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Regulating reaction pathways in Hybrid-electrolyte Li-CO_2 batteries via electrocatalytic CO_2 reduction reaction paradigm migration

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Owing to the high theoretical energy density, rechargeable lithium-carbon dioxide (Li-CO_2) batteries attract significant attention for synergistic energy storage and carbon fixation. However, the performance of conventional single organic electrolyte systems is hindered by issues such as the deposition of insulating Li_2CO_3 and inefficient CO_2 mass transport, which makes breakthroughs difficult. Hybrid-electrolyte systems isolate the anode and cathode environments via solid electrolytes, constructing an aqueous cathode to accommodate CO_2 reduction reaction (CO_2RR). This design enhances CO_2 solubility, facilitates proton-coupled electron transfer, and suppresses solid-phase deposition, thereby significantly optimizing battery performance. Nevertheless, the cathode reaction mechanism remains unclear, with the evolution of key intermediates, proton/electron transfer pathways, and catalyst-electrolyte synergies yet to be clarified. This work elucidates the limitations of conventional systems, highlights the advantages of hybrid-electrolyte designs, and integrates established principles from CO_2RR electrocatalysis, such as the regulation of reaction pathways by pH, salt concentration, and current density. This study aims to provide a theoretical framework for developing next-generation Li-CO_2 batteries with high energy density and long cycle life while emphasizing the critical value of electrocatalytic insights in deepening the mechanistic understanding.

Against the strategic backdrop of accelerating carbon neutrality globally, the development of technologies capable of simultaneously achieving CO_2 fixation and high-density energy storage has become an urgent priority. Rechargeable lithium-carbon dioxide (Li-CO_2) batteries, which are based on their unique working principle ($4Li + 3CO_2 \leftrightarrow 2Li_2CO_3 + C$), theoretically offer an energy density of up to 1876 Wh kg^{-1}, far exceeding that of existing energy storage systems.[1,2] However, the traditional configuration employing a single organic electrolyte, while able to accommodate the relatively stable operation of the lithium metal anode and provide lithium ion conduction, creates fundamental contradictions with the intrinsic requirements of efficient CO_2 electrochemical reduction reactions (CO_2RR). This fundamental incompatibility stems from several core issues inherent to the organic medium. (1) The two-phase interface formed in organic electrolytes leads to extremely sluggish CO_2 diffusion kinetics; (2) the absence of proton sources impedes proton-coupled electron transfer (PCET) processes essential for efficient CO_2RR; (3) the high overpotential for CO_2 activation in aprotic media favors the thermodynamically stable but insulating Li_2CO_3 as the dominant product, leading to irreversible electrode passivation. These issues collectively undermine the reversibility and energy efficiency of conventional Li-CO_2 batteries.

To address this bottleneck, hybrid electrolyte systems have emerged, the innovation of which lies in the physical isolation of anode and cathode reaction environments. The anode compartment retains organic electrolytes to maintain the stability of the lithium metal anode, whereas the cathode compartment is filled with aqueous electrolytes.[3,4] This configuration offers several decisive advantages over conventional single-electrolyte systems, including enhanced CO_2 solubility and mass transfer in the aqueous phase, efficient proton-coupled electron transfer enabled by water, and tunable product selectivity via pH regulation. By fundamentally avoiding the formation of insulating Li_2CO_3, this design promises higher energy efficiency, lower overpotentials, and extended cycle life. The revolutionary significance of this configuration lies in the fact that its cathode compartment essentially functions as an aqueous reactor highly adapted to the CO_2RR. The aqueous environment offers four key advantages. First, the moderate surface tension of water enables the formation of a stable solid-liquid-gas triple-phase interface within the nanopores of gas diffusion electrodes, driven by capillary forces. This structure significantly expands the electrochemically active surface area and shortens the diffusion distance for CO_2 to active sites, synergistically enhancing mass transport. Second, water molecules act as intrinsic proton sources, efficiently facilitating PCET processes to unlock diverse reaction pathways,

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including 2e$^-$ reduction to CO or formate and even multi-electron reduction to C_{2+} products. Third, precise regulation of the electrolyte pH, concentration, and cation types can direct the reaction toward generating soluble or gaseous products, thereby fundamentally avoiding the formation of insulating solid-phase Li_2CO_3. This configuration directly addresses the fundamental bottlenecks of conventional single-electrolyte batteries. As a result, it not only holds promise for reducing charging overpotentials to below 3.5 V but also directly utilizes the proven high current density tolerance and rapid reaction kinetics of aqueous CO_2RR systems.

However, the development of hybrid-electrolyte batteries faces a critical scientific challenge in that their cathode reaction mechanism remains poorly defined. Although existing studies hypothesize that the product may be soluble formate, direct in situ experimental evidence is still lacking. Key uncertainties persist, including the evolution pathways of critical intermediates (such as *COOH and *CO), the steps of electron/proton transfer, and the regulatory mechanisms by which pH and cations influence reaction selectivity.[5] This knowledge gap underscores the necessity of revisiting the well-established framework of aqueous CO_2RR research. Given that the cathode compartment of hybrid electrolyte batteries shares identical core elements with those of conventional CO_2RR systems, decades of accumulated insights into the CO_2RR field can be directly translated. Thus, the central proposition of this article is to elaborate on the integration of hybrid electrolyte systems with electrocatalytic CO_2RR principles, focusing on the following key aspects: (1) the scientific nature of how conventional systems are limited by the insulating properties of Li_2CO_3; (2) how the compartmentalized design of hybrid electrolytes avoids the solid-phase product deposition via an aqueous cathode environment; (3) how core principles from CO_2RR research (regarding pH, current density, and electrolyte concentration) can be translated to hybrid electrolyte batteries to resolve unknown reaction mechanisms, predict product distributions, and optimize kinetic performance; and (4) the unique challenges facing this system and potential solutions. This work aims to provide a theoretical framework and technical roadmap for developing next-generation Li-CO_2 batteries with high energy density, low overpotential, and long cycle life.

Limitations of organic electrolytes and inhibition mechanisms of solid products in hybrid electrolyte systems

Conventional organic electrolyte systems encounter core constraints in the CO_2RR of Li-CO_2 batteries, including CO_2 mass transfer limitations, irreversible deposition of the insulating solid-phase product Li_2CO_3, and catalyst efficiency bottlenecks. This chapter systematically dissects the physicochemical origins of these limitations and elaborates on the breakthrough mechanisms by which the hybrid electrolyte strategy achieves solid-phase deposition suppression via reaction pathway reconstruction, as well as the prevailing challenges in this field.

Multiple constraints on the CO_2RR in organic electrolyte systems

Conventional Li-CO_2 batteries adopt a single organic electrolyte design, which is beneficial for stabilizing the lithium metal anode. However, multiple systemic defects of this design have been well validated by extensive experiments, serving as fundamental bottlenecks that limit the improvement of battery performance. These defects primarily stem from three interrelated core issues.

The primary limitation lies in the excessive wetting behavior of organic electrolytes on porous electrodes, which restructures the CO_2 mass transfer pathway and significantly slows the reaction kinetics. Owing to their high compatibility with porous electrodes, organic electrolytes fully penetrate and fill the electrode pores, forming a continuous and enclosed organic phase environment. In this system, CO_2 must first dissolve to saturation in the bulk phase of the organic electrolyte and then diffuse across the two-phase interface between the electrolyte and the electrode active sites. The core bottleneck of this mass transfer pathway is the extremely low diffusion rate of CO_2 in the organic phase, with a diffusion coefficient of only approximately 10^{-6} cm^2 s^{-1}, which is lower than the value of 4.4×10^{-6} cm^2 s^{-1} in aqueous systems. This discrepancy arises from the larger molecular size of organic solvents and stronger intermolecular van der Waals forces, which strongly hinder the migration of CO_2 molecules, leading to a significant reduction in the transport efficiency of CO_2 from the saturated electrolyte across the two-phase interface to the electrode surface. More critically, the complete wetting of porous structures by organic electrolytes results in a much thicker CO_2 mass transfer layer (reaching 40-160 μm) compared to flowing aqueous systems (only 0.01-10 μm), further extending the mass transfer distance.[6] The combination of these two factors directly causes the rate of CO_2 reaching the electrode surface to be unable to match the reaction demand, leading to significantly retarded reaction kinetics and ultimately manifesting as generally low limiting current densities of the battery. Under high current density conditions, CO_2 at the electrode surface is more prone to rapid depletion, triggering severe concentration polarization and further deteriorating the reaction efficiency.[7–9]

The greater core challenge resides in the thermodynamic inevitability, insulating nature of Li_2CO_3, and the irreversible blocking it induces. Theoretical calculations confirm that the formation free energy of Li_2CO_3 is significantly lower than that of other potential products (e.g., $Li_2C_2O_4$). Its reaction pathway, which often involves Li_2O intermediates, possesses a lower energy barrier, whereas competing pathways have much higher energy barriers, rendering the formation of Li_2CO_3 both thermodynamically and kinetically unavoidable (Figure 1). Nevertheless, Li_2CO_3 has extremely poor electrical conductivity: its electronic band gap is as wide as 5.06 eV (with an electronic conductivity of ~10^{-15} S cm^{-1}), and the migration activation energy of Li^+ in its crystal lattice is high (with an ionic conductivity of <10^{-12} S cm^{-1}). In-situ experimental observations reveal that Li_2CO_3 tends to intertwine with amorphous carbon in the form of nanocrystals, forming a dense and insulating deposition layer on the electrode surface with a thickness of up to 15-30 nm. This deposition layer not only physically covers active sites and blocks electrode pores but also completely blocks electron and ion transport

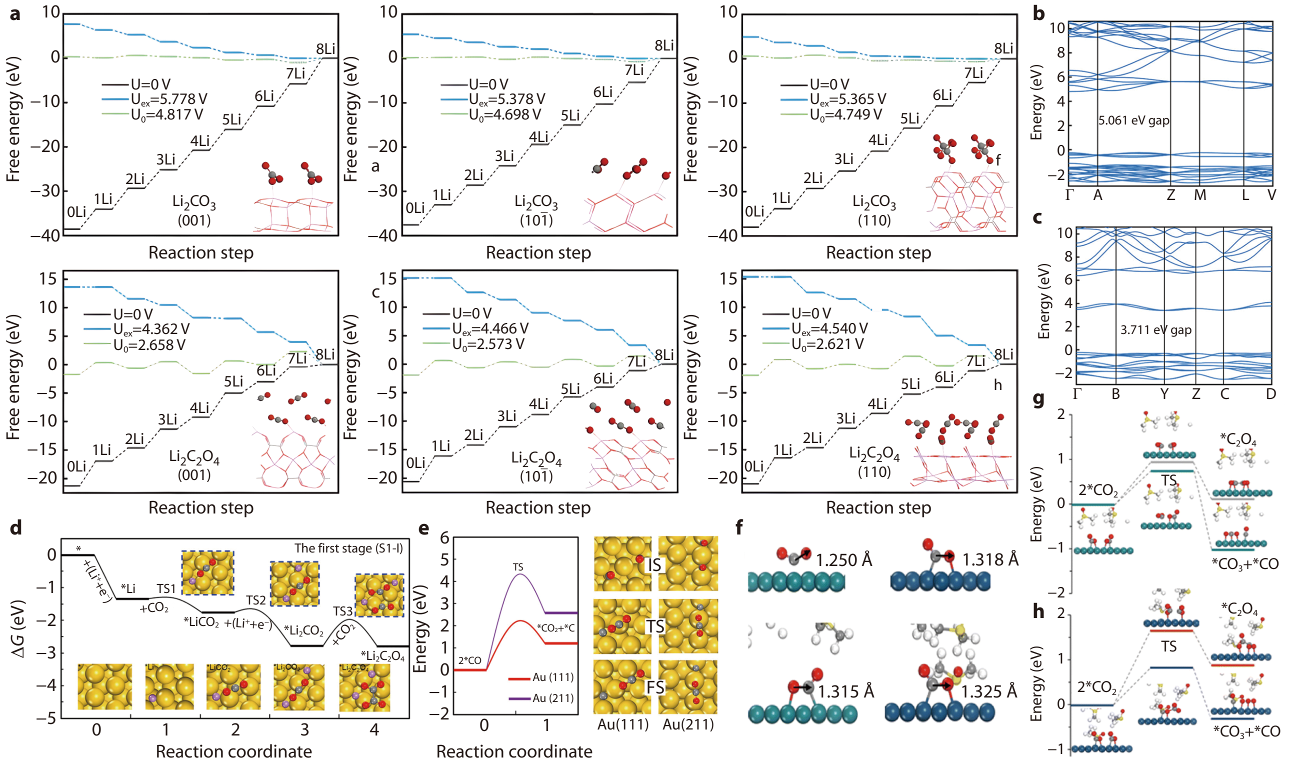

Fig. 1 Key evidence for the thermodynamics and reaction pathways of Li_2CO_3 formation. **a** Variation of decomposition free energy of Li_2CO_3 and $Li_2C_2O_4$ with reaction steps. **b**, **c** Electronic band structures of Li_2CO_3 and $Li_2C_2O_4$.[10] **d** Free energy curve for the formation of $^*Li_2C_2O_4$ in the first stage; the rate-determining step (C-C coupling) has an energy barrier of 0.81 eV. **e** Free energy and energy barriers (2.24-4.33 eV) for CO disproportionation [11] **f** CO_2 adsorption structures on Ru (0001) and Ir (111) surfaces in DMSO solvent, with C-O bond lengths of 1.315-1.325 Å. **g**, **h** Energy barrier diagrams for CO_2 disproportionation pathways (0.76-0.83 eV).[12]

pathways due to its insulating nature. Even with the aid of catalysts, its decomposition is often incomplete; the residual products provide nucleation sites for uneven deposition in subsequent cycles, forming a vicious cycle of deposition-passivation-more severe deposition and ultimately leading to rapid decay of battery capacity and shortened cycle life.[10–15]

Additionally, catalysts face a systemic ceiling in terms of efficiency within organic systems. Even when highly active catalysts or soluble catalysts are employed, their performance improvement is severely constrained by the aforementioned fundamental defects. The slow mass transfer rate of CO_2 directly limits the utilization efficiency of catalyst active sites under high current density conditions, making it difficult to exploit their high activity advantages. The inherent insulating property of Li_2CO_3 and the incompleteness of its deposition/decomposition cause the catalyst surface to be covered by residual products and active sites to be deactivated; moreover, the residual carbon layer further accelerates the blocking of electrode pores during subsequent deposition processes, undermining the durability of the catalytic decomposition effects. More critically, interfacial interactions between the organic electrolyte and the catalyst may accelerate catalyst deactivation, further narrowing the room for performance improvement. Therefore, although catalyst optimization can slightly improve the reaction efficiency at low current densities and in initial cycles, it is unable to overcome the performance and lifespan upper limits imposed by the physicochemical constraints of the organic system itself.[16–18]

Mechanisms and pathway regulations for hybrid-electrolyte systems

The core value of the hybrid electrolyte strategy in Li-CO_2 batteries lies in reconstructing reaction pathways via an aqueous cathode environment, thereby avoiding the deposition of insulating solid-phase products. This design logic utilizes a breakthrough in addressing the contradiction between lithium metal stability and reaction kinetics in Li-O_2 batteries. Early studies by Zhou et al.[4] used a LISICON-type solid-state electrolyte to separate the organic phase from an alkaline aqueous electrolyte, achieving 500 hours of continuous discharge. Visco et al.[3] further confirmed that NASICON-type electrolytes can ensure the stability of lithium anodes in aqueous environments. This paradigm was directly migrated to Li-CO_2 systems to solve the dual challenges of Li_2CO_3 deposition caused by limited CO_2 mass transport in organic phases and the need for aqueous environments compatible with lithium anodes.

The aqueous stability of $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) is the cornerstone for practical implementation of the system. Systematic studies by Zhou et al.[19] showed that this NASICON-type electrolyte maintains a complete crystal structure after soaking for 6 months in weakly acidic to neutral environments, with an ionic conductivity stable at 2.5×10^{-4} S cm^{-1}. Degradation only occurs under strongly alkaline conditions (0.1 M LiOH), thus providing material guarantees the dual functions of Li^+ conduction and aqueous phase isolation.

On the basis of this material foundation, the Li | organic phase | LAGP | aqueous phase (NaCl--LiCl) | Pd cathode system developed by Xue et al.[5,20] demonstrated breakthrough performance: in a neutral aqueous environment, the Pd catalyst efficiently reduces CO_2 to soluble HCOOH via a PCET mechanism, with a Faradaic efficiency >97%. Its reaction energy barrier, 0.8 eV, is significantly lower than that of the Li_2CO_3 formation pathway (>1.3 eV), avoiding solid-phase deposition from a thermodynamic source. Moreover, CO_2 solubility increases to 90 mM (3 times greater than that of organic phases), and the high diffusion coefficient of HCOOH has a 10-order-of-magnitude advantage over that of solid Li_2CO_3, completely suppressing electrode blockage. After performance optimization, the nanoporous Pd membrane catalyst stabilized the discharge voltage at 2.61 V, reduced the charge voltage to 2.87 V, achieved an energy efficiency exceeding 91%, and a cycle life of over 300 hours (Figure 2a, b). The universality of this strategy was cross-validated in the Na-CO_2 system, which targeted HCOOH generation by regulating the H^+/OH^- concentration in the aqueous electrolyte, further confirming the universal ability of hybrid electrolyte design to inhibit solid-phase deposition.[21]

However, recent studies have revealed the complexity of reaction pathways and cognitive limitations. Feng et al.[22] found that when water-in-salt (WiS) electrolytes are used in the same aqueous environment, catalyst types can lead to significant differences in product pathways. The Mo_2C/CNT cathodes selectively generate $Li_2C_2O_4$, whereas the CNT cathodes mainly produce insulating Li_2CO_3. Combined, DFT and in situ DEMS analysis revealed that the strong adsorption energy of Mo_2C surfaces for $Li_2C_2O_4$ (-5.09 eV) can stabilize this intermediate and inhibit its decomposition, whereas the weak adsorption ability of CNTs (−1.12 eV) causes $C_2O_4^{2-}$ to dissolve and disproportionate into Li_2CO_3 and elemental carbon. This phenomenon completely contradicts the traditional perception that aqueous environments inevitably generate soluble products, highlighting the dominant role of the synergistic effect between catalysts and electrolytes in reaction pathways. Notably, even in high-concentration WIS electro-

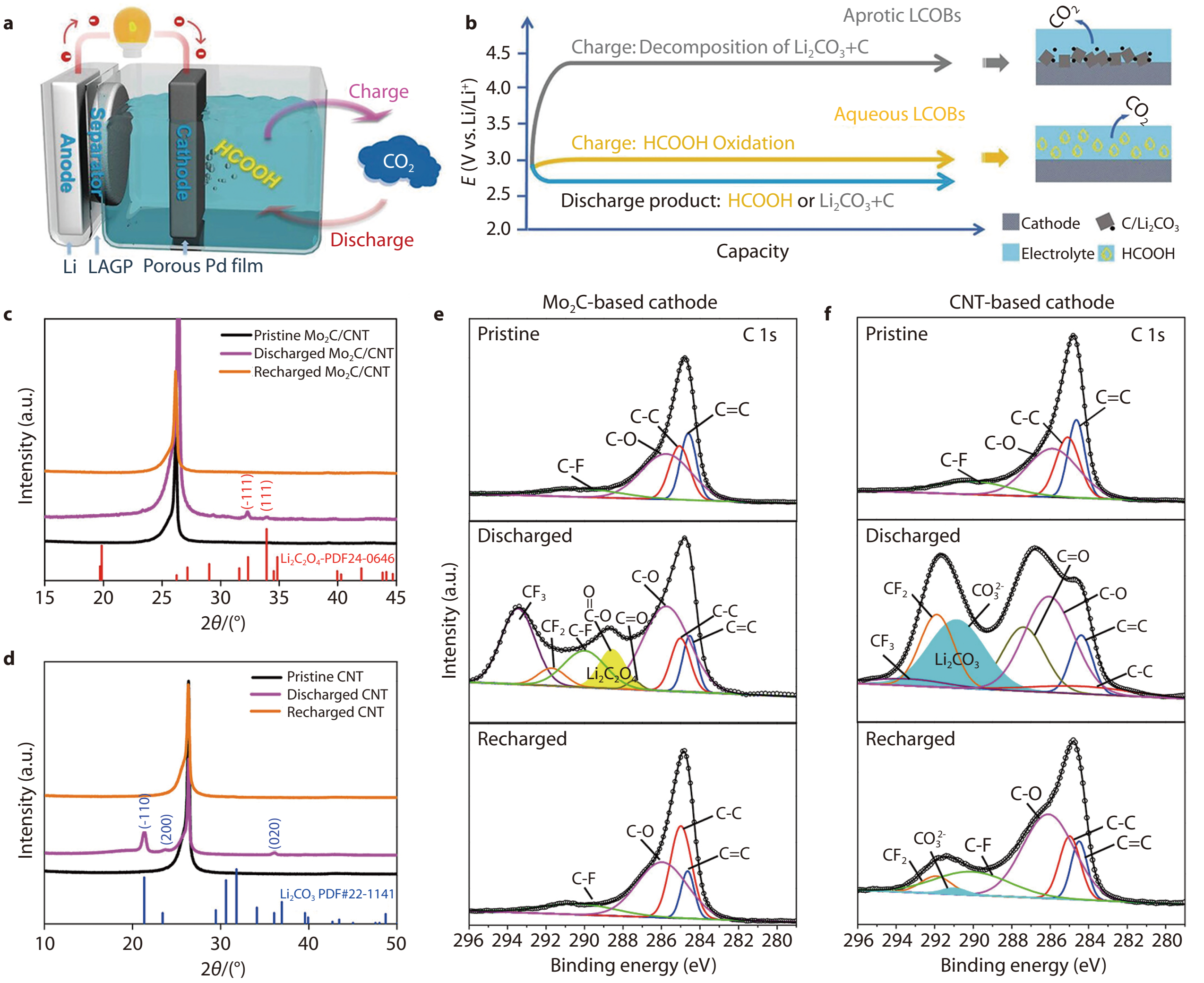

Fig. 2 Path regulation of hybrid-electrolyte Li-CO_2 batteries. **a** Schematic diagram of the porous Pd-based hybrid electrolyte battery structure. **b** Comparison of aqueous and conventional aprotic Li-CO_2 batteries.[20] (c-d) XRD patterns of **c** Mo_2C/CNT and **d** CNT cathodes. (e-f) XPS spectra of C 1s for the pristine, discharged, and recharged cathodes in WIS-based electrolyte: **e** Mo_2C/CNT and **f** CNT cathode.[22]

lytes, CNT cathodes still lead to the formation of Li_2CO_3, contradicting the formate pathway observed in low-concentration systems with Pd catalysts. This finding underscores that the electrolyte environment alone is insufficient to dictate the reaction pathway; the catalyst's adsorption properties and interfacial interactions play equally critical roles. Consequently, the triangular regulatory relationship between electrolyte concentration, catalyst properties, and product selectivity demands further clarification (Figure 2c-f).

The core dilemma in current research is that the dynamic coupling mechanism between electrolyte microenvironments and interfacial processes has not been clarified: how the reorganization of solvation structures induced by high-concentration Li^+ quantitatively regulates the stability of *COOH/OCHO* intermediates remains to be elucidated; there is a lack of in situ evidence for the impact of switching between neutral/alkaline electrolytes on proton transfer efficiency at solid/liquid interfaces and the competition between Li_2CO_3/HCOOH pathways; and the disturbance mechanism of current density fluctuations on electric double layer structures and $C_2O_4^{2-}$ formation kinetics is even more unexplored. These challenges essentially stem from the complex synergistic effects at the solid/liquid/gas three-phase interface. Currently, the application of *in situ* characterization techniques in such complex hybrid systems is still in its infancy. The primary limitations lie in the difficulty of probing the buried solid-liquid interfaces and in distinguishing the transient, low-concentration intermediates against the background signals from the multi-phase environment. Techniques like *in situ* Raman, XAS, and DEMS face significant challenges in signal sensitivity, spatial resolution, and the design of specialized electrochemical batteries that can accommodate the hybrid architecture without compromising performance**.** To elucidate these multi-parameter coupling mechanisms, a mature research paradigm of electrocatalytic CO_2 reduction (CO_2RR) systems is urgently needed.

Cross-system transfer of CO_2RR regulation mechanisms

Given that the cathode of hybrid electrolyte Li-CO_2 batteries is inherently an aqueous CO_2RR system containing Li^+, the inhibition of solid-phase deposition and regulation of reaction pathways in such batteries essentially rely on precise control of microscopic mechanisms of the CO_2RR. The mature mechanisms and theoretical frameworks in electrocatalytic CO_2RR, which describe how reaction pathways are regulated by pH, electrolyte concentration, and current density, provide robust paradigms for clarifying the complex correlations between electrolyte, catalyst, and product in battery systems. The validity of this cross-system paradigm transfer is powerfully underscored by the latest research. For instance, Martínez et al.[23] directly visualized the dynamic restructuring of bimetallic catalysts under operating conditions, revealing that the synergistic Cu-Au interfaces, stabilized by specific electrolyte cations, are crucial for steering the CO_2RR pathway towards C_{2+} products. In a complementary study, Wang et al.[24] deciphered the decisive role of interfacial water structure regulated by the electric double layer, which governs the proton transfer efficiency and effectively suppresses the competing hydrogen evolution reaction. These seminal works exemplify the depth of understanding now achievable in CO_2RR electrocatalysis, providing a clear roadmap for resolving the analogous interfacial complexities in hybrid-electrolyte Li-CO_2 batteries. This chapter will therefore transfer these established and emerging regulatory laws to construct a theoretical framework for pathway optimization.

To establish this framework, we first highlight representative aqueous electrolyte systems in electrocatalytic CO_2RR. Table 1 shows the recent literature on aqueous CO_2RR at GDEs and the electrolytes applied. Alkali metal bicarbonate electrolytes (e.g., 0.1-1.5 M $KHCO_3$ or $NaHCO_3$) rely on the dynamic $HCO_3^-/CO_2(aq)$ equilibrium to continuously supply active carbon sources. Meanwhile, leveraging their buffering property, they stabilize the reaction interface within the pH range of 6-8 and effectively suppress local pH fluctuations.[25–28] To meet the demand for C_2 product synthesis under high current densities, strong alkaline electrolytes (e.g., 1-10 M KOH/NaOH) utilize a high-pH environment (pH 12-14) to significantly increase the protonation energy barrier of water molecules by 0.3-0.5 eV, thereby inhibiting the hydrogen evolution side reaction. However, it is noteworthy that CO_2 reacts rapidly with OH^- to form CO_3^{2-} with a rate constant $k = 10^4\ M^{-1}\ s^{-1}$, and subsequent reconstruction of active CO_2 species is required via carbonate-bicarbonate chemical equilibrium.[29–32] Phosphate systems (e.g., KH_2PO_4/K_2HPO_4) achieve precise regulation over a broad pH range of 2-12 through their triprotic dissociation characteristics. In contrast, sulfate electrolytes (e.g., K_2SO_4) leverage the strong acidity of HSO_4^- to directionally optimize proton trans-

Table 1. Comparison of CO2RR performance in different electrolyte systems.

Catalyst/GDE Support	Electrolyte	Potential E_{WE}/V	Current Density i/mA·cm^{-2}	Faradaic Efficiency FE/-	Reference
Sn GDE	0.1 M $KHCO_3$	−0.8 V~−1.7 V vs Ag/AgCl	6	~90%	25
SGDE	0.5 M $KHCO_3$	−1.8 V vs Ag/AgCl	~22.17±3.30	~78.60±0.11%	26
Tin Catalyst GDE	0.5 M $KHCO_3$	−1.4~-2.0 V vs Ag/AgCl	~21.67±1.29	~86.75±2.89%	28
Ag/C GDE	1 M KOH	−1.2~−2.0 V vs Ag/AgCl	~101	>90%	29
Gold nanoparticles GDE	2.0 M KOH	−0.04~−0.72 V vs RHE	~158	~98.3%	30
Tin Electrode	0.1 M H_3PO_4/1 M NaH_2PO_4	−1.0~−1.6 V vs Ag/AgCl	0.5~3	~85%	31
Nano-porous Copper-Silver Alloy GDE	1 M KOH	−0.7 V vs RHE	~300	~85%	32
Ag GDE	1 M KCl	−0.04~−0.72 V vs RHE	~51.3	>80%	33
PtRu	0.5 mol·L^{-1} K_2SO_4		~391.6	~94.7%	34
Ag GDE	0.5/0.8 M K_2SO_4	~−2.19 V vs Ag/AgCl	10 ~ 160	~90%	35
NiPc-OMe MDE	0.5 mol·L^{-1} K_2SO_4	~−1.26 V vs RHE	20 ~ 400	>99%	36

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fer kinetics. Together, these two types of electrolytes satisfy the proton supply requirements of reaction pathways.[33–36] Halide electrolytes (e.g., 0.5-2 M KCl/KBr/KI) modify the surface electronic structure of catalysts via anion-specific adsorption. Among them, heavy halide ions (I^-/Br^-) can regulate the position of the surface d-band center due to their high adsorption coverage, selectively stabilizing key intermediates (COOH or CO) while inhibiting competitive hydrogen evolution. This significantly enhances the selectivity of C_1/C_2 products.[37–40]

Among these electrolyte properties, pH emerges as the most pivotal regulatory factor, as it directly governs CO_2 speciation, proton activity, and Li^+ compatibility in hybrid systems. The following section 3.1 will therefore focus on the effect of pH on electrocatalytic CO_2 reduction pathways, establishing a theoretical basis for balancing efficient CO_2 reduction and Li_2CO_3 inhibition in hybrid electrolyte Li-CO_2 batteries.

Effects of pH on electrocatalytic CO_2 reduction pathways

In the electrocatalytic CO_2RR system, catalysts significantly alter the reaction pathways and product distribution by regulating the adsorption energy of intermediates. However, on inert electrodes without catalysts (such as Hg and glassy carbon), the intrinsic pathway of the CO_2RR is entirely dependent on the pH of the electrolyte. This phenomenon reveals the underlying chemical principles of PCET processes. In inert electrode systems (e.g., Hg, glassy carbon) free from catalyst interference, the electrolyte pH directly determines the intrinsic pathway of the reduction reaction by regulating the dissolved forms of CO_2 and proton transfer pathways. This rule provides a fundamental theoretical framework for the design of cathode electrolytes.

The pH of an electrolyte is jointly determined by the types and concentrations of cations (such as K^+ and Li^+) and anions (such as HCO_3^- and Cl^-) within the system. In addition to influencing the solubility of carbon dioxide (Figure 3a), pH affects the thermodynamic properties of the carbon dioxide reduction reaction according to the Nernst equation. As H^+ ions are consumed during the reaction, the activity of protons directly influences the equilibrium potential E. The dependence of the standard potential on pH is typically illustrated via a Pourbaix diagram (Figure 3b). In aqueous media, water serves as both a proton donor for CO_2 reduction products and an intermediate proton donor. Consequently, for the CO_2RR and hydrogen evolution reaction (HER), depending on the solution pH, either OH^- is formed or H^+ is consumed during the reaction process. In a strongly acidic environment (pH < 4), the high concentration of H^+ in the electrolyte significantly inhibits the reaction between CO_2 and H_2O through protonation, leading to CO_2 predominantly existing in the molecular form (CO_2(aq)), which accounts for more than 95% of the H^+ present. The reduction of CO_2 in this form is initiated by an initial electron transfer step: $CO_2 + e^- \rightarrow CO_2^{-*}$. However, experimental and theoretical analyses by Hori et al.[41] showed that the activation energy barrier for this step is as high as 1.8 eV, far exceeding that for the reduction of H^+ to H^* (≈ 0.2 eV). To eliminate the interference of catalysts on the reaction pathway, experiments used a mercury electrode. Linear sweep voltammetry was employed to record the reduction current in a 0.1 M HCl electrolyte. The results indicated that the onset potential for CO_2 reduction to CO was -1.9 V vs. SHE, with an overpotential exceeding 1.5 V; when the potential was negatively shifted to -2.0 V, the Faraday efficiency (FE) for CO remained below 5%, whereas the FE for the HER was > 95%. Further analysis revealed that a high H^+ concentration drastically reduces the proton transfer resistance, enabling H^+ to more easily accept electrons on the electrode surface to form H_2 and thus create strong competition for the CO_2RR. Additionally, the secondary dissociation of strongly acidic electrolytes further maintains a high H^+ concentration, exacerbating the dominance of the HER. In sharp contrast to the high-barrier pathway in strongly acidic environments, the near-neutral environment (pH 6--8) achieves a significant increase in CO_2RR activity through the transformation of CO_2 into HCO_3^-. In this pH range, the reaction between CO_2 and H_2O reaches equilibrium, with HCO_3^- accounting for 60%-80%. The molecular structure of HCO_3^- functions as both a carbon source and a proton source; it can directly provide a carbon source for the CO_2RR without undergoing the high activation

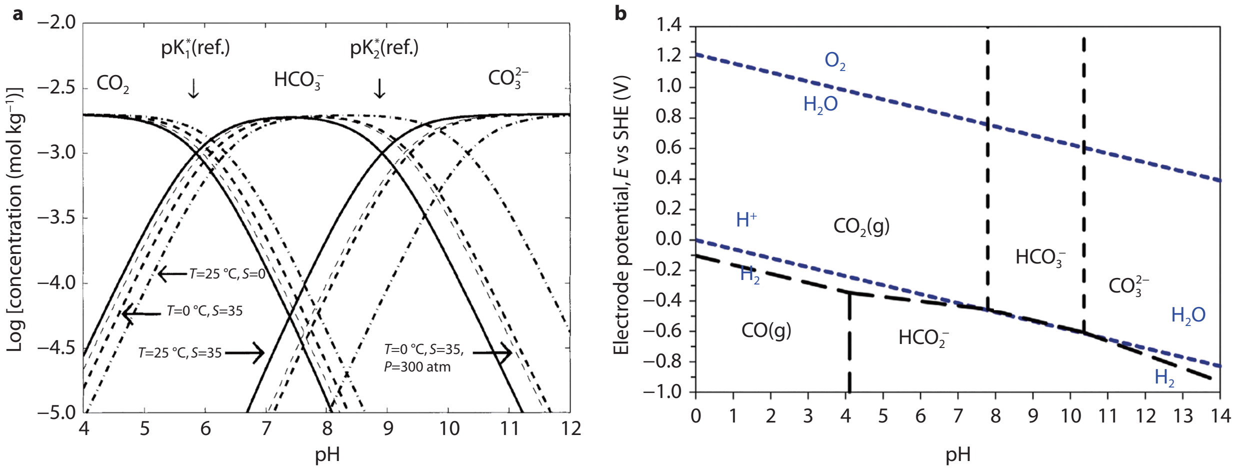

Fig. 3 Regulatory role of pH in key properties of CO_2 in aqueous systems. **a** Solubility of CO_2 in water as a function of the pH value at the indicated temperatures, salinities, and pressures. **b** Pourbaix diagram of CO_2 and its related substances.[46]

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energy step of CO_2(aq) and can participate in PCET through its inherent -OH group, reducing the reliance on free H^+. As a result, the energy barrier for the direct reduction pathway of $HCO_3^- + 2e^- + H^+ \rightarrow HCOO^- + OH^-$ decreases to 1.0 eV at pH=7, which is 0.8 eV lower than that for the reduction of CO_2(aq). To verify the role of HCO_3^- as the active species, Seshadri et al.[42] conducted control experiments using a Pt electrode with no CO_2RR activity. The experimental group used a 0.5 M $KHCO_3$ buffer solution, whereas the control group used a 0.1 M HCl solution. The results revealed that approximately 5% HCOOH was detected in the experimental group without the formation of CO or H_2; no CO_2RR products were detected in the control group, and only a weak HER was observed (FE < 1%). When $KHCO_3$ was added dropwise to the control group until pH=6.0, the FE of HCOOH gradually increased to 3%, confirming that HCO_3^- is the key to initiating the CO_2RR. To eliminate the interference of mass transfer limitations, the research group of Varela et al.[43] used a rotating glassy carbon electrode and quantified the regulatory effect of pH on the CO_2RR in a 0.5 M $KHCO_3$-HCl mixed buffer solution. They reported that the HCOOH yield was only 0.8% at pH=2.0, increased to 4.0% at pH=5.0, and further increased to 8.5% at pH=7.0. Moreover, as the pH increased from 2.0 to 5.0, the concentration of HCO_3^- increased from 0.01 M to 0.45 M, and the yield increased by 5 times, confirming the positive correlation between the HCO_3^- concentration and CO_2RR activity. In a strongly alkaline environment (pH > 10), a high concentration of OH^- converts CO_2 into CO_3^{2-} through two rapid reaction steps: the first step is $CO_2 + OH^- \rightarrow HCO_3^-$, and the second step is $HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$. The second step proceeds at a faster rate, making CO_3^{2-} the dominant form of dissolved CO_2. Dinh et al.[44] confirmed via in situ Raman spectroscopy that over 90% of CO_2 is converted to CO_3^{2-} before reaching the electrode at pH=14. However, the strong C-O bond in CO_3^{2-} results in an extremely high reduction energy barrier. Thermodynamic analysis by Burdyny et al.[45] indicated that the standard potential for the reduction of CO_3^{2-} to CO is -1.43 V vs. SHE, which is much lower than the standard potential of the HER (-0.83 V vs. SHE). Additionally, the activation energy barrier for the rate-determining step ($CO_3^{2-} \rightarrow HCO_3^-$) exceeds 2.0 eV, leading to a negligible actual reaction rate. Thus, only the HER occurs in catalyst-free strongly alkaline systems. More critically, the binding constant of CO_3^{2-} with Li^+ (logKsp=8.66) is much lower than that with K^+ (logKsp=3.17). Experiments by König at al. showed that after adding 0.5 M Li^+ to 1 M KOH, Li_2CO_3 particles with a particle size of 1–5 μm were observed to deposit on the cathode within 10 cycles, blocking the gas diffusion channels.[46]

The pH-dependent intrinsic electrocatalytic CO_2RR on inert electrodes provides critical guidance for cathode electrolyte design in hybrid Li-CO_2 batteries, where balancing efficient CO_2 reduction and suppressing irreversible Li_2CO_3 deposition demands in-depth consideration of the unique coupling between CO_2 speciation, proton transfer, and Li^+ kinetics. In strongly acidic environments, the high energy barrier for CO_2(aq) reduction renders this regime inapplicable; furthermore, such conditions form Li^+-H^+ complexes that disrupt charge transfer, alongside competitive HER and solid electrolyte corrosion, all of which conflict with the fundamental operating principles of Li-CO_2 batteries. In contrast, the near-neutral pH range (6~8) serves as a universal design criterion; here, HCO_3^- acts as both a carbon source and proton shuttle, overcoming the high energy barrier of CO_2(aq) reduction to accelerate kinetics for matching battery discharge rates, neutralizing OH^- generated during the CO_2RR to prevent Li_2CO_3 formation, and maintaining moderate H^+ activity to avoid the HER, which ensures that the CO_2 is the primary electron acceptor, whereas the positive correlation between the HCO_3^- concentration and CO_2RR activity guides the electrolyte formulation to 0.5-1 M $KHCO_3$, optimizing CO_2 utilization and guaranteeing Li^+ transport. Under strongly alkaline conditions, high OH^- concentrations, although they inhibit the HER, convert CO_2 to CO_3^{2-}, which binds tightly to Li^+ to form cathode-clog Li_2CO_3 precipitates, with Li-CO_2 systems requiring a more stringent pH threshold (<10) than standalone CO_2RR systems do. Thus, applying CO_2RR pH regulation mechanisms to Li-CO_2 batteries confirms that near-neutral electrolytes are a strategic choice, mediated by HCO_3^-, as they simultaneously achieve efficient CO_2 reduction, proton balance, and Li^+ compatibility, resolving the conflict that plagues conventional single-electrolyte systems.

Dynamic control of the electrocatalytic CO_2RR by varying the electrolyte concentration

The salt concentration in electrolytes is a key parameter regulating the reaction mechanism of the CO_2RR. It directly reshapes reaction pathways and rate-determining steps by altering the ionic solvation environment and free water activity. Research on WiS electrolytes by Suo et al.[47] stands as a landmark breakthrough. This work is the first to reveal that ultrahigh salt concentrations reconstruct the solvation sheath, forming a solid electrolyte interphase (SEI) in aqueous environments and expanding the electrochemical stability window to 3.0 V. This work provides a fundamental theoretical basis for the subsequent regulation of CO_2RR pathways and offers a unique platform to elucidate the role of H_2O in the CO_2RR (Figure 4a-c). Studies by Qi et al.[48] revealed that WiS electrolytes not only enhance CO selectivity by suppressing the H_2O concentration but also provide a new perspective for pathway regulation in hybrid-electrolyte Li-CO_2 batteries by altering the rate-determining step.

In traditional aqueous electrolytes, a high H_2O concentration exacerbates the HER, resulting in low selectivity for carbon products in the CO_2RR. In WiS electrolytes, ultra-high concentrations of Li^+ form tight solvation sheaths with H_2O molecules, drastically reducing the free water content from 55.5 mol L^{-1} in traditional dilute electrolytes to 12.4 mol L^{-1}. This drastic regulation of water activity directly triggers a sudden change in CO_2RR selectivity: the FE of CO on the Au catalysts increases from 30% in the traditional 0.5 M $NaHCO_3$ system to a maximum of 80%, with the HER significantly suppressed. The root cause of this change lies in the fact that high salt concentrations weaken the ability of H_2O to act as a proton source, reducing competition between the HER and CO_2RR, thus highlighting the decisive role of salt concentration in product selectivity. More critically, the increase in salt concentration completely altered the kinetic mechanism of the reaction. Electrodynamic analysis revealed that in the low overpotential region (-0.32 to -0.42 V vs. RHE), the rate of CO formation exhibited a quasi-zero-order dependence on the

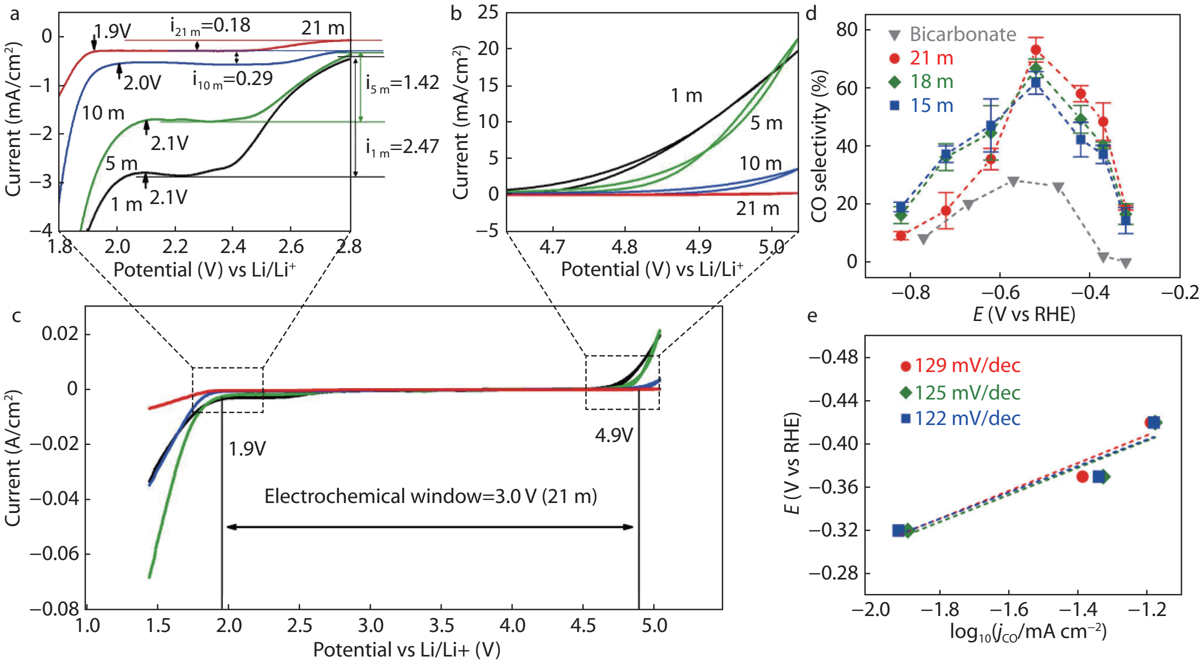

Fig. 4 Regulation of the electrochemical CO_2RR by WIS electrolytes. **a** Overall electrochemical stability window. **b** and **c** Magnified view of the regions outlined near the anodic and cathodic extremes.[47] **d** All electrolytes were saturated with CO_2. **e** Tafel analyses of WiS with different H_2O concentrations.[48]

H_2O concentration, with a Tafel slope close to 118 mV dec^{-1}. This indicates that the rate-determining step of the reaction has shifted from possible CPET in traditional systems to a pure electron transfer (ET) process ($CO_2^* + e^- \rightarrow CO_2^{-*}$). This means that high salt concentrations, by suppressing free water activity, make proton-involved steps no longer rate limiting, and the transfer of electrons to adsorbed CO_2 becomes the core of regulating the reaction rate, clearly demonstrating the role of salt concentration in reshaping the rate-determining step of the reaction (Figure 4d, e).

This mechanism has important implications for the design of hybrid-electrolyte Li-CO_2 batteries. The reduced free water content in WiS not only inhibits the HER but also reduces the probability of CO_2 reacting with H_2O to form HCO_3^-/CO_3^{2-}, thereby lowering the risk of forming solid-phase products such as Li_2CO_3 by combining with Li^+. Moreover, the fact that ET is the rate-determining step suggests that directional regulation of product pathways can be achieved by optimizing the promotion effect of cathode catalysts on electron transfer processes in conjunction with regulating H_2O activity via WiS electrolytes. In addition, although the $[Li(H_2O)_n]^+$ solvation structure in WiS is tight, it still maintains a certain Li^+ conductivity, which matches the Li^+ selective conduction requirement of solid electrolytes in hybrid electrolyte systems, providing a new idea for balancing inhibiting solid-phase deposition and ensuring ion transport.

Dynamic control of the electrocatalytic CO_2RR by the current density

As one of the most critical operating parameters in the CO_2RR, the current density directly reshapes the local microenvironment on the electrode surface, including the CO_2 concentration, pH gradient, and intermediate coverage, by altering the balance between the reaction kinetics and mass transfer efficiency, thereby governing continuous shifts in product selectivity. While such dynamic regulatory patterns vary in detail with catalyst type, their core mechanisms are universal, providing a foundational logic for understanding fluctuations in product pathways within hybrid electrolyte systems.

At low current densities (<10 mA cm^{-2}), CO_2 mass transfer is sufficient, and the reaction pathways are dominated primarily by the intrinsic selectivity and thermodynamic preferences of the catalyst. Timoshenko et al.[49] utilized in situ X-ray absorption spectroscopy combined with machine learning to demonstrate that at 5 mA cm^{-2}, the Ni-N_4 active sites of Nickel-based Transition Metal-Nitrogen-Carbon (Ni-TMNC) single-atom catalysts exhibit specific adsorption of COOH intermediates, stabilizing CO selectivity above 90% while significantly suppressing the HER. At this stage, the catalyst maintains a single-atom dispersed structure without agglomeration (Figure 5a). Similarly, Mistry et al.[50] reported that defect-rich Ag catalysts operating in battery systems at 8 mA cm^{-2} achieve an FE of 92% for CO due to adequate activation of CO_2 by surface defect sites, with no pathway deviation induced by mass transfer limitations (Figure 5b). Liu et al.[51] Furthermore, at 6 mA cm^{-2}, the RuPC/NPC catalyst, through the synergistic effect of Ru polypyridyl carbene and N-doped porous carbon, stabilizes CO intermediates and promotes C-C coupling, resulting in an FE of 27.5% for ethanol (Figure 5c). This finding reinforces the decisive role of the catalyst-support interface in determining product selectivity under low-current conditions. As the current density increases to 10-50 mA cm^{-2}, mass transfer limitations become increasingly prominent, forming a CO_2-deficient zone on the electrode surface. Dramatic changes in the local microenvironment, such as pH shifts, then emerge as the dominant factors regu-

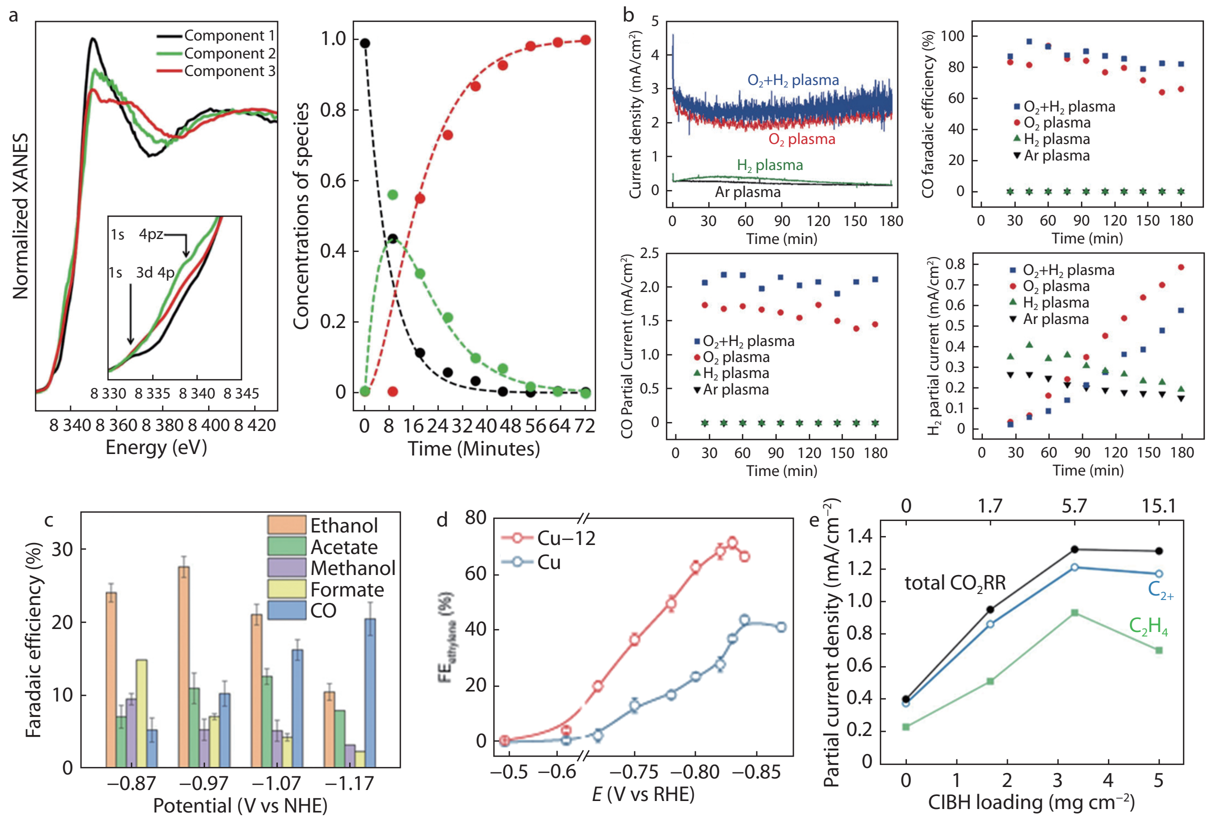

Fig. 5 Mechanisms Governing Current Density Regulation in the CO_2RR. **a** XANES spectra for the extracted pure species and related concentration profiles (filled circles) extracted via the TM approach from the experimental Ni K-edge XANES data for the HTNi-TMNC sample.[49] **b** CO2 electroreduction over plasma-treated Ag foil catalysts at -0.6 Vvs. RHE in 0.1 m $KHCO_3$.[50] **c** Faradaic efficiencies for ethanol, acetate, methanol, formate, and CO production on RuPC/NPC over a 1-h period.[51] **d** FE using CO2-saturated 1 M $KHCO_3$ as the supporting electrolyte.[52] **e** Partial current density for total CO2RR reactions, with C_{2+} and C_2H_4 at the maximum cathodic energy efficiency.[44]

lating reaction pathways. Li et al.[52] modified Cu catalyst surfaces with N-aryl tetrahydrobipyridine molecules; even at a high current density of 230 mA cm^{-2}, these molecules stabilized *CO intermediates to maintain an FE of 72% for ethylene. However, in situ characterization revealed that the local pH increased from 7 to 10, with CO_3^{2-} accounting for 60% of the species, necessitating buffer systems to inhibit the formation of solid-phase precursors. When current densities exceed 100 mA cm^{-2}, mass transfer limitations become an absolute bottleneck, requiring structural design to overcome diffusion limits (Figure 5d). García de Arquer et al.[44] developed a catalyst-ionic polymer bulk heterojunction (CIBH) structure, which reduces CO_2 diffusion distances from 100 μm to 10 μm via 5-20 μm porous channels. Even at 1.3 A cm^{-2}, this structure maintains a 65% FE for C_2 products. Its core advantage lies in achieving efficient coupling of the gas-liquid-solid three-phase interface through hydrophobic-hydrophilic domain separation, mitigating local CO_2 depletion and pH fluctuations (Figure 5e). Therefore, the regulation of CO_2RR pathways by current density follows a consistent pattern: low current densities are catalyst-dominated, whereas medium to high current densities are codominant by microenvironmental factors and mass transfer. This cross-system commonality provides direct guidance for optimizing current density matching strategies in hybrid electrolyte Li-CO_2 batteries.

The dynamic current density-product selectivity relationship established in the electrocatalytic CO_2RR offers critical operational principles for hybrid Li-CO_2 batteries but requires adaptation to address battery-specific constraints, including Li^+ flux limitations imposed by solid electrolyte conductivity ($\sigma \sim 10^{-4}$ S cm^{-1}) and depth of discharge (DoD) dependent electrolyte evolution. At low current densities (<10 mA cm^{-2}), catalyst-dominated selectivity enables high Faradaic efficiency for soluble products such as formate but risks incomplete lithium utilization. Medium currents (10-100 mA cm^{-2}) necessitate buffered electrolytes (e.g., 0.5 M $KHCO_3$) and pH-robust catalysts (e.g., MoS_2@CNT) to counteract local alkalization (pH >9) that triggers carbonate precipitation, whereas high currents (>100 mA cm^{-2}) demand hierarchical electrodes with shortened CO_2 diffusion paths (<10 μm, CIBH-type) and lithiophilic solid electrolyte coatings (e.g., Li_3N) to mitigate concurrent CO_2/Li^+ depletion. Future work must establish operando diagnostics to resolve transient microenvironment changes under battery cycling conditions.

According to the above discussion, the regulation of CO_2RR pathways in hybrid-electrolyte Li-CO_2 batteries is a complex multi-factor process that is determined by pH, the electrolyte concentration, and the current density. By synergistically adjusting these factors, CO_2RR kinetics can be aligned with Li^+ flux, thereby resolving the core issues of solid product deposition and insufficient stability in traditional single-electrolyte systems. This mechanism transfer from the electrocatalytic

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CO_2RR not only verifies the feasibility of using mature CO_2RR insights for Li-CO_2 battery design but also identifies clear optimization directions, laying a solid foundation for conclusions and future perspectives to be discussed in Chapter 4.

Conclusions and perspectives

The core value of hybrid-electrolyte Li-CO_2 batteries lies in realizing the synergy between energy storage and carbon conversion through environmental isolation design. The key to overcoming the limitations of traditional systems lies in combining the efficient CO_2 reduction characteristics of aqueous environments with the high energy density advantages of lithium metal, fundamentally avoiding the bottleneck of insulating Li_2CO_3 deposition. However, there remain unresolved gaps in the understanding of the in-depth mechanisms of this system, which precisely highlights the necessity of deep integration with the field of the electrocatalytic CO_2RR. This integration is not a simple technical migration but rather leverages the decades-long accumulated research paradigms of the latter to provide a new perspective for clarifying the ambiguity of its mechanisms in hybrid electrolyte systems.

The core breakthrough in future research lies in moving beyond fragmented empirical optimization to embrace holistic, mechanism-driven rational design, an effort centered on resolving the intrinsic contradictions of hybrid electrolyte systems (Figure 6). Targeted pH control requires the dynamic maintenance of near-neutral conditions to optimize bicarbonate-mediated CO_2RR pathways. This involves quantifying interfacial pH gradients to regulate the carbon species distribution. Precise neutralization of hydroxyl ions inhibits Li_2CO_3 nucleation while avoiding hydrogen evolution at low pH or Li^+-carbonate precipitation at high pH. The complexity of this multi-parameter optimization makes it an ideal application for artificial intelligence (AI) and machine learning, which can predict optimal electrolyte compositions and operational windows. Meanwhile, the electrolyte concentration synergy between aqueous and organic phases needs to balance competing demands; it must maximize CO_2RR activity and Li^+ conductivity while minimizing electrolyte decomposition. First-principles simulations of ion solvation structures are critical here, as they help navigate trade-offs where diluted electrolytes impair conductivity and concentrated electrolytes accelerate side reactions. Practical current density adaptability is essential for real-world applications. High-current operation exacerbates Li_2CO_3 deposition and hydrogen evolution, so addressing this requires co-engineering modulating catalyst electronic states via d-band center tuning paired with buffering the catholyte microenvironment using HCO_3^- to sustain stable performance under variable current loads. Machine learning models trained on operando data will be key to establishing the dynamic structure-activity relationships needed for this co-engineering under fluctuating operational conditions. Technical validation tools are indispensable for supporting the above regulation and adaptability designs. In situ diagnostics must track key interfacial intermediates such as *COOH and *CO as well as transient pH changes, which link catalyst active site behavior to Li^+ solvation dynamics. Additionally, the long-term stability of solid electrolytes represents a fundamental challenge for practical deployment. Degradation mechanisms such as Li^+ channel blockage and mechanical failure at the interfaces with organic or aqueous electrolytes can severely limit cycle life. Future work must focus on developing novel solid electrolytes with high ionic conductivity (>10^{-3} S cm^{-1}), wide electrochemical windows, and robust interfacial compatibility, possibly through composite designs or surface modifications. Currently, a fundamental focus must be placed on mitigating solid electrolyte degradation by preventing Li^+ channel blockage and interfacial side reactions at the boundaries with organic and aqueous phases. Ultimately, success hinges on the tripartite coengineering of catalysts, catholytes, and solid–electrolyte interfaces, with the core closing the design loop. The integration of artificial intelligence, from high-throughput screening to inverse design, is poised to be the key enforcer for closing this complex design loop efficiently. Tuning adsorption energies stabilizes CO_2RR intermediates, pH-regulated catholytes suppress unwanted carbonate formation, and SEI nanostructuring resolves the critical trade-off between carbon fixation efficiency and ionic conductivity below 10^{-4} S cm^{-1}.

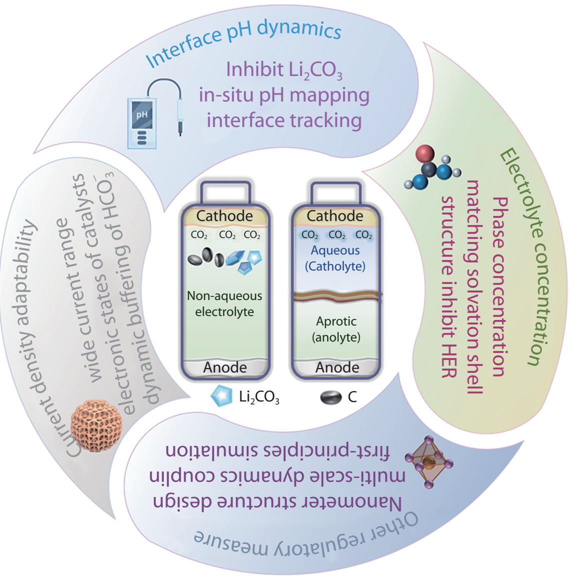

Fig. 6 Schematic illustration of multi-dimensional regulation strategies for hybrid electrolyte Li-CO_2 batteries.

The core value of such cross-field paradigm integration lies in transforming the quantitative laws of microenvironment-intermediates-selectivity in electrocatalytic CO_2RR into the mechanistic research language of hybrid electrolyte systems, promoting it from phenomenological observation to fundamental understanding and mechanistic innovation. Through this process, not only can the current bottlenecks such as ambiguous catalyst-electrolyte synergistic mechanisms and unclear proton-electron transfer pathways, be addressed, but a new research paradigm can also be established for the development of carbon fixation-energy storage integrated technologies, making it truly a core technology with both high energy density and negative carbon properties in the carbon neutrality strategy and accelerating the transition from fundamental mechanistic understanding to rationally designed systems.

AUTHOR CONTRIBUTIONS

Yasen Hao: Conceptualization, Investigation, Writing - original draft. Xu Xiao: Project administration, Supervision, Writing - review & editing. Zhuojun Zhang: Investigation. Zehui Zhao: Investigation. Aijing Yan: Investigation. Tenghui Qiu: Investigation. Peng Tan: Project administration, Supervision, Writing - review & editing.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

DATA AVAILABILITY

No data was used for the research described in the article.

REFERENCES

1. F. Wang, Y. Li, X. Xia, W. Cai, Q. Chen, M. Chen, *Adv. Energy Mater.*, 2021, 11, 2100667.
2. X. Mu, H. Pan, P. He, H. Zhou, *Adv. Mater.*, 2020, 32, 1903790.
3. S. J. Visco, E. Nimon, B. Katz, The Development of High Energy Density Lithium/Air and Lithium/Water Batteries with No Self-Discharge, ECS Meet. Abstr., 2006, MA2006-02, 389.
4. Y. Wang, H. Zhou, *J. Power Sources*, 2010, 195, 358.
5. R. Yang, Z. Peng, J. Xie, Y. Huang, R. A. Borse, X. Wang, M. Wu, Y. Wang, *ChemSusChem*, 2020, 13, 2621.
6. I. Bagemihl, C. Bhatraju, J. R. Van Ommen, V. Van Steijn, *ACS Sustain. Chem. Eng.*, 2022, 10, 12580.
7. X. Xiao, Z. Zhang, P. Tan, *Proc. Natl. Acad. Sci.*, 2023, 120, e2217454120.
8. Z. Zhang, X. Xiao, A. Yan, K. Sun, J. Yu, P. Tan, *Nat. Commun.*, 2024, 15, 9952.
9. X. Xiao, Z. Zhang, A. Yan, L. Shi, P. Tan, *Adv. Funct. Mater.*, 2025, 1, 2505676
10. L. Xiong, N. Q. Su, *Inorg. Chem.*, 2025, 64, 8376.
11. X. Zhang, Y. Wang, Y. Li, *J. Phys. Chem. Lett.*, 2023, 14, 1604.
12. X. Zhang, Y. Wang, Y. Li, *Chem. Sci.*, 2024, 15, 4804.
13. J. M. Garcia-Lastra, J. S. G. Myrdal, R. Christensen, K. S. Thygesen, T. Vegge, DFT+U Study of Polaronic Conduction in Li2O2 and Li2CO3 : Implications for Li-Air Batteries, *J. Phys. Chem. C*, 2013, 117, 5568.
14. T. Yang, H. Li, J. Chen, H. Ye, J. Yao, Y. Su, B. Guo, Z. Peng, T. Shen, Y. Tang, L. Zhang, J. Huang, *Nanoscale*, 2020, 12, 23967.
15. P. Jia, M. Yu, X. Zhang, T. Yang, D. Zhu, T. Shen, L. Zhang, Y. Tang, J. Huang, *Nano Res.*, 2022, 15, 542.
16. H. Wang, K. Xie, Y. You, Q. Hou, K. Zhang, N. Li, W. Yu, K. P. Loh, C. Shen, B. Wei, *Adv. Energy Mater.*, 2019, 9, 1901806.
17. Z. Zhang, W. Bai, Z. Cai, J. Cheng, H. Kuang, B. Dong, Y. Wang, K. Wang, J. Chen, *Angew. Chem. Int. Ed.*, 2021, 133, 16540.
18. Y. Bai, L. Wei, Y. Lian, Z. Wei, D. Song, Y. Su, X. Zhu, W. Huo, J. Cheng, Y. Peng, Z. Deng, *ACS Appl. Mater. Interfaces*, 2023, 15, 41457.
19. K. He, C. Zu, Y. Wang, B. Han, X. Yin, H. Zhao, Y. Liu, J. Chen, *Solid State Ion.*, 2014, 254, 78.
20. H. Xue, H. Gong, X. Lu, B. Gao, T. Wang, J. He, Y. Yamauchi, T. Sasaki, R. Ma, *Adv. Energy Mater.*, 2021, 11, 2101630.
21. X. Yang, D. Zhang, L. Zhao, C. Peng, K. Ren, C. Xu, P. Liu, Y. Zhou, Y. Lei, B. Yang, D. Xue, F. Liang, *Adv. Energy Mater.*, 2024, 14, 2304365.
22. N. Feng, B. Wang, Z. Yu, Y. Gu, L. Xu, J. Ma, Y. Wang, Y. Xia, *ACS Appl. Mater. Interfaces*, 2021, 13, 7396.
23. Y. Li, Q. Yin, B. Jia, H. Wang, H. Gu, Q. Hu, H. Yang, T. Guo, P. Hu, L. Li, L. Liu, L. Guo, *Angew. Chem. Int. Ed.*, 2025, 64, e202505668.
24. H. Ge, W. Shi, J. Liu, Y. Zhang, X. Wang, *J. Am. Chem. Soc.*, 2025, 147, 8367.
25. J. Wu, F. G. Risalvato, P. P. Sharma, P. J. Pellechia, F. -S. Ke, X. -D. Zhou, *J. Electrochem. Soc.*, 2013, 160, F953
26. Q. Wang, H. Dong, H. Yu, *J. Power Sources*, 2014, 271, 278.
27. J. Wu, P. P. Sharma, B. H. Harris, X. -D. Zhou, *J. Power Sources*, 2014, 258, 189
28. Q. Wang, H. Dong, H. Yu, H. Yu, *J. Power Sources*, 2015, 279, 1.
29. S. Ma, Y. Lan, G. M. J. Perez, S. Moniri, P. J. A. Kenis, *ChemSusChem*, 2014, 7, 866.
30. S. Verma, Y. Hamasaki, C. Kim, W. Huang, S. Lu, H. -R. M. Jhong, A. A. Gewirth, T. Fujigaya, N. Nakashima, P. J. A. Kenis, *ACS Energy Lett.*, 2018, 3, 193
31. P. Bumroongsakulsawat, G. H. Kelsall, *Electrochim. Acta*, 2014, 141, 216.
32. T. T. H. Hoang, S. Verma, S. Ma, T. T. Fister, J. Timoshenko, A. I. Frenkel, P. J. A. Kenis, A. A. Gewirth, *J. Am. Chem. Soc.*, 2018, 140, 5791.
33. B. Kim, S. Ma, H. -R. Molly Jhong, P. J. A. Kenis, *Electrochim. Acta*, 2015, 166, 271
34. X. Lu, D. Y. C. Leung, H. Wang, J. Xuan, *Appl. Energy*, 2017, 194, 549.
35. E. J. Dufek, T. E. Lister, M. E. McIlwain, *J. Appl. Electrochem.*, 2011, 41, 623
36. Z. Jiang, Z. Zhang, H. Li, Y. Tang, Y. Yuan, J. Zao, H. Zheng, Y. Liang, *Adv. Energy Mater.*, 2023, 13, 2203603.
37. X. Zhang, J. Li, Y. -Y. Li, Y. Jung, Y. Kuang, G. Zhu, Y. Liang, H. Dai, *J. Am. Chem. Soc.*, 2021, 143, 3245
38. T. Yuan, T. Wang, G. Zhang, W. Deng, D. Cheng, H. Gao, J. Zhao, J. Yu, P. Zhang, J. Gong, *Chem. Sci.*, 2022, 13, 8117.
39. H. “Molly” Jhong, F. R. Brushett, P. J. A. Kenis, *Adv. Energy Mater.*, 2013, 3, 589.
40. Y. Kang, Y. Kim, Y. Doh, J. Lee, J. Kim, K. T. Park, *Angew. Chem. Int. Ed.*, 2025, 137, e202504380.
41. C. G. Vayenas, R. E. White, M. E. Gamboa-Aldeco, *Modern Aspects of Electrochemistry*, Springer New York, New York, 2008.
42. G. Seshadri, C. Lin, A. B. Bocarsly, *J. Electroanal. Chem.*, 1994, 372, 145.
43. A. S. Varela, W. Ju, T. Reier, P. Strasser, *ACS Catal.*, 2016, 6, 2136.
44. F. P. García De Arquer, C. -T. Dinh, A. Ozden, J. Wicks, C. McCallum, A. R. Kirmani, D. -H. Nam, C. Gabardo, A. Seifitokaldani, X. Wang, Y. C. Li, F. Li, J. Edwards, L. J. Richter, S. J. Thorpe, D. Sinton, E. H. Sargent, *Science*, 2020, 367, 661
45. T. Burdyny, W. A. Smith, *Energy Environ. Sci.*, 2019, 12, 1442.
46. M. König, J. Vaes, E. Klemm, D. Pant, *iScience*, 2019, 19, 135.
47. L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, *Science*, 2015, 350, 938.
48. Q. Dong, X. Zhang, D. He, C. Lang, D. Wang, *ACS Cent. Sci.*, 2019, 5, 1461.
49. A. Martini, D. Hursán, J. Timoshenko, M. Rüscher, F. Haase, C. Rettenmaier, E. Ortega, A. Etxebarria, B. Roldan Cuenya, *J. Am. Chem. Soc.*, 2023, 145, 17351.
50. H. Mistry, Y. Choi, A. Bagger, F. Scholten, C. S. Bonifacio, I. Sinev, N. J. Divins, I. Zegkinoglou, H. S. Jeon, K. Kisslinger, E. A. Stach, J. C. Yang, J. Rossmeisl, B. Roldan Cuenya, *Angew. Chem. Int. Ed.*, 2017, 129, 11552.
51. Y. Liu, X. Fan, A. Nayak, Y. Wang, B. Shan, X. Quan, T. J. Meyer, *Natl. Acad. Sci.*, 2019, 116, 26353.
52. F. Li, A. Thevenon, A. Rosas-Hernández, Z. Wang, Y. Li, C. M. Gabardo, A. Ozden, C. T. Dinh, J. Li, Y. Wang, J. P. Edwards, Y. Xu, C. McCallum, L. Tao, Z. -Q. Liang, M. Luo, X. Wang, H. Li, C. P. O’

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