



Proton tunneling interfacial engineering enables selective CO₂ electroreduction on CoZn oxide nanoflowers

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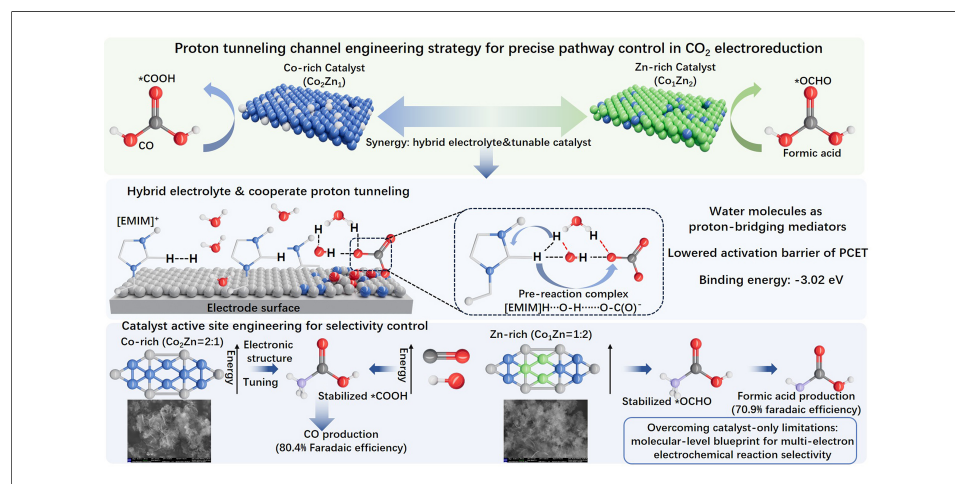
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Abstract

The electrochemical CO₂ reduction reaction (CO₂RR) holds great promise for closing the anthropogenic carbon cycle, yet conventional aqueous electrolytes epitomized by KHCO₃ suffer from intrinsically low CO₂ solubility, sluggish mass transport, and poor product selectivity, which collectively hamper catalytic efficiency and pathway controllability. Here, we report a rationally designed hybrid electrolyte system comprising 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) supplemented with KHCO₃, integrated with composition-tunable CoZn oxide nanoflower catalysts, that enables highly efficient and precisely switchable conversion of CO₂ to either CO or formic acid (HCOOH). Through an integrated approach combining electrochemical measurements, *in situ* infrared spectroscopy, and multiscale theoretical simulations (density functional theory + ab initio molecular dynamics), we uncover a previously unrecognized cooperative proton tunneling mechanism: water molecules act as proton-bridging mediators, constructing a linear [EMIM]-H...O-H...O-C(O)⁻ pre-reaction complex at the electrode interface that dramatically lowers the activation barrier of the proton-coupled electron transfer step. Critically, the Co:Zn ratio dictates the electronic structure of active sites; Co centers stabilize *COOH intermediates for CO evolution, whereas Zn centers favor *OCHO

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stabilization for HCOOH formation. Under optimized conditions, the Co:Zn = 2:1 catalyst achieves a Faradaic efficiency of 80.4% for CO, whereas the Co:Zn = 1:2 counterpart delivers 70.9% for HCOOH. This work establishes a paradigm of “proton tunneling channel engineering” via electrolyte-catalyst synergy, offering a molecular-level blueprint for precise control over multi-electron electrochemical transformations beyond CO₂RR.

INTRODUCTION

The electrochemical CO₂ reduction reaction (CO₂RR) offers a transformative route to convert waste CO₂ into value-added chemicals using renewable electricity, thereby closing the anthropogenic carbon cycle. Among the possible products, C₁ molecules such as carbon monoxide (CO) and formic acid (HCOOH) are particularly attractive from both economic and industrial standpoints: CO is a key syngas component for the Fischer-Tropsch process, while HCOOH serves as a promising hydrogen carrier and platform chemical^[1-3]. However, CO₂RR inherently involves multi-electron/proton transfer steps, competing reaction intermediates, and the ubiquitous hydrogen evolution reaction (HER), which collectively impose stringent challenges in achieving high Faradaic efficiency (FE), low overpotential, and precise product selectivity^[4,5]. Consequently, the rational design of CO₂RR systems that can selectively steer the reaction toward a single C₁ product, either CO or HCOOH, represents a central frontier in electrocatalysis.

Considerable efforts have been devoted to developing cost-effective, earth-abundant alternatives to noble metal catalysts. The earliest strategy employed monometallic catalysts: cobalt-based materials selectively reduce CO₂ to CO via favorable *COOH binding, achieving FE of 60%-80% but suffering from pronounced hydrogen evolution, *CO poisoning, and an inability to produce HCOOH; conversely, zinc-based catalysts favor the *OCHO intermediate for HCOOH generation yet exhibit poor intrinsic activity, rapid corrosion, and FE typically below 70%^[6-9]. Neither monometallic Co nor Zn can simultaneously achieve high activity, high selectivity, and long-term stability for a single C₁ product. To overcome these limitations, bimetallic CoZn oxide systems leverage complementary properties: Co provides high intrinsic activity for CO₂ activation, while Zn modulates the electronic structure of adjacent Co sites via ligand and strain effects and introduces its own selectivity toward *OCHO. The synergistic effects manifest as (i) d-band center tuning that optimizes intermediate adsorption energies, (ii) geometric ensemble effects that isolate Co sites to suppress C-C coupling, (iii) bifunctional active sites where Co activates CO₂ and Zn facilitates subsequent protonation, and (iv) composition-dependent selectivity switching that steers the dominant product from CO (Co-rich) to HCOOH (Zn-rich). Indeed, adjusting the Co:Zn ratio enables precise control over the reaction trajectory. Despite these advances, catalyst-centric optimization alone quickly reaches performance ceilings imposed by conventional aqueous electrolytes such as KHCO₃, which suffer from low CO₂ solubility (≈34 mM), an electric double layer that poorly stabilizes the key *CO₂⁻ intermediate, and a high overpotential for CO₂ activation^[10,11]. As a result, even optimally tuned bimetallic catalysts in KHCO₃ exhibit restricted reaction rates, persistent HER competition, and moderate FE ceilings (typically < 85% for CO and < 75% for HCOOH). Thus, there is an urgent need to move beyond purely catalyst-focused strategies and develop innovative electrolyte systems that synergistically interact with the catalyst, rather than serving merely as inert conductive media.

Beyond the constraints of conventional electrolytes, the CO₂RR field faces more fundamental challenges that cannot be resolved by catalyst engineering alone. The reaction operates at a gas-liquid-solid three-phase interface, where multiple competing processes CO₂ dissolution and diffusion, proton transfer from the electrolyte to the catalyst surface, and electron/proton injection into adsorbed intermediates must be orchestrated simultaneously. From a thermodynamic perspective, the linear scaling relationship between binding energies of key intermediates (*COOH, *CO, *OCHO) imposes an intrinsic limitation: optimizing the catalyst for one intermediate inevitably destabilizes others, making it difficult to achieve both high

activity and exclusive selectivity for a single C₁ product^[12–15]. Moreover, the initial one-electron reduction of CO₂ to *CO₂^{•−} requires a highly negative equilibrium potential (−1.90 V vs. standard hydrogen electrode), representing a substantial thermodynamic barrier that is poorly mitigated by most catalyst designs. From a kinetic standpoint, the proton-coupled electron transfer (PCET) step, the hydrogenation of *CO₂^{•−} to *COOH (or *OCHO), is rate-determining for most CO₂RR pathways. The kinetics of this step are exquisitely sensitive to the interfacial proton availability and local electric field, yet these parameters are difficult to control in conventional aqueous electrolytes where water serves as both the proton source and the solvent^[16,17].

The poorly defined hydrogen-bonding network at the electrode/electrolyte interface leads to inefficient proton delivery, forcing the reaction to proceed through high-energy transition states. Furthermore, the competing HER pathway, which involves more facile PCET kinetics, often outruns CO₂RR in aqueous media, especially at high overpotentials. These thermodynamic and kinetic bottlenecks represent field-wide challenges that call for innovative strategies beyond conventional catalyst optimization. Recent advances have further demonstrated that interfacial electrolyte engineering can effectively modulate the local reaction environment to enhance CO₂RR performance^[18,19]. Herein, we report a conceptually distinct hybrid electrolyte system composed of [EMIM]Cl with a controlled amount of KHCO₃, which not only retains the CO₂-activation benefits of the ionic liquid but also improves mass transfer and supplies a necessary proton source. Integrated with composition-tunable CoZn oxide nanoflower catalysts, this electrolyte-catalyst ensemble achieves a remarkable performance leap: the Co:Zn = 2:1 catalyst delivers a FE of 80.4% for CO, whereas switching the ratio to Co:Zn = 1:2 shifts the selectivity to HCOOH with an FE of 70.9%. Using *in situ* infrared spectroscopy and density functional theory (DFT) calculations, we unravel the interfacial origin of this enhancement. In conventional KHCO₃, the weak K⁺-H₂O interaction yields a loosely structured interface with weak CO₂ adsorption and sluggish kinetics. In neat [EMIM]Cl, proton transfer is severely hindered by steric constraints and the high energy barrier for C₂-H bond cleavage. Remarkably, in the hybrid [EMIM]Cl/KHCO₃ electrolyte, water molecules establish a linear hydrogen-bonded chain [EMIM]-H...O-H...O-C(O)^{•−} forming a “pre-reaction complex” that enables a cooperative proton tunneling mechanism. This mechanism synergistically couples proton transfer with electron donation, achieves functional separation (water as the proton shuttle, [EMIM]⁺ as the proton reservoir), and markedly reduces the activation barrier of the PCET step. By systematically correlating macroscopic electrochemical performance with molecular-level interfacial dynamics, this work establishes a rational electrolyte catalyst design strategy for precise pathway control in CO₂RR and underscores the transformative potential of proton tunneling channel engineering for advancing sustainable CO₂ conversion technologies beyond conventional catalyst-centric paradigms.

EXPERIMENTAL

Materials

All chemical reagents were used as received without further purification. Specifically, cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99%), zinc chloride (ZnCl₂), tetraethyl orthosilicate (TEOS, > 99%), urea (99.5%), ammonium hydroxide solution (25%~28%), and cetyltrimethylammonium bromide (CTAB) were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was employed for the preparation of all solutions throughout the experimental process.

Material synthesis

Synthesis of mesoporous SiO₂ nanospheres

Mesoporous SiO₂ nanospheres (MSN) were synthesized according to a reported method^[20]. In a typical procedure, 53.2 mL of deionized water was mixed with 64 mL of n-butanol under stirring for 5 min. Then, 2.56 g of CTAB was added, and the mixture was stirred for another 10 min. Subsequently, 28 mL of ammonium hydroxide was quickly injected, and the container was sealed, followed by stirring for 30 min.

Table 1. Metal precursor ratios for the three CoZn oxide catalysts

Catalyst ID	Co (NO ₃) ₂ ·6H ₂ O/mmol	ZnCl ₂ /mmol	Co:Zn molar ratio
1	1.25	1.25	≈1:1
2	1.70	0.80	≈2:1
3	0.83	1.67	≈1:2

Finally, 11.2 mL of TEOS was added, and the reaction was allowed to proceed under sealed conditions with continuous stirring for 24 h. The entire process was conducted at a constant temperature of 27 °C. After the reaction, the white solid product was collected, thoroughly washed alternately with deionized water and ethanol, and dried overnight in an oven at 85 °C. The resulting yellowish solid was calcined at 500 °C for 6 h to obtain the final MSN support.

Synthesis of CoZn oxide catalysts

Three catalysts with different Co/Zn molar ratios were prepared. The general synthesis procedure was as follows: A total of 2.5 mmol of cobalt nitrate and ZnCl₂ (specific quantities for each ratio are listed in Table 1) were dissolved in 10 mL of deionized water and stirred at 500 rpm for 5 min. Then, 1.2 g of urea and 1.5 mL of ammonium hydroxide were added, and the mixture was stirred for another 5 min. Subsequently, 0.3 g of the as-synthesized MSN support was quickly introduced. The mixture was immediately transferred to an oil bath at 80 °C and reacted with continuous stirring at 350 rpm for 5 h. The resulting blue solid was collected by centrifugation, washed three times with deionized water, and vacuum-dried overnight at 60 °C. Finally, the product was calcined in an air atmosphere with a heating rate of 10 °C/min to 300 °C and maintained at this temperature for 4 h to obtain the final catalyst.

Physical characterization

Scanning electron microscopy (SEM) was conducted on a Zeiss GeminiSEM300 instrument (Carl Zeiss Microscopy Ltd.). Transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) with energy-dispersive X-ray spectroscopy mapping were performed using a FEI Talos F200X instrument (Thermo Fisher Scientific, Waltham, MA, USA). X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250Xi instrument (Thermo Fisher Scientific, Waltham, MA, USA) using monochromatic Al K α radiation. X-ray diffraction (XRD) patterns were collected on a Rigaku Ultimate IV diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu K α radiation. Nitrogen adsorption-desorption isotherms were measured using a Micromeritics 3Flex instrument (Micromeritics Instrument Corporation, Norcross, GA, USA). For *in situ* attenuated total reflection-fourier-transform infrared spectroscopy (ATR-FTIR) studies, a Thermo Fisher Nicolet IS 50 FTIR spectrometer configured with an MCT/B detector and a VeeMAX III ATR accessory was utilized. A custom three-electrode spectroelectrochemical cell was employed. The working electrode was fabricated by applying a catalyst film onto a gold-sputtered silicon prism. An Ag/AgCl electrode and a platinum wire served as the reference and counter electrodes, respectively. The electrochemical environments consisted of two separate electrolyte systems: (i) 0.1 M KHCO₃ aqueous solution saturated with CO₂, and (ii) the hybrid electrolyte system composed of 0.06 M KHCO₃ + 0.1 M [EMIM]Cl saturated with CO₂. The cell was interfaced with a potentiostat, and IR spectra were collected during controlled potential holds across a range from open-circuit potential, 0 to -1.1 V vs. reversible hydrogen electrode (RHE).

Electrochemical evaluation

The electrochemical measurements were performed using a CHI760E electrochemical workstation (CH Instruments, Shanghai) in a conventional two-compartment H-cell separated by a Nafion 117 membrane. A standard three-electrode configuration was employed, consisting of a catalyst-coated working electrode, an

Ag/AgCl reference electrode, and a Pt sheet counter electrode. Electrochemical characterization involved linear sweep voltammetry (LSV) conducted at a scan rate of 5 mV/s in CO₂-saturated and Ar-saturated electrolytes. The hybrid electrolyte system was prepared by mixing 0.1 M KHCO₃ aqueous solution with 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) in a 3:2 volume ratio. (The hybrid electrolyte system was prepared by first diluting commercial [EMIM]Cl ($\geq 98\%$ purity, molecular weight 146.62 g/mol) with deionized water to prepare a 0.25 M [EMIM]Cl stock solution. e.g., 30 mL of 0.1 M KHCO₃ + 20 mL of [EMIM]Cl for larger-scale preparations, or 15 mL + 10 mL for smaller-scale experiments, 0.06 M KHCO₃ + 0.1 M [EMIM]Cl. The final electrolyte thus contains approximately 0.06 M KHCO₃ and 0.1 M [EMIM]Cl. Electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency range of 100 kHz to 0.1 Hz with an AC amplitude of 5 mV. The electrocatalytic CO₂RRs were conducted under potentiostatic control in both a 0.1 M KHCO₃ solution and a hybrid electrolyte system comprising 0.06 M KHCO₃ + 0.1 M [EMIM]Cl. A constant CO₂ flow of 30 mL/min was maintained throughout the electrolysis experiments, with each compartment of the H-cell containing 25 mL of electrolyte. The gaseous effluent from the cathodic compartment was continuously monitored and quantitatively analyzed using online gas chromatography. The FE for a given product *i* was determined by the relation: $FE_i = (n_i \times z_i \times F)/Q \times 100\%$, where the terms *n_i*, *z_i*, *F*, and *Q* denote the moles of product generated, the electron transfer number per molecule, the Faraday constant, and the total charge consumed, respectively. Potentials referenced to the Ag/AgCl electrode were converted to the RHE scale using the formula: $E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.197 + 0.0596 \times \text{pH}$ (The pH measurements were performed at 27 °C, and the Nernstian slope was calculated accordingly as 0.0596 V per pH unit). First-principles calculations based on DFT were carried out using the Vienna Ab-initio Simulation Package (VASP). The projector augmented-wave (PAW) method and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional were employed in the calculations. DFT computations were performed to systematically investigate the interaction energies between the [EMIM]⁺ cation and CO₂ molecules, as well as reaction intermediates (COOH and OCHO) on Co and Zn sites. The reaction energy barriers in different systems were also evaluated.

RESULTS AND DISCUSSION

Hierarchical CoZn oxide nanoflowers: morphology, phase and pore architecture

The CoZn oxide catalysts supported on MSN were first examined by SEM and TEM. Regardless of the Co:Zn ratio, all catalysts self-assemble into uniform three-dimensional (3D) flower-like architectures composed of interlaced nanosheets (SEM images of the catalysts are provided in [Supplementary Figure 1](#)). This open hierarchical structure provides a high density of accessible active sites and facilitates reactant diffusion, a distinct structural advantage for CO₂RR^[21,22]. Increasing the Zn content systematically reduces the nanoflower size [[Figure 1A-C](#)]. Mechanistically, Zn²⁺ ions promote nucleation while suppressing Ostwald ripening, acting as a “morphology-directing agent” that balances nucleation promotion and growth inhibition^[23,24]. Elemental mapping [[Figure 1D](#)] confirms homogeneous distribution of Co, Zn, and Si, verifying successful catalyst loading.

The crystal phase composition and structural evolution of the mesoporous SiO₂-supported CoZn oxide catalysts were probed by XRD. As depicted in [Figure 2A](#), the bare mesoporous SiO₂ (SiO₂-supported CoZn oxide catalysts) support exhibits a characteristic broad diffraction halo centered at around 22.47°, which is indicative of its amorphous nature. Upon the integration of Co and Zn species, distinct crystalline phases emerge. For the catalysts with Co:Zn ratios of 2:1 and 1:1, the XRD patterns reveal well-defined diffraction peaks at 35.31° and 58.90°^[25,26]. These peaks can be indexed to the characteristic reflections of a cobalt-zinc composite oxide phase, suggestive of the formation of a crystalline spinel-type structure (e.g., ZnCo₂O₄)^[27]. Notably, a significant phase evolution is observed with a further increase in Zn content. Specifically, the pattern for the Co:Zn = 1:2 catalyst not only retains the aforementioned peaks but also manifests an additional distinct peak at 64.64°. The emergence of this new diffraction feature coincides with the overall

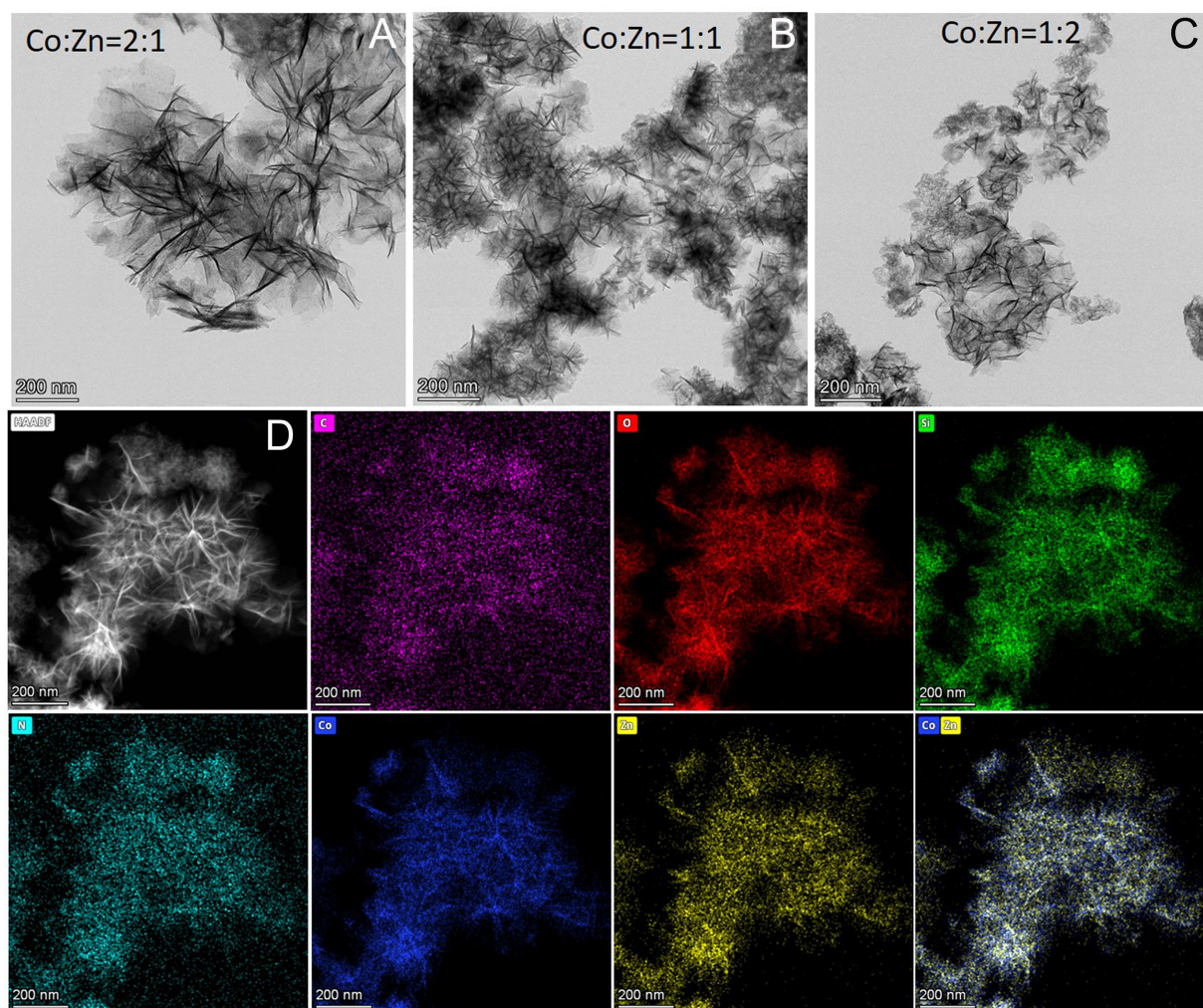


Figure 1. (A–C) TEM images of the three-dimensional flower-like hierarchical catalysts with different Co/Zn molar ratios, revealing their fine morphological features. (D) High-angle annular dark-field scanning TEM image and the corresponding elemental maps of C, O, Si, N, Co, and Zn for the catalyst with a Co/Zn molar ratio of 2:1, confirming the spatially homogeneous distribution of each element within the architecture.

pattern more closely aligning with that of a zinc-rich phase, such as ZnO (zincite, JCPDS No. 36-1451), where the peak at $\sim 64.64^\circ$ corresponds to its (103) crystal plane^[28]. This systematic shift in the XRD profiles unequivocally demonstrates that increasing Zn incorporation redirects the crystallization pathway, favoring the formation of ZnO alongside or in place of the bimetallic spinel phase, thereby altering the catalyst's intrinsic phase composition. It should be noted that the as-synthesized catalysts are oxide-based materials (ZnCo_2O_4 spinel and ZnO phases), as confirmed by XRD analysis, rather than CoZn metallic alloys. CoZn oxide nanoflower catalysts with different Co:Zn atomic ratios exhibit distinct pore structural characteristics, which are closely correlated with their CO_2RR catalytic performance and product selectivity. From the pore size distribution curves [Figure 2B], clear composition-dependent mesoporous features can be observed across the three catalysts. The Co:Zn = 2:1 catalyst shows a dominant mesopore distribution in the 10–20 nm range, with a differential pore volume of $\sim 0.4 \text{ cm}^3/\text{g}$. This narrower and more uniform mesoporous structure effectively restricts the over-hydrogenation of intermediates and promotes CO desorption, leading to a FE of 80.4% for CO at this ratio. In contrast, for the Co:Zn = 1:2 catalyst, a sharp and intense mesopore peak centered at approximately 10–40 nm is evident, with a differential pore volume ($dV/d\log \text{ Pore Volume}$) reaching $\sim 0.6 \text{ cm}^3/\text{g}$, indicating the formation of a highly developed and uniform mesoporous network. This large-sized mesoporous structure facilitates the rapid diffusion of CO_2 and reaction intermediates, providing

sufficient reaction space for the formation of HCOOH, thereby achieving a FE of 70.9% for formic acid at this ratio. The Co:Zn = 1:1 catalyst, however, shows a relatively broad pore-size distribution with a distinct peak at smaller pore sizes, and delivers a lower maximum differential pore volume. This observation aligns well with its moderate catalytic activity and broad product distribution trend in CO₂RR.

Electronic structure modulation by Co:Zn ratio: the origin of selectivity switching

To establish a comprehensive correlation between catalyst composition, physicochemical properties, and CO₂RR performance, we first conducted systematic compositional and textural characterization of the three CoZn oxide nanoflower catalysts. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis [Supplementary Table 1] confirms that the actual Co:Zn molar ratios (0.98:1, 1.95:1, and 0.49:1 for the three catalysts, respectively) are in excellent agreement with the nominal target ratios ($\approx$ 1:1, $\approx$ 2:1, and $\approx$ 1:2), validating our precise synthetic control over catalyst composition. Complementary Brunauer-Emmett-Teller (BET) surface area and total pore volume measurements [Supplementary Table 2] reveal systematic textural variations as a function of composition. The Co:Zn = 2:1 catalyst exhibits a BET surface area of 142 m²/g and a total pore volume of 0.38 cm³/g (with a pore size of approximately 20 nm), whereas the Co:Zn = 1:2 catalyst shows substantially higher values of 186 m²/g and 0.57 cm³/g, consistent with its larger mesopores centered at roughly 25–40 nm [Figure 2B]. The Co:Zn = 1:1 catalyst displays intermediate values (165 m²/g and 0.45 cm³/g). These systematic textural variations directly correlate with the observed product selectivity: the narrower mesopores of the Co-rich catalyst favor CO desorption and suppress over-hydrogenation, while the larger mesopores of the Zn-rich catalyst facilitate rapid diffusion of CO₂ and reaction intermediates, providing sufficient reaction space for HCOOH formation. Moreover, XPS survey scans [Supplementary Table 3] reveal that the residual nitrogen content from the CTAB template and urea is consistently low ($\sim$ 1.2–1.5 at%) across all three catalysts with no systematic variation, confirming that residual nitrogen does not contribute to the observed selectivity trends. Having established the composition-property relationships, we next examined the electronic structure modulation induced by the Co:Zn ratio using high-resolution XPS analysis. XPS was employed to gain deep insights into the surface elemental chemical states and electronic structures of the mesoporous SiO₂ and the CoZn oxide nanoflower catalysts supported thereon. High-resolution scans of the C 1s region revealed characteristic peaks at 283.0, 284.1, 285.4 and 287.3 eV [Figure 2C], which are assigned to metal carbide/carbon-silicon bonds (C-M/C-Si), adventitious carbon/amorphous carbon (C-C/C-H, commonly used as an internal reference), hydroxyl/ether carbon (C-O) and carboxyl/carbonyl carbon (C=O), respectively^[29]. Notably, a negative binding energy shift of 0.1–0.4 eV was observed for the C-O and C=O peaks with decreasing Co:Zn ratio (i.e., increasing Zn content), indicating enhanced electron-donating character in Zn-rich regions and a weakening of the C-O bond polarity^[30,31]. For the Si 2p spectrum [Figure 2D], the pristine mesoporous SiO₂ support exhibited peaks at 101.5, 101.8, and 102.5 eV, corresponding to Si²⁺ (sub-oxide), Si³⁺ (intermediate oxide), and Si⁴⁺ (SiO₂), respectively, confirming its partially oxidized surface state^[32,33]. However, upon deposition of the CoZn oxide nanoflowers, the Si 2p peaks underwent a systematic negative shift (up to 0.8–0.9 eV) to 100.6, 101.6, and 102.2 eV. This clearly demonstrates electron transfer from the metal nanoflowers to the SiO₂ support, reducing the silicon oxidation state, with the effect being more pronounced at higher Zn contents due to promoted interfacial electron coupling and delocalization facilitated by Zn's electronegativity. Further analysis of the metal active sites showed that the Co 2p spectrum featured main peaks at 780.2 eV (Co 2p_{3/2}) and 796.5 eV (Co 2p_{1/2}) [Figure 2E], indicative of Co²⁺ oxidation states (in phases like CoO or ZnCo₂O₄ spinel), along with satellite peaks at 785.3 and 802.4 eV consistent with a high-spin d⁷ electronic configuration^[34,35]. As the Co:Zn ratio decreased, the Co 2p_{3/2} main peak exhibited a positive binding energy shift (up to +0.5 eV), revealing a decreased electron density at the Co sites, originating from the competition of Zn²⁺ for lattice oxygen, which weakens the covalency of the Co-O bond^[36]. In stark contrast, the Zn 2p spectrum [Figure 2F], with characteristic peaks at 1,021.0 eV (Zn 2p_{3/2}) and 1,043.9 eV (Zn 2p_{1/2}), confirming the presence of Zn²⁺ species, showed a negative shift of approximately 0.4 eV for the Zn 2p_{3/2} peak when the

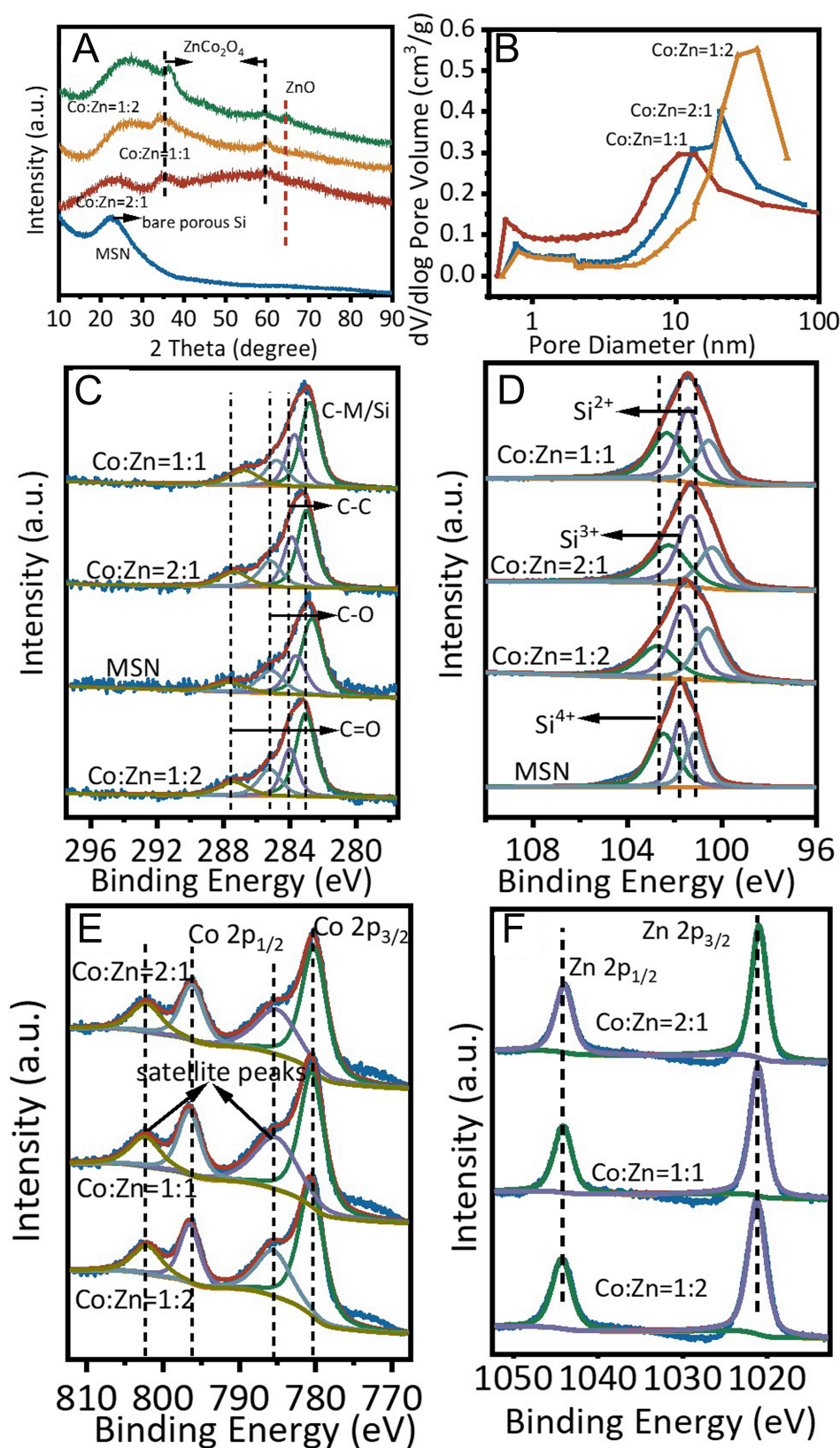


Figure 2. (A) XRD patterns of the three-dimensional flower-like hierarchical catalysts with varied Co/Zn molar ratios. (B) Pore size distribution curves derived from N_2 adsorption-desorption isotherms for the corresponding three catalysts. (C-F) High-resolution XPS spectra of catalysts with different Co/Zn molar ratios: (C) C 1s, (D) Si 2p, (E) Co 2p, and (F) Zn 2p core levels.

Co:Zn ratio increased^[37]. This suggests an increased electron density at Zn sites, likely associated with electron transfer from Co^{2+} to the Zn 4s-p orbitals, thereby optimizing the interfacial Lewis acidity. XPS analysis unequivocally reveals that variations in the Co:Zn ratio modulate the intermetallic charge distribution, inducing systematic binding energy shifts (positive for Co, negative for Zn and SiO_2). This pronounced electronic effect profoundly influences the adsorption behavior of key reaction intermediates on the catalyst surface, thereby providing crucial evidence at the electronic structure level for understanding the switching mechanism of the CO_2RR pathway selectivity (CO vs. HCOOH).

Dramatic enhancement of CO_2RR kinetics in hybrid [EMIM]Cl/ KHCO_3 electrolyte

EIS analysis reveals significant differences between the conventional KHCO_3 electrolyte and the innovative [EMIM]Cl/ KHCO_3 composite electrolyte in the electrocatalytic CO_2RR . Bode plots demonstrate that the impedance modulus of the composite electrolyte system is markedly lower than that of the pure KHCO_3 system at the same applied potential, indicating a substantial reduction in interfacial charge transfer resistance (Nyquist plots, Figure 3A and B). The difference is most pronounced at less negative potentials and diminishes at more negative potentials due to the increased driving force for charge transfer, which accelerates the kinetics in both systems. Quantitative analysis using equivalent circuit fitting [Supplementary Table 4] confirms that the charge transfer resistance (R_{ct}) of the hybrid electrolyte is consistently lower than that of pure KHCO_3 across all tested potentials. This phenomenon is attributed to the unique interfacial layer formed by the adsorption of $[\text{EMIM}]^+$ on the electrode surface, which interacts with CO_2 molecules to form $[\text{EMIM}]^+-\text{CO}_2$ complex intermediates, substantially lowering the overpotential for CO_2 reduction to CO^[14,38,39]. As the potential shifts negatively from -0.3 to -0.9 V vs. RHE, the impedance values of both electrolytes gradually decrease, reflecting enhanced charge transfer kinetics at higher overpotentials. However, the composite electrolyte consistently exhibits lower impedance values across all tested potentials, demonstrating the additional catalytic promotion provided by the imidazolium cations^[38]. The evolution of phase and phase angle plots offers further critical insights into the interfacial kinetics (Bode magnitude plots, Figure 3C and D). The shift of the phase angle peak to higher frequencies in the composite electrolyte indicates a decrease in the time constant of the electrode interface process, corresponding to an accelerated charge transfer rate (Bode phase-angle plots, Figure 3E and F). The sharpening of the phase angle peak suggests a more concentrated distribution of time constants, reflecting improved uniformity of the electrode/electrolyte interface and enhanced synergy in the reaction process. The overall shift of the phase angle peak to more negative values (e.g., from -30° to -40°) signifies enhanced interfacial capacitive behavior, originating from the restructured electric double layer at the electrode surface with higher double-layer capacitance due to the imidazolium cations. This reconstituted double layer not only promotes CO_2 enrichment but also reduces the reaction activation barrier by stabilizing the CO_2 radical anion intermediate. The interfacial enhancement mechanism in the composite electrolyte system can be summarized in three aspects: First, the $[\text{EMIM}]^+$ adsorbed on the electrode surface forms hydrogen bonds with the CO_2 radical anion via $\text{C}_2\text{-H}$ or $\text{C}_4/\text{C}_5\text{-H}$, stabilizing key reaction intermediates^[40]. Second, the adsorption layer of $[\text{EMIM}]^+$ alters the structure and thickness of the electric double layer^[41], increasing the local electric field strength and facilitating the initial electron transfer step to CO_2 ^[42]. Finally, this unique interfacial microenvironment may also suppress the competing HER, further improving the selectivity of CO_2RR . These factors collectively contribute to the substantially enhanced efficiency of CO_2RR , providing an important theoretical foundation for the design of highly efficient electrocatalytic interfaces^[43]. It is worth emphasizing that the advantages of our [EMIM]Cl/ KHCO_3 hybrid electrolyte system are fundamentally distinct from and complementary to those provided by gas diffusion electrode (GDE) architectures. Our hybrid electrolyte actively participates in the reaction mechanism through multiple functions that GDE architecture alone cannot provide: (i) the $[\text{EMIM}]^+$ cations form strong non-covalent interactions with the negatively charged CO_2^- intermediate via $\text{C}_2\text{-H}$ hydrogen bonding, stabilizing this high-energy species and lowering the activation barrier for the initial electron transfer step; (ii) the electrolyte establishes a linear hydrogen-bonded $[\text{EMIM}]\text{-H}\cdots\text{O-H}\cdots\text{O-C(O)}^-$

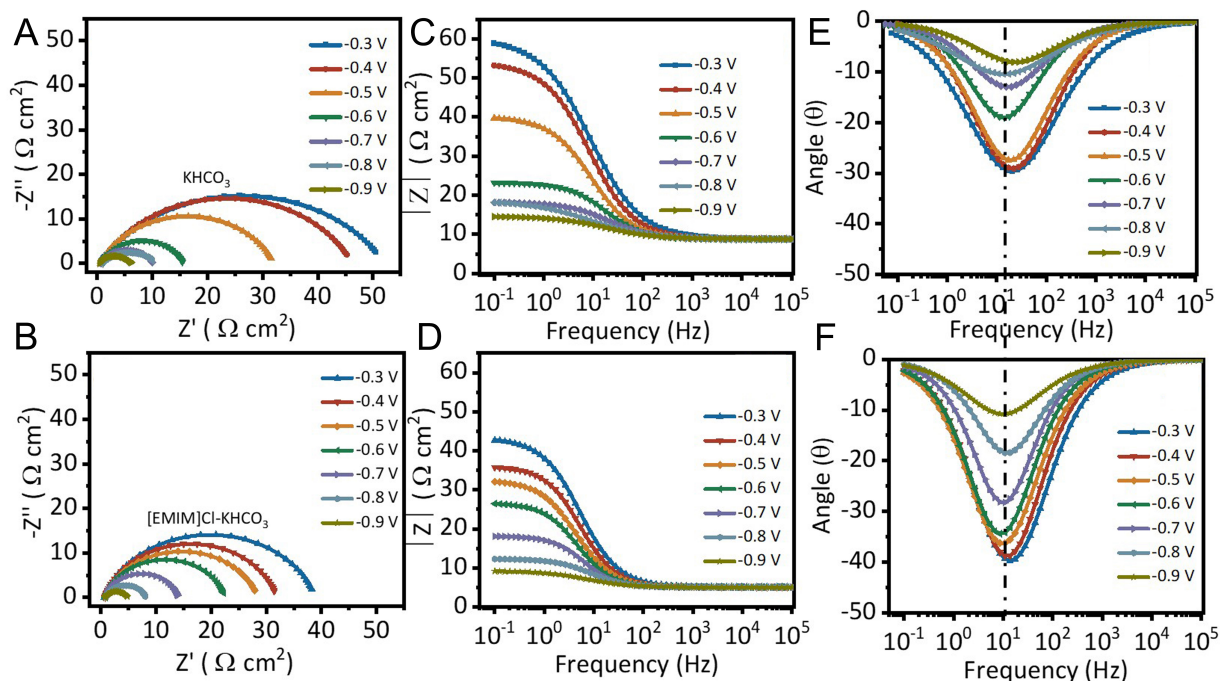


Figure 3. Electrochemical impedance spectroscopy of the catalyst with a Co/Zn molar ratio of 2:1 in (A, C, E) 0.1 M KHCO_3 and (B, D, F) 0.06 M KHCO_3 + 0.1 M [EMIM]Cl electrolyte. (A and B) Nyquist plot, (C and D) Bode magnitude plot, and (E and F) Bode phase angle plot.

pre-reaction complex that enables a cooperative proton tunneling mechanism, fundamentally altering the PCET kinetics and substantially reducing the overpotential; and (iii) the imidazolium cation adsorption layer inherently suppresses HER by excluding water molecules from the active sites. These are intrinsic molecular-level benefits that arise from the electrolyte's chemical composition, independent of the electrode architecture. While GDEs effectively address the physical mass transport limitations of CO_2 , our electrolyte engineering strategy targets the thermodynamic and kinetic bottlenecks at the molecular level, offering a synergistic and complementary design principle that can be readily integrated with GDE-based systems for enhanced practical performance.

Precise pathway switching: CO vs. HCOOH with record selectivities

This study systematically investigates the regulatory mechanism and synergistic enhancement effects of CoZn oxide nanoflower catalysts in a [EMIM]Cl/ KHCO_3 composite electrolyte system for the electrocatalytic CO_2 RR. In the conventional KHCO_3 electrolyte [Figure 4A], the LSV curves of all CoZn oxide catalysts under CO_2 and Ar atmospheres are nearly superimposable, indicative of negligible electrocatalytic activity toward CO_2 RR. Here, the current response for CO_2 RR is indistinguishable from the background current associated with the HER, highlighting the inefficiency of bare KHCO_3 in facilitating CO_2 activation. In stark contrast, incorporation of the [EMIM]Cl/ KHCO_3 electrolyte [Figure 4B] elicits a dramatic enhancement in cathodic current density for all catalysts under CO_2 , with the Co:Zn = 2:1 catalyst exhibiting a significantly enhanced current density ($P < 0.01$, Student's t-test, $n = 3$) compared to the other compositions. This observation unequivocally demonstrates that the composite electrolyte synergizes with the CoZn oxide catalysts to accelerate CO_2 RR kinetics and suppress parasitic side reactions. In the pure KHCO_3 electrolyte [Figure 4C–E], the product landscape is dominated by CO, HCOOH, and H_2 , with substantial HER contribution across all potentials and catalyst compositions. A clear composition-dependent selectivity trend emerges: increasing Zn content shifts the primary product from CO (Co:Zn = 2:1) to HCOOH (Co:Zn = 1:2), while the Co:Zn = 1:1 catalyst yields a mixed distribution of CO and HCOOH [Table 2]. This selectivity divergence stems from intrinsic differences in intermediate binding energies at Co and Zn active sites: Co sites bind $^*\text{COOH}$ and $^*\text{CO}$ intermediates with moderate strength, favoring the sequential proton-electron transfer steps leading to CO desorption. Conversely, Zn sites exhibit negligible affinity for $^*\text{CO}$ and

preferentially stabilize the $^*\text{OCHO}$ intermediate, thus steering the reaction toward HCOOH formation via the formate pathway. The product distribution is profoundly altered in the $[\text{EMIM}]\text{Cl}/\text{KHCO}_3$ electrolyte [Figure 4F–H]. Most notably, the $\text{Co}:\text{Zn} = 2:1$ catalyst achieves a total FE of 89.5% for C_1 products ($\text{CO} + \text{HCOOH}$) at a low overpotential of -0.9 V vs. RHE in the $[\text{EMIM}]\text{Cl}/\text{KHCO}_3$ hybrid electrolyte [Figure 4F]. The maximum total C_1 FE of $93.81\% \pm 1.8\%$ is achieved at -1.0 V vs. RHE , accompanied by a marked suppression of HER^[7,44–47]. This performance enhancement is attributed to the multi-faceted synergistic effects of the ionic liquid component: (1) $[\text{EMIM}]^+$ cations form a robust interfacial adsorption layer, where their $\text{C}_2\text{-H}$ moieties engage in strong non-covalent interactions with negatively charged $^*\text{CO}_2^-$ intermediates, stabilizing this high-energy species and lowering the activation barrier for CO_2 reduction; (2) the high CO_2 solubility and viscosity of the ionic liquid establish a CO_2 -enriched microenvironment at the electrode electrolyte interface, ensuring a sustained supply of reactant; (3) the unique electric double-layer structure induced by $[\text{EMIM}]\text{Cl}$ generates a strong interfacial electric field, which polarizes and activates CO_2 molecules, while simultaneously excluding water molecules from the active sites to kinetically suppress HER. Collectively, these effects enable the precise compositional tuning of Co/Zn ratios to act as a "selectivity switch" for CO_2RR pathways, underscoring the critical role of electrolyte-catalyst engineering in achieving efficient and selective CO_2 conversion. To evaluate the stability of $[\text{EMIM}]\text{Cl}$ under our operating conditions, we performed ^1H NMR (nuclear magnetic resonance) spectroscopy on the $[\text{EMIM}]\text{Cl}/\text{KHCO}_3$ hybrid electrolyte before and after 12 h of chronoamperometry at -1.0 V vs. RHE , which corresponds to the optimal CO_2RR potential for the $\text{Co}:\text{Zn} = 2:1$ catalyst. The NMR spectra (presented in Supplementary Figure 2) show that all characteristic proton resonances of the $[\text{EMIM}]^+$ cation, specifically, the $\text{C}_2\text{-H}$ proton at $\sim 9.2\text{ ppm}$, the $\text{C}_{4/5}\text{-H}$ protons at $\sim 7.5\text{ ppm}$, the N-CH_2 protons at $\sim 4.2\text{ ppm}$, and the N-CH_3 protons at $\sim 3.8\text{ ppm}$, remain essentially unchanged in both chemical shift and integration intensity after prolonged electrolysis. Importantly, no new peaks corresponding to potential decomposition products (such as deprotonated imidazole species or ring-opened products) were detected within the detection limit of NMR spectroscopy. Additionally, post-electrolysis FTIR analysis of the electrolyte showed no emergence of new absorption bands that would indicate degradation of the imidazolium cation. To investigate the structural evolution of the oxide-based CoZn catalysts under CO_2RR operating conditions, we performed post-electrolysis characterization of the $\text{Co}:\text{Zn} = 2:1$ catalyst after 12 h of chronoamperometry at -1.0 V vs. RHE in the $[\text{EMIM}]\text{Cl}/\text{KHCO}_3$ electrolyte. As shown in Supplementary Figure 3, the XRD pattern of the spent catalyst retains the characteristic diffraction peaks of the spinel ZnCo_2O_4 phase, although a slight decrease in peak intensity is observed, suggesting that the overall crystalline framework remains largely intact. Post-electrolysis high-resolution XPS analysis of the spent $\text{Co}:\text{Zn} = 2:1$ catalyst [Supplementary Figure 4A–C] reveals notable yet subtle changes in the $\text{Co } 2\text{p}$ spectrum compared to the pristine catalyst. Specifically, a small shoulder emerges at approximately 778.5 eV , which is characteristic of metallic Co^0 formed via the electrochemical reduction of Co^{2+} species under cathodic polarization ($\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}^0$). This observation confirms that a minor fraction of surface Co^{2+} species undergoes reduction during CO_2RR electrolysis. Concurrently, the main $\text{Co } 2\text{p}_{3/2}$ peak remains centered at approximately 780.2 eV , indicative of Co^{2+} species in the spinel oxide structure, while a small feature at approximately 781.5 eV , previously ambiguously assigned, is more appropriately attributed to Co^{3+} species inherently present in the octahedral sites of the ZnCo_2O_4 spinel lattice or to surface hydroxylation resulting from air exposure during sample transfer, rather than to cathodic reduction. The $\text{Zn } 2\text{p}$ spectrum, in contrast, exhibits no discernible changes after electrolysis. Collectively, these observations indicate that the majority of Co species retain the Co^{2+} oxidation state, confirming that the spinel oxide framework is largely preserved under reaction conditions. The emergence of the metallic Co^0 shoulder, however, suggests that only a minor fraction of surface Co^{2+} species undergoes reduction during electrolysis, potentially generating the true active sites for CO_2RR while the bulk spinel structure remains intact. Importantly, the characteristic spinel oxide phase is maintained as the dominant structure, with only minor surface reconstruction occurring at the outermost

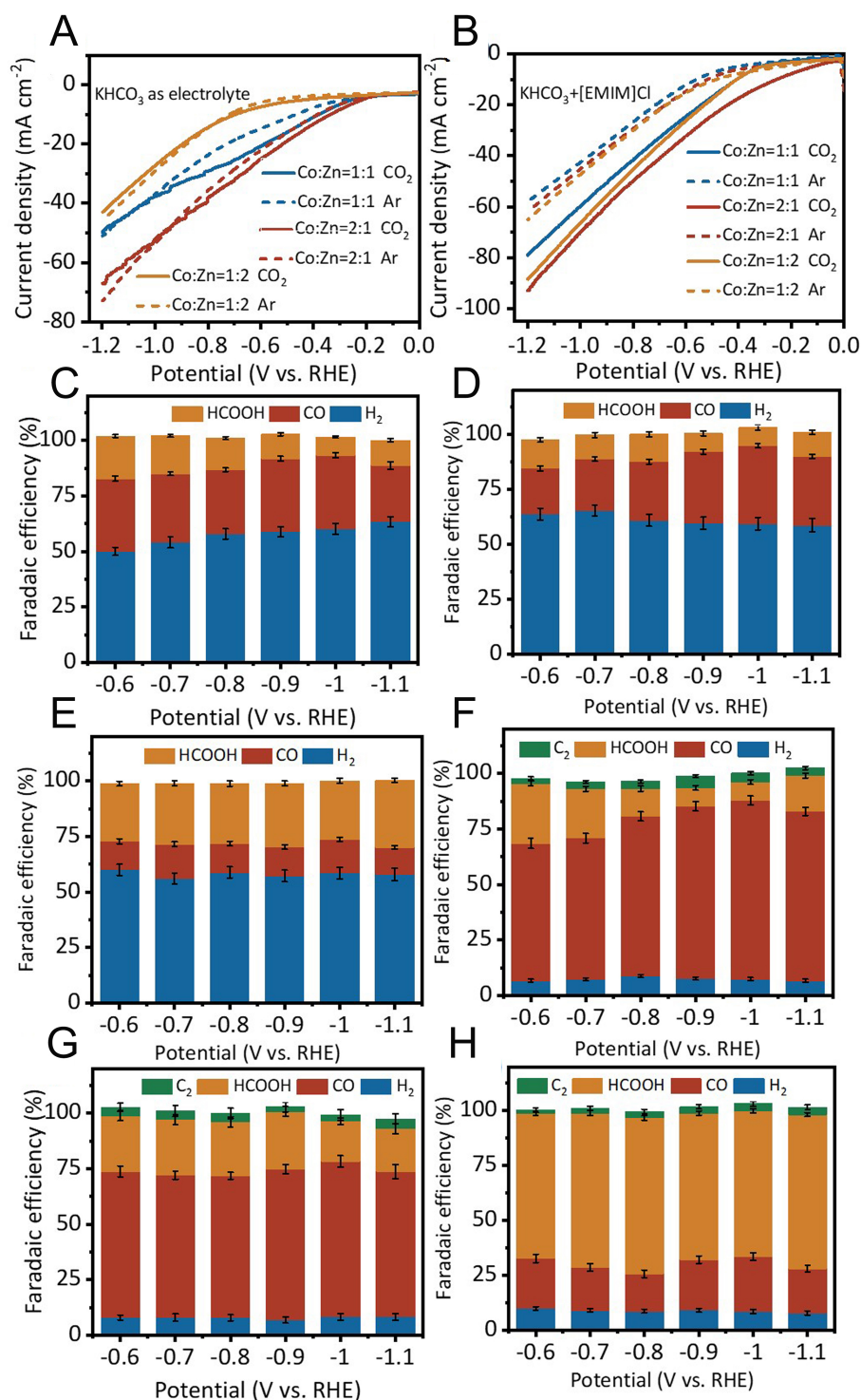


Figure 4. (A) CO₂RR polarization curves of catalysts with different Co/Zn molar ratios in 0.1 M KHCO₃ electrolyte. (B) CO₂RR polarization curves of catalysts with different Co/Zn molar ratios in the composite electrolyte of 0.06 M KHCO₃ + 0.1 M [EMIM]Cl. (C-E) Faradaic efficiencies for major products at various applied potentials in 0.1 M KHCO₃ electrolyte: (C) Co:Zn = 2:1, (D) Co:Zn = 1:1, (E) Co:Zn = 1:2. (F-H) Faradaic efficiencies for major products at various applied potentials in the composite electrolyte: (F) Co:Zn = 2:1, (G) Co:Zn = 1:1, (H) Co:Zn = 1:2. All potentials are reported vs. the reversible hydrogen electrode (RHE). All error bars represent the standard deviation (SD) from $n = 3$ independent measurements performed using separately prepared catalyst samples and fresh electrolytes.

atomic layers. These results collectively demonstrate that the CoZn oxide nanoflowers serve as stable precatalysts that undergo minimal structural evolution while preserving their hierarchical architecture, with surface reduction potentially generating the true active sites for CO₂RR.

Table 2. Comparison of CO₂RR performance under different catalysts and electrolyte conditions

Catalyst	Electrolyte system	Main product	Faradaic efficiency (%) at -0.9 V vs. RHE	Total faradaic efficiency CO + HCOOH (%) at -0.9/-1.0 V vs. RHE
Co:Zn = 2:1	0.1 M KHCO ₃	CO	33.1 ± 1.4	51.82 ± 1.2
Co:Zn = 2:1	0.06 M KHCO ₃ + 0.1 M [EMIM]Cl	CO	80.4 ± 2.1	89.5 ± 2.3/93.81 ± 1.8
Co:Zn = 1:2	0.1 M KHCO ₃	HCOOH	30.1 ± 2.8	42.22 ± 1.3
Co:Zn = 1:2	0.06 M KHCO ₃ + 0.1 M [EMIM]Cl	HCOOH	70.9 ± 1.5	89.97 ± 1.9/91.49 ± 2.5

Values are reported as mean ± standard deviation (SD) from $n = 3$ independent measurements. The total C_1 FE (main product CO) for Co:Zn = 2:1 in the hybrid electrolyte at -0.9 V vs. RHE is 89.5% ± 2.3% (see main text). The maximum total C_1 FE of 93.81% ± 1.8% is achieved at -1.0 V vs. RHE. The total C_1 FE (CO + HCOOH) for Co:Zn = 1:2 in the hybrid electrolyte at -0.9 V vs. RHE is 89.97% ± 1.9% (see main text). The maximum total C_1 FE (main product HCOOH) of 91.49% ± 2.5% is achieved at -1.0 V vs. RHE.

In situ spectroscopy reveals enhanced intermediate stabilization

In situ Fourier transform infrared spectroscopy was employed to systematically compare the mechanistic pathways of CO₂RR over CoZn oxide catalysts in conventional KHCO₃ vs. a [EMIM]Cl/KHCO₃ electrolytes. In the conventional KHCO₃ electrolyte [Figure 5A and B], the characteristic spectral signals corresponding to the C-OH deformation and asymmetric O-C-O stretching vibrations of the *COOH intermediate (within the 1,190–1,350 cm⁻¹ region) and chemisorbed *CO (at 1,015 cm⁻¹) remained weak, showing only a gradual increase as the potential shifted negatively. This indicates limited catalytic activity toward the CO formation pathway under these conditions. In contrast, within the [EMIM]Cl/KHCO₃ electrolyte [Figure 5C and D], the signal intensities in the same spectral regions were substantially enhanced and rose rapidly with increasingly negative potential. This observation can be attributed to the ionic liquid's role in elevating the local CO₂ concentration and modulating the interfacial electric field, thereby effectively promoting the formation of the *COOH intermediate and the desorption of *CO. Simultaneously, the Zn-C vibrational peak observed around ~842 cm⁻¹ reveals the synergistic role of Zn sites, whose electronic interaction with the ionic liquid may further optimize the electronic structure of adjacent Co active centers.

Molecular mechanism: cooperative proton tunneling via a linear hydrogen-bonded pre-reaction complex

To systematically elucidate the intrinsic influence of the electrolyte microenvironment on the performance of the electrocatalytic CO₂RR, this study integrates macroscopic electrochemical experiments with multiscale theoretical simulations. By constructing three characteristic interfacial models, namely, the conventional KHCO₃ aqueous solution, the anhydrous [EMIM]Cl ionic liquid, and [EMIM]Cl/KHCO₃, and combining DFT calculations with ab initio molecular dynamics (AIMD) simulations, we unravel at the molecular level the regulatory mechanism of the interfacial hydrogen-bonding network on proton transfer pathways and reaction energy barriers. The computational results reveal that in the conventional KHCO₃ system, the interface features a disordered weak interaction network of K⁺...OH⁻...OC(O)⁻ formed by water molecules and K⁺, with a binding energy of only -1.1 eV [Figure 6A]. This nonspecific adsorption is identified as the key factor responsible for the high overpotential. In the pure [EMIM]Cl system, although [EMIM]⁺ cations are enriched at the cathode interface, proton transfer is severely hindered due to steric hindrance between the imidazole ring and the -CO₂⁻ intermediate, as well as the excessively high energy barrier for direct cleavage of the C₂-H bond. The binding energy is even lower (-0.73 eV, Figure 6B), confirming the thermodynamic and kinetic unfavorability of the direct proton transfer pathway in the absence of a proton carrier. Upon introducing water to form the [EMIM]Cl/KHCO₃ hybrid electrolyte, the interfacial proton transfer mechanism undergoes a fundamental transformation. DFT calculations reveal that water molecules act as proton-bridging media, simultaneously forming strong hydrogen bonds with the C₂-H of [EMIM]⁺ and the oxygen atom of -CO₂⁻, thereby constructing a linear [EMIM]-H...O-H...O-C(O)⁻ pre-reaction complex. This configuration, through cooperative hydrogen bonding, substantially enhances the binding energy to -3.02 eV

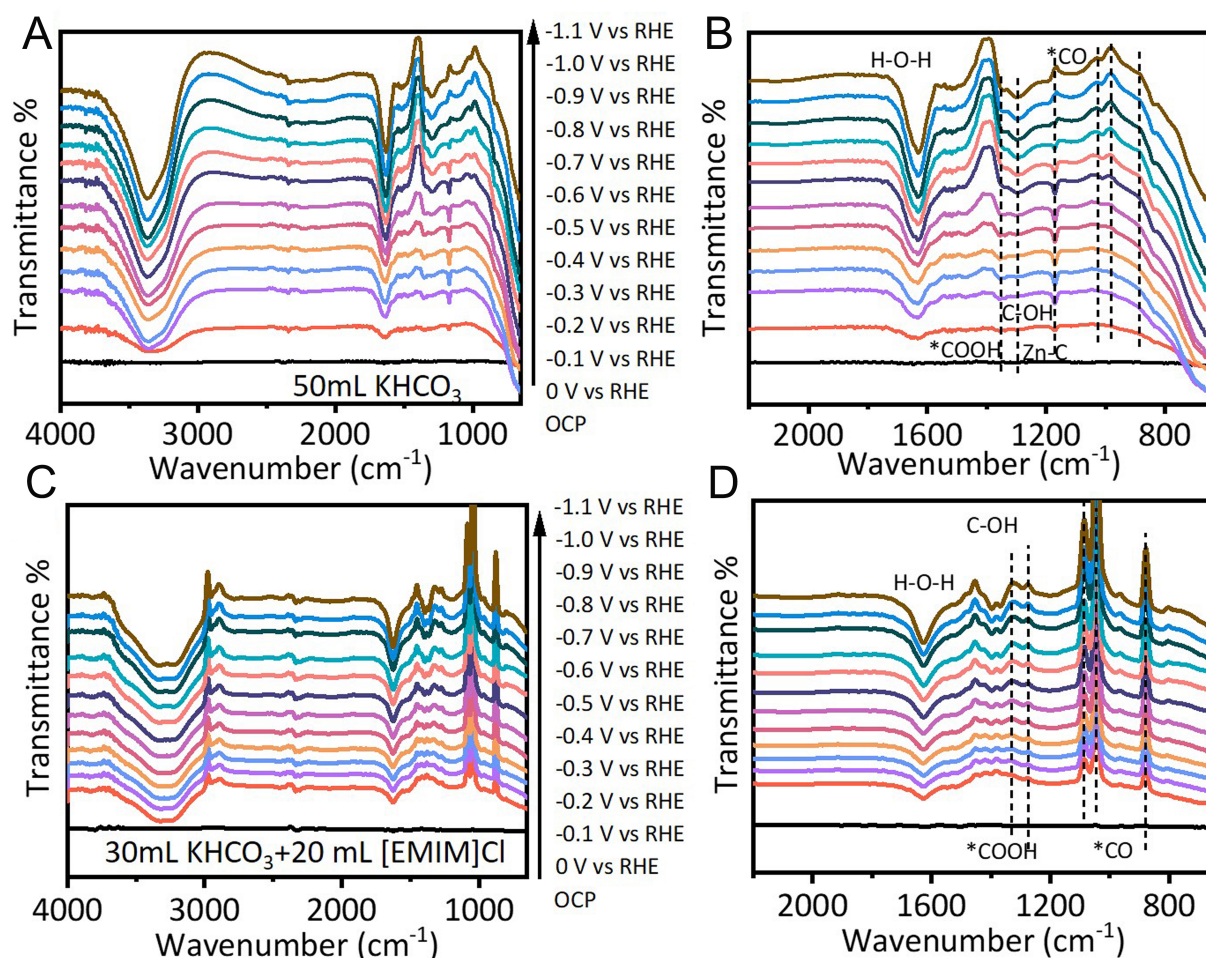


Figure 5. *In situ* infrared spectra acquired at different applied potentials for the catalyst with Co:Zn = 2:1 in (A and B) KHCO_3 and (C and D) KHCO_3 /[EMIM]Cl electrolyte, showing (A and C) the full-range spectra and (B and D) the spectral features in specific wavenumber regions. All four subfigures share the same color scheme, where each color corresponds to a specific applied potential (from 0 to -1.1 V vs. RHE, as indicated in the legend of (A), which applies to all panels).

[Figure 6C], greatly stabilizing the key intermediate. The core of this mechanism lies in the synergistic proton tunneling process: the formation of the hydrogen-bond chain weakens the $\text{C}_2\text{-H}$ and O-H bonds, coupling proton transfer with electron donation. This process achieves functional separation $[\text{EMIM}]^+$ serves as the proton donor, while water molecules act as an efficient proton transfer shuttle, thereby substantially reducing the activation energy of the PCET step.

Furthermore, the adsorption behavior of the pre-reaction complex $[\text{EMIM}]\text{-H}\cdots\text{O-H}\cdots$ on the CoZn oxide nanoflower catalyst surface was calculated, yielding a binding energy as high as -1.47 eV [Figure 6D], confirming the effective stabilization of this active species on the catalyst surface. Combined with the analysis of the reaction free energy diagram [Figure 6E], the thermodynamic favorability of this pathway for CO production is validated. To capture the dynamic interfacial behavior under realistic operating conditions, we performed AIMD simulations [Figure 6F]. The results show that during a 10 ps dynamic evolution, water molecules continuously construct and reconstruct transient linear $[\text{EMIM}]\text{-H}\cdots\text{O-H}\cdots\text{O-C(O)}^-$ hydrogen-bond networks between $[\text{EMIM}]^+$ and $\cdot\text{CO}_2^-$. This dynamic hydrogen-bridging mechanism provides atomistic evidence for the existence and sustainability of the aforementioned synergistic proton tunneling pathway, revealing the efficient synergy between proton supply and transfer channels in the hybrid electrolyte system. These findings offer a clear molecular-level foundation for designing low-overpotential electrolyte environments for CO_2RR .

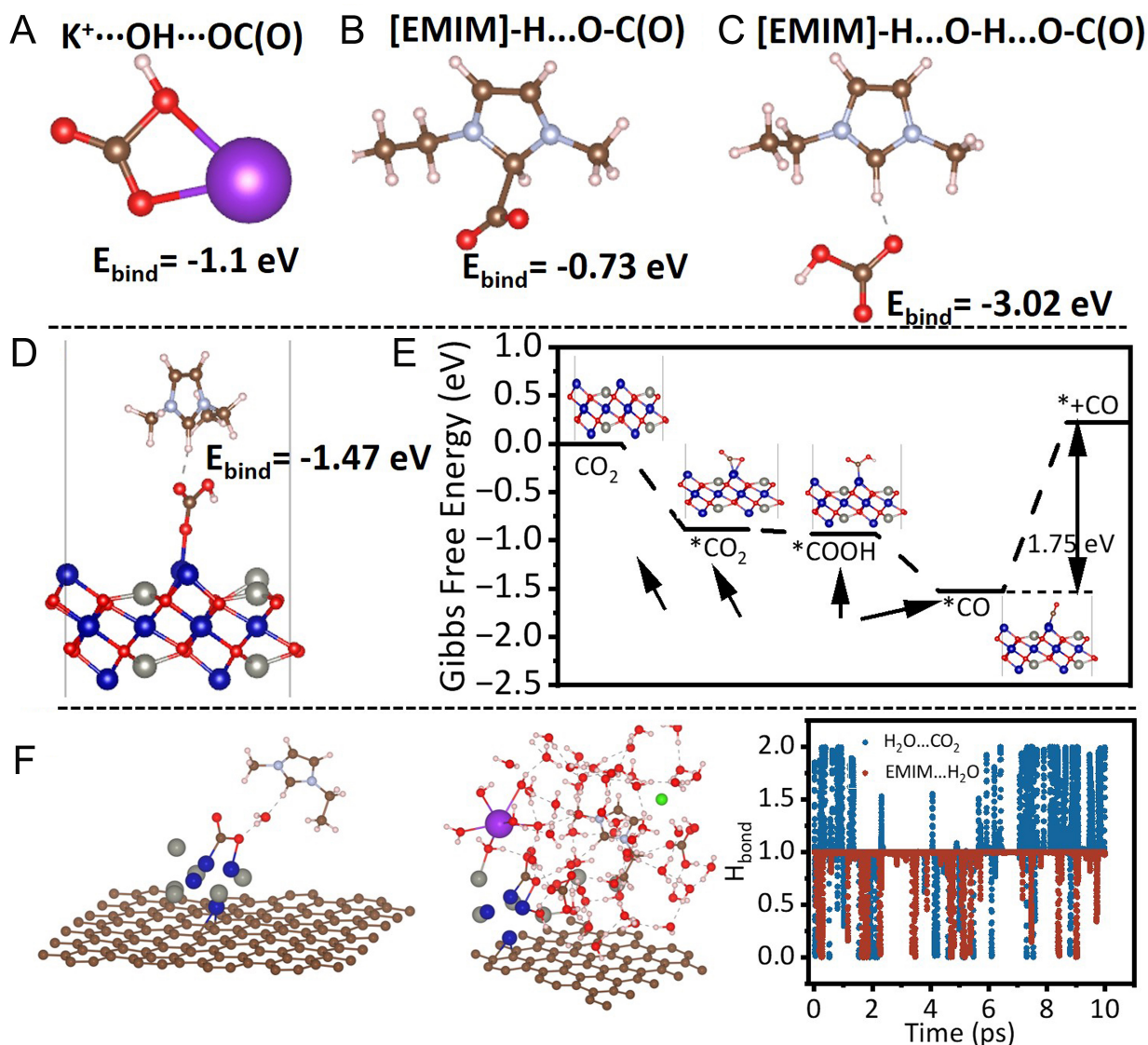


Figure 6. (A) Disordered $\text{K}^+\cdots\text{OH}\cdots\text{OC}(\text{O})^-$ in conventional KHCO_3 ; weak interactions, -1.1 eV . (B) Pure $[\text{EMIM}]\text{Cl}$; steric hindrance lowers binding to -0.73 eV , hindering direct proton transfer. (C) Linear $[\text{EMIM}]\text{-H}\cdots\text{O-H}\cdots\text{O-C}(\text{O})^-$ network in $[\text{EMIM}]\text{Cl}/\text{KHCO}_3$ hybrid: binding enhanced to -3.02 eV , highlighting water as proton-bridging mediator. (D) Adsorption of key $[\text{EMIM}]\text{-H}\cdots\text{O-H}\cdots$ complex on CoZn oxide nanoflower: binding energy -1.47 eV , confirming active species stabilization. (E) Reaction free energy diagram: thermodynamic favorability of CO production pathway validated. (F) AIMD snapshot (10 ps): transient linear H-bonding network between $[\text{EMIM}]^+$ and $\cdot\text{CO}_2^-$ mediated by water, evidencing the synergistic proton tunneling mechanism.

CONCLUSION

In summary, we have established a synergistic electrolyte-catalyst engineering strategy that enables precise manipulation of CO₂ reduction pathways through a cooperative proton tunneling mechanism. By integrating a hybrid $[\text{EMIM}]\text{Cl}/\text{KHCO}_3$ electrolyte with composition-tunable CoZn oxide nanoflower catalysts, we achieved exceptional selectivity control: the Co:Zn = 2:1 catalyst delivers a FE of 80.4% for CO, while the Co:Zn = 1:2 counterpart yields 70.9% for HCOOH, both at substantially reduced overpotentials compared to conventional KHCO_3 systems. Mechanistically, we unraveled a previously unrecognized cooperative proton tunneling pathway enabled by the unique interfacial hydrogen-bonding network. Water molecules act as proton-bridging mediators, constructing a linear $[\text{EMIM}]\text{-H}\cdots\text{O-H}\cdots\text{O-C}(\text{O})^-$ pre-reaction complex at the electrode/electrolyte interface. This configuration dramatically enhances the binding energy to -3.02 eV and lowers the activation barrier of the PCET step, as revealed by DFT calculations. AIMD simulations further

demonstrate the dynamic persistence of this hydrogen-bonded architecture under operating conditions, confirming its functional role in sustaining efficient proton transfer. Critically, the electronic structure modulation arising from tunable Co/Zn ratios, evidenced by systematic XPS binding energy shifts, governs the adsorption energetics of key intermediates (*COOH vs. *OCHO), thereby dictating the ultimate product selectivity. The hybrid electrolyte does not merely serve as a passive medium; it actively participates in the rate-determining PCET step, amplifying the intrinsic selectivity differences between Co and Zn sites. This work introduces the concept of “proton tunneling channel engineering” as a design principle for next-generation CO₂ reduction systems. Beyond achieving record-high selectivities, our findings establish a molecular-level blueprint for electrolyte-catalyst synergy that transcends conventional catalyst-centric paradigms. The demonstrated strategy opens new avenues for precise control over multi-electron electrochemical reactions, including but not limited to CO₂RR, and underscores the transformative potential of rational electrolyte design in advancing sustainable energy conversion technologies.

DECLARATIONS

Authors' contributions

Made substantial contributions to formal analysis, visualization, and writing, review and editing: Hu, Y.; Wang, N.

Made substantial contributions to project administration, funding acquisition, and supervision: Lin, X.; Liu, Q.

All authors have read and approved the final manuscript.

Availability of data and materials

The data supporting the findings of this study are available within the article and its [Supplementary Materials](#). Additional raw data (including original microscopy images, electrochemical measurements, and DFT calculation inputs and outputs) are available from the corresponding authors upon reasonable request.

AI and AI-assisted tools statement

During the preparation of this manuscript, the AI tool Deepseek (version DeepSeek-V3.2, released 2025-12-01) was used solely for language polishing and grammar checking. The tool did not influence the study design, data collection, analysis, interpretation, or the scientific content of the work. All authors take full responsibility for the accuracy, integrity, and final content of the manuscript.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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Supplementary Materials

[Supplementary Materials](#)

REFERENCES

1. Zhang, W.; Jin, Z.; Chen, Z. Rational-designed principles for electrochemical and photoelectrochemical upgrading of CO₂ to value-added chemicals. *Adv. Sci.* **2022**, *9*, 2105204. DOI PubMed PMC
2. Jiang, M.; Wang, H.; Zhu, M.; et al. Review on strategies for improving the added value and expanding the scope of CO₂ electroreduction products. *Chem. Soc. Rev.* **2024**, *53*, 5149-89. DOI
3. Kumar De, S.; Won, D.; Kim, J.; Kim, D. H. Integrated CO₂ capture and electrochemical upgradation: the underpinning mechanism and techno-chemical analysis. *Chem. Soc. Rev.* **2023**, *52*, 5744-802. DOI
4. Liu, L.; Deng, C.; Xu, Y.; et al. Advancing CO₂ upgrading to multicarbon products: synergies between photo/electrochemical and biological conversion. *Adv. Funct. Mater.* **2025**, *36*, e13716. DOI
5. Wang, C.; Lv, Z.; Feng, X.; Yang, W.; Wang, B. Recent advances in electrochemical CO₂-to-multicarbon conversion: from fundamentals to industrialization. *Adv. Energy. Mater.* **2023**, *13*, 2302382. DOI
6. Chen, Z.; Zhang, G.; Du, L.; Zheng, Y.; Sun, L.; Sun, S. Nanostructured cobalt-based electrocatalysts for CO₂ reduction: recent progress, challenges, and perspectives. *Small* **2020**, *16*, 2004158. DOI
7. Li, N.; Si, D.; Wu, Q.; Wu, Q.; Huang, Y.; Cao, R. Boosting electrocatalytic CO₂ reduction with conjugated bimetallic Co/Zn polyphthalocyanine frameworks. *CCS. Chem.* **2023**, *5*, 1130-43. DOI
8. Zhu, W.; Zhang, L.; Liu, S.; et al. Enhanced CO₂ electroreduction on neighboring Zn/Co monomers by electronic effect. *Angew. Chem. Int. Ed.* **2020**, *59*, 12664-8. DOI
9. Gong, Y.; Yang, X.; Zhang, Y.; et al. Constructing asymmetric-electron-density Pd-Zn dual-atoms on N-doped defective mesoporous carbon for electrochemical reduction of CO₂. *Chem. Eng. J.* **2024**, *500*, 156603. DOI
10. Khirak, B. N.; Da Silva, G. T. S. T.; Lai, H. D. T.; et al. Integrated carbon dioxide capture and electrochemical conversion: chemistry, electrode and electrolyzer design, and economic viability. *Adv. Energy. Mater.* **2025**, *16*, e02564. DOI
11. Lai, W.; Qiao, Y.; Wang, Y.; Huang, H. Stability issues in electrochemical CO₂ reduction: recent advances in fundamental understanding and design strategies. *Adv. Mater.* **2023**, *35*, 2306288. DOI PubMed
12. Zeng, S.; Zhang, X.; Bai, L.; et al. Ionic-liquid-based CO₂ capture systems: structure, interaction and process. *Chem. Rev.* **2017**, *117*, 9625-73. DOI
13. Wang, Y.; Wang, Y.; Zhao, Y.; Fu, J.; Liu, Z. Ionic liquids promoted transformation of carbon dioxide. *Chem. Rev.* **2025**, *125*, 6057-129. DOI
14. Fortunati, A.; Risplendi, F.; Re Fiorentin, M.; et al. Understanding the role of imidazolium-based ionic liquids in the electrochemical CO₂ reduction reaction. *Commun. Chem.* **2023**, *6*, 84. DOI PubMed PMC
15. Dongare, S.; Zeeshan, M.; Aydogdu, A. S.; et al. Reactive capture and electrochemical conversion of CO₂ with ionic liquids and deep eutectic solvents. *Chem. Soc. Rev.* **2024**, *53*, 8563-631. DOI
16. Eisele, L.; Bica-Schröder, K. Photocatalytic carbon dioxide reduction with imidazolium-based ionic liquids. *ChemSusChem* **2025**, *18*, e202402626. DOI PubMed PMC
17. Fu, Z.; Zhang, J.; Wu, H.; et al. Ionic liquids functionalized copper catalytic systems for electrocatalytic carbon dioxide reduction. *ChemCatChem* **2024**, *16*, e202401049. DOI
18. Liu, M.; Zhang, C.; Ying, Y.; et al. Optimization strategies for enhancing the stability of Cu-based catalysts. *Mater. Rep. Energy.* **2025**, *5*, 100355. DOI
19. Ke, X.; Xu, W.; Liu, C.; et al. Innovative electrode designs for low-temperature electrochemical CO₂ reduction with ampere-level performance. *Energy. Environ. Sci.* **2025**, *18*, 7792-858. DOI
20. Song, J.; Sun, H.; Yao, S.; et al. Semi-confinement effect enhances CH₄ and C₂H₄ production in CO₂ electrocatalytic reduction. *Small* **2025**, *21*, 2411491. DOI
21. Long, Y.; Tao, Y.; Shang, T.; et al. Roles of metal ions in MXene synthesis, processing and applications: a perspective. *Adv. Sci.* **2022**, *9*, 2200296. DOI PubMed PMC
22. Cai, G.; Yan, P.; Zhang, L.; Zhou, H.; Jiang, H. Metal-organic framework-based hierarchically porous materials: synthesis and applications. *Chem. Rev.* **2021**, *121*, 12278-326. DOI

-
23. Chu, L.; Shen, H.; Wei, H.; Chen, H.; Ma, G.; Yan, W. Morphology engineering of ZnO micro/nanostructures under mild conditions for optoelectronic application. *Int. J. Miner. Metall. Mater.* **2024**, *32*, 498–503. DOI
24. Zheng, Y.; Yang, J.; Liu, Z.; Qiao, Z. A. Multi-component crystalline mesoporous materials: synthesis principle and application. *Adv. Mater.* **2025**, *37*, e10911. DOI
25. Lin, Z.; Li, L.; Xi, C.; et al. Fabrication of the hollow dodecahedral NiCoZn layered double hydroxide for high-performance flexible asymmetric supercapacitor. *J. Colloid. Interface. Sci.* **2024**, *657*, 91–101. DOI
26. Han, G.; Liu, C.; Pan, Y.; et al. Artificial photosynthesis over tubular In₂O₃/ZnO heterojunctions assisted by efficient CO₂ activation and S-scheme charge separation. *Adv. Sustain. Syst.* **2022**, *7*, 2200381. DOI
27. Khelifi, N.; Ihzaz, N.; Toulemonde, O.; et al. Cobalt-doped ZnO nanoparticles and PLD-deposited thin film forms: structure, optical properties and nature of magnetic anisotropy. *RSC. Adv.* **2024**, *14*, 27622–33. DOI PubMed PMC
28. Meng, K.; Zhang, J.; Cheng, B.; et al. Plasmonic near-infrared-response S-scheme ZnO/CuInS₂ photocatalyst for H₂O₂ production coupled with glycerin oxidation. *Adv. Mater.* **2024**, *36*, 2406460. DOI
29. Hao, H.; Wang, Y.; Katyal, N.; et al. Molybdenum carbide electrocatalyst in situ embedded in porous nitrogen-rich carbon nanotubes promotes rapid kinetics in sodium-metal-sulfur batteries. *Adv. Mater.* **2022**, *34*, 2106572. DOI
30. Shao, W.; Ling, Y.; Peng, H.; et al. Ion irradiation-induced coordinatively unsaturated Zn sites for enhanced CO hydrogenation. *J. Am. Chem. Soc.* **2025**, *147*, 5703–13. DOI
31. Dong, C.; Mu, R.; Li, R.; et al. Disentangling local interfacial confinement and remote spillover effects in oxide-oxide interactions. *J. Am. Chem. Soc.* **2023**, *145*, 17056–65. DOI
32. Deng, S.; Li, J.; Zewdie, G. M.; et al. Mg-doped porous silicon derived from silica aerogels for fast and stable zinc-ion hybrid capacitors with high capacitance. *Adv. Funct. Mater.* **2023**, *34*, 2311259. DOI
33. Zhao, Y.; Zhang, L.; Liu, Q.; et al. An ultrafast charge-driven topological intercalation prelithiation strategy for carbon-silicon composite anodes. *Adv. Sci.* **2025**, *12*, e06636. DOI PubMed PMC
34. Mittal, S. K.; Yadav, K. L. A sustainable synthesis of mesoporous Mn_{1-x}Ni_xCo₂O₄ nanoparticles: exploring calcination effects on supercapacitor performance. *Nanoscale* **2025**, *17*, 26257–70. DOI PubMed
35. França, M. C.; Lima, I. S.; Ghorbani, A.; et al. Co_(1-x-y)Fe_xZn_y-glycerolate microspheres as electrocatalysts for the oxygen evolution reaction. *ACS Appl. Energy Mater.* **2025**, *8*, 12618–26. DOI PubMed PMC
36. Wang, Z.; Wu, P.; Zou, X.; et al. Optimizing the oxygen-catalytic performance of Zn-Mn-Co spinel by regulating the bond competition at octahedral sites. *Adv. Funct. Mater.* **2023**, *33*, 2214275. DOI
37. Jiang, H.; Zhang, Y.; Waqar, M.; et al. Anomalous Zn²⁺ storage behavior in dual-ion-in-sequence reconstructed vanadium oxides. *Adv. Funct. Mater.* **2022**, *33*, 2213127. DOI
38. Nkurunziza, F.; Dongare, S.; Chatterjee, S.; et al. Alkali cation inhibition of imidazolium-mediated electrochemical CO₂ reduction on silver. *J. Am. Chem. Soc.* **2025**, *147*, 7564–77. DOI
39. Dongare, S.; Coskun, O. K.; Cagli, E.; et al. A bifunctional ionic liquid for capture and electrochemical conversion of CO₂ to CO over silver. *ACS Catal.* **2023**, *13*, 7812–21. DOI PubMed PMC
40. Wang, Q.; Liu, Y.; Tan, Y.; et al. Enhanced acidic CO₂-to-C₂₊ reduction via ionic liquid layer modification. *Small* **2025**, *21*, 2412293. DOI
41. Chi, L. P.; Zhang, Y. C.; Niu, Z. Z.; et al. Acidic CO₂ electrolysis with near-ideal selectivity and carbon efficiency enabled by overcoming its inherent trade-off. *Angew. Chem. Int. Ed.* **2025**, *64*, e202503539. DOI
42. Zhang, Q.; Musgrave, C. B.; Song, Y.; et al. A covalent molecular design enabling efficient CO₂ reduction in strong acids. *Nat. Synth.* **2024**, *3*, 1231–42. DOI
43. Zhang, H.; Liu, S.; Zhang, C.; et al. Lattice hydrogen participation and mass transport acceleration improve CO₂ electroreduction to C₂ products. *Angew. Chem. Int. Ed.* **2025**, *65*, e18519. DOI
44. Liu, T.; Luo, H.; Ouyang, T.; Liu, Z. Q. In situ exsolved CuZn alloy electrocatalysts for CO₂ conversion to tunable syngas production. *Adv. Funct. Mater.* **2024**, *35*, 2415367. DOI
45. Rooney, C. L.; Lyons, M.; Wu, Y.; et al. Active sites of cobalt phthalocyanine in electrocatalytic CO₂ reduction to methanol. *Angew. Chem. Int. Ed.* **2023**, *136*, e202310623. DOI
46. Rosen, J.; Hutchings, G. S.; Lu, Q.; Forest, R. V.; Moore, A.; Jiao, F. Electrodeposited Zn dendrites with enhanced CO selectivity for electrocatalytic CO₂ reduction. *ACS Catal.* **2015**, *5*, 4586–91. DOI
47. Zhou, J.; Nie, W.; Tarnopol, D. E.; Mccrory, C. C. Co-Co and Co-Zn bimetallic complexes for electrocatalytic CO₂ reduction: the role of interrelated intramolecular effects on activity. *Chem. Catal.* **2024**, *4*, 101006. DOI

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