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Optimizing Hydrophobicity of Cu@Zn Foam Catalysts for Efficient CO₂ Electroreduction in a Microchannel Reactor

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Abstract: CO₂ electrochemical reduction is a promising way to convert CO₂ to valuable fuels and chemicals. This study presents a porous Cu@Zn foam catalyst with a tailored hydrophobic surface for enhanced CO₂ reduction. The catalyst is synthesized via a modified dynamic hydrogen bubble template method, incorporating polytetrafluoroethylene (PTFE) during electrodeposition to control wettability. This strategy creates a hydrophobic microenvironment that significantly increases the three-phase (gas–liquid–solid) contact area, promoting CO₂ mass transfer and suppressing the competing hydrogen evolution reaction. The optimized Cu@Zn-8PTFE catalyst achieves a CO Faraday efficiency (FE_{CO}) of 87.53% at -35 mA cm^{-2} , a 40% improvement over the unmodified Cu@Zn. Furthermore, it also exhibits excellent stability, maintaining FE_{CO} > 90% for 64 h at -15 mA cm^{-2} . While hydrophobic modification is beneficial, excess PTFE loading reduces performance by covering active sites and diminishing the three-phase interface. This work highlights the importance of controlling catalyst wettability to optimize the three-phase interface for enhanced CO₂ electroreduction.

Keywords: CO₂ electroreduction; hydrophobically modified; microchannel reactor; three-phase interface



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1. Introduction

CO₂ electroreduction (CO₂ER) presents a compelling strategy to address climate change concerns and establish a sustainable carbon cycle by transforming CO₂ to valuable chemicals and fuels [1]. However, realizing the full potential of CO₂ER, particularly in aqueous electrolytes, is hampered by significant hurdles. Primarily, the inherently low solubility of CO₂ in water ($\sim 30 \text{ mmol L}^{-1}$ at 1 bar, 25 °C) [2] severely restricts mass transport to the catalyst surface, thereby limiting achievable current densities [3]. Concurrently, the parasitic hydrogen evolution reaction (HER) competes for electrons and active sites, diminishing the selectivity towards desired CO₂ reduction products [4,5]. Overcoming these mass transfer and selectivity limitations is paramount for practical CO₂ER application.

Efforts to mitigate these challenges primarily follow two interconnected pathways: optimizing the reactor configuration and engineering the catalyst's surface properties. Microchannel reactors, for instance, offer distinct advantages over conventional cell designs due to their high surface-area-to-volume ratio, leading to enhanced mass transfer, simplified operation, and improved scalability [6]. Notably, employing specific flow regimes, such

as the Taylor flow (alternating gas/liquid plugs) demonstrated by Zhang et al. [7], can continuously regenerate the crucial gas–liquid–solid interface within the microchannel, further boosting CO₂ availability. Complementing reactor design, tailoring the catalyst's surface wettability offers a powerful lever to control reactant access. While hydrophilic surfaces necessitate CO₂ diffusion through a liquid boundary layer, creating a hydrophobic microenvironment can significantly enlarge the three-phase contact area where gaseous CO₂, liquid electrolyte, and solid catalyst converge [8–10]. This facilitates direct CO₂ transport from the gas phase to the active sites, potentially alleviating diffusion limitations and suppressing HER by limiting water access. Prior studies using hydrophobic modifiers like zinc myristate [11] or PTFE incorporation [12] have indeed shown enhanced CO Faradaic efficiency, especially at higher current densities. However, maximizing the benefit of hydrophobicity requires careful control, as the specific wetting state—ideally the Wenzel–Cassie coexistent state—is crucial for establishing an optimal and stable three-phase interface [13].

Beyond transport phenomena, the intrinsic nature of the catalyst material is critical. Zinc–copper (Zn–Cu) systems have emerged as promising non-precious metal catalysts for selective CO production [14–16]. Zn's weak binding affinity for the *CO intermediate facilitates its desorption [17], while Cu can synergistically enhance activity, potentially through improved conductivity or favorable binding of other intermediates like *COOH [18]. Various Cu–Zn structures have shown promising CO production; for example, modified nanosheets [19] reported FE_{CO} values greater than 90%, while phase-separated catalysts [20] also achieved FE_{CO} values around 94% under their optimal conditions.

While these strategies—microchannel reactors, hydrophobic surfaces, and Cu@Zn catalysts—show individual promise, effectively integrating them to create a highly efficient and stable CO₂ER system presents ongoing challenges. Specifically, achieving a well-controlled, uniform, and robustly integrated hydrophobic character within a high-surface-area, porous catalyst structure remains difficult using conventional post-synthesis modification techniques [21,22]. Building on this, we hypothesize that the incorporation of polytetrafluoroethylene (PTFE) during the dynamic hydrogen bubble template (DHBT) synthesis of porous Cu@Zn foam offers a superior approach. This method aims to create an intimately integrated hydrophobic network throughout the catalyst's porous architecture, allowing for the precise tuning of surface wettability.

This work, therefore, introduces such a hydrophobic, porous Cu@Zn foam catalyst and systematically investigates the impact of varying PTFE content (0, 4, 8, and 16 mL added to the electrolyte) on the catalyst's morphology, wettability, and resulting three-phase interface formation. We correlate these properties with CO₂ER performance (FE_{CO}, activity, stability) within a microchannel reactor operating under optimized Taylor flow conditions. The central goal is to elucidate how controlling the degree of integrated hydrophobicity influences the balance between enhanced CO₂ mass transport, HER suppression, and potential drawbacks like increased charge transfer resistance, ultimately aiming to identify the optimal conditions for maximizing CO₂-to-CO conversion efficiency and stability. This combined strategy seeks to provide a robust solution addressing the critical mass transport and selectivity challenges in aqueous CO₂ER.

2. Materials and Methods

2.1. Materials and Chemicals

Zinc rod (99.99%, 1.0 mm in diameter), potassium bicarbonate (99.99%, Macklin, Shanghai, China), sulfuric acid (>96%, Sinopharm Reagent, Shanghai, China), ethanol (99.5%, Sinopharm Reagent, Shanghai, China), zinc sulfate heptahydrate (99.5%, Lingfeng Chemical Reagent, Shanghai, China), copper sulfate pentahydrate (99.99%, Macklin, Shanghai, China), and PTFE (60 wt%, Meryer, Shanghai, China). Platinum gauze (Pt315) and

sandpaper (5000 mesh) were purchased from Tianjin Ida. Saturated calomel electrode (CHI150, SCE, CH Instruments, Shanghai, China) was acquired from CH instruments. All solutions were prepared using ultrapure water. A CHI660E electrochemical workstation (CH Instruments, Shanghai, China) was used to conduct the electrochemical processes.

2.2. Preparation of Catalysts

The zinc rod substrate was pre-treated by cutting, polishing (5000 mesh sandpaper), activating in 0.1 M H_2SO_4 (10 s), and sequentially using ultrasonic cleaning in ethanol and deionized (DI) water (5 min each), followed by N_2 drying. This prepared Zn rod served as the cathode.

The porous foam catalysts were then synthesized via electrodeposition in a two-electrode cell with a platinum mesh anode, immersed in 100 mL of aqueous electrolyte containing 0.19 M ZnSO_4 , 0.01 M CuSO_4 , and 1.5 M H_2SO_4 . To introduce hydrophobicity, varying volumes ($x = 4, 8$, or 16 mL) of PTFE dispersion (60 wt%) were added to this electrolyte; $x = 0$ corresponds to the unmodified catalyst. Electrodeposition was carried out at a constant current density of -3 A cm^{-2} for 15 s.

As schematically illustrated in Figure 1, this synthesis employs the dynamic hydrogen bubble template (DHBT) method: the high current density drives vigorous hydrogen evolution at the cathode, with the bubbles acting as dynamic templates. Simultaneously, Cu^{2+} and Zn^{2+} ions are reduced and deposited onto the bubble-free areas, forming the porous foam structure. When PTFE is present in the electrolyte ($x > 0$), its particles become incorporated within the growing metallic framework during this co-deposition process, yielding hydrophobic Cu@Zn-PTFE composites distinct from the standard Cu@Zn foam formed without PTFE ($x = 0$).

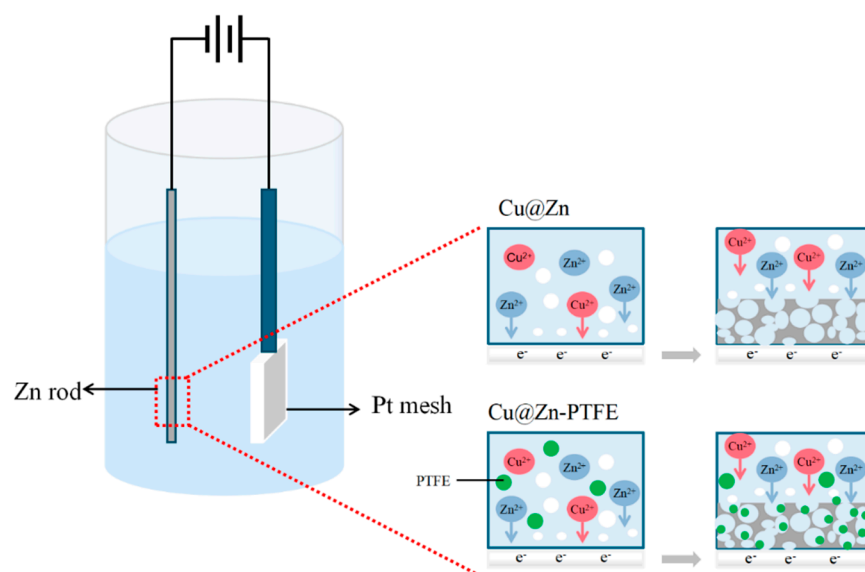


Figure 1. Schematic illustration of the catalyst synthesis via the dynamic hydrogen bubble template (DHBT) method.

After deposition, the catalyst-coated Zn rods were rinsed thoroughly with DI water and dried overnight in a vacuum oven. The samples were designated Cu@Zn ($x = 0$), Cu@Zn-4PTFE ($x = 4$), Cu@Zn-8PTFE ($x = 8$), and Cu@Zn-16PTFE ($x = 16$). A control Zn foam catalyst was also prepared using the same method but omitting both CuSO_4 and PTFE.

2.3. Electrocatalytic Measurements and Product Analysis

All electrochemical measurements in this study were conducted using a standard three-electrode configuration, where potential was reported relative to the respective reference electrode used in each setup.

CO₂ electroreduction (CO₂ER) performance evaluations, including product analysis and long-term stability tests, were conducted in a three-electrode microchannel reactor (Figure 2) with anolyte and catholyte separated by a Nafion 117 membrane (DuPont), chosen for its high proton conductivity and electrochemical stability. The electrolyte, 0.1 M KHCO₃, was pre-saturated with CO₂ by bubbling through a 5-meter polyethylene tube. A saturated calomel electrode (SCE) and platinum mesh served as reference and counter electrodes, respectively, with the working electrode positioned in the center of the Nafion tube. Gas–liquid ratios were controlled using flow controllers. Gaseous products were analyzed by in-line gas chromatography Synpec M3000, TCD (Synpec Technologies, Shanghai, China). To ensure that the reported data reflected steady-state performance, the system was first stabilized under the desired operating conditions for 900 s prior to data collection. Subsequently, product measurements were taken every 300 s for three consecutive intervals, and the final reported values represent the average of these three measurements. The separated aqueous KHCO₃ electrolyte was continuously recirculated via a pump back to a pre-mixing unit, ensuring a continuous, closed-loop operation for the electrolyte throughout the experiment. All experiments in this study were conducted at a controlled temperature of 25 °C.

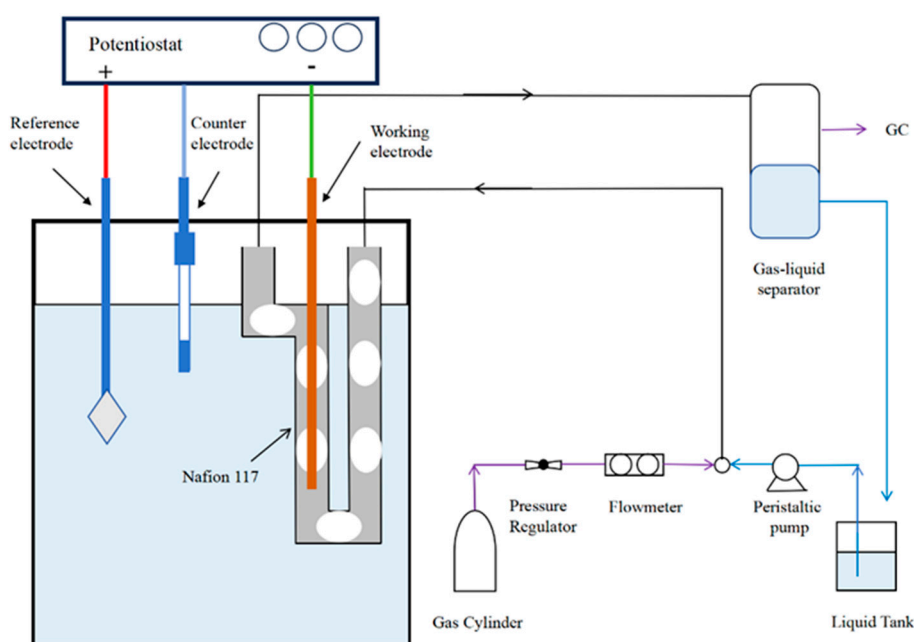


Figure 2. Schematic of the three-electrode microchannel reactor setup for CO₂ electroreduction experiments [3,11].

Separately, electrochemical characterizations, specifically Cyclic Voltammetry (CV) measurements for double-layer capacitance (C_{dl}) determination and Electrochemical Impedance Spectroscopy (EIS), were conducted in a 50 mL single-compartment batch cell. Due to material compatibility and setup constraints specific to this batch cell configuration, an Ag/AgCl electrode was employed as the reference electrode for these characterization measurements.

2.4. Computational Fluid Dynamics (CFD) Simulations

Computational fluid dynamics (CFD) simulations were performed using COMSOL Multiphysics to investigate the gas–liquid two-phase flow behavior within the microchannel reactor.

(1) Continuity Equation

$$\frac{\partial \alpha_q}{\partial t} + \nabla \cdot (\alpha_q \mathbf{u}_q) = 0 \quad (1)$$

where α_q is the volume fraction of phase q (liquid or gas). The sum of volume fractions is 1 ($\alpha_l + \alpha_g = 1$). $\mathbf{u}$ is the velocity vector (shared by both phases).

(2) Momentum Equation

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla p + \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{g} + F_{\text{surface}} \quad (2)$$

where ρ is the mixture density: $\rho = \alpha_l \rho_l + \alpha_g \rho_g$; $\mathbf{u}$ is the mixture velocity; p is the pressure; $\boldsymbol{\tau}$ is the stress tensor (for the mixture); $\mathbf{g}$ is the gravitational acceleration; F_{surface} is the surface tension force.

(3) Surface Tension Force

$$F_{\text{surface}} = \sigma \kappa \mathbf{n} \delta_s \quad (3)$$

where σ is the surface tension coefficient (between CO_2 and the 0.1 M KHCO_3 solution). We used a value of 0.072 N/m, which is a reasonable estimate for the CO_2 –water interface; κ is the curvature of the interface; $\mathbf{n}$ is the unit normal vector to the interface; δ_s is a Dirac delta function, which is non-zero only at the interface.

2.5. Catalyst Characterization

Water contact angles (CAs) were measured using a Dataphysics DCAT21 goniometer via the sessile drop method with 3 μL DI water droplets. Measurements were conducted at 25 ± 1 °C and $50 \pm 5\%$ relative humidity (RH).

3. Results and Discussion

3.1. Characterization of Catalysts

The morphology and structure of the prepared catalysts were initially characterized using scanning electron microscopy (SEM). As depicted in Figure 3, all synthesized catalysts exhibit a highly porous, interconnected structure, a characteristic outcome of the dynamic hydrogen bubble template (DHBT) method used during electrodeposition. This technique relies on simultaneously evolved hydrogen bubbles acting as transient templates on the cathode, leading to the formation of porous architectures that are beneficial for mass transport after the bubbles detach or merge [23]. The baseline Cu@Zn catalyst (Figure 3a,b), prepared without PTFE, features relatively large, well-defined pores (~50–100 μm) with walls constructed from intricate leaf-like or dendritic structures, clearly visible at higher magnification.

Significant morphological alterations occurred upon the incorporation of PTFE into the synthesis electrolyte (Figure 3c–h), modifying the baseline structure observed without PTFE (Figure 3a,b), which resembles typical dendritic or porous features often seen in electrodeposited copper or copper–zinc alloys [24]. A distinct trend of decreasing average pore size was observed with increasing PTFE content. This phenomenon aligns with observations in other electrodeposition systems, where the co-deposition of inert particles can

lead to grain refinement and altered porosity [25]. Furthermore, high-magnification images (Figure 3d,f,h) reveal a transformation in the fine structure of the pore walls: the leaf-like morphology gives way to interconnected, sheet-like structures decorated with embedded particles, particularly noticeable in the PTFE-containing samples. This morphological evolution is attributed to the co-deposition of hydrophobic PTFE particles alongside the metal ions. Specifically, PTFE particles could influence both metal ion reduction kinetics and, crucially, hydrogen bubble dynamics (formation, adhesion, detachment). However, at the highest PTFE loading (Cu@Zn-16PTFE, Figure 3g,h), a significant aggregation of these particles becomes apparent on the surface, suggesting that further increases in PTFE concentration could lead to the excessive coverage and potential blockage of catalytically active sites. Consequently, catalysts with PTFE loadings higher than 16 mL were not pursued further.

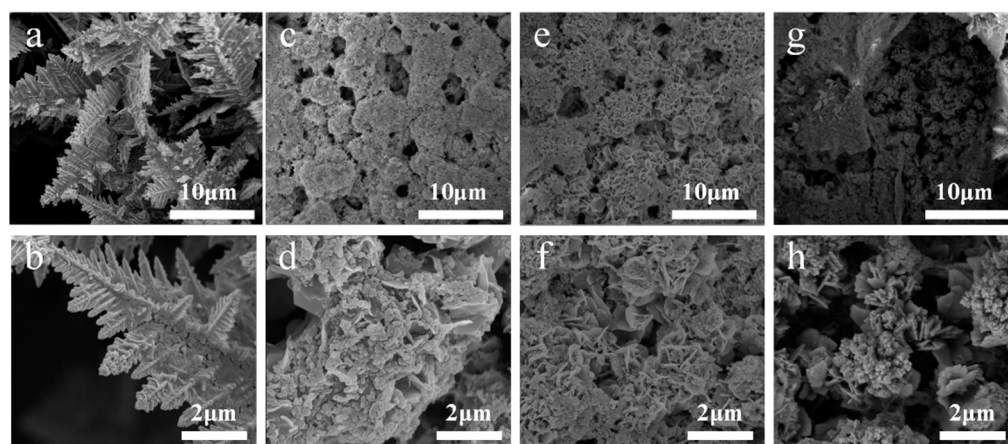


Figure 3. SEM micrographs illustrating the morphological evolution of catalysts with increasing PTFE content: (a,b) Cu@Zn, (c,d) Cu@Zn-4PTFE, (e,f) Cu@Zn-8PTFE, and (g,h) Cu@Zn-16PTFE at low (top row) and high (bottom row) magnifications.

To confirm the elemental composition and distribution, particularly the successful incorporation of PTFE, energy-dispersive X-ray spectroscopy (EDS) mapping was performed. Figure 4 presents the results for the representative Cu@Zn-8PTFE catalyst, showing the SEM image of the analyzed area alongside the corresponding elemental maps. The maps clearly indicate a uniform distribution of zinc (Zn), copper (Cu), and fluorine (F, serving as a marker for PTFE) across the catalyst's porous structure. This confirms the homogeneous integration of all components, including the PTFE, during the synthesis process.

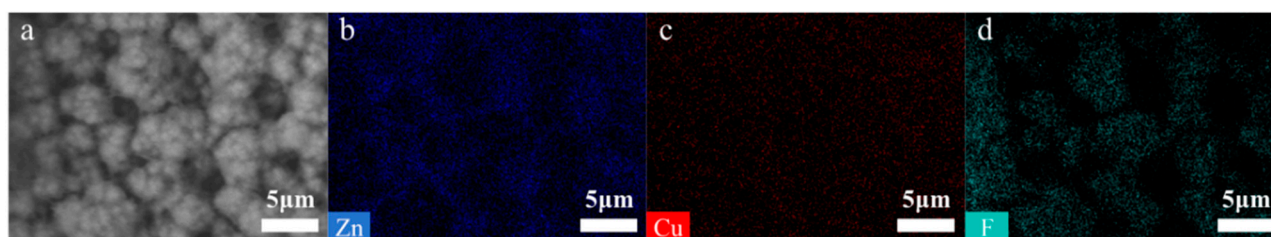


Figure 4. EDS elemental mapping of the representative Cu@Zn-8PTFE catalyst: (a) SEM image of the mapped area, and corresponding distributions of (b) Zn, (c) Cu, and (d) F, confirming uniform component incorporation.

Following the morphological analysis, XRD and XPS were employed to investigate the composition and chemical states of the catalysts. As shown in Figure 5a, the XRD patterns of both Cu@Zn and Cu@Zn-8PTFE are dominated by peaks characteristic of

metallic Zn (PDF#04-003-5661), with Cu_2O (111) also identified at 36.49° (PDF#97-002-6963). The absence of Cu–Zn alloy peaks suggests distinct Cu and Zn phases. The broad peak at 18.08° in the Cu@Zn-8PTFE pattern is characteristic of the (100) reflection of semi-crystalline PTFE [26].

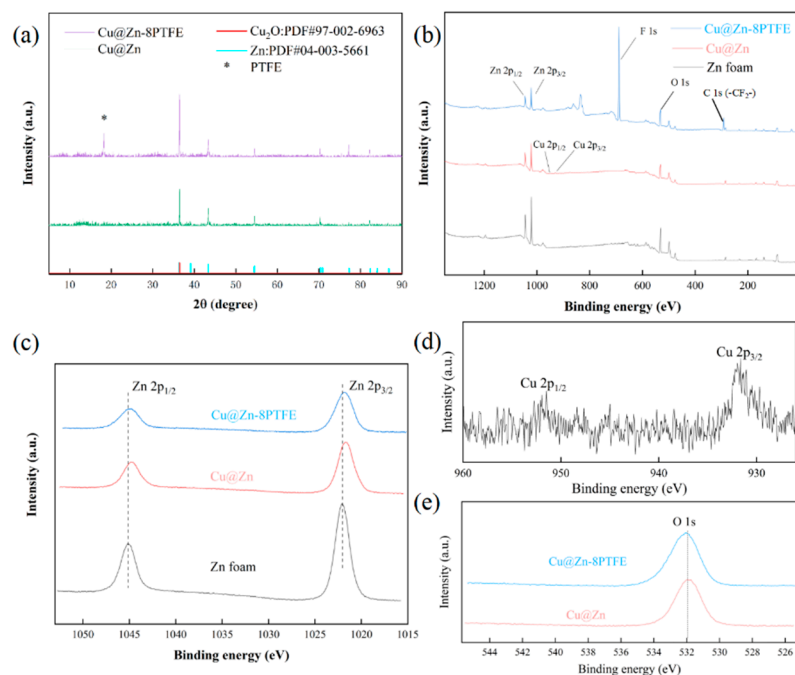


Figure 5. (a) XRD patterns of Cu@Zn and Cu@Zn-8PTFE; (b) XPS spectra of survey scan, (c) High-resolution XPS spectrum in the Zn 2p region for Zn foam, Cu@Zn, and Cu@Zn-8PTFE samples, (d) High-resolution XPS spectrum in the Cu 2p region for the Cu@Zn sample, (e) High-resolution XPS spectrum in the O 1s region for Cu@Zn, and Cu@Zn-8PTFE samples.

XPS provided further insight into surface composition and chemical states (Figure 5b–e). The survey scan (Figure 5b) confirmed the presence of Zn and O in both samples, with Cu also detected in the Cu@Zn sample. Significantly, for the Cu@Zn-8PTFE sample, the survey scan revealed strong signals for fluorine (F 1s at ~689 eV) and a characteristic carbon peak (C 1s at 291.99 eV, originating from -CF₂- in PTFE), which are definitive indicators of the PTFE coating and were absent in the Cu@Zn precursor. Within this coated sample, however, the Cu signal was below the detection limit in the Cu@Zn-8PTFE survey scan, likely owing to the low copper loading and signal attenuation effects from the PTFE coating [27].

High-resolution Zn 2p spectra (Figure 5c) provided crucial insights into the electronic interaction between Cu and Zn. Compared to the pristine Zn foam (shown as reference), the Zn 2p_{3/2} (around 1022 eV) and Zn 2p_{1/2} (around 1045 eV) peaks for the Cu@Zn and Cu@Zn-8PTFE samples both exhibited a slight but noticeable shift towards higher binding energies. This positive shift suggests a modification of the electronic environment of Zn, specifically a decrease in electron density around Zn atoms upon Cu deposition. This observation directly demonstrates the electronic interaction between Cu and Zn.

The high-resolution Cu 2p spectrum (Figure 5d) further clarifies the copper state. For the Cu@Zn sample, it clearly reveals the presence of Cu/Cu₂O species (Cu 2p_{3/2} at 932.6 eV), consistent with the survey scan findings.

High-resolution O 1s spectra were examined to gain deeper insight into the surface oxygen speciation (Figure 5e). Both the Cu@Zn and Cu@Zn-8PTFE samples exhibit a primary O 1s peak centered at approximately 532 eV. The notable breadth of this peak indicates overlapping contributions from multiple oxygen species with differing chemical

states but similar binding energies. According to literature reports, the region around the peak maximum (~ 532 eV) is primarily associated with surface hydroxyl groups ($-\text{OH}$) and adsorbed water (H_2O), species commonly formed on metal/oxide surfaces upon exposure to ambient air [28]. This suggests that the outermost layer probed by XPS is enriched in these hydroxyl and adsorbed water species.

While the signal around 532 eV is dominant, the peak's breadth, particularly its extension towards the lower binding energy side, likely encompasses contributions from lattice oxygen (O^{2-}) within the underlying ZnO, typically expected around 530–531 eV [29,30]. Overall, the O 1s spectra indicate that the sample surfaces are predominantly covered by hydroxyl groups and adsorbed water, potentially with minor contributions from ZnO lattice oxygen embedded within the broad spectral envelope.

3.2. Cu@Zn Catalyst Performance and Reactor Optimization

Temperature is a critical parameter in CO_2 electroreduction, as it significantly influences both CO_2 solubility in the aqueous electrolyte (generally decreasing with increasing temperature, potentially impacting mass transport) and the kinetics of electrochemical reactions (typically accelerating with temperature according to the Arrhenius relationship, affecting reaction rates and selectivity) [31,32]. Variations in temperature would therefore directly impact the measured performance, making comparisons difficult. To ensure consistent experimental conditions and enable a reliable comparison of the differently modified catalysts presented below, all experiments in this study were conducted at a controlled ambient temperature of 25 °C.

This section investigates the impact of incorporating Cu into Zn-based catalysts for enhanced CO_2 electroreduction (CO_2ER) performance. To this end, the electrocatalytic activity of a plain Zn rod, a porous Zn foam, and the Cu@Zn catalyst were systematically compared in a microchannel reactor. These experiments were all conducted using 0.1 M KHCO_3 electrolyte at an initial gas–liquid (G/L) ratio of 1:1. The resulting Faradaic efficiency for CO (FE_{CO}) as a function of current density is presented in Figure 6a.

While the porous Zn foam exhibits higher FE_{CO} than the Zn rod due to the increased electrochemically active surface area [33], the Cu@Zn catalyst demonstrates a significantly greater improvement. Specifically, the Cu@Zn catalyst achieves FE_{CO} values exceeding 80% at lower current densities (82.97% at -5 mA cm^{-2} and 82.53% at -15 mA cm^{-2}) and maintains a substantial 75.6% FE_{CO} , even at -25 mA cm^{-2} , representing a $\sim 20\%$ enhancement over the Zn foam at that current density. This marked improvement is attributed to the enhanced electrical conductivity imparted by Cu, facilitating efficient charge transfer at the electrode–electrolyte interface [15,18]. The concurrent suppression of the hydrogen evolution reaction (HER) is evident from the lower Faradaic efficiency for H_2 (FE_{H_2}) observed for Cu@Zn compared to Zn foam (Figure 6b).

Subsequently, the influence of the G/L ratio on CO_2ER performance was investigated using the Cu@Zn catalyst at a fixed current density of -20 mA cm^{-2} and 0.1 M KHCO_3 electrolyte. Figure 6c illustrates the dependence of FE_{CO} on the G/L ratio, revealing a pronounced peak of FE_{CO} that is observed at a ratio of 1:1. This optimal performance clearly coincided with the establishment of a stable Taylor flow regime within the microchannel reactor, as visualized in Figure 6d. The enhanced mass transfer characteristics of Taylor flow, arising from the internal recirculation within the liquid slugs and near the bubble caps [7], are responsible for the optimized performance at this ratio. Deviations from the optimal 1:1 G/L ratio disrupted the beneficial Taylor flow regime, leading to diminished FE_{CO} . Specifically, at ratios lower than 1:1 (e.g., 1:2), the increased proportion of the liquid phase likely hindered efficient CO_2 mass transport to the catalyst surface. Conversely, at ratios higher than 1:1 (e.g., 4:3 and 2:1), the elongated gas slugs potentially reduced the

wetted electrode area, limiting the formation of the extensive three-phase (gas–liquid–solid) interface necessary for efficient CO₂ER. Consequently, a G/L ratio of 1:1 was employed for all subsequent electrochemical measurements.

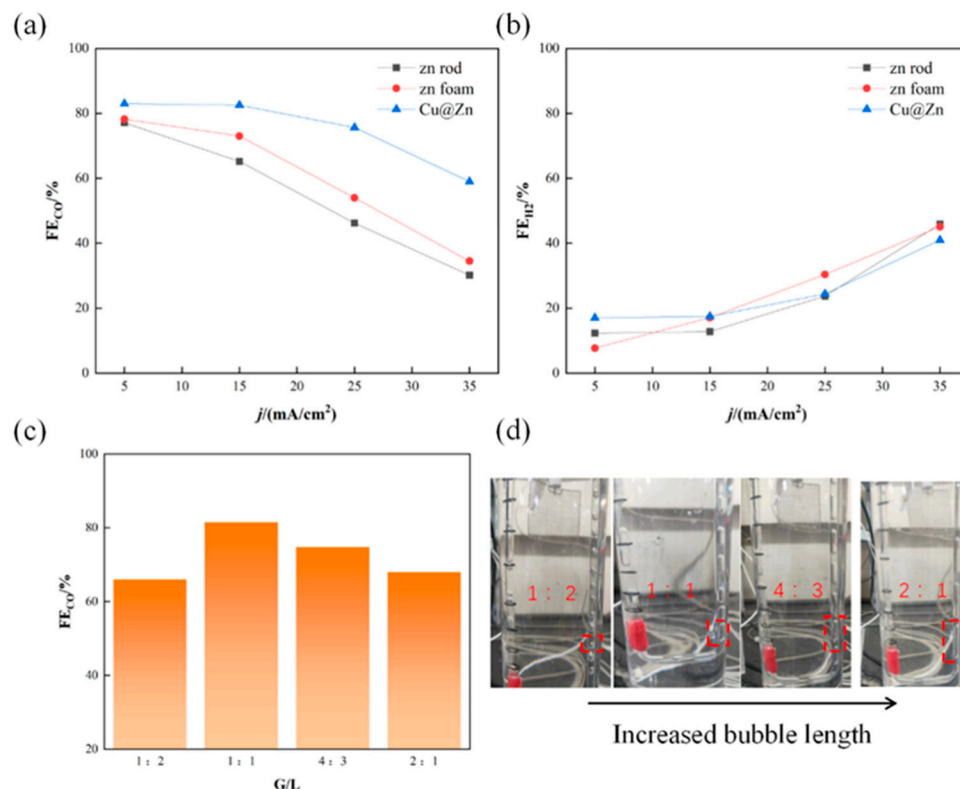


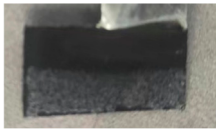
Figure 6. Enhanced CO₂ electroreduction performance of Cu@Zn catalyst. (a) FE_{CO} and (b) FE_{H₂} as a function of current density for a Zn rod, Zn foam, and Cu@Zn catalyst. (c) FE_{CO} of the Cu@Zn catalyst at various gas–liquid (G/L) ratios. (d) Visualization of flow patterns in the microchannel reactor at different G/L ratios.

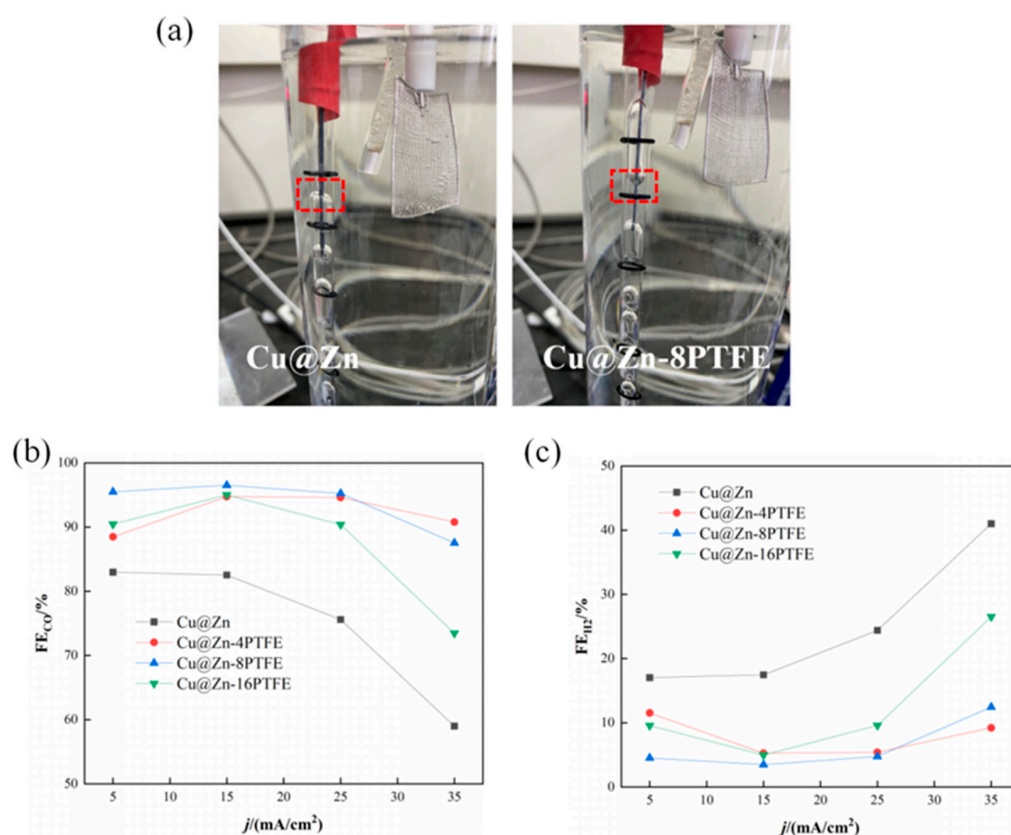
3.3. Hydrophobic Modification of Cu@Zn Catalysts

The influence of catalyst wettability on CO₂ER performance was investigated by modifying the Cu@Zn catalyst with varying amounts of PTFE (detailed preparation was shown in Section 2.2). Table 1 presents the water contact angles (CAs) and corresponding images of the catalyst surfaces. The pristine Cu@Zn exhibited a hydrophilic nature (CA = 38.59°), while increasing PTFE content led to progressively more hydrophobic surfaces, reaching a CA of 144.73° for Cu@Zn-16PTFE. This controlled wettability modification directly impacts the gas–liquid–solid interface crucial for CO₂ER [34].

Figure 7 illustrates the performance of these catalysts. The hydrophilic Cu@Zn showed reasonable FE_{CO} at low current densities (Figure 7b), but this selectivity declined sharply at higher currents, accompanied by increased H₂ evolution (Figure 7c). This is attributed to CO₂ mass transfer limitations at the hydrophilic surface, hindering gas access to active sites under high reaction rates. Introducing PTFE significantly improved CO selectivity, especially at higher currents. The moderately hydrophobic catalysts, Cu@Zn-4PTFE and Cu@Zn-8PTFE, demonstrated excellent performance, with FE_{CO} values exceeding 90% at −35 mA cm^{−2} and a peak of 96.5% at −15 mA cm^{−2} for Cu@Zn-8PTFE. This enhancement stems from the increased hydrophobicity, which promotes CO₂ transport by creating a favorable gas–liquid interface (Figure 7a). However, excessive hydrophobicity (Cu@Zn-16PTFE) proved detrimental, resulting in lower FE_{CO} than Cu@Zn-8PTFE, likely due to hindered electrolyte access and ionic conductivity [13].

Table 1. Contact angle of catalysts with different wettability.

Catalyst	Cu@Zn	Cu@Zn-4PTFE	Cu@Zn-8PTFE	Cu@Zn-16PTFE
Image				
Water contact angle				

**Figure 7.** CO₂ electroreduction performance and interfacial phenomena on PTFE-modified Cu@Zn catalysts. (a) Gas bubble comparison; (b) FECO₂; and (c) FEH₂.

3.4. Mechanistic Insights into the Role of Hydrophobicity

The electrochemical characterization provides further insights into the impact of PTFE modification on the Cu@Zn catalysts. Linear Sweep Voltammetry (LSV) measurements comparing the total current density in CO₂-saturated electrolyte with the background/HER current density in Ar-saturated electrolyte are presented for each catalyst in Figure 8g. These control experiments reveal the contribution of non-CO₂ reduction processes. A direct comparison of the total current densities under CO₂ saturation (also shown compiled in Figure 8f for clarity) confirms the superior performance of the Cu@Zn foam catalysts compared to the Zn rod benchmark. As previously discussed, the moderately hydrophobic Cu@Zn-4PTFE and Cu@Zn-8PTFE catalysts exhibit higher current densities than the unmodified Cu@Zn, especially at more negative potentials. This enhanced activity suggests improved CO₂ transport to the active sites, facilitated by the hydrophobic modifica-

tion. Conversely, the excessively hydrophobic Cu@Zn-16PTFE shows lower activity than Cu@Zn-8PTFE, indicating that overly hydrophobic surfaces hinder the reaction, likely due to restricted electrolyte access [10].

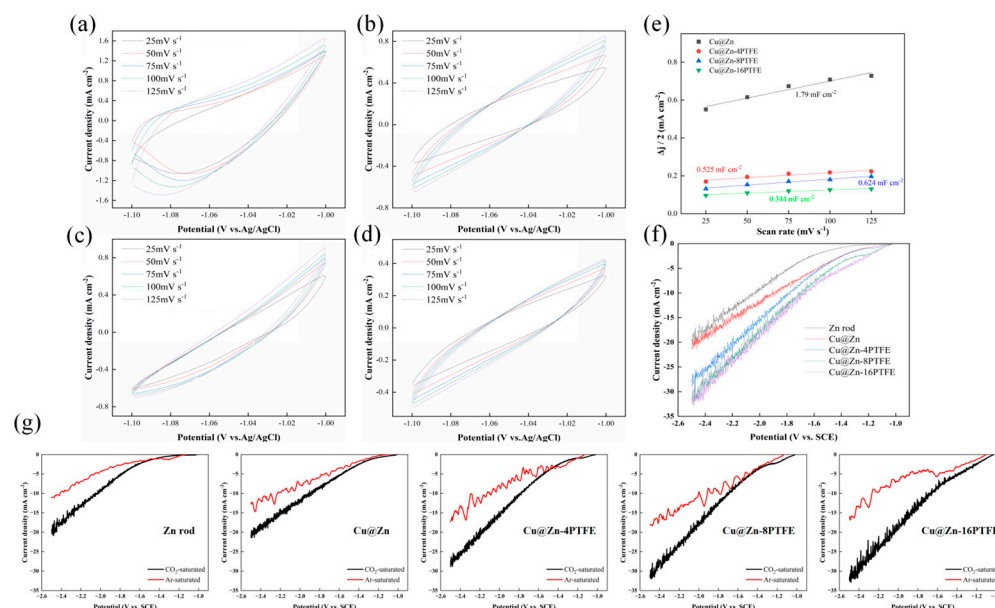


Figure 8. Cyclic voltammograms (CVs) at various scan rates (25–125 mV s^{−1}) for (a) Cu@Zn, (b) Cu@Zn-4PTFE, (c) Cu@Zn-8PTFE, and (d) Cu@Zn-16PTFE. (e) Corresponding current density difference ($\Delta j/2$) vs. scan rate. (f) Linear sweep voltammetry (LSV) curves. (g) Comparison of LSV curves for the indicated electrodes in 0.1M KHCO₃ electrolyte saturated with CO₂ (black lines) and Ar (red lines).

Cyclic voltammetry (CV) measurements at various scan rates (Figure 8a–d) reveal further details about the electrochemical behavior. From these scan-rate-dependent CVs, the double-layer capacitance (C_{dl}) was determined, which serves as a proxy for comparing the relative electrochemical active surface area (ECSA) of the catalysts.

The determination involved the following steps. First, CV scans were conducted within a narrow potential window selected for its non-Faradaic characteristics, where significant redox peaks are not expected. Within this potential window, CV scans were performed at multiple scan rates (ν): 25, 50, 75, 100, and 125 mV s^{−1}. For each scan rate, the capacitive current density was measured. This was achieved by selecting a medium potential within the non-Faradaic window and measuring the difference between the anodic (j_a) and cathodic (j_c) values.

$$\Delta j = j_a - j_c \quad (4)$$

A plot of half of this current density difference ($\Delta j/2$) versus the scan rate (ν) was then generated (Figure 8e). The C_{dl} value was extracted from the slope of the linear fit applied to the data points in the $\Delta j/2$ vs. ν plot, according to the relationship

$$\Delta j/2 = C_{dl} \cdot \nu \quad (5)$$

The different slopes for the various catalysts in Figure 8e indicate that PTFE modification affects the number of accessible active sites. The pristine Cu@Zn exhibits the highest C_{dl} (1.79 mF cm^{−2}). The most substantial decrease in C_{dl} occurs upon the initial addition of PTFE, as seen with Cu@Zn-4PTFE (0.525 mF cm^{−2}). Interestingly, the C_{dl} for Cu@Zn-8PTFE

(0.624 mF cm^{-2}) is slightly higher than that for the 4% PTFE sample, before decreasing again for Cu@Zn-16PTFE, which shows the lowest C_{dl} (0.344 mF cm^{-2}).

This complex trend suggests a trade-off: while PTFE enhances surface hydrophobicity, potentially aiding CO_2 transport, it simultaneously hinders electrolyte penetration and can block active sites, thus reducing the ECSA. The initial sharp drop (Cu@Zn to Cu@Zn-4PTFE) indicates a significant impact of even low PTFE loading on site accessibility. The slight increase at Cu@Zn-8PTFE might reflect an optimal balance or complex interfacial wetting phenomena at this specific loading under these conditions. However, the further, albeit more modest, decrease from Cu@Zn-8PTFE to Cu@Zn-16PTFE PTFE aligns with the general expectation that excessive PTFE loading increasingly obstructs active sites and limits electrolyte access, thereby diminishing the overall ECSA [12,35]. Optimizing PTFE content is therefore crucial, balancing improved reactant transport against maintaining sufficient active site availability.

These observations are consistent with the concept of a tunable three-phase interface. The increasing hydrophobicity created by PTFE incorporation leads to gas trapping within the catalyst pores, as evidenced by the decrease in electrochemical double-layer capacitance (C_{dl}) with increasing PTFE content (Figure 9). This reduction in C_{dl} , which is proportional to the electrochemically active surface area (ECSA), indicates a decrease in the solid–liquid contact area. However, this decrease is not detrimental to performance because the hydrophobic modification simultaneously establishes a gas–liquid–solid three-phase boundary. This three-phase interface facilitates CO_2 access to the catalyst active sites, leading to the observed enhancements in CO selectivity and overall activity for the moderately hydrophobic catalysts. The lower activity of the Cu@Zn-16PTFE catalyst reinforces the importance of balancing hydrophobicity and electrolyte access for optimal performance. While hydrophobicity promotes CO_2 transport, excessive hydrophobicity restricts electrolyte access and ionic conductivity, ultimately hindering the reaction.

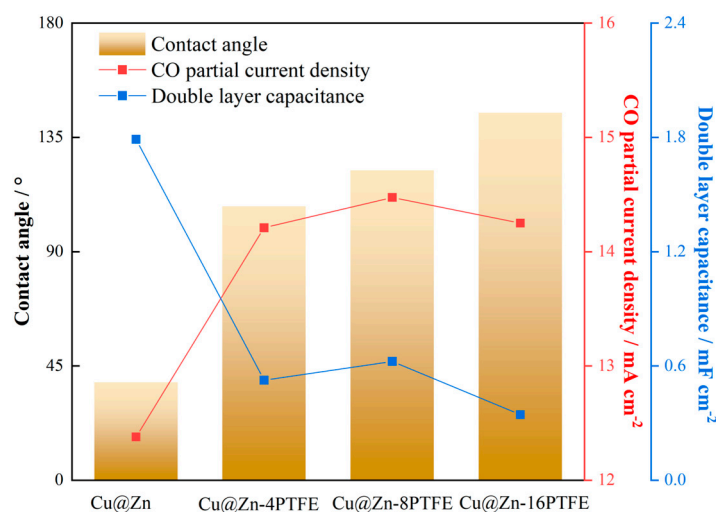


Figure 9. Contact angle, double-layer capacitance, and CO partial current density plotted against PTFE content for Cu@Zn catalysts.

The interplay between surface hydrophobicity, electrochemically active surface area (ECSA), and catalytic performance is effectively summarized in Figure 9. As PTFE content increases, the catalyst surface becomes progressively more hydrophobic, evidenced by the rising contact angle. This increased hydrophobicity is initially beneficial, facilitating CO_2 transport to the catalyst surface and mitigating mass transfer limitations, which leads to a significant increase in the CO partial current density (red line) when moving from Cu@Zn to Cu@Zn-4PTFE and further to Cu@Zn-8PTFE. However, the incorporation of

PTFE also tends to decrease the electrochemically active surface area, as indicated by the general downward trend in double-layer capacitance (C_{dl} , blue line), likely due to partial coverage or blockage of active sites. The Cu@Zn-8PTFE catalyst emerges as the optimal formulation because it strikes the most effective balance between these competing factors. It achieves a sufficiently high contact angle ($\sim 115^\circ$) to promote efficient CO_2 delivery, resulting in the highest CO partial current density among the tested catalysts (Figure 7b). Crucially, this enhancement in mass transport is achieved without an excessive loss of active surface area compared to the Cu@Zn-16PTFE sample, which, despite being the most hydrophobic, suffers from a lower C_{dl} and consequently a reduced CO partial current density. Therefore, the moderate hydrophobicity and relatively preserved active site accessibility of Cu@Zn-8PTFE synergistically contribute to its superior CO_2 electroreduction performance, validating it as the most promising catalyst composition identified in this study.

Electrochemical Impedance Spectroscopy (EIS) was employed to further probe the interfacial charge transfer kinetics and understand the resistance components influencing catalyst performance. Figure 10 displays the Nyquist plots obtained for the different electrodes, measured across a frequency range of 100 kHz to 0.1 Hz. Equivalent circuit fitting parameters, including solution resistance (R_s), charge transfer resistance (R_{ct}), and calculated effective double-layer capacitance (C_{dl}), are summarized in Table 2.

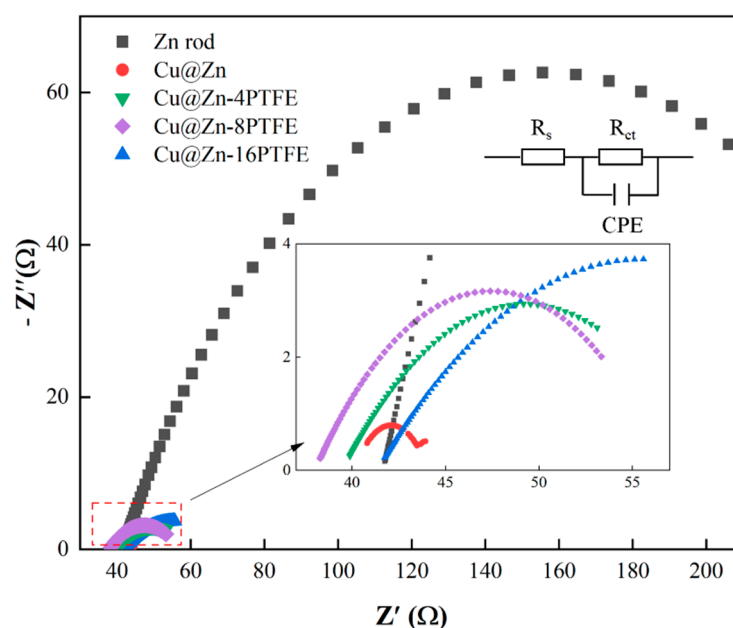


Figure 10. Nyquist plots for the prepared electrodes (Zn rod, Cu@Zn, Cu@Zn-xPTFE where $x = 4, 8, 16$). Insets show the magnified high-frequency data and the equivalent circuit model.

Table 2. EIS of different catalysts.

Electrode	R_s/Ω	R_{ct}/Ω	C_{dl}/mF
Zn rod	41.66	229.3	0.70532
Cu@Zn	40.14	3.93	0.101171
Cu@Zn-4PTFE	41.34	18.86	3.29605
Cu@Zn-8PTFE	39.5	19.55	8.558368
Cu@Zn-16PTFE	38.01	28.38	27.530152

As expected, the bare Zn rod exhibits a very large semicircle, indicating significantly higher overall impedance compared to the porous foam catalysts. The Cu@Zn catalyst,

devoid of PTFE, shows the smallest semicircle diameter among all foam samples, which corresponds to the lowest charge transfer resistance ($R_{ct} = 3.93 \Omega$). This reflects its inherently good metallic conductivity and relatively facile charge transfer in the absence of the insulating PTFE component.

Upon the incorporation of PTFE, a clear increase in the semicircle diameter is observed for all modified catalysts (Cu@Zn-4PTFE, Cu@Zn-8PTFE, Cu@Zn-16PTFE) compared to the baseline Cu@Zn. This directly confirms the statement that the insulating nature of PTFE inherently increases the charge transfer resistance (R_{ct}). As shown in Table 2, R_{ct} increases progressively with PTFE content. Simultaneously, C_{dl} shows a dramatic increase with PTFE loading. This significant rise in C_{dl} indicates that PTFE addition substantially enlarges the electrochemically accessible surface area, likely by fostering the formation of a complex, porous three-dimensional network within the electrode structure.

While increasing PTFE content enhances hydrophobicity, potentially improving CO_2 mass transport, it simultaneously impedes charge transfer kinetics, as evidenced by the rising R_{ct} [36]. The Cu@Zn-8PTFE catalyst ($R_{ct} = 19.55 \Omega$, $C_{dl} = 8.56 \text{ mF}$) appears to represent the point where the benefits of an enlarged, accessible surface area (high C_{dl} relative to Cu@Zn) and potentially enhanced mass transport are optimally balanced against the detrimental effect of increased, but still moderate, charge transfer resistance.

In contrast, the significantly higher R_{ct} observed for Cu@Zn-16PTFE (28.38Ω) strongly suggests that, at this high loading, the impedance to charge transfer becomes a dominant limiting factor. Although the C_{dl} value is the highest (27.53 mF), indicating the largest physical interfacial area, the severely increased R_{ct} implies that efficient electron transfer across this extensive interface is significantly hindered. This kinetic limitation, possibly coupled with increasingly tortuous pathways or reduced electrolyte penetration, effectively limiting the utilization of parts of the active surface within the dense PTFE network, overrides any further potential gains from increased hydrophobicity or surface area [12].

3.5. Long-Term Stability Evaluation

To evaluate the operational stability and rigorously assess the impact of the hydrophobic modification, long-term electrolysis experiments were conducted for both the optimized Cu@Zn-8PTFE catalyst and the unmodified Cu@Zn catalyst at a constant current density of -15 mA cm^{-2} . The catalyst exhibited excellent long-term performance, maintaining an FE_{CO} consistently greater than 93% for 55 h with relatively stable applied potential (Figure 11c), a selectivity comparable to that previously measured under identical conditions (Figure 7b), demonstrating its excellent operational stability. In stark contrast, the unmodified Cu@Zn catalyst, tested under identical conditions (Figure 11d), showed considerably lower stability. While its initial FE_{CO} was high (around 85%), a noticeable decline in both FE_{CO} and potential stability occurred after approximately 15–20 h of operation. This direct comparison (Figure 11c,d) unequivocally confirms that the PTFE modification substantially improves the long-term operational durability of the Cu@Zn catalyst under CO_2 reduction conditions [37].

This superior stability can be partly attributed to the microchannel reactor's Taylor flow regime, which promotes efficient product removal and interface regeneration [7], mitigating issues common in GDEs. However, post-mortem analysis revealed insights into potential degradation pathways. SEM images showed subtle morphological changes after the reaction (Figure 11a,b), and, more critically, EDS analysis indicated a significant decrease in surface fluorine content from 3.08 wt% to 0.52 wt% (Table 3). This substantial loss of fluorine strongly suggests the gradual detachment or degradation of the hydrophobic PTFE component during prolonged operation. Therefore, while stable for extended periods, the ultimate performance decay likely involves a combination of subtle structural evolution

and the loss of the crucial hydrophobic modifier, which would diminish the beneficial three-phase interface effect over time.

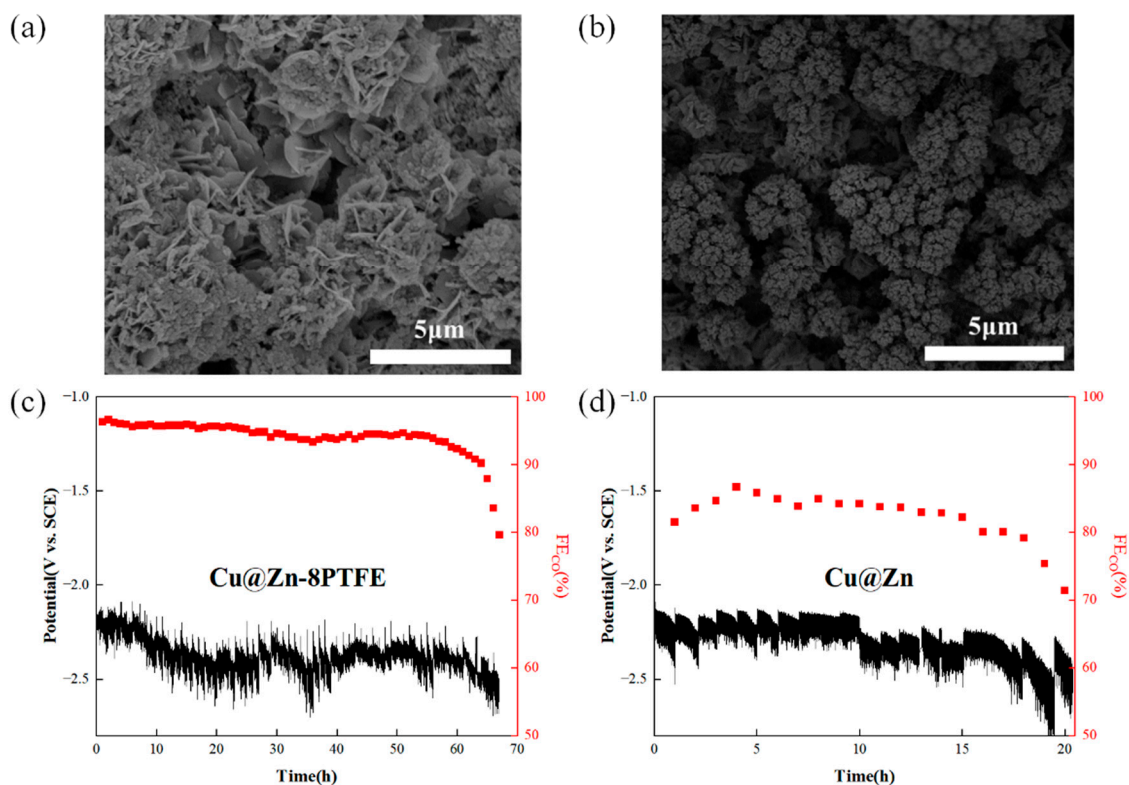


Figure 11. (a) SEM images of Cu@Zn-8PTFE before stability; (b) SEM images of Cu@Zn-8PTFE after stability; (c) FE_{CO} and applied potential of Cu@Zn-8PTFE vs. reaction time; (d) FE_{CO} and applied potential of Cu@Zn vs. reaction time.

Table 3. Proportion of elements of Cu@Zn-8PTFE before and after the reaction.

Element	Weight Content (%)		
	Zn	Cu	F
Before stability	86.32	10.6	3.08
After stability	88.36	11.12	0.52

Nevertheless, the demonstrated 64-hour stability at high FE_{CO} (>93%) represents a significant advancement in durability compared to many recently reported systems summarized in Table 4, which often show stability for less than 25 h under comparable conditions, highlighting the effectiveness of our integrated hydrophobic modification and microchannel reactor approach.

Table 4. Comparison of CO_2 ER performance for Cu@Zn-8PTFE and other catalysts.

Catalyst	$FE_{CO}/\%$	Electrolyte	Stability/h	Reference
Cu@Zn-8PTFE	93	0.1M $KHCO_3$	65	This work
Np Zn-Cu	50	0.5M $KHCO_3$	18	[14]
Cu-ZnO-2	75.6	0.1M $KHCO_3$	12	[38]
Cu_2Zn_8	73.1	0.1M $KHCO_3$	24	[39]
$Cu_{0.3}Zn_{9.7}$	90.69	0.1M $KHCO_3$	8	[33]
CuZn-MOF	90	0.1M $KHCO_3$	/	[40]
Zn-1P	92.6	0.5M $KHCO_3$	12	[41]
ZnAg-40-F/0	97.4	0.1M $KHCO_3$	10	[35]
Zn NS-8% PTFE	90.2	0.1M $KHCO_3$	12	[42]

3.6. CFD Modeling of Hydrophobicity Effects on Gas–Liquid Interface

To gain deeper mechanistic insight into how surface wettability influences catalytic performance by modulating mass transport, computational fluid dynamics (CFD) simulations were performed. Figure 12 addresses the critical role of mass transport limitations in aqueous CO₂ER. Figure 12a provides a schematic illustration that defines the diffusion layer thickness (δ) near the catalyst surface. Figure 12b then quantitatively illustrates the theoretical impact of this diffusion layer by plotting the mass transfer-limited current density (j_{lim}) calculated directly from Equation (6) [10]:

$$j_{lim} = \frac{nFD_0C_0}{\delta} \quad (6)$$

where n is the number of electrons, F is the Faraday constant, D_0 is the diffusion coefficient, and C_0 is the bulk reactant concentration. This calculated plot clearly demonstrates the strong inverse dependence of the maximum achievable current density on the diffusion layer thickness, showing a sharp decrease in j_{lim} as δ increases. This theoretical relationship highlights the inherent challenge posed by liquid-phase reactant diffusion in achieving high current densities.

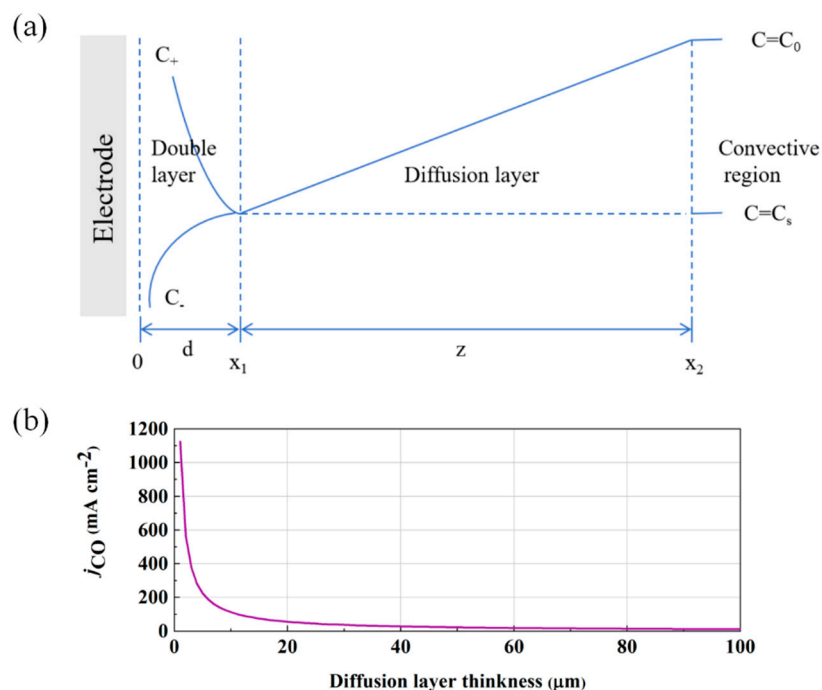


Figure 12. Impact of diffusion layer thickness on CO₂ reduction rate. (a) Concentration profile schematic at the electrode interface. (b) Calculated CO partial current density as a function of diffusion layer thickness.

The microchannel reactor configuration employed in this study (schematically depicted in Figure 13) is designed to mitigate this by fostering a direct three-phase interface, thereby reducing the liquid-phase diffusion path for CO₂ compared to fully immersed electrodes.

Simulations presented in Figure 14 directly assess the critical role of engineered hydrophobicity within the microchannel by demonstrating the impact of varying catalyst surface contact angle on electrolyte distribution. At a low contact angle (60°), representative of the hydrophilic Cu@Zn surface, an extensive flooding of the catalyst structure occurs. This configuration creates a substantial liquid film barrier, impeding CO₂ diffusion to active sites and limiting performance, consistent with the mass transport principles illustrated

in Figure 12. Conversely, increasing the contact angle to 105° , and particularly 120° , simulating the hydrophobic PTFE-modified surfaces, leads to electrolyte recession and significantly enhances gas penetration into the catalyst layer. The simulation at 120° indicates the formation of a stable, thin electrolyte film coating the catalyst structures, which are otherwise predominantly exposed to the CO_2 gas phase. This simulated thin-film configuration represents a near-optimal scenario for mass transport, minimizing the CO_2 diffusion distance through the liquid while theoretically maintaining sufficient electrolyte contact for proton/ion conduction and water supply. Therefore, these CFD results strongly corroborate the experimental findings, demonstrating that increasing surface hydrophobicity effectively tailors the TPI structure to alleviate CO_2 mass transport limitations. The superior performance observed experimentally for Cu@Zn-8PTFE (contact angle $\sim 115^\circ$) likely arises from achieving an optimal balance in the real system, maximizing the benefits of reduced diffusion path length (approaching the 120° simulation) without significantly compromising other factors such as overall ionic conductivity or complete active site wetting.

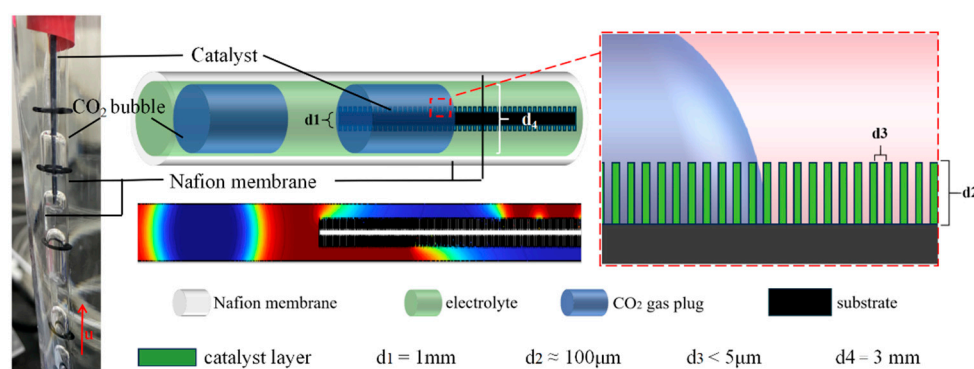


Figure 13. Photograph (left) illustrating the segmented CO_2 bubble flow in the actual device, alongside a schematic diagram (right) detailing the design of the microchannel reactor, including catalyst layer architecture and key dimensions.

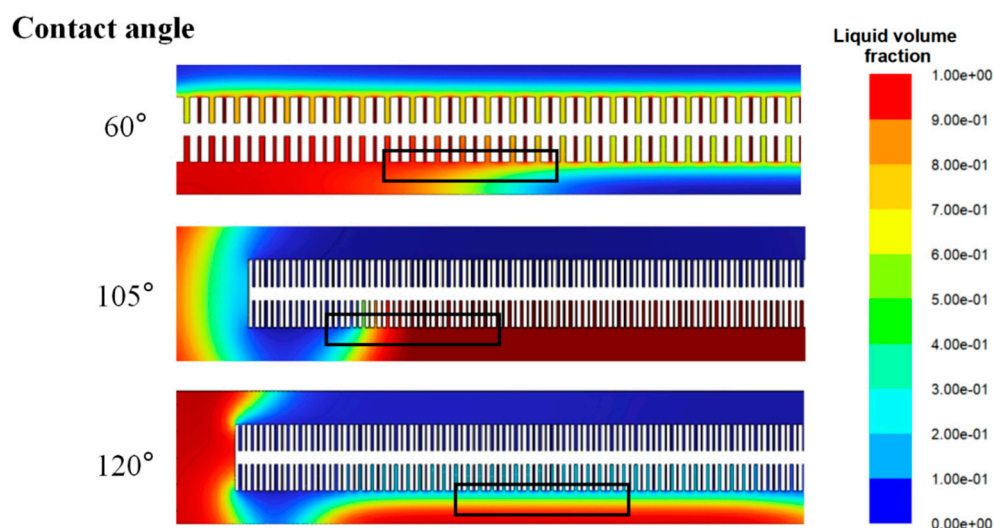


Figure 14. Impact of surface wettability on electrolyte distribution within the catalyst layer.

4. Conclusions

In summary, this study successfully developed hydrophobic, porous Cu@Zn foam catalysts using a straightforward dynamic hydrogen bubble template method and incorporating PTFE. When employed in a microchannel reactor for CO_2 electroreduction, these

catalysts demonstrated significantly enhanced performance. The optimized Cu@Zn-8PTFE achieved a remarkable CO Faradaic efficiency (FE_{CO}) of 96.5% at -15 mA cm^{-2} and exhibited excellent stability, maintaining $FE_{CO} > 90\%$ for 64 h. The key to this improvement lies in the tailored hydrophobicity, which creates an efficient three-phase (gas–liquid–solid) interface, thereby promoting CO_2 mass transfer to the active sites while suppressing the competing hydrogen evolution reaction. However, our results also reveal a critical trade-off: excessive hydrophobicity (Cu@Zn-16PTFE) negatively impacts performance by increasing charge transfer resistance and hindering electrolyte access. This underscores the importance of optimizing the degree of hydrophobicity, likely targeting a Wenzel–Cassie coexistent state, to balance enhanced mass transport with sufficient catalyst conductivity and active site availability. Ultimately, this work validates controlled hydrophobic modification as a powerful strategy for boosting selectivity and activity in CO_2 electroreduction and provides valuable guidelines for designing advanced electrocatalysts.

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