfer limitations. This prevents further increase in current density and hinders the maintenance of high Faradaic efficiencies, posing a significant challenge for scaling up the gas-phase electrochemical reduction process for industrial applications.^[4,36]

Impressively, flow-through HFGDEs have demonstrated remarkable performance, achieving ampere-level current densities,[37-41] e.g., an extraordinary partial current density of CO with 4.3 A cm⁻² has been achieved on nanostructured Ag-based HFGDE in acidic conditions.^[41] This exceptional performance of HFGDEs is attributed to the unique flowthrough architecture, which delivers convective gas directly to catalytic sites, significantly enhancing mass transport and providing superior gas accessibility at the triple-phase interfaces (Figures 1d,e).^[36] The inner wall of hierarchically porous hollow fibers consists of fused metal particles forming an interconnected 3D network, while the outer surface is decorated with densely packed nanostructured electrocatalysts (Figure 1e). This unique architecture of HFGDEs provides a compact, self-supported structure, enabling a simplified cell design by allowing direct immersion into the catholyte with sealed ends. The lumen side of HFGDEs can serve as a gas chamber, while the porous hollow fiber walls function as gas diffusion layers. The high surface-to-volume ratio of HFGDEs also enables dense packing, making them highly suitable for industrial applications. Moreover, the convective flow provided by HFGDEs configuration effectively mitigates flooding, a common issue during the CO₂RR.^[42,43] Flooding arises from a significant loss of GDE hydrophobicity caused by electrowetting under applied potentials. This further causes the infiltration of electrolytes into the GDE pore structure, blocking the CO₂ diffusion pathways and compromising both performance and stability.^[44,45]

To underscore the advances of flow-through HFGDE at ampere-level current density, CO2 transportation in HFGDEs operating in gas-penetrating mode and non-gas penetrating modes has been modeled and evaluated.^[42,43] In gas-penetrating mode (Figure 2a), the end of HFGDE was sealed, forcing CO_2 to permeate through the hollow fiber walls and interact with the active catalytic sites, providing an ample CO₂ concentration and maximizing the formation of triple-phase boundaries, thereby promoting reaction kinetics. Conversely, the non-gas-penetrating mode (Figure 2b) featured an open end, allowing CO₂ to flush directly into the electrolytes, which resulted in a limited CO₂ supply near active sites. For instance, bismuth HFGDEs operating in gas-penetrating mode achieved an ampere-level partial current density of formate, outperforming its non-gas-penetrating counterparts, which reached a maximum value of only 36 mA cm⁻².^[43] These results highlight the importance of maintaining sufficient CO₂ supply near active sites to enhance reaction kinetics (Figure 2c). Modeling studies further visualized CO_2 distribution on the Bi HFGDE in both modes (Figure 2d). In gaspenetrating mode, CO₂ continuously rushes through the hollow fiber micron channels to reach electrode-electrolyte interfaces, while the turbulent flow also promotes localized mixing of reactants. In contrast, in non-gas-penetrating mode, the pore structure of HFGDE becomes flooded, and CO_2 is primarily supplied from bulk electrolytes, limiting mass transport and reaction rates.^[43] CO_2 velocity (Figure 2e) and pressure (Figure 2f) profiles in gas-penetrating mode indicate that CO_2 initially accelerates through the micron-channels before gradually decreasing outward, effectively spreading around active sites.^[42] However, in non-gas-penetrating mode, lower CO_2 velocity (Figure 2g) and pressure (Figure 2h) result in minimal CO_2 flow through the hollow fiber walls, with most CO_2 relying on diffusion from bulk electrolytes.^[42] Therefore, the flow-through HFGDE configuration facilitates an adequate and continuous gas supply at triplephase boundaries, significantly enhancing mass transport and reaction kinetics to achieve ampere-level current densities, making it a robust design for industrial-scale applications.

Regarding the development of HFGDEs, early hollow fiber configurations for flow batteries and solid-oxide fuel cells demonstrated the advantages of tubular architecture over conventional planar designs.^[46–48] In this context, we acknowledge I.D. Raistrick's research on porous electrodes, which provides key insights and fundamental theories into the evolution of cathodes from planar to porous materials.^[49,50] For gas-phase electrochemical reduction, Kas et al. pioneered the development of hierarchically porous Cu HFGDE in 2016, achieving at least an order-of-magnitude higher partial current density of CO compared to polycrystalline Cu electrodes.^[51] Since then, the design of HFGDEs has been focused on the fabrication and metal selection (e.g., Cu, Ag, Ti) for bulk HFGDE to optimize product selectivity and catalytic activity.^[37,52–56] The performance of metallic HFGDEs is intricately linked to their porosity, conductivity, and mechanical strength, all of which can be tailored by adjusting fabrication parameters such as reduction temperature.^[57] Beyond bulk properties, surface engineering can further enhance the performance of bare-surface HFGDE by providing more active sites, while introducing heteroatom (alloying or doping) modifies the electronic structure, and fine-tunes the product selectivity.^[38,58,59] Finally, engineering of the electrode-electrolyte interface plays a pivotal role in realizing the full potential of HFGDEs, enabling ampere-level current densities with improved efficiency and selectivity.[37,60,61]

Excellent material-focused reviews for gas-phase electrolysis have been published in recent years, focusing on electrocatalyst development, electrode and electrolyzer design.^[62-71] This review specifically aims to provide a comprehensive overview of the material selection and design strategies for advanced HFGDEs, offering guidance for their application in gas-phase electrochemical reactions. We start by outlining the key design criteria for fabricating HFGDEs, including metal selection and geometric considerations. Next, we explore the fabrication techniques for various metallic HFGDEs (e.g., Cu, Ag, Bi, Ti, Ni, Zn). The review also delves into recent progress in HFGDEs for gas-phase electrolysis processes such as CO₂ reduction reaction (CO₂RR), CO reduction reaction (CORR), and nitrogen reduction reaction $(N_2 RR)$. Finally, we provide a forward-looking perspective on the future of HFGDEs, offering insights and recommendations for addressing existing challenges and exploring new opportunities for their application in scalable, high-performance electrochemical processes.

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Figure 2. a) gas penetrating and b) non-gas penetrating modes for dislocated lattice bismuth hollow fiber (D-Bi HF). c) Partial current densities of format for D-Bi HF in gas penetrating and non-gas penetrating modes. d) Finite element simulations based on COMSOL Multiphysics. CO₂ concentration diffusion of CO₂-penetrating and non-penetrating modes for D-Bi HF. Reproduced with permission.^[43] Copyright 2023, Elsevier B.V. Simulation results of e) velocity and f) pressure distributions for bismuth hollow fiber (Bi HF) in gas-penetrating mode. g) velocity and h) pressure distributions for Bi HF in non-gas-penetrating mode. Reproduced with permission.^[42] Copyright 2023, Elsevier B.V.







Figure 3. Design criteria for preparing metallic hollow fiber gas-diffusion electrodes.

2. Design Criteria for Hollow Fiber Gas-Diffusion Electrodes

The design criteria for HFGDEs are outlined in **Figure 3**, where factors such as conductivity, abundance, and intrinsic catalytic activity play a crucial role in the selection of metals. Additionally, fabrication conditions must be carefully integrated to assess other essential properties, including reducibility, porosity, gas permeance, and mechanical strength. Achieving a high-performance HFGDE requires a balanced optimization of these factors to ensure efficient gas diffusion and electrochemical performance. For example, a medium reduction temperature, such as 600 °C, was chosen for reducing HFGDEs, as higher temperatures (above 625 °C) can improve mechanical strength but tend to reduce porosity significantly.^[72,73] This review specifically focuses on Cu, Ag, Ni, Bi, and Ti-based hollow fibers, as these materials have shown significant contributions to various gas-phase electrochemical conversions.

A high conductivity of the metal is crucial for enhancing the availability of active sites, which directly influences the electro-

chemical performance of HFGDEs.^[74,75] The conductivity of several primary metals can be ranked in the following order: Ag > Cu > Al > Zn > Ni > Fe > Pt > Sn > Ti > Bi. From an economic and scalability perspective, it is of great significance to consider the Earth's abundance of these metals.^[76,77] The abundance of these metals can be ranked as follows: Al > Fe > Ti >> Ni > Zn > Cu > Sn >> In > Ag > Pd > Bi >> Pt > Au. Therefore, noble metals such as Pt and Au are typically excluded from the fabrication of related HFGDEs due to their low abundance and high cost.

The intrinsic activity of metals plays a crucial role in determining the product selectivity during the electrochemical reduction of small gas molecules.^[4,12,78] Specifically, for the electrochemical conversion of CO₂, metals such as Ti, Fe, Ni, and Pd facilitate the HER.^[79] In contrast, Au, Ag, and Zn are effective in producing carbon monoxide.^[25,28,80] In, Sn, Bi, and Pb tend to favor the production of formic acid, while Cu is known for its activity in producing hydrocarbons or alcohol. The unique d-band electronic structure of Cu, combined with its moderate binding strength for CO intermediates, enables the stabilization of key reaction intermediates (e.g., CO, CHO, OCCO), promoting C-C coupling

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and facilitating the formation of C₂₊ products.^[8,20,81–83] For the electrochemical reduction of N₂, noble metals like Au and Ag have shown promising potential as electrocatalysts for nitrogen reduction reaction (N₂RR).^[84,85] Cost-effective transition metals, such as Mo, Fe, Ti, and Mn, have garnered significant interest for N₂RR due to their valence electrons being near the Fermi level in their d bands, which results in favorable intrinsic activation barriers and improved reaction kinetics.^[78,86] Additionally, main group metals like Sn and Bi are also considered potential candidates for N₂RR because of their affordability, adjustable electronic structures, and low HER activity.^[87,88]

Among these intrinsic properties of metals, the fabrication process can influence other essential features (e.g., microstructure, mechanical strength) of HFGDE. During fabrication, hollow fibers must undergo air calcination to eliminate the nonconductive polymer binders, which results in the formation of corresponding metal oxide.^[51,72] Typically, a straightforward hydrogen reduction at medium temperature is performed to convert the metal oxide into its reduced form.^[51] Therefore, certain metals with stable oxides (e.g., Al2O3) are not suitable candidates for fabricating metallic hollow fibers. It should be noted that the reduction temperature is related to the growth of metal particles, which in turn affects the porosity, conductivity, and mechanical strength of HFGDEs. In light of this, we have expanded the discussion on section 3, which focused on the fabrication of Cu HFGDEs. At last, it is of great importance to evaluate these features via suitable methods for further enhancing the performance of related HFGDEs.^[72] For instance, a mercury porosimeter, or a porosimeter that uses the capillary flow porosimetrybased liquid extrusion technique, provides a more accurate measurement of the micron pore size distribution in HFGDEs. The bending strength can be assessed using the four-point method on a mechanical strength testing system. Additionally, resistivity can be measured using a four-probe method with a potentiostat. In summary, the optimal design of high-performance HFGDEs requires excellent electrical conductivity, facile reducibility, sufficient material abundance, high gas permeability, and moderate mechanical strength. Conductivity and reducibility are crucial for minimizing ohmic resistance and enabling efficient electron transfer. Material abundance must also be considered to ensure economic feasibility for large-scale implementation. Moreover, excessive mechanical strength compromises gas permeability; thus, a balance between structural integrity and efficient gas transport is preferred. Finally, intrinsic catalytic activity is not a primary criterion, as a tailored catalyst layer can be applied to the outer surface of HFGDEs to facilitate the desired electrochemical reaction.

3. Fabrication Methods

3.1. Fabrication of Cu Hollow Fiber

The earth's abundance, affordability, excellent conductivity, reducibility, and intrinsic activity toward electrochemical conversion make Cu an ideal candidate for fabricating HFGDEs. The fabrication of Cu HFGDE can serve as a typical example for preparing metal-based HFGDEs, and the following section highlights this process in detail.

The fabrication of Cu hollow fibers builds on established methodologies for fabricating polymeric microtubular electrodes, primarily relying on phase inversion and thermal calcination (Figure 4).^[89] Specifically, the polymeric dope is prepared by dispersing copper precursors (e.g., Cu, CuO) and polymer binders (e.g., polyethersulfone, polysulfone) into organic solvents like N-Methyl-2-Pyrrolidone (NMP) and Dimethylformamide (DMF) using ultrasonication to prepare a homogeneous dope solution. The polymeric dope is extruded through a spinneret rig into a non-solvent bath, typically water, where phase inversion occurs. During this process, the organic solvents migrate into the non-solvent bath and are replaced by the water, causing polymer solidification. Various factors, including the composition, viscosity, flow rate of the extruding dope and bore water, the air gap, and the temperature of the non-solvent, significantly influence the phase-inversion process and the resulting porosity of the fibers.^[90]

Furthermore, the non-conductive polymer binder is removed through a two-step thermal calcination process, which involves burning out the polymer in air and subsequently reducing the oxidized metal precursors in a reducing atmosphere (e.g., H2/inert gas mixture). The micron porous structure of HFGDE primarily develops during the oxidation step. Optimization of the oxidation step, including the temperature and duration, is essential to ensure complete removal of the polymer binder while preserving the desired porosity. The thermogravimetric analysis revealed that the primary weight loss for Cu hollow fiber occurs between 300-380 °C, corresponding to the decomposition and combustion of the polymer binder. Following this, the weight begins to increase due to the oxidation of copper particles, stabilizing between 550-1000 °C, which indicates that the majority of polymer can be removed when the temperature exceeds 600 °C.^[57] The impact of calcination duration on pore size distribution was also investigated. Samples subjected to different calcination durations (1-4 h) showed no significant differences in pore size distribution, suggesting once the majority of polymer is removed, extending the calcination duration has minimal influence on the microstructure of fibers.^[57]

The reduction process is a critical step in determining the final properties of hollow fibers, such as porosity, mechanical strength, and conductivity. H₂-temperature programmed reduction analysis revealed that the reduction of CuO starts at temperatures above 250 °C, reaching its peak reduction rate at 300 °C, confirming efficient reduction at temperatures beyond this threshold. X-ray diffraction further validated the conversion of CuO into metallic Cu during the reduction.^[51] Reduction at lower temperatures (<400 °C) preserves the micron-scale porous structure crucial for gas permeance.^[51] However, fibers reduced at these temperatures tend to exhibit fragility and insufficient mechanical strength. On the other hand, higher reduction temperatures enhance mechanical strength and conductivity due to the growth, fusion, and bonding of copper particles. For instance, as the reduction temperature rises from 400 to 625 °C, the pore size decreases from \approx 3 to 1 µm, with negligible micron-scale pores observed at 700 °C.^[72] Correspondingly, N₂ permeance decreased from 1.23×10^{-4} to 9.11×10^{-5} mol m⁻² so p, with a drastic drop to 1.19×10^{-9} mol m⁻² so p at 700 °C.^[72] In contrast, mechanical strength improves significantly, rising from 52 MPa at 400 °C to 124 MPa at 700 °C.^[72] Electrical resistance also decreased with





Figure 4. Schematic of fabrication of hollow fiber electrode via dry-wet process. Reproduced with permission.^[89] Copyright 2023, Elsevier B.V.

increasing reduction temperature, with fibers at 400 °C exhibiting four times higher resistance compared to those reduced at 700 °C. The improvement in conductivity is attributed to the wellfused copper particles and enhanced metallic bonding.^[72] Despite these benefits, the loss of porosity at high reduction temperatures compromises the fiber's function as a gas diffuser, which is critical for electrochemical reactions. Striking a balance between porosity, mechanical strength, and conductivity is essential to fully leverage the potential of HFGDEs.

3.2. Fabrication of Non-Cu Hollow Fibers

While Cu hollow fibers offer high conductivity, mechanical strength, and affordability, their broad activity in CO₂RR results in various products (e.g., CO, formate, C2+), which motivates the exploration of non-Cu HFGDEs for the selective production of high-yield single products. In the following section, we delve into the fabrication of non-Cu hollow fibers. The preparation of non-Cu hollow fibers involves reduction processes tailored to the specific properties of each metal and its precursors, which employ distinct reduction gases and temperatures. Ni fibers are typically fabricated using Ni-based precursors (e.g., Ni, NiO), which are reduced in the H₂ atmosphere to achieve the metallic Ni structure.^[90-93] Ag fibers leverage the thermal decomposition of silver oxide. These fibers are calcined in air at 600 °C, as silver oxide decomposes at temperatures above 200 °C, directly forming metallic Ag fibers without additional reduction steps.^[94] Bi fibers, due to the low melting point of Bi (274.1 °C), require a more intricate preparation process involving multiple steps to ensure structural integrity and the desired properties. First, the green Bi fibers

are first sintered in air at 550 °C for 6 h and then reduced in hydrogen at 250 °C for 12 h. Following this, the fibers are calcinated in argon at 720 °C for 6 h, and subsequently in air at 500 °C for 4 h to produce Bi_2O_3 HF. Finally, Bi_2O_3 HF is reduced in 0.1 M NaBH₄ for 2 h to obtain Bi/Bi_2O_3 HF. The Bi/Bi_2O_3 HF electrode is then electrochemically reduced at a fixed potential of -0.3 (V vs RHE) to obtain pure metallic Bi HF.^[42,43] The intrinsic structural stability of ZnO hinders its reduction in a hydrogen atmosphere. To address this, Zn fibers are synthesized via a two-step electrochemical reduction process in a three-electrode system. Initially, a constant potential of -1.4 V vs Ag/AgCl is applied for 900 s to reduce surface ZnO and enhance electron conductivity. Subsequently, a high current density of -400 mA cm⁻² is applied to facilitate the rapid reduction of bulk ZnO to metallic Zn.^[95]

The fabrication of Ti fibers differs significantly from those used for Cu, Ni, Ag, and Bi fibers due to the unique properties of Ti. Specifically, H₂ treatment at elevated temperatures leads to the embrittlement of Ti. Additionally, Ti is highly reactive at high temperatures, readily oxidizing and interacting with various substrates. For instance, Ti can reduce Al_2O_3 at 800 °C and interactions between Ti and SiO₂ have been observed at temperatures exceeding 800 °C. Regarding this, Al_2O_3 crucibles were used for thermal oxidation, SiO₂(quartz) tubes for 800 °C treatment, and Mo foil for applying 1100 °C treatment. The oxidation process was performed at 475 °C for 8 h with a slow ramping rate of 3 °C min⁻¹ to carefully remove the non-conductive polymer binder without premature oxidation, and the reduction process was conducted at 800 °C for 8 h in argon to metallic Ti fibers.^[56]

Figure 5 presents SEM images of cross-sections and outer surfaces of hollow fibers fabricated from different metals. The cross-sectional images of hollow fibers exhibit macro voids





Figure 5. SEM images of a) cross-sectional and b) outer surface of Cu HF (scale bar 100 µm for a, 1 µm for inset, and b). Reproduced with permission.^[52] Copyright 2021, Elsevier B.V. SEM images of c) cross-sectional of Cl-SnO₂@Ni HF, and outer surface of Ni HF. Reproduced with permission.^[93] Copyrights 2025, Wiley-VCH GmbH. SEM images of e) cross-sectional and f) outer surface of Ag HF. Reproduced with permission.^[37] Copyrights 2022, Wiley-VCH GmbH. SEM images of g) cross-sectional of Bi/Bi₂O₃ HF and h) outer surface of Bi HF. Reproduced with permission.^[42] Copyright 2023, Elsevier B.V. SEM images of i) cross-sectional and j) outer surface of Zn HF. Reproduced with permission.^[95] Copyright 2025, American Chemical Society. SEM images of k) cross-sectional and l) outer surface of Ti HF. Reproduced with permission.^[56] Copyright 2023, Royal Society of Chemistry.

extending from the interior toward a denser, sponge-like outer structure (Figure 5a,c,e,g,i,k). The images of the external surface of the fibers show that the fibers are composed of aggregated metal particles forming an interconnected 3Dporous structure (Figure 5b,d,f,h,j,l). The extent of metal fusion is strongly influenced by the melting point and the applied reduction temperature. The relatively lower melting points of Cu, Ni, and Ag resulted in the fused metal particles from the outer surface of Cu HF (Figure 5b), Ni HF (Figure 5d), and Ag HF (Figure 5f), while the Ti spheres in Ti HF (Figure 51) are connected less extent due to a high melting point of Ti. The Bi HF (Figure 5h) and Zn HF (Figure 5) develop rough surfaces after an additional electrochemical reduction of their respective metal oxides, leading to increased catalytic sites and morphology evolution. The 3Dporous architecture of hollow fiber electrodes provides a compact, selfsupported structure, offering significant potential for high-rate and efficient gas-phase electrochemical reduction through enhanced mass transport.

4. Design Strategies of Hollow Fiber Gas-Diffusion Electrodes

In this section, we have summarized the design strategies for HFGDEs into four parts (Figure 6), including fabrication en-

gineering, surface engineering, introducing heteroatoms, and electrode-electrolyte interface (EEI) engineering.

4.1. Fabrication Engineering

The engineering design of HFGDE can be initiated by optimizing the fabrication parameters. Critical factors such as metal type, particle size, and reduction conditions significantly influence the electrode properties, including the structure of the electrocatalyst, electrochemical surface area (ECSA), conductivity, mechanical strength, and porosity, resulting in different electrochemical performance of HFGDEs.

The selection of appropriate metals for HFGDEs fabrication enables precise control over product selectivity. For instance, Ag HFGDE or Zn HFGDDE can achieve a Faradaic efficiency exceeding 90% for carbon monoxide, while Bi HFGDEs demonstrate over 90% Faradaic efficiency in formate production.^[42,95,96] Cu HFGDEs are particularly effective for generating C₂₊ products such as hydrocarbons and alcohols.^[104] Additionally, Ti HFGDE offers excellent stability, facilitating efficient electrochemical conversion of nitrate to ammonia in acidic electrolytes.^[56] Beyond single-metal systems, the incorporation of mixed-metal powders offers a strategy to fine-tune product





Figure 6. Designing strategies of hollow fiber gas-diffusion electrodes.

selectivity by adjusting metal-powder ratios. For example, the Faradaic efficiency for formate in CuSn HFGDEs varies depending on the Cu/Sn content ratio, while modifying Sb content in CuSb HFGDEs can tune CO selectivity.^[98,99]

In addition to optimizing product selectivity through metal selection, increasing the ECSA is a straightforward method to enhance the current density of HFGDEs. For instance, CuAl alloy powders have been used to fabricate porous Cu HFGDEs via the alloying-dealloying method.^[100] This process involves sacrificing the templated metal Al, resulting in a surface area increase by a factor of 50 compared to the non-porous precursor. The enlarged surface area contributed to a high current density of -18 mA cm⁻² at -0.4 V vs RHE, surpassing the performance of Cu HFGDEs reported by Kas's group.^[51]

The use of smaller metal powder sizes can further enhance the ECSA of HFGDEs by providing more accessible corner and edge catalytic sites, in addition to tuning product selectivity. A series of Cu HFGDEs were prepared by using different sizes of Cu powders (10 nm, 100 nm, and 10 μ m). The Cu-10 nm and Cu-100 nm HFGDEs predominantly produced CO, while the Cu-10 μ m electrode favored the production of formate. The smaller particles, with a higher density of corner and edge sites, facilitated CO production, whereas the larger particles, with more flat sites, preferentially promoted formate formation.^[101]

The variation in reduction conditions can modulate grain boundaries and crystal facets, thereby influencing the product selectivity of HFGDEs. Cu HFGDEs prepared under different reduction conditions exhibited distinct product selectivity at lower potentials. For instance, the Cu (1-2 μ m) HFGDE reduced at 280 °C in 4% H₂/Ar exhibited a high CO FE of 75% at a -0.4 V (vs RHE).^[51] In contrast, Cu (1 μ m) HFGDE reduced at 650 °C in H₂/Ar mixture exhibited mixed Cu (110) and Cu (100) crystal facets, resulting in a formate selectivity of 77% at -0.9 V (vs RHE).^[73] Furthermore, a Cu (500 nm) HFGDE reduced at 500 °C in 5% H₂/Ar exhibited a predominant Cu (111) crystal facet, delivering a high formate FE of 86% at -0.9 V (vs RHE). The DFT calculation revealed that the formation of formate is particularly favorable on the Cu (111) crystal facet through the second protonelectron transfer step.^[102]

4.2. Surface Engineering

Building upon the advancements in fabrication engineering, surface engineering emerges as a vital approach to further enhance the electrocatalytic performance of HFGDEs. This enhancement is achieved by in-situ surface restructuring or depositing nanostructured electrocatalysts, effectively transforming smooth bulk surfaces into rough surfaces enriched with abundant active sites. In this section, we provide a comprehensive overview of surface engineering strategies, emphasizing their role in improving the performance of HFGDEs.

4.2.1. Surface Re-Structuring

In-situ surface re-structuring via oxidation and reduction is an effective method for increasing the electrochemical surface area and enhancing the electrocatalytic activity of metallic HFGDEs. Through oxidation and reduction, substantial enhancement has been achieved for Ag, Cu, and Bi HFGDEs, exhibiting beneficial properties such as increased surface roughness and active sites, introduced oxygen vacancies, contractive metal bonds, dislocated lattice, reaction-favorable crystal facet, and distinguished grain boundaries.

Surface re-structuring via anodic oxidation combining electrochemical reduction can effectively enhance the surface roughness and active sites of HFGDEs. This strategy also enables precise tailoring of surface crystal morphology by introducing surface modifiers (e.g., $\rm Cl^-$, $\rm CO_3^{2-}$) during the oxidation stage. For ADVANCED SCIENCE NEWS www.advancedsciencenews.com

instance, the Ag HF enriched with silver nanosheets (NS@Ag HF) was prepared by anodizing Ag HF in NaCl solution.^[39] During this process, metallic Ag was first oxidized to AgCl nanosheets, which were subsequently reduced to Ag nanosheets (Figure 7a). Compared to the smooth surface of pristine Ag HF (Figure 7b), the structured electrode exhibited a dense and thick layer of silver nanosheets (Figures 7c,d), leading to a significantly enlarged ECSA. Tafel slope analysis (Figure 7e) showed that NS@Ag HF displayed the smallest slope, indicating the reconstructed nanosheets facilitate electron transfer, optimize the adsorption and activation of reaction intermediates, and accelerate reaction kinetics (Figure 7f). In a similar study, Ag HF (Figure 7g) underwent oxidation and reduction in KHCO₃ solution, transforming its smooth surface (Figure 7h) to activated structure with hierarchical micro/nanostructures (Figure 7i), resulting in more than a threefold increase in ECSA and at least an order-of-magnitude higher partial current density for CO compared to bare Ag HF (Figure 7j).^[38]

Surface restructuring through electrochemical oxidization and reduction can create surface oxygen vacancy, which can lead to an electronic-rich surface, adjusting the adsorption of intermediates and thereby enhancing reaction kinetics. An oxygen vacancy-rich E-Cu HF was prepared by cyclic voltammetry (CV) scanning acid-etched Cu HF in a 0.5 м КНСО₃ solution (Figure 7k). The surface atomic ratio of Ov in E-Cu HF was 1.8 times higher than that of Cu HF, indicating the formation of a substantial number of low-coordinated Cu sites that facilitate CO₂ activation.^[103] Operando Ramen spectroscopy confirmed the presence of abundant surface-adsorbed *CO₂ intermediates on the E-Cu HF electrode. Similarly, AgHF(O)-ER was fabricated by electro-oxidization in a 0.2 M NaOH solution, followed by in-situ electrochemical reduction in a 0.5 м КНСО₃ solution (Figure 7l). The resulting electrode with unique micro/nanostructure can stabilize the *COOH intermediate, promoting the CO2RR kinetics for CO formation.^[94]

Surface restructuring through in-situ electrochemical oxidization and reduction can induce metal bond contraction and dislocated lattices, creating high-energy interfaces that reduce energy barriers and modify the adsorption behavior of reaction intermediates. The Bi HF with contraction of Bi-Bi bonds was fabricated by in-situ electro-reduction of Bi/Bi₂O₃ HF (Figure 8a).^[42] Wavelet transform plot showed a slight contraction of Bi-Bi bond length (Figure 8b). This was further corroborated by the shift of the Bi (012) diffraction peak to a high degree (Figure 8c), indicating the compression of unit cell and the contraction of Bi-Bi bonds. Density functional theory (DFT) calculations revealed that the contracted Bi-Bi bonds reduce the free energy of forming key intermediates (*OCHO), critical for format formation, making the reaction more thermodynamically favorable (Figure 8d). In another study, the lattice-dislocated Bi HF (D-Bi HF) was prepared by electrochemical oxidation and reduction in the KCl solution, and the formed BiO_vCl_v species can rapidly release non-metallic elements to create lattice defects.^[43] Highresolution TEM analysis revealed a lattice spacing of 0.34 nm in the "T" region (Figure 8e), representing a $\approx 6\%$ lattice plane expansion due to dislocations. The strained lattice reduced the free energy for HCOO* formation to 0.64 eV, compared to 0.96 eV for Bi HF without lattice dislocation (Figure 8f). As a result, D-Bi HF achieved an almost perfect Faradaic efficiency for format (99.5%)

www.advmat.de with a remarkable partial current density of 1010 mA $\rm cm^{-2}$ at -0.98 V vs RHE (Figure 8g). Surface restructuring via in-situ electrooxidation and reduction could also promote the formation of reaction-favorable crystal facets and create distinctive grain boundaries, which can significantly enhance the selectivity of copper-based catalysts for C₂₊ products. A Cu (100)-rich Cu HF with a distinctive grain boundary between Cu (100) and Cu (111) was prepared via insitu electrooxidation of Cu HF to CuO nanowire in 3 M KOH and then electrochemical reduction to Cu HF with plentiful microparticles and dense nano spines (Figure 8h).^[97] Compared to Cu HF (Figure 8i) with a smooth surface, the activated Cu HF (Figure 8j) with hierarchical micro-nano structures possessed more than three times ECSA. The HR-TEM confirmed the existence of Cu (100) and Cu (111) grain boundaries in activated Cu HF (Figure 8k), in contrast to Cu HF (Figure 8l), which only ob-

served the Cu (111) crystal facet. The surface ratio of Cu (100) to Cu (111) is closely related to the product distribution (C_{2+}/C_1) , the Cu (100) facet is thermodynamically favorable for C–C coupling. A higher C_{2+}/C_1 ratio (ca. 4.8 at 2.3 A cm⁻², -1.94V) was achieved in activated Cu HF, higher than that of Cu HF (ca. 0.7 at 1.6 A cm⁻², -3.66V), as the surface area ratio of Cu (100) to Cu (111) in activated is about 6 times higher than that of Cu HF.

4.2.2. Surface Deposition

Aligning with in-situ surface restructuring, the direct deposition of nano-structured electrocatalysts can also be an effective method to increase the electrochemical surface area while also fine-tuning the selectivity of HFGDEs. Unlike powder-based electrocatalysts, the deposited electrocatalysts do not require a binder, which maximizes the active surface area and enhances the mechanical stability.^[104,105] Additionally, the interconnected porous structure of these electrocatalysts facilitates better gas distribution and excellent charge transfer. As a result, the metallic HFGDEs can serve as efficient gas diffusers and electron conductors for loading various nanostructured electrocatalysts. Techniques such as electrodeposition, galvanic replacement reaction (GRR), chemical vaporing deposition (CVD), hydrothermal growth, and spraying coating have been utilized to grow nanostructured electrocatalysts on the outer surface of HFGDE, resulting in tuned surface morphology, ECSA, electronic state, surface wettability, crystal facet of deposited electrocatalysts on HFGDEs.

Electrodeposition is a straightforward and effective strategy for depositing nanostructured electrocatalysts, offering precise control over catalyst morphology and performance. Several deposition parameters, including metal substrates, composition and concentration of electrolytes, surfactants, deposition techniques, applied current or potentials, and deposition duration, influence the final properties of electrocatalysts.^[106–111] For instance, the pulse electrodeposition technique has been demonstrated to facilitate the uniform growth of 2D morphology nanosheets on HFGDE surfaces (**Figure 9a**).^[52,112] This technique could help maintain a stable concentration of metal ions near the electrode, promoting consistent nucleation and uniform crystal growth. As a result, dense bismuth nanosheets (Figure 9b) with a thick layer (Figure 9c) were successfully deposited on Cu HF, achieving



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Figure 7. a) Schematic of in-situ fabrication of silver nanosheet-based silver hollow fiber (NS@Ag HF). SEM image of the outer surface of b) silver hollow fiber (Ag HF), c) NS@Ag HF, and cross-sectional SEM image of d) NS@Ag HF. e) Tafel slopes of NS@Ag HF electrodes. f) Reaction steps for silver catalysts with smooth or nanosheet-standing surface for electrochemical reduction CO₂ to CO. Reproduced with permission.^[39] Copyrights 2023, Wiley-VCH GmbH. g) Optical image of the as-prepared Ag HF tubes. SEM image of the outer surface of h) Ag HF, and i) activated Ag HF, scale bars in h and i are 5 µm and 500 nm. j) Partial current density of CO for different silver-based electrodes. Reproduced with permission.^[38] Copyright 2022, spring nature limited. k) Schematic of Cu-based hollow fiber preparation. Reproduced with permission.^[103] Copyrights 2023, Elsevier Ltd. I) Schematic of preparation of silver microparticle rich Ag HF via electrochemical oxidation and reduction. Reproduced with permission.^[94] Copyrights 2024, American Chemical Society.



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Figure 8. a) Schematic of the preparation of Bi HF. b) Wavelet transforms for the k3-weighted Bi K-edge EXAFS signals of different bismuth samples. c) Enlarged XRD diffraction peaks of (012) plane. d) Free-energy profiles for formation production over different Bi crystal planes with contractive and normal Bi—Bi bonds, respectively. Reproduced with permission.^[42] Copyright 2023, Elsevier B.V. e) IFFT patterns of (012) plane of dislocated-lattice bismuth. f) Calculated free energy change diagram for CO_2 reduction to HCOOH. g) Long-term performance test at -0.90 (V vs RHE). Reproduced with permission.^[43] Copyright 2023, Elsevier B.V. h) Optical image of Cu HF, electrooxidated Cu HF, and activated Cu HF. SEM image of the outer surface of i) Cu HF, and j) activated Cu HF. High-resolution TEM image of k) activated Cu HF, and l) Cu HF. Reproduced with permission. Copyright 2022, The Royal Society of Chemistry.^[97]

an ECSA more than 5 times that of Cu HF with bulk bismuth particles. $^{\left[52\right] }$

The varying standard reduction potentials among metals enable the in-situ growing electrocatalyst on HFGDEs through the GRR method.^[108,113,114] For instance, bismuth nanosheet arrays were successfully grown on the Cu HF by simply immersing Cu HF in 20 μ M BiCl₃ DMSO solutions (Figure 9d).^[114] Element mapping (Figure 9e) of the resulting electrode showed the formation of bismuth nanosheets (Figure 9f) that grew uniformly from the inner to the outer surface of the HFGDE, significantly improving gas distribution and increasing ECSA. Additionally, the abundant metal surface of HFGDEs provides a conducive environment for the growth of carbon-based materials, such as Ndoped carbon nanotube (NCNT) arrays. These NCNTs, embedded with NiFe alloy nanoparticles, were grown on the outer surface of Ni HF through the CVD method.^[92] **ADVANCED** SCIENCE NEWS _

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Figure 9. a) Schematic of Bi deposition on Cu HFGDE from pulse electrodeposition. b) SEM image and c) cross-sectional SEM image of Cu–Bi PE prepared by pulse electrodeposition bismuth nanosheets, scale bars in b and c are 1 μ m, Reproduced with permission.^[52] Copyright 2021, Elsevier B.V. d) Schematic of fabricating bismuth nanosheet arrays on Cu HF (Bi NSAs@Cu HF) via galvanic replacement reaction. e) EDS Bi mapping images of cross-section, and f) Surface SEM image of Bi NSAs@Cu HF. Reproduced with permission.^[114] Copyright 2024, The Royal Society of Chemistry. g) Schematic illustration of electrodeposition of Sn on Cu HFGDE. h) Composition of Sn species on HFGDEs. i) Comparison of electrochemical reduction CO₂ to formate for Sn-based electrocatalysts. Reproduced with permission.^[53] Copyright 2020, American Chemical Society. j) Zn 2p, and k) Ag 3d XPS spectra of HFGDEs. Reproduced with permission. Copyright 2024, Wiley-VCH GmbH.^[115]

The electronic interaction between metals offers opportunities to adjust the electronic states of the electrocatalyst by fine-tuning the electron interaction, and it can be further achieved by regulating the duration of electrodeposition or GRR.^[53,115] For instance, the valence state of Sn was modified by changing the Sn deposition time on Cu HF (Figure 9g), and the ratio of Sn²⁺/Sn⁴⁺ increased with increased Sn deposition time, reaching its highest value at 120 s (Figure 9h). The resulting electrode with the highest Sn²⁺/Sn⁴⁺ ratio achieved optimal performance for formate production (Figure 9i).^[53] Additionally, extending the GRR duration could also lead to the enhancement in electronic interaction. For example, the enhanced electronic interaction between Zn and Ag was observed by the XPS analysis; the Zn $2p_{3/2}$ shifted to higher binding energies (Figure 9j), and the Ag $3d_{3/2}$ shifted slightly toward lower binding energy (Figure 9k) with increased GRR duration.^[115]

Exposing reaction-favorable crystal facets of metal electrocatalysts can significantly enhance the selectivity of the target product by lowering the energy barrier for key intermediates.^[116] For instance, the Cu (100) facet can facilitate the CO dimerization,



leading to the formation of ethylene.[89,97] The Zn (101) facet favors the production of CO, while the Zn (002) facet exhibits high selectivity for producing H₂.^[24,112] The Sn (101) facet can promote the production of formate.^[117,118] Electrodeposition and hydrothermal methods have been utilized to deposit nano-structured electrocatalysts with predominant crystal facets on HFGDEs, thereby improving their performance for targeted products. For instance, Cu cubic electrocatalysts, enriched with Cu (100) crystal facets, were grown on Cu HF via 30 cycles of alternating reducing and oxidizing potential (Figure 10a), resulting in a dense Cu nano-cube structure (Figure 10b), significantly increasing the ECSA for HFGDE. X-ray diffraction analysis confirmed the dominance of the Cu (100) crystal facets (Figure 10c). The resulting electrode demonstrated exceptional performance, achieving a high FE of over 90% for C_{2+} products and more than 65% for ethylene.^[89] Furthermore, the addition of surfactants during electrodeposition can regulate the nucleation and crystal growth process by modulating the surface free energy of the facets. For instance, a zinc nanosheets-based HFGDE with a controlled ratio of Zn (101)/Zn (002) crystal facet was fabricated by adding cationic surfactant cetyltrimethylammonium bromide (CTAB) (Figure 10d). With 1 mM CTAB, smaller zinc nanosheets were formed (Figure 10e), achieving a high ratio of Zn (101)/Zn (002) crystal facet of 9.58 (Figure 10f), optimizing the electrode for CO production.^[112]

The deposition of SnO₂ with distinct crystal facets on the outer surface of Ni HF can be achieved via a hydrothermal method by varying the titration rate of the growing solution (Figure 10g). The formation of abundant nanoflower structures (Figure 10h) in Ni HFGDE markedly enhances the ECSA, providing more active sites for the reaction. X-ray diffraction analysis revealed the presence of distinct crystal facets for different SnO₂ deposits, and the diffraction peak located at 33.9°, corresponding to the (101) crystal facet (Figure 10i). The resulting electrode dominant SnO₂ (101) crystal facet achieved the lowest onset potential and the highest partial current for formate production (Figure 10j). The DFT calculation revealed that the SnO₂ (101) crystal facet could help reduce the energy barrier for *OCHO formation, and the weak *HCOOH adsorption ability can promote HCOOH desorption (Figure 10k), facilitating the high selectivity of formate production.[118]

Modifying the deposition process can enhance the electrochemically active surface area and the intrinsic activity of electrocatalysts. However, since the CO₂ reduction reaction is confined to the gas-electrolyte-catalyst interface, it is crucial to optimize surface wettability, control the reaction area, and maximize the triple-phase boundary to facilitate reaction kinetics.^[16,44] The coexistence of the Cassie-Wenzel state (partially wetted area) is arguably the ideal case for promoting gas-liquid-solid interface reactions.^[16] A super-hydrophilic surface may lead to flooding and blockage of the porous structure, while a super-hydrophobic surface may hinder sufficient contact between catalysts and electrolytes.^[29] To optimize the reaction depth and maximize the formation of triple-phase boundaries, we reported a surface deposition and post-treatment method to precisely control the wetting depth of the electrolytes (Figure 11a).^[54] CNT-Bi electrocatalysts were first electrodeposited on the Cu HF to enhance the ECSA of the Cu HF electrode, with the color change to black (Figure 11b), indicating the uniform growth of CNT-Bi layer \approx 14–15 µm thick (Figure 11c). The wettability was subsequently modulated via in-situ electrochemical oxidation of CNTs to create hydrophilic-hydrophobic regions for CO_2RR . The CNT-Bi electrode turned more hydrophilic with greater anodic voltage and oxidation duration (Figures 11d,e). Anodic treatment at 15 s yielded optimal wettability, resulting in a fourfold increase in catalyst utilization ratio (Figure 11f) and a significantly enhanced partial current density of formate (Figure 11g) compared to the untreated electrode.

In addition to adjusting the wetting depth of electrolytes, we conducted another study to enhance pore utilization and optimize triple-phase boundaries by regulating the surface wettability of the electrode.^[119] Zinc nanosheets electrocatalysts were first electrodeposited on the outer surface of the Cu HFGDE to provide an active catalyst layer, followed up with infiltration and melting of hydrophobic polytetrafluoroethylene (PTFE) (Figure 11h). The decoration of PTFE could help regulate the capillary pressure, mitigating electrolyte flooding. Electrolyte flooding refers to the excessive penetration of the electrolyte into the gas-diffusion electrode, which disrupts gas transport, accelerates mechanical degradation, and reduces the efficiency and selectivity of CO₂RR products. Confocal laser fluorescent microscopy was employed to monitor flooded pores, and PTFE-treated electrode (Figure 11i) dropped by almost 66.7% of fluorescent area compared to untreated counterpart (Figure 11i). Furthermore, the treated electrode exhibited a significantly reduced pressure drop (Figure 11k) and enhanced CO₂ bubbling (Figure 11l), confirming improved pore utilization for CO₂ distribution, which facilitates the formation of triple-phase boundaries around the PTFE particles (Figure 11m). With optimized PTFE loading, the HFGDE achieved the highest partial current density for CO production (Figure 11n).

The spray coating method has also been effectively employed to enhance the surface roughness and tune the selectivity of HFGDEs. For instance, a Cu-Ti HF was prepared by spray coating Cu powder on Ti HF, and the resulting electrode achieved a high Faradaic efficiency of almost 90% for ammonia, while the unmodified Ti HFGDE requires a more negative potential window to initiate the reaction.^[120]

In short conclusion, HFGDE surface engineering via in-situ surface restructuring and the deposition of nano-structured electrocatalysts could not only enhance the ECSA of the electrode but also boost the intrinsic activity of electrocatalysts. In-situ surface reconstruction could lead to the introduced oxygen vacancies, contractive of metal bonds, lattice dislocation, and distinctive grain boundaries to benefit the reaction. By tuning the deposition process, it is possible to regulate the electronic states and expose reaction-favorable crystal facets. Furthermore, the combination of deposition and post-treatment techniques allows for the precise control of surface wettability, optimizing reaction depth, improving pore utilization, and maximizing the formation of triple-phase boundaries, thereby accelerating the reaction kinetics.

4.3. Introducing Heteroatoms

Introducing another heterogenous atom into the host metal HFGDE through alloying or doping can be an effective method for modulating the electronic state of the electrocatalyst and





Figure 10. a) Schematic of HFGDEs and growing nanocubes on the outer surface for CO reduction. b) SEM image of the outer surface of CuCube HFGDE with nanocubes covering (scale bar: 50 nm). c) XRD of pristine and CuCube HFGDEs. Reproduced with permission.^[89] Copyrights 2023, Elsevier B.V. d) Schematic of preparing Zn catalysts-based HFGDEs via pulse electrodeposition. e) SEM image of the outer surface of Zn nanosheets covered HFGDE. f) Texture coefficient data of different Zn crystal facets on HFGDEs. Reproduced with permission.^[112] Copyrights 2024, Elsevier B.V. g) Schematic of 3D hierarchical SnO₂ deposited Ni HF (SnO₂@Ni HF) electrodes for CO₂ electroreduction to format. h) Surface SEM image of nanoflowers structure of SnO₂@Ni HF electrode. i) XRD results of Ni HF electrodes with different deposited SnO₂ crystal facets. j) Partial current density of format over Ni HF electrodes. k) DFT calculation for free energy of format production over SnO₂ with different main crystal facets. Reproduced with permission.^[118] Copyrights 2025, Elsevier Inc.

tuning the selectivity of products.^[121,122] In this section, we summarize the key engineering strategies employed to modulate the electronic structure of HFGDEs via alloying or doping, highlighting their impact on catalytic performance and product selectivity.

4.3.1. Alloying

Alloying another metal site to the hosting HFGDE could tune the selectivity and activity of host catalysts by regulating their electronic states and offering additional binding sites for the





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Figure 11. a) Schematic of dual-layer HFGDE fabrication. b) Optical image of Cu HFGDEs. c) Cross-sectional SEM image of dual-layer HFGDE prepared with 10 min of electrophoretic deposition (scale bar: 50 nm). d) Contact angle of dual-layer HFGDE after 10 s wettability regulation via anodic voltage at various voltage values. e) The effect of duration of anodic voltage treatment at 2.0 V. f) the ratio of catalyst layer utilization. g) Partial of format for dual-layer HFGDEs at applied potentials. Reproduced with permission.^[54] Copyrights 2022, Elsevier B.V. h) Schematic of preparing HFGDEs with enhanced CO₂ distribution with PTFE decoration. Confocal fluorescent area image of i) pristine HFGDE, and j) HFGDE with enhanced CO₂ distribution in pristine HFGDE with enhanced CO₂ distribution in pristine HFGDE and HFGDE with enhanced CO₂ distribution. m) CO₂ transportation and CO₂ electrochemical reduction at optimized triple-phase boundary. n) Partial current density of CO for HFGDEs at applied potentials. Reproduced with permission.^[119] Copyrights 2024, Elsevier B.V.

adsorption of intermediates.^[122] For instance, introducing a small amount of Sn into Cu has been shown to suppress hydrocarbon formation, while the bronze alloy Cu_6Sn_5 , with a Cu/Sn atomic ratio of 6/5, achieves high FE for formation production.^[109,110] We reported an electrodeposition-thermal annealing method to selectively grow the Cu₃Sn or Cu₆Sn₅ phase on the outer surface of Cu HF.^[59] A thinner Sn layer (5 min electrodeposition) with a 12 h thermal aging at 220 °C promotes the formation of the Cu₃Sn phase, while a thick Sn catalyst layer

(20 min electrodeposition) with a 24 h thermal aging at 220 °C can form the Cu₆Sn₅ phase (**Figure 12**a). After Sn electrodeposition, the Cu HF turned to light grey (Figure 12b), and further thermal annealing at 220 °C resulted in dark grey appearance (Figure 12b), indicating the formation of bronze alloy on the surface of Cu HF. A thick layer of bronze alloy was clearly observed on the outer surface of Cu₆Sn₅ HFGDE (Figure 12c). X-ray diffraction analysis confirmed the presence of the Cu₆Sn₅ phase (Figure 12d), and the HR-TEM analysis revealed a







Figure 12. a) Diffusion pathways of Cu and Sn atoms in the interface of Sn layer and Cu substrate during aging step and growth of bronze alloy phases. b) Optical image of HFGDEs. c) Cross-sectional SEM image of CuSn alloy HFGDE (scale bars: 100 μ m, 1 μ m for inset). d) XRD patterns of HFGDEs. e) High-resolution TEM image of Cu₆Sn₅ HFGDE. Faradic efficiency of different products over f) Cu HFGDE, and g) Cu₆Sn₅ HFGDE. Reproduced with permission.^[59] Copyrights 2021, Elsevier B.V. h) Schematic of fabricating Cu–Sn alloy hollow fibers. i) XRD patterns of Cu–Sn_{45%} HF with adding 45% of Sn during fabrication. j) Faradaic efficiency of HFs toward CO₂ electrochemical reduction at -0.7 (V vs RHE). k) Potential dependence for format and CO and partial current density of format over Cu–Sn_{45%} HF electrode at applied potentials. Reproduced with permissions.^[98] Copyrights 2020, Wiley-VCH GmbH. I) Schematic of the fabrication process for Cu–Sb HFGDEs. m) XRD patterns of HFGDEs. n) Faradaic efficiency of formate, CO, and H₂ over CuSb-HFGDE at -1.0 (V vs RHE). Reproduced with permissions.^[99] Copyrights 2023, Elsevier Inc.

lattice spacing of 0.29 nm, consistent with the Cu₆Sn₅ crystal structure (Figure 12e). Compared to unmodified Cu HFGDE, which exhibits multiple product selectivity (Figure 12f), the Cu₆Sn₅ HFGDE exhibited an FE of 90% for formate production (Figure 12g) at -1.1 V (vs RHE), highlighting its enhanced performance for CO₂ reduction.

Pre-mixing desired metal powders during the early stage of HFGDE extrusion provides a simple and effective method for fabricating alloy-based HFGDEs. By varying the ratio of metal powders, the product selectivity can be finely tuned. For instance, a CuSn (bronze) HF was fabricated by mixing Cu and Sn powder (Figure 12h), resulting the formation of $Cu_{6.26}Sn_5$ and Cu_3Sn crystal facets in the Cu- $Sn_{45\%}$ HF with 45% Sn addition (Figure 12i). The FE for formate of CuSn HF varies with the ratio of Cu/Sn contents, with the Cu- $Sn_{45\%}$ HF achieving the highest FE of 90% (Figure 12j) and the highest partial current density for format production (Figure 12k).^[98] It is important to note that metals with a low melting temperature, such as Sn and Bi,

are prone to melting during the annealing process, which could potentially reduce the porosity of hollow fiber. In another study, CuSb HFs were fabricated by adjusting the amount of added Sb (Figure 12l), and both crystal facets of Cu and Sn were observed in the CuSb HF (Figure 12m). The product selectivity of Cu HF was tuned by varying the Sb content (Figure 12n), and the CuSb-3 HF with optimal Sb addition, achieved a FE CO of 72.82% at -1(V vs RHE), demonstrating the influence of Sb addition on CO selectivity.^[99]

In addition to alloying, bimetal electrocatalysts can be directly grown on the surface of HFGDE to further enhance their selectivity and performance. The synergistic effects between bimetals play a critical role in modulating the adsorption of key intermediates, thereby improving reaction kinetics.^[123,124] For instance. the interaction between N dopants and enclosed NiFe alloy particles, with electrons transferring from NiFe alloy to N-doped carbon shell, can lower the energy barrier of generating *COOH intermediates to promote CO production. The resulting electrode achieved a high FE CO over 90% with a CO partial current density of 171.7 mA cm⁻² at -1.03 V (vs RHE).^[92] In a similar approach, the synergistic effect between Ag and Zn could increase the adsorption of *COOH intermediates, thereby boosting the CO₂RR kinetics. The bimetal AgZn nanosheet-based electrode achieved a twice-partial current density of CO compared to the single Znbased HFGDE.[115]

4.3.2. Doping

Doping with heteroatoms, both metallic and non-metallic, is an effective strategy to modulate the electronic structure of host atoms and optimize intermediate adsorption, thereby enhancing catalytic efficiency.^[125–127] Unlike alloying, which typically involves the incorporation of larger quantities of another metal, doping integrates a limited amount of dopant atoms to modify the properties of the host metal. For instance, a boron-doped Cu HF was fabricated by a wet chemical reduction method using NaBH₄ solution to introduce the B atom to the Cu host (Figure 13a).^[58] Compared to pristine Cu HF with a smooth surface (Figure 13b), the B-Cu HF exhibited increased surface roughness, with abundant squama-like structures (Figure 13c). Boron, being electron-withdrawing, dopes into the Cu lattice, increasing the Cu-Cu interatomic distance and promoting the formation of $Cu^{\delta+}$ species with positive oxidation states. This was confirmed by the observed expansion in the lattice distance (Figures 13d,e) of Cu (111) lattice (0.209 nm), as well as the 0.2° downshift in Cu diffraction peak (Figure 13f). X-ray absorption near-edge structure spectra (Figure 13g) further confirmed the successful doping of boron, showing an oxidation state of $Cu^{\delta+}$ (0.47) and a lower coordination number (4.9), compared to pristine Cu HF (12). The B-doped electrode demonstrated exceptional performance in CO_2 conversion to ethanol (Figure 13h), achieving a high FE of 52.4% and an ultrahigh partial current density of 1.25 A cm⁻². DFT calculations revealed that the B-Cu (111) surface facilitates CO₂RR by lowering the energy barrier for *COCHO formation (Figure 13i), a crucial intermediate for the branching of ethylene and ethanol production. The lower Gibbs free energy of *CH₃CHO formation and higher energy for C_2H_4 production on B-Cu HF surface suggest that B-doping increases the selectivity for ethanol production (Figure 13j). In a similar study, chlorine incorporation into SnO₂ was found to enhance electron transfer and CO₂ adsorption, effectively reducing the energy barrier for the formation of the key intermediate *OCHO. The resulting Cl-SnO₂@Ni HF demonstrated exceptional stability, sustaining a formate selectivity exceeding 94% over 520 hours at a current density of 3 A cm⁻¹.^[93]

4.4. Electrode-Electrolyte Interface Engineering

As mentioned, the gas delivery regime in HFGDE is flowthrough with full contact between the gas and the electrolyte, therefore electrode-electrolyte interface engineering matters greatly. The compositions and local environments in electrolytes, comprising solvents, local pH, cations, anions, impurities, additives, and modifiers, play a crucial role in tuning the electrode-electrolyte interface (EEI) and shaping the local catalytic microenvironment. For a detailed discussion of interfacial engineering, we refer readers comprehensive reviews.^[14,128,129] In this section, we focus on optimizing electrolytes for HFGDE applications in gas-phase electrochemical reactions, with a particular emphasis on the introduction of halides, cationic surfactants, and cations. During electrochemical reactions, such as the CO₂RR, the cathode becomes negatively charged, inducing an enrichment of cations and a depletion of anions near its surface. This process establishes an electric double layer (EDL) at the EEI, which comprises the inner Helmholtz plane (IHP), where specifically adsorbed ions and solvent molecules reside, and the outer Helmholtz plane (OHP), where the solvated ions are located. The structure and dynamics of this EDL significantly influence the reaction kinetics and product selectivity, highlighting the importance of EEI engineering in enhancing the performance of HFGDEs.

Anions can adsorb onto negatively charged electrodes, effectively modulating the electronic states and facilitating the adsorption of key reaction intermediates.^[130] For example, a breakthrough ampere-level current density was reported on Ag HFGDE using a 3.0 м KCl electrolyte.^[37] The low-coordinated adsorption of Cl⁻ ions on the Ag HFGDE surface significantly suppressed the HER while enhancing CO₂RR kinetics (Figure 14a). Specifically, the HER selectivity dramatically declined upon adding 2.7 mol L^{-1} Cl⁻ to the KHCO₃ electrolyte (Figure 14b). The Tafel slope (Figure 14c) decreased from 160 to 73 mV dec⁻¹ with a 3 M Cl⁻ electrolyte, indicating an accelerated electron transfer rate for CO₂ activation. This observation was corroborated by the lowest interfacial charge transfer resistance (Figure 14d) for Ag HFGDE in the presence of 3 M Cl⁻. DFT calculations (Figure 14e) revealed that Cl- adsorption on the Ag (111) surface reduces the energy barriers for the formation of *COOH and *CO intermediates while increasing the energy barrier for *H production, thereby promoting CO₂RR over HER. Moreover, Cl- ions can function as catalyst surface modifiers, inducing structural changes through electrochemical oxidation and reduction processes.^[128] For instance, an NS@Ag HF electrode with abundant nanosheets was fabricated by electrooxidizing and reducing Ag HFGDE in a Cl⁻-rich electrolyte.^[39] The synergistic effects of the silver nanosheets and Cl- adsorption enhanced the reaction kinetics. The resulting electrode achieved an ultra-high

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Figure 13. a) Schematic of fabrication process of pristine Cu HF (H-Cu HF) and boron doped Cu HF (B-Cu HF). SEM image of the outer surface of b) H-Cu HF, and c) B-Cu HF. High-resolution TEM image with corresponding FFT pattern of d) H-Cu HF, and e) B-Cu HF. f) XRD patterns, and g) Cu K-edge XANES spectra (average oxidation state of $Cu^{\delta+}$ species) of H-Cu HF and B-Cu HF, reference Cu foil, and Cu_2O . h) Partial current densities of C_{2+} products and ethanol over HFGDEs. The Gibbs free energy diagrams for i) the CO₂ to *CH₂CHO intermediate, and j) the adsorbed *CH₂CHO intermediate to ethylene and ethanol HFGDEs. Reproduced with permissions.^[58] Copyrights 2023, American Chemical Society.



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Figure 14. a) Schematic illustrations showing the process of CO₂ electroreduction over Ag HF electrode in KCl electrolytes. b) Faradaic efficiency of CO and H₂ on Ag HF electrode at 1 A cm⁻² in different electrolytes. c) Tafel slopes of Ag HF. d) Electrochemical impedance spectroscopy (EIS) Nyquist plots and equivalent circuit as insert for Ag HF at -500 mA cm⁻². e) Calculated Gibbs free energy diagrams for forming CO and H₂ over Ag and Cl-Ag. Reproduced with permissions.^[37] Copyrights 2022, Wiley-VCH GmbH. f) Schematic of adsorbed halide ions favor CO₂ adsorption and coupling. g) Projected density of state, and h) top views of the deformation charge density of the halide-HFGDEs. Activation energy of *CO coupling i), and HER j) of the halide-HFGDEs. Reproduced with permissions.^[61] Copyrights 2024, Elsevier B.V. k) Schematic of CO₂ electrochemical reduction on Ag HFGDE with CTAB regulating the electrolytes interfaces. I) Faradaic efficiency of CO for Ag HFGDE in 0.5 mM CTAB and CTAB-free electrolytes. o) Partial current density of CO for Ag HFGDE in 0.5 mM CTAB and CTAB-free electrolytes at applied potentials. Reproduced with permissions.^[131] Copyrights 2024, Wiley-VCH GmbH.

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partial current density of CO (2.13 A cm^{-2}) at -0.97 V (vs RHE), with a CO FE of 97.03% using 3 M KCl as the catholyte.

Other halides, such as Br⁻ and I⁻, have also been demonstrated to enhance the CO₂RR activity of Cu HFGDEs.^[61,132] The adsorption strength of halide ions on Cu HFGDEs positively correlates with their ability to activate CO₂ molecules. This is attributed to the efficient electron transfer from halides to the vacant orbital of CO₂ through X_{ads}-C bonds, which stabilize and active CO₂ molecules on the electrode surface (Figure 14f). DFT calculation (Figures 14g,h) revealed that I⁻ exhibits the strongest adsorption among halides, accompanied by a pronounced negative charge transfer from I⁻ to Cu in the deformation charge density distribution. This indicates a robust electron accumulation and transfer between I⁻ and Cu sites. The I-Cu interaction showed the lowest energy barrier for *CO dimerization (Figure 14i) and the highest energy barrier for *H formation (Figure 14j), favoring the selectivity of CO₂RR over HER and promoting the formation of C₂₊ products. Experimental results corroborated these findings, as the Cu HFGDE performed at 3.0 м KI electrolyte achieved the highest FE of 68.8% for C_{2+} products at a current density of 3.0 A cm⁻², outperforming 63.8% at 3 м KBr and 61.8% at 3м KCl.^[61]

The modification of EEI with cationic surfactant represents another effective method to enhance the performance of HFGDEs.^[133,134] Cationic surfactants such as cetyltrimethylammonium bromide (CTAB) could accumulate in EDL, greatly reducing the availability of protons and thereby suppressing HER.^[133] For instance, the CO₂RR performance of an Ag HFGDE was significantly improved by adding CTAB to the KHCO₃ solution.^[131] The increased bias potential facilitated the alignment of hydrophobic long-alkyl chains of CTAB, which repels isolated water to suppress HER (Figure 14k). This modification enabled the resulting electrode to achieve a high FE of CO of 98.15% at -0.9 (V vs RHE), compared to only 67.9% in the electrolytes without CTAB addition (Figure 14l). Moreover, the ordered structure of CTAB enhances ion diffusion and charge transfer, further improving reaction kinetics. This was evidenced by the lower charge transfer resistance (Figure 14m) and reduced Tafel slope value (Figure 14n) observed with 0.5 mM CTAB, indicating fast electron transfer and efficient CO2 activation. Consequently, the Ag HFGDE operating with 0.5 mM CTAB exhibited a significantly higher partial current density of CO compared to the electrode in CTAB-free electrolytes (Figure 140).

The role of cations in acidic electrolytes is critical for suppressing HER and stabilizing adsorbed intermediates Cations readily accumulate at the inner Helmholtz plane (IHP) under negative potentials, shifting the reduction potential to more positive values.^[41,60,135] This shift reduces proton concentration and increases the overpotential for HER at the outer Helmholtz layer (OHL), as illustrated in Figures 15a,b.^[41] A Cu HFGDE (0.75mm, 100 µm) (Figure 15c) with integrated molten copper particles on the porous surface (Figure 15d) was employed in strong acid electrolytes for CO₂RR at ampere lever current densities.^[60] When operated at pure acid electrolyte, hydrogen was the only detected product (Figure 15e). However, the introduction of K⁺ cations into the electrolytes significantly altered the product distribution. At lower K^+ concentrations (0.5–2.0 M), the formation of C_1 products was slightly enhanced, while higher K⁺ concentrations favored C₂₊ product formation (Figure 15f). In optimized conditions (3 M KCl + H₂SO₄, pH 0.71), the Cu HF achieved an FE

of 73.4% for C_{2+} products with a partial current density of 2.2 A cm⁻². DFT calculation (Figure 15g,h) revealed the mechanistic insights into this behavior. The protonation of *CO to *CHO was determined to have a lower activation energy barrier (1.10 eV) compared to *CO dimerization to form *OCCO (1.77 eV). This indicates a preference for the pathway involving *CO protonation followed by *CO + *CHO coupling, rather than direct *CO dimerization. The co-adsorption of H⁺ and K⁺ on the Cu crystal facet further reduced the energy barrier, accelerating the ratedetermining step of *CO protonation to *CHO, thereby enhancing CO₂RR kinetics and favoring C₂₊ product formation. Surface engineering of the Cu HFGDE was also shown to improve performance. A tensile-strained Cu HFGDE exhibited a FE of 84.5% and a partial current density of as high as $3.1 \,\mathrm{A \, cm^{-2}}$ for C_{2+} products at $(3 \text{ M KCl} + 0.05 \text{ M H}_2\text{SO}_4)$.^[135] For CO production, a nanostructured Ag HFGDE demonstrated exceptional performance, achieving a CO FE of 95% and a partial current density as high as 4.3 A cm⁻² under the same electrolyte conditions. These findings underscore the importance of electrolyte composition and electrode design in optimizing CO₂RR activity and selectivity.^[41]

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The CO₂RR usually involves a proton-coupled electron transfer (PCET) step, resulting in a large overpotential for CO₂ activation in a nonaqueous solvent. However, the unique properties of ionic liquids (ILs), such as their high CO₂ solubility, excellent stability, and high ionic conductivity, make them promising electrolytes for CO2RR despite the inherent challenges of nonaqueous environments.^[128] A capsule-like Ni HF was fabricated via encapsulating Bi@Zeolite catalysts, and the Bi@Zeolite catalyst was locked into the pores of hollow fiber due to the inner-outer pressure difference with applied vacuum force from the outer surface of Ni HF.[91] After sealing one end side of the hollow fiber, the CO₂ and ionic liquid-based electrolytes (MeCN:[Bmim]PF₆:H₂O = 14:6:0.04) were fed through the lumen side of the hollow fiber and forced to extrude out through the porous wall. In this case, the CO₂ mass transportation improved, and the diffusion path was significantly shortened. The high FE CO of 74.1% was achieved at an overpotential of 260 mV, around 2.6 and 2.5 times than those Ni foil-loaded Bi@Zeolite (28.1%) and pristine Ni HF (29.6%), respectively.

4.5. Summary of Design Strategies

In summary, **Table 1** highlights the key design strategies and performance of HFGDEs for gas-phase electrochemical conversion. Advanced fabrication engineering techniques enable the construction of highly structured HFGDEs, ensuring efficient CO₂ delivery and minimizing mass transport resistance. Surface engineering and the introducing heteroatoms through alloying or doping, significantly enhance catalytic activity and selectivity. Furthermore, engineering the electrode-electrolyte interface stabilizes reaction intermediates and mitigates side reactions, thereby enabling the attainment of ampere-level current densities.

To advance the development of scalable and cost-effective hollow fiber gas-diffusion electrodes, we provide a systematic framework for selecting metal hollow fibers based on scalability, durability, and cost considerations. From a scalability perspective, metal selection and fabrication engineering are critical. Cu and Ni hollow fibers stand out as promising candidates due to their





Figure 15. Schematic diagram of electric double layer near cathode in a) $H_2SO_4 + KCl$, and b) H_2SO_4 electrolytes during CO_2 electrochemical reduction. Outer Helmholtz Plane (OHP). Reproduced with permissions. Copyrights 2024, Springer nature.^[41] c) Cross-sectional, and d) surface SEM image of Cu HF. e) Faradaic efficiency of H_2 on Cu HFGDE in H_2SO_4 with pH 1. f) K⁺ concentration-dependent Faradaic efficiency and partial current density of C_{2+} . g) A reaction energy diagram for *CO to *OCCHO on Cu HFGDE in $H_2SO_4 + KCl$ electrolytes, either via a direct *CO dimerization pathway or *CO hydrogenation to *CHO and then dimerization with *CO. h) A reaction energy diagram for *CO to *OCCHO via the *CO + *CHO coupling pathway on Cu HFGDEs with different electrolyte compositions. Reproduced with permissions.^[60] Copyrights 2024, The Royal Society of Chemistry.

facile and mature hydrogen reduction process, ensuring both scalability and practical implementation. Ni hollow fibers serve as robust substrates for the direct deposition of tailored catalysts to achieve selective electrochemical transformations. For instance, SnO₂-Ni hollow fibers, synthesized via hydrothermal methods, exhibited excellent stability for format production under amper-

level current density, offering a more practical and scalable alternative to the complex fabrication of Bi HF.^[42,93,118] Similarly, Cu hollow fibers demonstrate strong potential for C₂₊ product generation, with selectivity enhancements achievable through insitu surface engineering, heteroatom doping, and electrolyte optimization to sustain ampere-level current densities.^[40,58,135]

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Table 1. Design strategies and performance of HFGDEs for	gas-phase electrochemical reduction reaction in recent year
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Design strategies	HFGDEs	Electrolytes	рН	Flow rate [mL min ⁻¹]	Applied potential [vs RHE]	FE % [Product]	Current density [mA cm ⁻²]	Stability [h]	Refs
Fabrication	Cu	0.3 м КНСО ₃	≈7.0	20	-0.41 V	72.4 (CO)	8.4	24	[<mark>51</mark>]
engineering	Ag	0.5 м КНСО ₃	≈7.2	30	-1.2 V	92.7 (CO)	141	150	[<mark>96</mark>]
	Bi	2 м КНСО ₃	NA	30	-1.26 V	93 (format)	1130	40	[<mark>42</mark>]
	CuAl	0.5 M KHCO ₃	≈7.2	NA	-0.4 V	NA (format)	18	20	[100]
	CuSn	0.5 м КНСО ₃	≈7.2	30	-0.75 V	91 (format)	75	6	[<mark>98</mark>]
	CuSb-3	0.5 м КНСО ₃	≈7.2	20	-1.0 V	72.82 (CO)	206.4	15	[<mark>99</mark>]
	Cu-10nm	1 м КНСО ₃	≈7.2	20	-0.9 V	48.6 (CO)	≈200	20	[101]
	Cu	0.1 м КНСО ₃	≈6.8	10	-0.9 V	77.1 (format)	34.7	15	[73]
	Cu	0.5 м КНСО ₃	≈7.2		-1.1 V	80 (format)	210	120	[102]
	Zn	3 м KCl	≈6.8	20	-1.24	90.3 (CO)	800	110	[<mark>95</mark>]
Surface engineering	Cl-NS@Ag	3 м KCl	≈6.8	30	-0.95 V	97.13 (CO)	2000	200	[<mark>39</mark>]
	Activated Ag	1.5 м КНСО ₃	NA	60	-0.86 V	90.6 (CO)	1467.6	170	[<mark>38</mark>]
	E-Cu	0.5 м КНСО ₃	≈7.2	10	-1.18 V	92.3 (format)	91.4	NA	[103]
	Ag HF (O)-ER	0.5 м КНСО ₃	≈7.2	20	-1.3 V	93 (CO)	120.6	6	[<mark>94</mark>]
	Bi	2 м КНСО ₃	≈8.1	30	-1.26 V	93 (format)	1130	40	[42]
	D-Bi HF	3 м KCl	NA	10	-0.98 V	99.5 (format)	1010	100	[43]
	Activated Cu	3.5 м KCl	NA	20	-0.95 V	64.8 (C ₂₊)	2000	170	[97]
	Bi/Bi ₂ O ₃ NS	0.5 м КНСО₃	≈7.2	20	-1.0 V	85 (format)	141	24	[52]
	Bi NSAs	0.5 м КНСО ₃	≈7.2	NA	-1.11	80 (format)	300	60	[114]
	NiFe@NCNTs	0.5 м KCl	NA	30	-0.86 V	80 (CO)	90	42	[92]
	CuSn120	0.5 м КНСО₃	≈7.2	20	-1.2 V	78 (format)	88	4	[53]
	Ag30ZnNS	0.5 м KCl	≈3.8	20	-1.3 V	88.6 (CO)	93.1	24	[115]
	CuCube	1 м КОН	≈14	20	-0.8 V	90 (C ₂₁)	418	36	[89]
	ZncNS	0.5 м KCl	≈3.8	20	-1.3 V	72 (CO)	73.3	6	[112]
	SnO₂	2 м КНCO₂	NA	10	-1.1 V	94 (format)	1300	300	[118]
	CNT-Bi	0.5 м КНСО₂	≈7.2	20	-1.0 V	90 (format)	148	24	[54]
	ECD	3 м KCl	≈6.8	30	-1.3 V	81.2 (CO)	310.2	25	[119]
	Cu-Ti	0.05м Na₂SO₄	NA	40	-0.6 V	90% (ammonia)	NA	NA	[120]
Introducing	Cu ₂ Sn ₂	0.5 м КНСО ₂	≈7.2	10	-1.1 V	89 (format)	136	24	[59]
heteroatoms	CuSn	0.5 м КНСО	≈7.2	30	-0.75 V	91 (format)	75	6	[98]
	CuSb-3	0.5 м КНСО,	≈7.2	20	-10V	72 82 (CO)	206.4	15	[99]
	NiFe@NCNTs	0.5 м KCl	NA	30	-0.86 V	80 (CO)	90	42	[92]
	Ag307nNS	0.5 M KCl	~3.8	20	-13V	88 6 (CO)	93 1	24	[115]
	B-Cu HE	3 M KCl	NA	20	_0.91 V	78 9 (C-)	2400	150	[58]
	Cl-SnO ₂		NA	30	0.51 V	94% (format)	3000	520	[90]
Electrode-	Cl-Ag	3 M KC	~6.8	30	_0 91 V	92 2 (CO)	1000	$150 (1 \ \text{cm}^{-2})$	[33]
electrolytes	Cl-aAg	3 M KCl	~0.0 NA	20	-1.08 V	90.3 (CO)	3500	$200 (2 \text{ A cm}^{-2})$	[40]
engineering		3 M KI	NA	20	-1.26 V	50.5 (CC)	3000	200 (2 A Chi)	[61]
	Br Cu	3 M KBr	NA	20	-1.20 V	$63.8(C_{2+})$	3000	NA	[01]
	Cl Cu	3 M KCl	NA	20	-1.27 V	$61.8(C_{2+})$	3000	NA	[01]
	ClaCu	3 M KCl	NA	20	-0.95 V	$90.5(C_{2+})$	2000	$200(2 \ \text{cm}^{-2})$	[40]
			0.71	20	-0.95 V	$30.3 (C_{2+})$	2000	200 (2 A Chi)	[40]
		(pH 0.71)	0.71		5.0 A CIII	$73.4 (C_{2+})$	3000		[00]
	NSL-Cu	3 м КСІ + H ₂ SO ₄ (рН 1)	1	30	3.7 A cm ⁻	84.5 (C ₂₊)	3000	240 (3 A cm ⁻²)	[135]
	CD-Ag	3 м KCl + 0.05 м H ₂ SO ₄	1	30	-1.41 V	95 (CO)	4500	200 (2 A cm ⁻²)	[41]
	Bi@Zeolite	MeCN: [Bmim]PF ₆ :H ₂ O = 14: 6:0.04	NA	30	–1.8 V (vs SHE)	74.1 (CO)	6.6	16	[91]





Figure 16. Perspectives for the development of hollow fiber gas-diffusion electrodes.

From an economic perspective, Zn hollow fibers present a more economically viable option for CO production compared to the high electrode cost of Ag-based hollow fibers.^[95] In terms of durability, acidic electrolytes are preferred for long-term operation due to their effectiveness in mitigating salt precipitation, necessitating the use of corrosion-resistant metals to ensure electrode longevity. In conclusion, a scalable and cost-effective HFGDE substrate should be fabricated through a facile reduction process using cost-effective, corrosion-resistant metals, allowing for the deposition of tailored catalysts with optimized wettability. This integrated design strategy balances scalability, durability, and economic feasibility, paving the way for industrial applications.

5. Conclusion and Perspectives

The well-engineered electrodes can optimize the formation of reactive gas-catalyst solid-electrolyte liquid interfaces, promoting a high local concentration of gas molecules at catalytic sites, which, in turn, advances the gas-phase electrochemical reduction toward industrial-scale applications. Flow-through hollow fiber gas-diffusion electrodes (HFGDEs) or hollow fiber gas penetration electrodes (HFGPEs) demonstrate significant promise in this domain by continuously delivering convective gas to active sites, achieving current densities of multiple amperes per square centimeter in liquid electrolytes, underscoring their robustness as an electrode design for industrial-scale applications. This review highlights recent progress in HFGDEs for the electrochemical reduction of gaseous molecules, focusing their design criteria, fabrication methods, and strategies for improving electrochemical performance. Special attention is given to HFGDEs applied in the electrochemical conversion of CO₂. The architecture of HFGDEs is particularly impactful in ensuring an adequate supply of reactive gases to active sites and fostering the formation of abundant triple-phase interfaces, thereby accelerating reaction kinetics. HFGDEs operating in gas-diffusion conditions have demonstrated at least an order-of-magnitude higher partial current densities compared to their non-gas-diffusion condition counterparts. Despite these achievements, the optimization of HFGDEs remains an area of active development to fully unlock their potential.

Here are some recommendations (Figure 16) for further studies:

5.1. Tune the Microstructure of HFGDEs

The electrochemical performance of hollow fiber gas-diffusion electrodes (HFGDEs) is often underestimated due to the relatively uneven distribution of pore sizes. In HFGDE configurations, sufficient reactive gas availability near the active sites requires the convective flow pressure to exceed the capillary pressure, ensuring the formation of clear pathways for gas transport. Otherwise, the pore structure becomes flooded, obstructing gas pathways and limiting the supply of reactive gas to the catalytic sites. This dynamic is critical for flow-through HFGDEs to achieve high current densities. Since capillary pressure is directly linked to the pore sizes of HFGDEs, achieving a relatively uniform pore size distribution is essential to enhance convective flow and ensure that the majority of pores remain open for efficient gas transport.

To address the challenges associated with uneven pore size distribution of HFGDEs, several strategies are proposed. 1) Modification of fabrication step. Optimizing the fabrication process can balance the critical properties of metallic HFGDEs, such as mechanical strength, conductivity, porosity, and gas permeability. This can be achieved by selecting appropriate metal powders (considering metal type and particle size), fine-tuning the metal ADVANCED SCIENCE NEWS www.advancedsciencenews.com

powder/polymer binder/solvent ratio, and adjusting sintering and reduction conditions (e.g., temperature and duration). Drawing inspiration from established inorganic hollow fiber membrane techniques used in gas separation could provide valuable insights for improving the fabrication of metallic HFGDEs. 2) Construct a hydrophobic layer. Inspired by planar GDE design, incorporating a hydrophobic macroporous gas diffusion layer can enhance gas transport while preventing flooding, thus improving operational stability. Enhancing the hydrophobicity of porous metallic HFGDEs can optimize pore utilization by reducing electrolyte wettability, regulating the electrolyte contact angle, and minimizing capillary pressure. Hydrophobic treatments using hydrophobic reagents such as polytetrafluoroethylene (PTFE), 1-octadecyl thiol, or myristic acid can be applied to metallic HFGDEs to achieve these effects. 3) Introduce a catalyst layer with uniform pore size distribution. Introducing a catalyst layer with relatively uniform pore sizes can facilitate mass transport and improve reaction kinetics. Templating techniques are commonly used to fabricate porous catalysts with controlled pore size distribution. Applying this approach to metallic HFGDEs can significantly enhance gas distribution and electrochemical performance by reducing micron-sized pores to macro-, meso-, or nanopore dimensions.

5.2. Improve the stability of HFGDEs

Although some porous metallic HFGDEs have demonstrated ampere-level current densities sustained for hundreds of hours, achieving stability beyond 10 000 hours remains a significant challenge.^[7] Stability is crucial not only for the metallic HFGDEs themselves but also for the electrocatalysts applied. The degradation pathways of metal-based electrocatalysts primarily involve dissolution-deposition, fragmentation, detachment, oxidation-reduction, and redistribution, all of which are governed by the thermodynamic and kinetic mechanisms of atomic migration and chemical evolution.^[45] The in-situ growth of catalysts on HFGDEs offers a promising strategy to enhance stability by eliminating complications associated with immobilization, such as reduced activity and degradation, which are often observed in powder-based electrocatalysts requiring polymer binders and coatings on carbon-based GDEs.

Electrolyte flooding, a critical issue, occurs when excessive electrolyte penetration disrupts gas transport, accelerates mechanical degradation, and lowers CO₂RR efficiency and selectivity. To prevent flooding, HFGDEs require a convective gas flow capable of overcoming capillary pressure, necessitating continuous monitoring of gas flow pressure over time. Additionally, constructing a hydrophobic layer can further mitigate flooding by reducing capillary pressure.

Prolonged operation in near neutral or alkaline electrolytes at high current densities often leads to salt precipitation, which clogs HFGDE pores, compromising performance and stability. While acidic electrolytes can effectively mitigate salt accumulation, they impose stringent material requirements due to their corrosive nature. In such environments, selecting inherently corrosion-resistant metals is critical. Beyond single-metal systems, the development of anti-corrosive alloys represents a viable approach to enhancing stability under acidic conditions, paving the way for more durable HFGDEs in industrial applications.

5.3. Modelling Microenvironment of HFGDEs

Despite recent advancements in the development of porous metallic HFGDEs, understanding their local microenvironment under operando conditions remains limited. The interfacial microenvironment, such as local pH, gas concentration, and reaction intermediates, plays a pivotal role in determining the catalytic activity and selectivity of gas-phase electrochemical reactions. Advanced in-situ microscopy techniques, and electrochemical mass spectrometry, have proven effective in detecting intermediates during electrochemical reactions. However, under operando conditions, especially at high current densities, the presence of abundant gas bubbles in the HFGDE surface can significantly interfere with the detection signals of in-situ microscopy. Moreover, the design of custom cells tailored to specific in-situ techniques is required for accurate characterization. Complementing experimental approaches, molecular simulations, and finite element analyses using tools like COMSOL Multiphysics offers valuable insights into local gas concentrations and transport phenomena in HFGDEs. To further advance the field, comprehensive studies integrating operando characterizations and computational models are essential to elucidate the mechanisms governing HFGDE performance.

5.4. Exploring HFGDEs for Other Electrolysis Systems

Applications such as $CO/N_2/NO$ reduction and $CH_4/H_2/propylene$ oxidation can benefit from the unique structure of metallic HFGDEs to enhance reaction kinetics and efficiency. While pure gas streams are commonly employed in laboratory settings to evaluate performance, real-world applications often involve mixtures of gases with the target gas present in relatively low concentrations. In such scenarios, the development of bifunctional HFGDEs with integrated gas capture capabilities becomes critical. These electrodes could be designed with an inner layer to selectively adsorb and concentrate the desired gas, which would then diffuse to the outer layer for electrochemical reactions, addressing challenges of gas separation and utilization in practical settings.

5.5. Possible Scalability and HFGDEs Electrolyzer Design

To demonstrate the potential scalability of HFGDEs, arrays of 5, 10 Ag HFGDE were adhered into a metal tube (**Figure 17a**) and evaluated in flow cells for the conversion of CO_2 to CO (Figures 17b,c).^[41] The performance of single, 5-tub, and 10-tube arrays showed similar rapid growth trends with increasing current density.^[41] Although the performance of HFGDE array electrodes slightly declined with increasing tube number and current density, the 10-tube-HFGDE array still achieved over 90% of Faradaic efficiency for CO at 4 A cm⁻² in Figure 17d.

Existing studies have demonstrated that hollow fibers aligned in arrays could improve scalability; however, manufacturing







Figure 17. Optical images of a) 10-tube CD-Ag HPE array electrode. The two-compartment electrolysis cell b) from a side view, and c) from a crosssection view during CO₂ electroreduction reaction (CO₂RR). The CO₂RR performance of d) 10-tube CD-Ag HPE array at different current densities (0.5–4 A cm⁻²) CO₂-saturated 3 M KCl + 0.05 M H₂SO₄ catholytes. Reproduced with permissions.^[41] Copyrights 2024, Springer Nature. e) Schematic of electrically conductive, catalytic, and porous hollow-fiber (CCPHF) cathode with dual functions. Reproduced with permissions.^[45] Copyright 2018, Wiley-VCH f) cost compositions of over Zn HPE with those of recently reported Zn-based and other representative electrocatalysts for producing CO. Reproduced with permissions.^[95] Copyright 2025, American Chemical Society.

challenges associated with hollow fiber arrays may limit their widespread adoption. Future research may explore the development of an integrated hollow fiber bundle (Figure 17e), which has been utilized as a dual-functional cathode. Further optimization of HFGDE arrangement in reactors is required to refine the spatial configuration and fiber density, thereby improving processing capacity per unit volume. Computational fluid dynamics (CFD) simulations offer a valuable tool for optimizing mass and heat transfer within these systems. For the transition of hollow fiber electrodes from laboratory to pilot scale, insights can be drawn from the well-established hollow fiber nanofiltration process.^[136]

Additionally, a techno-economic analysis (TEA) of industrialscale CO_2 reduction reaction for CO production has been conducted (Figure 17f). Zn hollow fibers, fabricated from costeffective raw materials, exhibit a substantial cost advantage over Ag hollow fibers, underscoring their strong potential for industrial application in gas diffusion electrodes (HFGDEs). Therefore, TEA serves as a critical criterion for evaluating the industrial-scale development of HFGDEs, necessitating a comprehensive assessment of electrode cost, electricity cost, equipment cost, and electrolyte cost. The overall cell voltage in electrochemical systems is primarily determined by the slower reaction rate at either the anode or cathode. In such cases, optimizing the anode reaction to a more favorable reaction, such as the methanol oxidation reaction (MOR), can help reduce the overall cell voltage and improve the system's efficiency. Furthermore, designing electrolyzers based on HFGDEs that operate without liquid electrolytes offers several distinct advantages. Unlike traditional liquid-phase electrolysis, this design mitigates issues like flooding, enhances mass transfer, and reduces the high ohmic resistance typically encountered in liquid electrolytes.

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Conflict of Interest

The authors declare no conflict of interest.

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