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Review

Recent progress and challenges of surface coatings for electrochemical CO_2 reduction

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ABSTRACT

Electrochemical CO_2 reduction (ECR) is a promising technology for mitigating carbon emissions and producing valuable chemicals by converting CO_2 into useful products using renewable energy sources. However, achieving high efficiency, selectivity, and stability in ECR systems remains a significant challenge. Surface coatings can enhance catalyst stability, improve selectivity towards desired products, and suppress unwanted side reactions. Recent advances in coating strategies have shown that different coating materials can be tailored to optimize the catalyst structure and the interaction between the catalyst and reactants, leading to improved electrochemical performance. This review provides a comprehensive analysis of the recent progress in surface coatings for ECR, focusing on the mechanistic role coatings play in influencing catalyst behavior and electrochemical performance. It also highlights the current challenges in coating design, while suggesting directions for future research to address these challenges.

1. Introduction

The electrochemical co-electrolysis of H_2O and CO_2 offers a sustainable and environmentally friendly approach for transforming CO_2 into valuable chemicals and fuels. This process works by using electricity, typically derived from renewable sources like solar or wind power, to drive the conversion of CO_2 and H_2O into carbon-based products, such as carbon monoxide (CO), formic acid (HCCOH), methane (CH_4), ethylene (C_2H_4), and even C_{2+} hydrocarbons[1–9]. However, there are several limitations and challenges associated with the electrochemical co-electrolysis of CO_2 and H_2O. One of the primary concerns is the efficiency of the process. Current electrochemical systems for CO_2 reduction suffer from low selectivity, meaning that they often produce a mix of different products with low efficiency. For example, when using copper (Cu)-based catalysts, the reaction can lead to the formation of several hydrocarbons, but the yield of the desired product is often suboptimal.

Various strategies have been applied to tune the electronic structure and morphology of catalysts in order to ultimately enhance their selectivity and activity, including regulating exposed facets[10], catalyst surfaces curvature engineering [11], bimetallic catalyst [12], heteroatom doping[13,14], and single atom alloying[15–17]. Yet despite the impressive progress made through these methods, significant challenges and limitations remain that demand critical evaluation. A predominant concern lies in the reliance on precise atomic-level control over catalyst structure and composition, which is often difficult to achieve and maintain under practical reaction conditions due to dynamic surface reconstruction and degradation phenomena that undermine catalyst stability and performance. Many approaches are developed and validated under idealized laboratory settings but fail to account for the inherent complexity, heterogeneity, and dynamic nature of real catalytic environments, including factors such as fluctuating reactant concentrations, competing side reactions, and mass transport limitations. Therefore, there is a pressing imperative to incorporate comprehensive system-level

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con CO_2 reduction (ECR).

Recently, surface coating emerges as a versatile and effective strategy to tailor catalyst interfaces without fundamentally altering the bulk material properties in electrocatalysis[18–22]; coatings can selectively enhance catalytic selectivity and activity by modulating surface chemistry, electronic structure, mass transport, create protective layers that improve catalyst stability under harsh reaction conditions and mitigate deactivation mechanisms such as poisoning or corrosion. Specificlly, coatings can act as molecular filters or promoters that influence local reactant concentration and intermediate stabilization, thereby improving product specificity. This strategy also enables the integration of multifunctional components, such as ionomers, polymers, and oxides. which can enhance electrode–electrolyte interactions and facilitate charge transfer. Moreover, surface coating strategies are often more readily adaptable for industrial applications because they provide a straightforward and scalable approach to modify existing catalyst surfaces without the need for complete redesign or synthesis of new materials[23–27]. Coatings can be applied through well-established techniques such as spray coating, dip coating, electrodeposition, or chemical vapor deposition, which are compatible with large-scale manufacturing processes and allow precise control over thickness and composition. Therefore, surface coating strategies strike a practical balance between performance enhancement and manufacturability, making them especially attractive for scaling up electrochemical CO_2 reduction technologies.

In related fields, such as fuel cells and water electrolysers, some comprehensive and well-articulated reviews have extensively covered advancements, challenges, and mechanistic insights of surface coatings[28–30]. And several reviews have been published in the field of ECR that focus specifically on the manipulation of interfacial microenvironments, particularly in relation to Cu-based catalysts [31], the selective production of multicarbon products [32], and ECR under acidic conditions[33]. However, to date, there exists a conspicuous gap in the literature regarding a systematic review that specifically summarizes recent progress in surface coating strategies within the context of ECR spanning from catalyst design to electrolyser integration. Addressing this deficiency, the present review aims to bridge this gap by providing a comprehensive analysis of how surface coatings function mechanistically to affect ECR performance. In this review, we examine the fundamental interactions occurring at the catalyst surface when a coating is applied, particularly focusing on how coatings influence the electrochemical performance of the catalyst. This includes the modulation of catalyst structure, the stabilization of reaction intermediates, and the enhancement of mass transport dynamics, all of which play a crucial role in improving the selectivity of electrochemical reactions (Fig. 1). Importantly, this review critically addresses the challenges associated with the use of surface coatings and the potential trade-offs between catalytic activity and long-term stability. By synthesizing recent experimental findings and theoretical studies, this work emphasizes the complex and multifaceted role of surface coatings in ECR and underscores the need for ongoing interdisciplinary research to advance materials design, reactor engineering, and system optimization for practical applications.

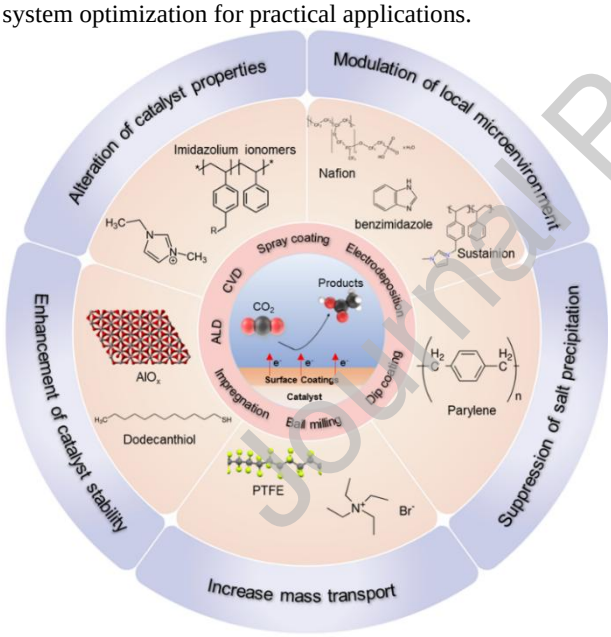

Fig. 1. Schematic overview of surface coating strategies for electrochemical CO_2 reduction.

2. Mechanisms by which coatings influence ECR

Coatings play a pivotal role in enhancing the performance and durability of ECR catalysts through several key mechanisms. Firstly, enhancing catalyst stability is one of the primary functions of coatings, which provide a protective layer that shields the catalyst from detrimental electrochemical conditions such as corrosion, oxidation, and mechanical degradation. This protective barrier helps preserve the structural integrity of the catalyst, thereby maintaining its active sites and ensuring prolonged catalytic efficiency. Secondly, coatings can alter the surface's physical and electronic properties by modifying factors such as charge distribution, electronic structure, and conductivity. These changes can significantly impact the catalyst's interaction with reactants, optimizing reaction kinetics and improving selectivity. Finally, coatings modulate the local reaction environment, influencing factors like local pH, ion concentration, and the electric double layer. By tuning these parameters, coatings can create a more favorable microenvironment for the catalytic process, enhancing reactant availability, stabilizing key intermediates, and facilitating efficient electron transfer. In the following discussions, we will explore these mechanisms in greater detail, highlighting how different coating strategies contribute to enhancing the stability and efficiency of ECR catalysts, and ultimately advancing the feasibility of large-scale CO_2 reduction technologies.

2.1 Enhancement of catalyst stability

S e of catalyst deactivation over time. Catalysts often degrade due to various factors such as corrosion, metal leaching, or aggregation/reconstruction of active sites during the electrochemical process. Surface coatings can serve as protective layers that shield the catalyst from harsh reaction conditions like high voltage, acidic environments, or extreme conditions. These coatings prevent corrosion by acting as a physical barrier, for instance, metal oxide coatings can prevent metal dissolution or oxidation, which are common causes of catalyst deactivation. Furthermore, coatings can stabilize active sites by preventing aggregation or leaching of catalytic materials, ensuring sustained catalytic performance over extended periods.

Early investigations have demonstrated that the incorporation of simple reduced graphene oxide (rGO) as a protective wrapper around Cu nanowires effectively maintains methane (CH_4) selectivity during electrochemical reactions. In contrast, Cu nanowires without this protective coating experience significant morphological degradation, which manifests as particle formation, wire bundling, disintegration, and fracturing [34]. While the rGO coating provides short-term stability by preserving the structure and CH_4 selectivity of Cu nanowires, it may not offer long-term protection under continuous electrochemical conditions. Over time, rGO coatings can degrade or fail to effectively shield the copper nanowires from corrosion and structural changes. In contrast, a more robust method for enhancing catalyst stability involves encapsulating Cu with alumina ($Cu@AlO_x$), which is achieved through a combination of colloidal synthesis and atomic layer deposition (ALD) (Fig. 2A) [35]. This method produces a unique hybrid organic/inorganic alumina coating with distinct characteristics. The process begins with a surface treatment using hydrogen peroxide, which introduces hydroxyl groups to the Cu surface, facilitating the attachment of the alumina shell during the initial nucleation phase. Subsequently, the alumina shell is grown around the copper nanocrystals through alternating injections of tri-methyl aluminum (TMA) and isopropanol. This stepwise deposition ensures the formation of a uniform and stable alumina layer, effectively encapsulating the Cu catalyst and enhancing its overall stability and performance.

Interestingly, the $Cu@AlO_x$ nanocrystals exhibit similar activity to that of the as-synthesized Cu nanocrystals (NCs) (Figs. 2B and C). This outcome highlights the distinctive nature of the thin alumina coating grown, as a thick alumina shell would typically serve as an insulator, preventing electron flow and resulting in a low current density. Regarding selectivity, the Cu NCs predominantly produce ethylene (C_2H_4) over CH_4. In contrast, the $Cu@AlO_x$ preferentially generates CH_4 rather than C_2H_4 across the entire potential range. Furthermore, the CH_4 selectivity of the $Cu@AlO_x$ remains stable for at least 24 h, while the Cu NCs experience a sharp decline in selectivity to zero after only 10 h. This rapid decline in the Cu NCs' performance is due to the dynamic restructuring of Cu, which negatively impacts the stability of CH_4 active sites. The most significant finding comes from post-ECR transmission electron microscopy (TEM) analysis (Fig. 2D). The Cu NCs undergo complete reconstruction into disordered catalysts during the initial stages of electrolysis as the potential increases to -1.1 V *vs.* RHE. In contrast, the $Cu@AlO_x$ retains their original structure, with negligible changes in particle size distribution, demonstrating enhanced stability. The identification of Cu^{2+}–O–Al with AlO_4 coordination as a critical motif for stabilization provides valuable insight into the catalytic mechanism. This unique structure likely plays a pivotal role in stabilizing the catalyst by facilitating the interaction between Cu and Al sites, which helps maintain the integrity of the catalyst under reaction conditions. The coordination of AlO_4 with Cu^{2+} also promotes electron redistribution, enhancing the stability of Cu sites and preventing their degradation.

Beyond morphology, surface coating can also stabilize catalyst valence state. For example, the application of polyvinylpyrrolidone ligand layers on Pd surfaces has been shown to effectively stabilize high-valence Pd species[36]. This stabilization promotes the formate pathway while inhibiting the formation of PdH, thereby suppressing the competing reactions of H_2 and CO formation. The protective function of coatings can be further extended to multilayer structures. For instance, Wang *et al.* proposed an effective strategy to preserve molecular additives on the electrode surface by applying a thin protective layer[37]. Specifically, using 4-dimethylaminopyridine (DMAP) as an example, they demonstrated that a thin hydrophobic protection layer of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) applied over the DMAP-functionalized Cu catalyst effectively prevents the leaching of DMAP during ECR. As a result, the DMAP-functionalized Cu catalyst exhibits >80 % selectivity towards multi-carbon products including ethanol, *n*-PtOH and ethylene.

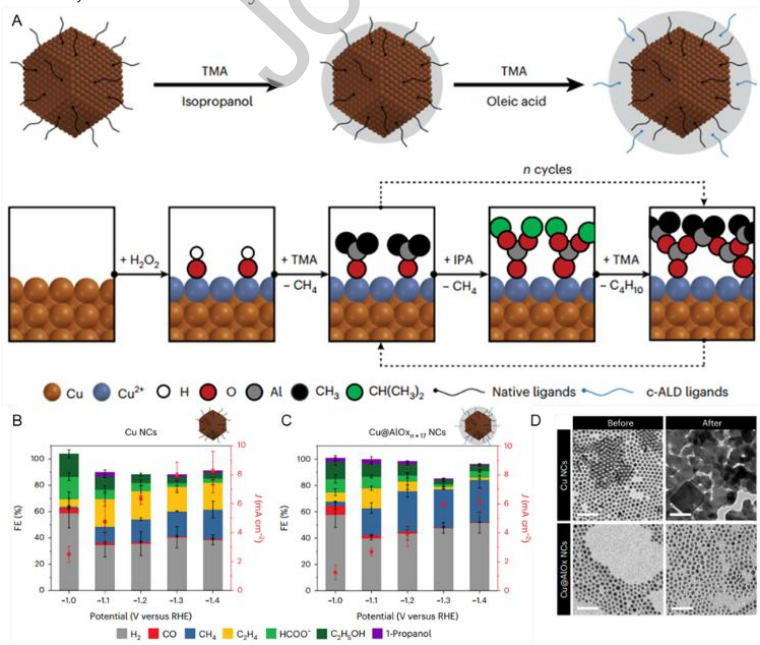

Fig. 2. (A) Schematic representation of the synthesis process for $Cu@AlO_x$. (B, C) The product distributions for the as-synthesized Cu and $Cu@AlO_x$, respectively. (D) TEM images of both Cu and $Cu@AlO_x$ before and after 4 h electrochemcial reduction at -1.1 V *versus* RHE. Reproduced with permissions [35] .Copyright 2024, Springer Nature.

The selectivity of electrochemical CO_2 reduction on Cu catalysts is strongly influenced by the crystallographic orientation of the exposed surface facets. Each facet presents a unique atomic arrangement and coordination environment, which alters the adsorption strength and stabilization of key intermediates involved in CO_2 reduction pathways [38]. For instance, the Cu(100) facet has been shown to favor the formation of C–C coupling products such as C_2H_4 and ethanol due to its ability to stabilize *CO intermediates and promote their dimerization [39,40]. In contrast, the Cu(111) facet, with its more close-packed structure, tends to favor methane production by facilitating hydrogenation of *CO species [41]. Meanwhile, high-index facets and stepped surfaces can provide undercoordinated sites that further diversify product distribution by offering multiple reaction pathways[42]. However, the electrochemical conditions, including applied potential and local pH, can lead to surface strain and atomic rearrangements which often results in the structure reconstruction during electrochemical CO_2 reduction due to the dynamic nature of the reaction environment.

Coating has been proven an effective way to prevent such reconstruction by selectively binding to specific crystallographic planes and dramatically lowering their surface energies. Through this preferential adsorption, the coating molecules passivate dangling bonds on the favored facets, making them significantly more stable than they would be in the bare crystal. As a result, the energetic driving force that normally pushes the crystal to reshape or expose different planes is greatly reduced, allowing the original facet geometry to be preserved even during growth, annealing, or other conditions that would otherwise trigger reconstruction.

Chen *et al.* demonstrated the application of a hierarchical nanostructural coating to enhance the stability and performance of Cu-based catalysts (Fig. 3A) [43]. Specifically, they engineered a hydrophobic CuO nanowire array on a Cu foam substrate through the annealing of electrodeposited $Cu(OH)_2$ nanowire arrays, which resulted in a well-ordered one-dimensional channel structure. This hierarchical design not only facilitated charge transfer but also increased the number of available active sites due to its high surface area. For surface coating, the researchers selected dodecanethiol (DDT) molecules via dip coating for their strong binding affinity to the Cu(100) facet, to stabilize the catalyst surface (CuO-SH). As a result, operando X-ray Diffraction (XRD) studies revealed that the CuO-SH catalyst exhibited a higher intensity of Cu(100) peaks during ECR compared to the uncoated CuO catalyst (Figs. 3B and C). After normalizing the XRD peak intensities, the Cu(100)/(111) intensity ratio for the CuO-SH catalyst was found to be more than three times greater than that of the CuO (Fig. 3D), indicating that the DDT molecules effectively stabilized the Cu(100) facets. Consequently, this design facilitated the electrochemical reduction of ECR toward ethylene production through two primary mechanisms: (1) Improving CO_2 transport and suppressed HER due to the hydrophobic nature of DDT. (2) Stabilizing the Cu(100) facet, which exhibits stronger *CO adsorption and a reduced activation barrier for the *CO–*CHO coupling step. Such facet stabilization can also be realized through the dynamic reconstruction processes[44]. For instance, when polycrystalline Cu is reduced in the presence of *N*,*N*′-ethylene-phenanthrolinium dibromide, the corrosion of the copper surface leads to the formation of well-defined nanocubes. And during electrocatalysis, these nanostructures are subsequently stabilized by a protective organic layer formed *in situ* through reductive dimerization of the phenanthrolinium dication. The combined effect markedly enhances C–C coupling while simultaneously suppressing the evolution of H_2 and CH_4.

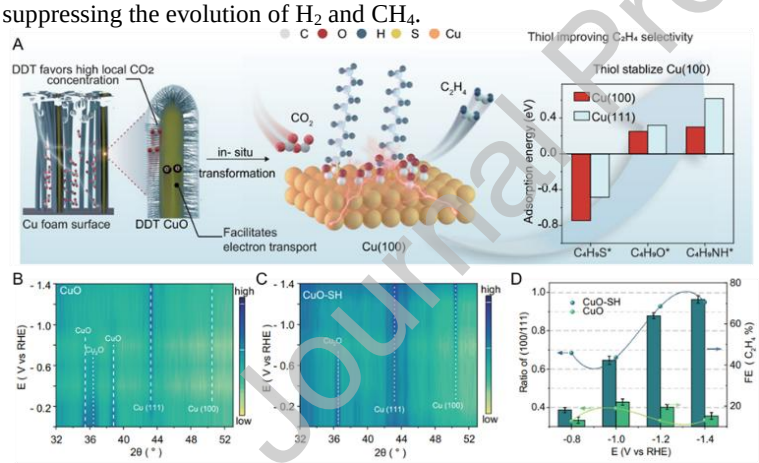

Fig. 3. (A) Schematic illustration of the design of DDT-functionalized CuO-SH catalysts. In situ XRD patterns of (B) CuO-SH and (C) CuO obtained at different applied potentials from 0 to −1.4 V. (D) Quantitative analysis of peak intensities. Reproduced with permissions [43]. Copyright 2024, Springer Nature.

2.2 Alteration of surface physical/electronic properties

Alteration of surface electronic properties through the application of coatings is another pivotal mechanism by which catalyst performance in ECR can be significantly enhanced. The electronic structure of a catalyst surface fundamentally governs the adsorption strength and configuration of key reaction intermediates, directly influencing reaction kinetics, selectivity, and overall efficiency. Surface coatings, ranging from conductive polymers and metal oxides to organic molecules with specific functional groups, can induce charge redistribution, modify the density of electronic states, and alter the catalyst's work function. These electronic perturbations affect how CO_2 molecules bind, how intermediates such as *COOH and *CO are stabilized or destabilized, and how competing reactions like hydrogen evolution are suppressed. By precisely tuning these electronic interactions, coatings provide a versatile approach to lower energy barriers, promote preferred reaction pathways, and improve catalyst durability. Therefore, surface coatings serve not only as protective or morphological modifiers but also as strategic electronic regulators, enabling precise control over surface reactivity and facilitating the design of highly effective electrocatalysts, understanding and controlling the alteration of surface electronic properties via coatings is essential for the rational design of highly selective and efficient ECR catalysts.

For example, various small organic molecules featuring distinct functional groups, such as oleylamine with an amine group, oleic acid with a carboxyl group, and dodecanethiol with a thiol group, have been investigated as surface modifiers on Ag nanoparticles for the ECR [45]. The nature of these functional groups plays a critical role in influencing the binding energies of key reaction intermediates (Fig. 4A). Notably, it was found that amine-capped Ag/C catalysts demonstrated superior CO selectivity compared with

carb y indicating that amine groups stabilize the *COOH intermediate while simultaneously destabilizing adsorbed hydrogen, thereby enhancing selective CO_2 reduction activity. In contrast, thiol-capped Ag nanoparticles demonstrate increased rates of both the HER and CO_2 reduction, resulting in less favorable selectivity toward CO_2 reduction compared to amine- or carboxyl-capped Ag nanoparticles. These results underline the importance of functional group in tuning catalyst selectivity and activity through surface modification strategies.

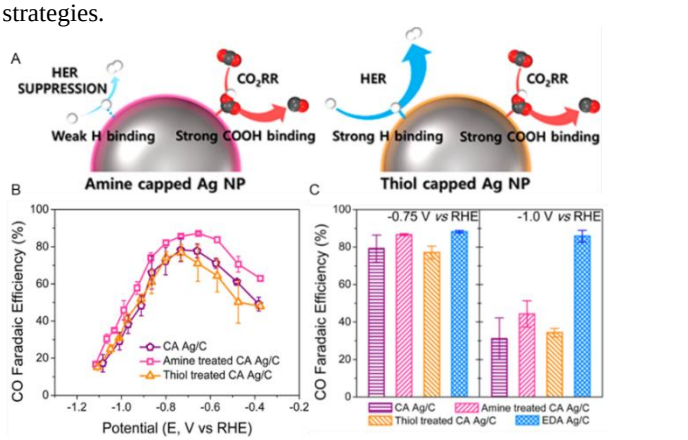

Fig. 4. (A) Diagram depicting the function of molecule-mediated Ag Nanoparticles. (B) CO Faradaic efficiency, depending on the applied potential for Ag/C, amine-treated Ag/C, thiol-treated Ag/C. (C) Comparison of CO Faradaic efficiency from different functionalized Ag surfaces. Reproduced with permission[45]. Copyright 2016, American Chemical Society.

Similarly, imidazolium-based monomers are employed as surface modifiers in ECR due to their unique chemical and electrochemical properties. The imidazolium cation features a positively charged heterocyclic structure capable of strong electrostatic interactions with the negatively charged catalyst surface and reactant species. Additionally, imidazolium groups can facilitate selective binding and stabilization of key CO_2 reduction intermediates, thereby modulating reaction pathways and improving product selectivity. Their tunable chemical structure allows for modification with various alkyl or functional groups, enabling fine control over hydrophobicity, steric effects, and electronic properties at the catalyst-electrolyte interface.

A series of imidazolium-based monomers were also evaluated as surface coatings for Ag-based catalysts (Figs. 5A and B), revealing that imidazolium-containing ionomers inherently promote the HER during ECR, without significantly affecting the kinetics of CO_2 reduction to CO (Fig. 5C) [46]. Interestingly, this finding indicates that the increased HER activity results from a faster bicarbonate proton-donor pathway facilitated by the ionomers, whereas the ECR rate remains unaffected because its rate-determining step does not involve proton transfer (Fig. 5D). Notably, modifying the imidazolium ring with various alkyl groups significantly influences the extent to which the bicarbonate-derived HER pathway is promoted. Analysis of kinetic parameters shows that the steric Taft parameter effectively correlates with HER promotion, indicating that increased steric bulk hinders the interaction between the ionomers and the Ag surface or bicarbonate/carbonate ions, thereby reducing proton transfer facilitation. DFT calculations further support these observations by demonstrating more favorable reaction energetics for bicarbonate reduction in the presence of imidazolium species, with the stabilization attributed to the close proximity of the imidazolium ring to both the Ag surface and bicarbonate ions.

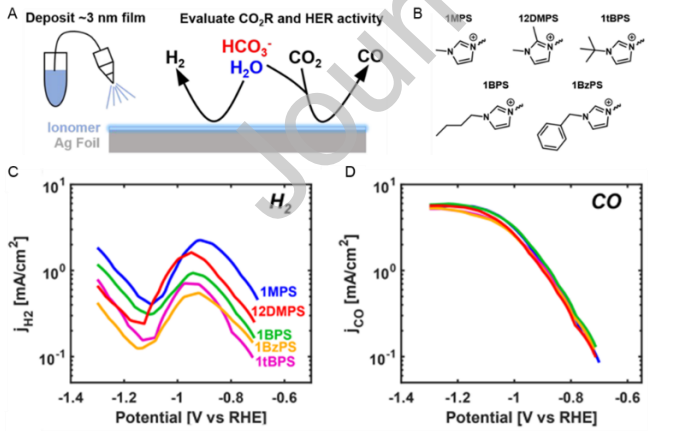

Fig. 5. (A) Schematic of the experimental setup illustrating the deposition of a thin ionomer film onto Ag foil via spray coating. (B) Structures of the five imidazolium groups tested. (C) Partial current density for H_2 as a function of electrode potential for a series of functionalized imidazolium ionomers, and D. Corresponding partial current density for CO under the same conditions. Reproduced with permission [46]. Copyright 2021, American Chemical Society.

Another noteworthy study offers an alternative perspective. Asadi *et al.* demonstrated that the functionalization of Mo_3P nanoparticles with imidazolium groups significantly enhances the electrocatalytic CO_2 activity of the Mo sites by precisely tuning their electronic structure and the local electric field at the catalyst surface [47]. The researchers applied an electrochemical method to coat the surface of Mo_3P nanoparticles with 1-ethyl-3-methylimidazolium, which was carried out using a standard three-electrode configuration (Fig. 6A). TEM characterization confirmed the formation of a uniform imidazolium coating approximately 1 nm thick on the surface of the Mo_3P nanoparticles, indicating successful surface modification (Fig. 6B). To probe the alterations in electronic properties induced by this functionalization, electron energy-loss near-edge structure (ELNES) spectroscopy was employed. The ELNES spectra of the Mo-M_3 edge revealed a distinct shift of approximately 0.7 eV toward higher energy in the imidazolium-functionalized Mo_3P (ImF-Mo_3P) compared to pristine Mo_3P (Fig. 6C). Additionally, an increase in the white-line intensity was observed, suggesting enhanced unoccupied density of states associated with Mo atoms after coating. These spectral changes signify a higher electrochemical potential

and [illegible] significantly upshifted relative to -0.77 eV in the unmodified Mo_3P. This upward shift of the d-band center correlates with stronger adsorption of CO_2 and CO intermediates, which is critical for facilitating the CO_2 reduction reaction. Collectively, these findings illustrate that imidazolium surface functionalization modulates the electronic structure of Mo active sites, thereby enhancing their affinity toward key reaction intermediates and improving catalytic performance. Electrochemical measurements reveal that the ImF-Mo_3P predominantly produces propane (C_3H_8) within the potential range of −0.2 V to −1.0 V *vs.* RHE (Fig. 6D). Propane formation initiates at −0.2 V with an FE of 38 %, reaching a peak efficiency of 91 % at −0.8 V. In stark contrast, pristine Mo_3P nanoparticles predominantly favor the production of CO and CH_4, attaining maximum Faradaic efficiencies of 75 % and 24 % respectively at −0.8 V. Importantly, only trace amounts of C_2H_6 and C_3H_8, with FE values below 2%, were detected on the pristine Mo_3P catalyst, underscoring the significant enhancement in multi-carbon hydrocarbon selectivity imparted by imidazolium surface functionalization.

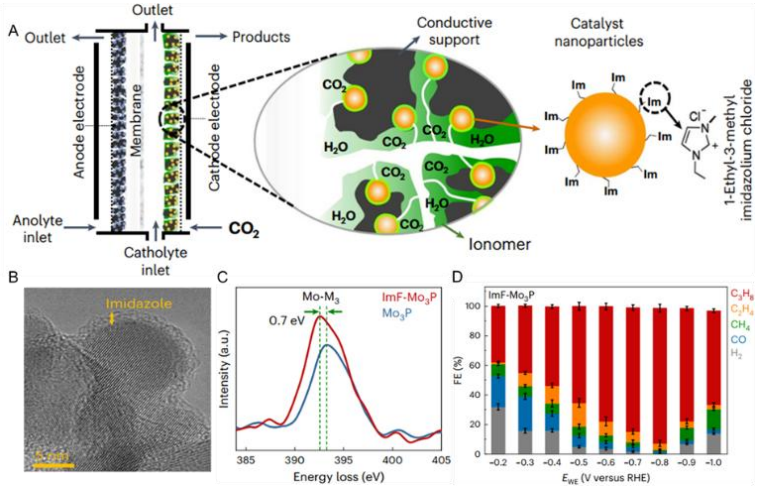

Fig. 6. (A) Illustration of the catalyst structure featuring Mo_3P nanoparticles coated with an imidazolium layer. (B) TEM image showing the structure of ImF-Mo_3P nanoparticles. (C) ELNES spectra of Mo-M_3 edge comparing imidazolium-functionalized ImF-Mo_3P and pristine Mo3P. (D) Faradaic efficiencies of the ImF-Mo_3P catalyst across various applied potentials. Reproduced with permission [47]. Copyright 2023, Springer Nature.

2.3 Modulation of local microenvironment

A critical factor influencing both the efficiency and selectivity of ECR is the microenvironment surrounding the electrocatalyst surface, which refers to the local chemical and physical conditions at the catalyst-electrolyte interface [48]. This microenvironment includes parameters such as local pH, concentrations of CO_2, anions, intermediate species, and the structure of the electric double layer (EDL), all of which directly impact the reaction dynamics. The local pH, for instance, governs proton availability and can influence the formation of hydrogen evolution reactions (HER) or CO_2 reduction pathways. Similarly, the concentration of CO_2 near the catalyst is essential, as its limited solubility in water can create concentration gradients that hinder its availability, thus impacting reaction rates. Anions and intermediate species, such as bicarbonate and carbonate ions, play an important role by stabilizing reaction intermediates and modifying the catalyst's electronic properties. The reactivity is further governed by the structure of the EDL, which modulates the distribution of ions and the local electrostatic potential at the electrode surface. An pioneering example involves manipulating the EDL using organic cations, such as alkylammonium species. Smaller alkylammonium cations, for instance, generate a stronger local electric field. This increased field strength was foudnt to promote the activation of the CO_2 and facilitates its reduction to CO [49]. These factors together govern the adsorption, activation, and reaction pathways of reactants and intermediates, ultimately dictating the efficiency and selectivity of product formation. Thus, controlling and optimizing this microenvironment is vital to enhance the performance of ECR, as even subtle changes in local conditions can lead to significant variations in product distribution, making it essential to design catalysts and coatings that regulate these parameters to favor desirable reactions.

ECR is fundamentally constrained by considerable kinetic overpotentials, primarily arising from the limited concentration of CO_2 molecules at the catalyst-electrolyte interface, which in turn promotes the competing HER in aqueous media and diminishes overall selectivity toward desired carbon-based products. Addressing this issue requires innovative strategies to tune the surface properties. One straightforward approach involves the application of hydrophobic surface coatings aimed at suppressing HER by restricting proton access to active catalytic sites. For instance, Liu *et al.* [50] demonstrated that polytetrafluoroethylene (PTFE) coatings on copper nanoneedles (CuNNs) effectively concentrated electrons and K^+ ions near the catalytic tips (Fig. 7A), thereby enriching the local CO_2 concentration while concurrently impeding proton supply. It was found that the accumulation of electrons at the apex of PTFE-coated CuNNs generates a substantially enhanced local electric field at the catalyst surface compared to that observed on pure Cu nanowires (CuNWs). In response to this intensified electric field, K^+ migrate toward the catalyst surface to preserve electrostatic equilibrium, leading to an increased local concentration of K^+ ions near the active sites (Fig. 7B). This modification resulted in a drastic reduction of the H_2 Faradaic efficiency (FE) to 5.9 % at 1.49 V *vs.* RHE, a significant decrease from the 41.6 % observed on uncoated CuNNs. Interestingly, the suppression of H_2 evolution was accompanied by dramatic improvements in C_1 and C_{2+} product selectivities, with FE(CH_4) and FE(C_2H_5OH) rising from 4.3 % and 7.7 % on CuNNs to 32 % and 25.8 % on PTFE coated CuNNs, respectively, while FE(C_2H_4) and FE(CO) similarly increased upon PTFE coating (Fig. 7C). Similarly, pyridinium-based molecular films can fulfill a comparable protective role[51,52]. Unlike PTFE coatings, these films form ultrathin and conformal layers that adhere closely to nanostructured catalyst surfaces. This intimate contact promotes efficient charge transfer while mitigating the mass transport limitations typically observed with thicker PTFE coatings. Notably, this strategy has demonstrated effectiveness for both Ag and Cu catalysts. For instance, in the case of Ag coated with a pyridinium-based molecular film, the hydrophobic layer not only suppresses HER but also

alte a proton-transfer step involving bicarbonate ions. These combined effects enable coated Ag electrodes to achieve >99 % FE_{CO} under aqueous conditions. When applied to Cu, the pyridinium-based coating selectively attenuates pathways leading to hydrogen and methane formation while leaving the fundamental C–C coupling chemistry of Cu largely unaffected. Partial-current analyses show that the production rates of ethylene, ethanol, and 1-propanol remain essentially unchanged, whereas the formation of H_2 and CH_4 is markedly reduced. This selective suppression suggests that the coating modulates the interfacial proton environment, thereby maintaining conditions favorable for high *CO coverage, an essential prerequisite for efficient multicarbon product formation. As a result, coated Cu electrodes exhibit FEs of 70 %–80 % for C_{2+} products.

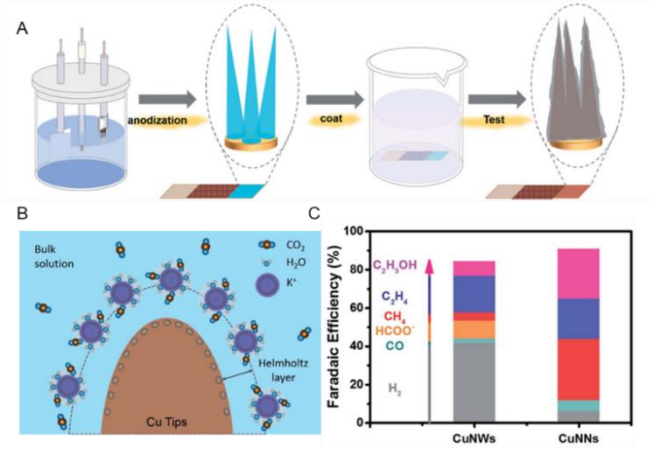

Fig. 7. (A) Diagram depicting the synthesis process of CuNNs. (B) Illustration showing the adsorption of K^+ in proximity to the copper tip surfaces. (C) Comparison of product distributions obtained from CuNWs and CuNNs at an applied potential of -1.49 V *versus* RHE. Reproduced with permission [50]. Copyright 2020, The Royal Society of Chemistry.

Unlike PTFE and other polymers, which are non-conductive, carbon coatings provide a combination of hydrophobicity and enhanced electrical conductivity, making them more suitable for facilitating electron transfer during electrochemical reactions. A related study investigated the synthesis of an amorphous carbon-coated silver nanoparticle (Ag/C) catalyst, utilizing a relatively simple and effective ultrasonic pyrolysis technique[53]. The approach aimed to introduce a thin carbon layer onto the silver nanoparticles (Ag NPs), this carbon layer is thought to enhance the accumulation of CO_2 at the catalyst surface, thereby increasing the local concentration of CO_2 within the catalytic layer. This localized concentration is crucial for optimizing the efficiency of CO_2 reduction reactions by facilitating more effective interactions between the catalyst and CO_2 molecules. Surface spectroscopic studies of the Ag/C catalyst revealed notable improvements in CO_2 adsorption properties, with significantly enhanced CO_2 peak intensities compared to the bare Ag catalyst. Furthermore, the emergence of the $*CO_2$ peaks at more positive potentials in the Ag/C system suggested a shift in the catalyst's electrochemical behavior, indicating improved activation of CO_2 molecules.

The incorporation of nitrogen into the carbon structure can further enhance the electronic properties of the material, providing increased conductivity and improved charge transfer at the electrode surface. Li *et al.* have reported a strategy involving the construction of a nitrogen-doped carbon (N_xC) shell on the surface of Ag nanoparticle cores to facilitate the formation of deep reduced ECR products[54]. This N_xC-coated catalyst demonstrated a notable increase in the H_2 FE (12 %), CH_4 (43.8 %), and C_2H_4 (8.4 %) compared to bare Ag NPs, which exhibited only 1 % H_2 FE and approximately 98% CO FE. The N_xC shell was found to significantly enhance HER kinetics over the Ag NPs because of the increased coverage of adsorbed H_2O. Furthermore, CO_2 adsorption/desorption measurements revealed that the N_xC-coated Ag NPs exhibited a significantly higher capacity for CO_2 adsorption compared to bare Ag NPs under identical pressure conditions. Furthermore, the desorption of CO_2 from the N_xC-coated surface occurred at a considerably lower pressure, indicating stronger interactions between CO_2 and the nitrogen species within the N_xC shell. This enhanced interaction likely contributes to the observed shift in product distribution. Specifically, the formation of CH_4 and C_2H_4 can be attributed to the following reason, in the absence of the N_xC shell, the CO intermediate rapidly desorbs from the Ag surface, predominantly leading to CO production due to its low adsorption energy and the lack of sufficient adsorbed hydrogen to drive further reduction. However, the presence of the N_xC shell stabilizes the CO intermediate by extending its residence time on the surface. Further, Bian *et al.* demonstrated that, in addition to enhancing the *CO binding strength, the incorporation of an N_xC shell on the Cu surface also influences the absorption geometry of *CO[55]. By coating the Cu surface with an N_xC shell, they found that the N_xC layer on the Cu/NC nanowire surface effectively traps CO on the Cu, promoting the stabilization and enhancement of the $*CO_{atop}$ intermediate through linear adsorption. This occurs because N can adsorb O, while Cu preferentially adsorbs C. This modification of the adsorption orientation not only stabilizes *CO but also facilitates C-C coupling, leading to significantly a high C_2H_4 FE of 53.5 % and 87.5 % FE for C_{2+} products.

Although the selectivity of ECR products can be notably improved under alkaline electrolyte conditions, primarily because elevated pH levels suppress the competing HER, thereby favoring CO_2 reduction pathways. However, this improvement in selectivity is accompanied by a significant drawback: At high pH, the local concentration of CO_2 near the copper catalyst surface diminishes substantially. This phenomenon arises from the rapid chemical equilibrium between CO_2 and hydroxide ions, which leads to the formation of HCO_3^- and CO_3^{2-} species. Consequently, the availability of free CO_2 molecules for direct reduction is limited, more importantly, these salts can accumulate and precipitate within the electrolyte or on the catalyst surface, creating a pronounced trade-off between maintaining high product selectivity and stability. Addressing this challenge requires innovative strategies to modulate the local CO_2 environment effectively. One promising approach involves incorporating organic components that can enhance the local CO_2/H_2O ratio at the catalyst surface in acidic electrolyte [56].

One of the pioneering studies in this field was conducted by Wang *et al.,* who observed that, beyond hydrophobicity, the polymer properties of gas permeability and water uptake capacity are more critical for controlling the local microenvironment in ECR [57]. They

syst [illegible] 2-(1,1,2,2,3-pentafluoro-3-(trifluoromethoxy)butyl)-5,5-bis(perfluoroethyl)tetrahydrofuran] (PCR), PT95 (poly[2-(1,1-difluoroethyl)-2-ethyl-4,4,5,5,6-pentafluoro-6-(trifluoromethyl)-1,3-dioxane]), polyvinylidene fluoride (PVDF), and Nafion 117. Upon evaluating the ECR performance of these Cu GDEs under identical conditions, it was found that their activity did not correlate with the hydrophobicity of the polymer. This suggests that hydrophobicity alone is not a reliable predictor for CO_2R activity or selectivity, particularly for multi-carbon product formation. Instead, they identified that CO_2 adsorption and water uptake capacity are the critical parameters for controlling the selectivity and activity of ECR. Similar findings were reported by Peters and Agapie *et al.,* who demonstrated that the *N*-tolylpyridinium additive effectively limits the transport of H^+ to the electrode while maintaining favorable CO_2 transport in acidic electrolyte [58]. This selective modulation of ion transport can mitigate the HER in favor of ECR. As a result, such ionomer-modified Cu electrodes have been shown to enhance the selective ECR to C_{2+} products, even in highly acidic electrolytes, under conditions of low alkali cation concentrations and low operating current densities.

Building on above knowledge, researchers have sought innovative strategies to enhance these properties at the electrode interface. One such approach involves the incorporation of ionomers. For instance, Sinton *et al.* introduced a novel approach by integrating a thin layer of ionomer containing immobilized benzimidazolium cationic functional groups (CG) at the Cu surface (Fig. 8A) [59]. This modification not only reduces the proton diffusion rate but also enhances the local pH, thereby promoting the selective production of C_{2+} products. Three types of CG-modified ionomers were prepared, designated as CG-low, CG-medium, and CG-high, by dissolving different types of dry ionomer resins (AP2-HNN2-00, AP2-HNN5-00, and AP2-HNN8-00 ionomers, respectively). The Cu electrodes modified with CG-functionalized ionomers were fabricated by spraying 1 wt% ionomer solutions with varying densities of cationic functional groups, allowing for the systematic evaluation of their influence on catalytic performance. They observed that the interfacial electric field generated by the CG layer was comparable in magnitude to that produced by alkali cation-containing solutions[60,61]. Such surface electric field plays a stabilizing role for the negatively charged CO_2, facilitating its adsorption and activation in acidic media. Furthermore, they employed molecular dynamics (MD) simulations to investigate the distribution of H_2O and CO_2 near the Cu surface (Fig. 8B). Their findings revealed that the CG-modified surface exhibited the lowest H_2O density compared to the K^+-rich electrolyte and pure water cases across various potentials, suggesting an effective H_3O^+-blocking function of the CG layer. Additionally, the CG modification led to an enhanced local CO_2 concentration at the Cu surface under constant potential, indicating improved CO_2 adsorption. The impact of CG loading on catalytic performance was also evaluated, and no significant improvement was observed since only a small amount of CG layer can fully cover the surface. The CG-low Cu showed a reduction in H_2 FE to 60 % compared with nearly 100 % H_2 FE in bare Cu (Fig. 8C). To better understand the underlying mechanism, cyclic voltammetry (CV) measurements were performed on CG-low Cu and bare Cu electrodes in H_2SO_4 electrolytes, with and without K^+. The results indicated that the onset of the plateau, representing H_3O^+ depletion at the Cu surface, occurred at a lower current density for CG-low Cu compared to bare Cu in K^+-rich electrolyte (Fig. 8D). This research introduces an innovative coating approach for developing ECR catalysts in acidic electrolytes without alkali ions.

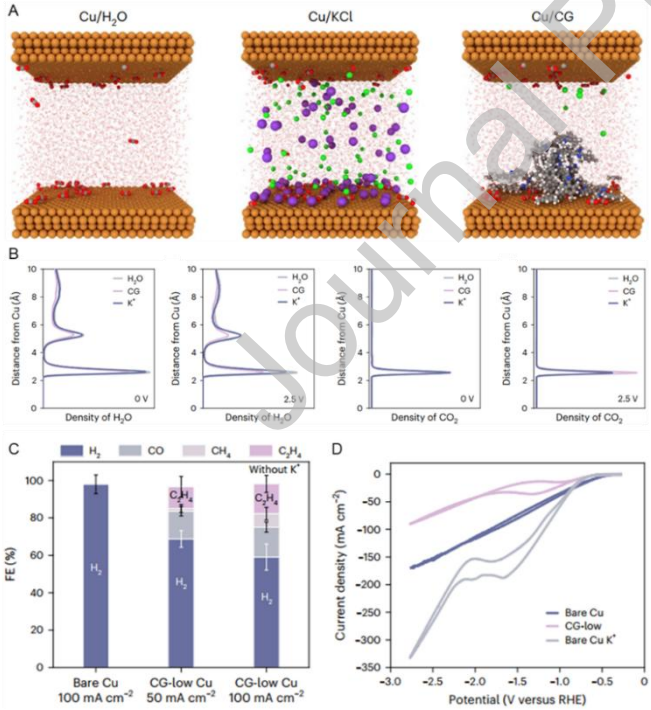

Fig. 8. (A) Theoretical simulations illustrating the atomic configurations for Cu/H_2O, Cu/KCl, and Cu/CG systems. Red, grey, yellow, green, purple, blue and white balls represent O, C, Cu, Cl, K, N and H, respectively. (B) Comparison of the simulated densities of H_2O and CO_2 as a function of distance from the Cu electrode. (C) Selectivity profiles for bare Cu and CG-modified Cu at different current densities. (D) curves for bare Cu, CG-modified Cu in 0.2 mol/L H_2SO_4 with Ar, and bare Cu in 0.2 mol/L H_2SO_4 + 3 mol/L KCl with Ar, at a scan rate of 100 mV/s. Reproduced with permission [59]. Copyright 2023, Springer Nature.

From the above work, it has seen demonstrated that ion-conducting polymers are an effective type of material for modulating the local concentrations of CO_2, H_2O, OH^-, and H^+ in electrocatalytic processes. The hydrophobic nature of their backbone chains, which typically contain $–CH_2–$ or $–CF_2–$ groups, coupled with the charged moieties at the ends of their side chains, allows for enhanced ion transport and selective modification of the interfacial environment. A more comprehensive study by Alexis *et al.* explored the impact of ionomer coatings on Cu electrodes during ECR [62], focusing on two representative ionomers: Nafion (a cation-conducting ionomer) and Sustainion (an anion-conducting ionomer). The study revealed that the Nafion layer did not significantly alter the current density compared to bare Cu electrodes. However, it induced substantial changes in the product distribution (Figs. 9A and B). Specifically, at

an a[illegible]%.

These results suggest that Nafion's cation-conducting properties likely reduce proton availability, favoring carbon-carbon coupling and enhancing the formation of C_{2+} products. In contrast, Sustainion exhibited only minor effects on product distribution across all tested potentials (Fig. 9C). However, it led to a noticeable increase in the total current density, indicating that Sustainion facilitated improved ion transport, thereby enhancing the overall reaction rate without significantly altering selectivity. This comparison underscores the distinct roles that cation- and anion-conducting ionomers play in modulating both the kinetics and selectivity of CO_2 electroreduction, providing valuable insights for the design of more efficient electrocatalytic systems.

To determine whether the observed selectivity enhancements were due to changes in the chemical microenvironment rather than intrinsic alterations in the Cu electronic structure, the effect of different ionomer-layer stacks was investigated (Figs. 9D and E). Notably, when a Sustainion layer was deposited on top of Nafion850-coated (Nafion with a lower mole mass) Cu (Naf850/Cu), the total current density increased relative to Naf850/Cu, but no significant changes were observed in the product distribution. Conversely, when a Nafion layer was added on top of a Sustainion-coated Cu electrode (Naf850/Sus/Cu), a marked increase in C_{2+} production was observed (C_{2+} FE rising from 61 % to 80 %). This configuration also led to a higher current density than that of Naf850/Cu. These findings indicate that, in the case of Sus/Naf850/Cu, all partial current densities were enhanced compared to Naf850/Cu, whereas in the Naf850/Sus/Cu configuration, there was a selective increase in the partial current density for C_{2+} products relative to Sus/Cu. Thus, these results suggest that the changes in product distribution and current densities are driven by the ionomer arrangement and its effect on the local microenvironment, rather than intrinsic modifications to the Cu surface.

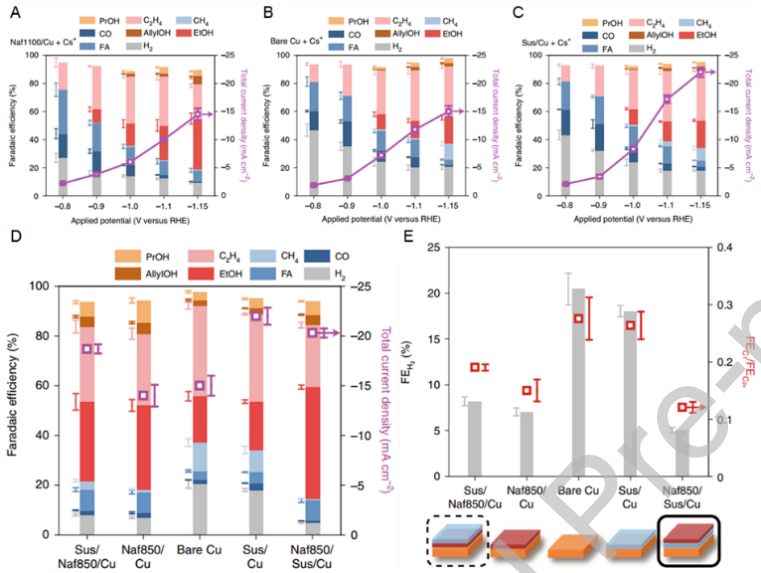

Fig. 9. (A-C) Catalytic performance of ECR using Nafion/Cu, bare Cu and Sustainion/Cu, respectively. (D) ECR performance using stacked ionomers on Cu. (E) Products analysis from the experiments in D. Reproduced with permission [62]. Copyright 2021, Springer Nature.

2.4 Increase mass transport

Surface coatings play a critical role in enhancing CO_2 mass transport in ECR by improving the surface area and creating efficient CO_2 transport channels. Coatings can increase the effective surface area of the electrode, providing more active sites for CO_2 adsorption and reducing the resistance to ion and gas transport. Additionally, specific surface modifications, such as the introduction of porous materials, can facilitate the formation of preferential pathways for CO_2 molecules, allowing for more efficient diffusion to the reaction sites, which are crucial for achieving high performance in ECR processes, especially at higher current densities.

Li *et al.,* reported the development of a solvent-free processing method to apply a porous nanocoating of PTFE onto commercial Cu nanoparticles, significantly enhancing the production of C_{2+} products [63]. The dry coating technique involves loading Cu and PTFE powders into a ball-milling chamber along with milling balls. The PTFE-coated Cu nanoparticles (NPs) aggregate into interconnected, porous 3D micro-granules, which are subsequently dispersed onto a carbon gas diffusion layer (GDL) through electrostatic deposition to form the cathode. This dry method results in nearly complete PTFE coverage on the Cu NPs, forming either a nanofilm or nanofiber structure (Fig. 10A). The PTFE coating, coupled with the increased porosity of the dry-coated sample, creates a more extensive catalyst–electrolyte–gas interface on the gas diffusion electrode. The increased surface area enhances the accessibility of active sites while also promoting more efficient CO_2 transport to the catalyst surface. This improvement in mass transport ensures a more uniform distribution of the reactant gas, which in turn optimizes the electrochemical reduction process and enhances the overall catalytic efficiency. As depicted in (Fig. 10B), for catalysts prepared with a fixed ball milling time of 30 min but varying PTFE mass loadings, the selectivity for C_{2+} products initially increased with the PTFE content. Specifically, the catalyst prepared with 20 % PTFE achieved a C_{2+} to C_1 ratio of 4.3, corresponding to a total FE for C_{2+} products of 71 %. However, when the PTFE loading was further increased, a notable shift in the electrochemical performance was observed, characterized by a significant increase in H_2 selectivity and a drastic reduction in C_{2+} FE to only 15 %. Additionally, the electrochemical performance was assessed across different ball milling times (Fig. 10C), with the results indicating that the highest C_{2+} selectivity was attained with 20 % PTFE and a 30-min ball milling time, achieving a C_{2+} FE of 78 % at a current density of 400 mA/cm^2. The improved performance observed with this particular configuration is attributed to the balance of mass transport kinetics and the insulating nature of PTFE.

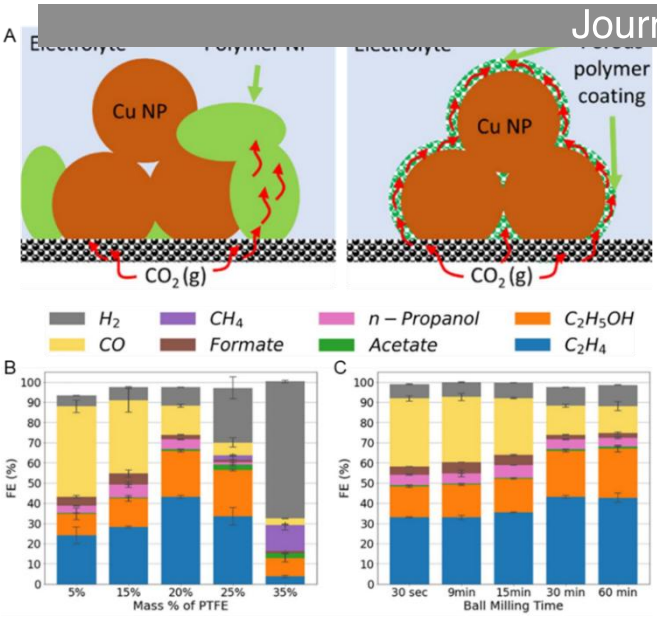

Fig. 10. (A) conventional airbrushing of a catalyst ink made of Cu–PTFE mixture and solvent-free dry processing method to coat PTFE on Cu. Effects of (B) PTFE mass loading and (C) ball milling time on the ECR products. Reproduced with permission [63]. Copyright 2023, The Royal Society of Chemistry.

Similarly, quaternary ammonium cation coatings are also investigated for their potential in modulating CO_2 mass transport, owing to their ability to enhance both ionic conductivity and CO_2 solubility at the electrode-electrolyte interface. Unlike PTFE, which is hydrophobic and functions primarily as a physical barrier, quaternary ammonium cation introduce charged sites that facilitate ion exchange and improve electrostatic interactions with CO_2 molecules. This enhancement promotes more efficient CO_2 adsorption and activation. For example, Guo *et al.* reported the use of quaternary ammonium cations immobilized on hydrophobic covalent organic frameworks (COFs) as coatings for nano Cu (Cu/Me-COF), which significantly enhances C_2H_4 production[64]. The incorporation of such hydrophobic cationic COFs effectively modulates the transport of CO_2 and H_2O, creating abundant triple-phase interfaces at the cathode (Fig. 11A). This structural modification improves the overall electrochemical performance, as demonstrated by a substantial increase in the C_2H_4 FE across a wide current density range of 200-800 mA/cm^2 (Fig. 11B). Furthermore, the Cu/Me-COF electrode demonstrated exceptional C_2H_4 production effeciency even with a diluted CO_2 feed (40 vol%, in Ar, Fig. 11C), suggesting an enhanced mass transfer of CO_2 within the cationic COF-modified cathode. This observation underscores the critical role of the COF modification in improving CO_2 transport and overcoming limitations associated with diluted feed conditions. Additionally, the immobilized quaternary ammonium cations within the COFs play a vital role in regulating K^+ migration *via* the Donnan effect, which enhances the local electric field at the interface. This modulation strengthens the *CO adsorption and promotes effective C–C coupling, which is essential for the production of C_2 products. Collectively, these findings highlight the significant improvements in both CO_2 transport and interface redulation brought about by the cationic COF modification, making it a promising strategy for enhancing the efficiency of CO_2 reduction processes.

Importantly, the concept of mass transport engineering is not limited to CO_2 but can be extended to other small-molecule reactants such as methane (CH_4) and CO. For instance, Wang *et al.* demonstrated that ionic liquid–TiO_2–CuO_x composite interfaces enable the selective conversion of CH_4 to ethanol (CH_3CH_2OH) under ambient conditions[65]. An aqueous electrolyte of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) was employed. The composite catalyst demonstrated efficient CH_4-to-CH_3CH_2OH conversion, attributed to the unique properties of the ionic liquid. Specifically, [bmim][BF_4] not only enhanced the solubility of CH_4 but also adsorbed and aggregated on the TiO_2–CuO_x surface under anodic polarization. Moreover, the synergistic interaction between the cation and anion in [bmim][BF_4] facilitated the formation of efficient CH_4 diffusion channels within the catalyst interface. This synergy enhanced CH_4 transport to the active sites, thereby enabling efficient C–H bond activation and subsequent ethanol production. Together, this study underscore the broader applicability of ionomeric coating strategies in tailoring mass transport pathways, offering generalizable design principles for optimizing electrochemical conversion of other hydrocarbons. Similarly, coating the Cu_2O surface with a fully fluorinated polymer has been demonstrated to effectively increase the local concentration of CO, thereby enhancing the formation of acetate [66].

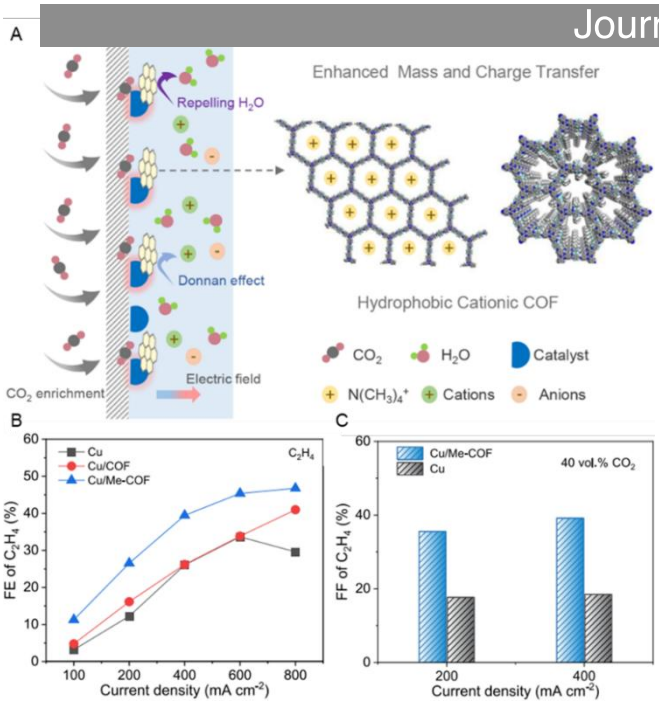

Fig. 11. (A) Schematic Illustrations of the mass and charge transfer effect by Me-COF. C_2H_4 FE on Cu, Cu/COF and Cu/Me-COF in (B) pure CO_2 and (C) Diluted CO_2 feed. Reproduced with permission [64]. Copyright 2025, ACS Publications.

The significant role of ionomers in enhancing mass transport and product selectivity was systematically investigated from a series of polystyrene-based ionomers. Specifically, ionomers containing alkali cations, such as K^+, have been shown to improve the efficiency of CO_2RR on metallic electrodes. The enhanced performance is theoretically attributed to a combination of factors, including an induced electric field from the positively charged functional groups and high local [CO_2] [67]. To investigate the correlation between K^+ content in ionomers and CO_2RR performance, a series of polystyrene-based ionomer films were tested on Cu electrodes (Fig. 12A) [68]. The electrodes were prepared by simply drop-casting the ionomer films. The results indicate that ionomers with higher K^+ concentrations exhibited a notable increase in C_{2+} selectivity compared to bare Cu (Fig. 12B).

Further analysis of the partial current densities revealed that the current density for C_{2+} products (j_{C2+}) also increased with increasing K^+ content in the ionomer. Interestingly, when replacing the electrolyte from 1 mol/L $KHCO_3$ to 1 mol/L MeN_4HCO_3, H_2 was the exclusive product, regardless of whether the electrodes were bare Cu or Cu electrodes coated with ionomer. Furthermore, when using 1 mol/L Me_4NOH as the electrolyte, no improvement in CO_2 reduction selectivity was observed with the ionomer coating compared to bare Cu (Fig. 12C). These findings suggest that the observed changes cannot be attributed solely to pH effects or microenvironment tuning from the ionomer coating. To explore the underlying reasons for these observations, the partial pressure of CO_2 (P_{CO2}) was varied. A monotonic increase in j_{C2+} was observed with rising P_{CO2}, indicating that the presence of ionomer coatings can effectively overcome the volcano plot behavior typically seen with unmodified Cu. Additionally, a log-log plot of P_{CO2} and j_{C2+} revealed a first-order relationship between the concentration of CO_2 and the formation of C_{2+} products in the presence of K^+-containing ionomers, suggesting efficient mass transport through the ionomer film (Fig. 12D). These results highlight the critical role of mass transport in driving CO_2RR.

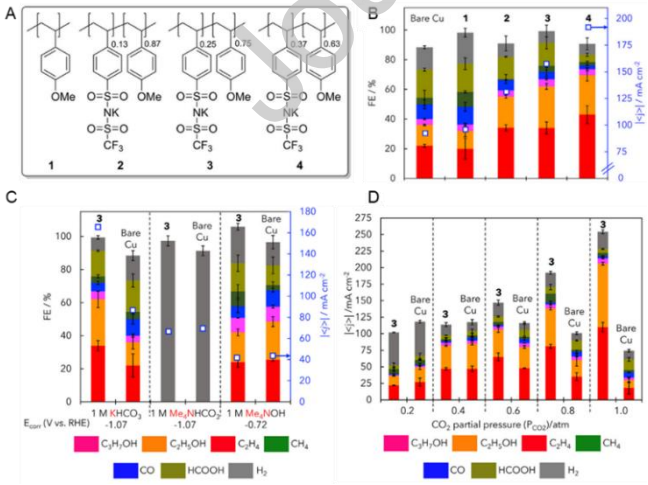

Fig. 12. (A) ionomers with different K^+ contents. (B) ECR performance of Bare Cu and K^+-ionomers-coated Cu. (C) ECR performance in different electrolytes. (D) ECR performance at various CO_2 partial pressures. Reproduced with permission [68]. Copyright 2024, Cell Press.

2.5 Suppression of salt precipitation

In addition to modifying the electrode and electrode-electrolyte interfaces, coatings can also be applied to the electrolyser assemblies to suppress the formation of salts that can accumulate and block flow channels. One of the most significant long-term stability concerns for anion exchange membrane (AEM)-based systems is the accumulation of salts, which can occur due to the electrochemical reactions

taki e efficiency of ion transport, limiting the effective use of the catalyst, and ultimately impeding the overall performance of the electrolyser.

Wang *et al.,* reported a pioneering approach utilizing a conformal parylene coating on the gas flow channel surface of a ECR membrane electrode assembly (MEA)[69]. The parylene coating was deposited via chemical vapor deposition (CVD) using dichlorodip-xylylene as the precursor, aimed at mitigating the issue of salt precipitation (Fig. 13A). The hydrophobic nature of the parylene coating facilitated the flow of $KHCO_3$ droplets by preventing premature drying and subsequent salt formation. However, the insulating nature of the coating necessitated manual removal of the parylene from the top surface of the endplate to ensure direct electrical contact between the current collector and the gas diffusion electrode (GDE) land area. To assess the impact of the hydrophobic parylene coating on salt distributions, control experiments were performed with a 1 × 2.5 cm^2 electrode positioned upstream in serpentine flow channels. The results revealed a marked difference in salt behavior: without the parylene coating, $KHCO_3$ precipitation occurred throughout the flow channels after a stability test at 100 mA/cm^2 with 0.5 mol/L $KHCO_3$, whereas the parylene-coated system showed no obvious salt buildup along the flow channels where the electrode was positioned (Fig. 13B). This coating strategy demonstrated significant improvements in the operational stability of the ECR MEA electrolyser (Fig. 13C). In the uncoated system, using a 0.1 mol/L $KHCO_3$ anolyte at 200 mA/cm^2, CO FE was maintained above 80% for approximately 100 h, after which salt accumulation obstructed the gas flow, leading to a significant decline in performance. In contrast, the parylene-coated device successfully extended operational stability to over 500 h, maintaining over 90 % CO FE without complete blockage of the flow channels. While this approach effectively facilitated the removal of liquid droplets before they dried into salt, it was not entirely immune to salt accumulation. Over time, as the GDE gradually became more hydrophilic, it became susceptible to adhesion of liquid droplets, which could lead to localized salt deposition. Therefore, further investigation into coatings with dynamic properties, or methods to rejuvenate the hydrophobicity of the GDE, could enhance long-term stability and performance by preventing the gradual onset of salt deposition.

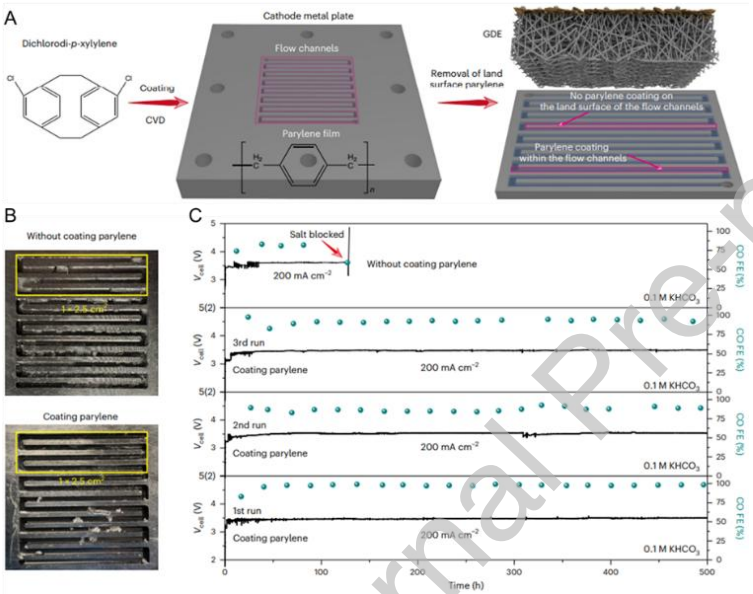

Fig. 13. (A) Schematic showing the hydrophobic coating to flow channels for the removal of $KHCO_3$ droplets. (B) Photographs showing $KHCO_3$ distribution in pristine flow channels *versus* parylene-coated cathode plates (Ag-NP@GDE located in yellow-marked area) after a 10-h control test at 100 mA/cm^2 in 0.5 mol/L $KHCO_3$. (C) Stability of the Ag-NP catalyst in MEA electrolyser with/without parylene coating. Reproduced with permission[69]. Copyright 2025, Springer Nature.

3. Conclusion

Surface coatings have emerged as a pivotal strategy for enhancing the performance of ECR by effectively modifying the electrode surface to optimize reaction conditions. These coatings, ranging from ionomers and organic polymers to carbon and metal oxide layers, serve multiple functions, improving both the reactivity and stability of catalysts. Broadly, these coatings can be categorized according to their specific roles. First, they function as physical barriers that stabilize the catalyst's morphology or selective crystallographic planes, thereby influencing the selectivity of the reaction. Additionally, coatings can induce charge redistribution and modify the electronic state of the catalyst, thereby allowing for precise control over surface reactivity. This adjustment directly impacts key processes such as reactant adsorption, intermediate stabilization, and product desorption. Furthermore, coatings can tune the microenvironment at the electrode surface by enhancing charge transfer, adjusting local pH, and concentrating specific ions. They also improve mass transport by facilitating the formation of preferential pathways for CO_2 molecules. Finally, these coatings help prevent salt precipitation by promoting the removal of liquid droplets before they can dry into salts, ensuring more efficient catalyst performance. The electrochemical performance of the representative studies with surface coating is summarized in Table 1, which showed significant improvement compared with that of catalyst without surface coating under the same conditions.

Table 1 Electrochemical properties of the reported catalysts with/without surface coating.

Catalysts	Coating method	Coating materials	Target product	Potential/V (*vs.* RHE)	Faradaic efficiency	Partial current density (mA/cm^2)	Stability	Ref.
$Cu@AlO_x$ NCs	ALD	AlOx	CH_4	-1.2	~26 %	~3	24 h	[35]
Cu NCs					~15 %	~1.7	10 h	

CuO-SH	Dip coating	DDT	C_2H_4	-1.2	75.3 %	242	mA/cm^2	[43]
CuO					44.8 %	169.3	/	
CuNNs	Dip coating	PTFE	C_{2+}	-1.49	47 %	~14	2500 s	[50]
CuNWs					~27 %	~10	/	
IMF-Mo_3P	Electrochemical deposition	IMF	C_3H_8	-0.8	91 %	361	100 h	[47]
Mo_3P					75 %	～285	/	
CG/Cu	Spray coating	Aemion$^+$	C_{2+}	/	～80 %	～80	>150 h	[59]
Bare Cu					～1 %	100	/	
Naf1100/Cu	Drop casting	Nafion and Sustainion	C_{2+}	-1.15	～70 %	～6	/	[62]
Bare Cu					～60 %	～4	/	
DRY 20 %PTFE/Cu	Ball milling	PTFE	C_{2+}	/	78 %	312	12 h at 200 mA/cm^2	[63]
WET 20 %PTFE/Cu					56 %	112	/	
Cu/Me-COF	Spray coating	Me-MOF	C_2H_4	/	46.8 %	374.2	89.6 h at 200 mA/cm^2	[64]
Bare Cu					～30 %	～240	/	
K^+-STFSI/Cu	Drop coasting	K^+-STFSI	C_{2+}	-1.15	82 %	225	/	[68]
Bare Cu					40 %	～35	/	
AgNP+Parylene	CVD	Parylene	CO	-3.4	～90 %	180	500 h	[69]
AgNP					～80 %	160	100 h	

DDT: 1-dodecanethiol; PTFE: polytetrafluoroethylene; IMF: 1-ethyl-3-methylimidazolium; Me-MOF: tetramethylammonium bromide-modified MOF; K^+-STFSI: 4-methoxystyrene and potassium (4-styrenesulfonyl)(trifluoromethanesulfonyl)imide.

It is important to recognize that, in addition to their most direct effects, surface coatings can influence ECR performance through multiple mechanisms [70-75]. Given the complexity of these interactions, surface coatings are not merely a passive feature but an active component that can finely tune the electrochemical process. Turning to the techniques employed to apply these coatings, a variety of approaches have been explored in recent studies, with ionomers and polymers being the most commonly used materials. Coating techniques range from simple physical deposition methods, such as impregnation, drop-casting, to more sophisticated approaches like chemical vapor deposition or atomic layer deposition, each offering different levels of control over coating thickness, uniformity, and material properties. Still, while these coatings show great promise in improving the efficiency and selectivity of the ECR, several challenges remain that must be addressed for their widespread application

Many surface coatings used in ECR degrade over time under prolonged electrolysis, which limits their practical application in large-scale systems. The degradation of these coatings is a complex process that can involve several mechanisms, including electrochemical corrosion, mechanical wear, and chemical instability. Understanding the degradation mechanisms of surface coatings is therefore essential for improving the stability and longevity of ECR systems. Detailed studies on the interaction between the coating material and the electrolyte, as well as the behavior of the catalyst under different electrochemical conditions, can provide valuable insights into how coatings deteriorate and the factors that influence their degradation rates. By identifying the key degradation pathways, researchers can design more robust coatings that are resistant to these forms of damage. This could involve the development of hybrid coatings that combine the desirable properties of different materials, such as the strength of metal oxides with the flexibility and ion conductivity of polymers, or the incorporation of protective layers that prevent the penetration of corrosive species. Additionally, surface coatings with self-healing properties or those that can undergo reversible changes in response to the electrochemical environment could offer promising solutions to mitigate degradation and extend the lifespan of the catalysts.

Another significant challenge is the poor conductivity of the coatings, which can severely limit the efficiency and performance of the overall electrochemical system. Surface coatings, particularly those made from insulating or low-conductivity materials such as organic polymers, metal oxides, or certain composite materials, can create barriers to efficient electron transfer between the electrode and the electrolyte. When the conductivity of the coating is insufficient, it increases the resistance at the interface, hindering the flow of electrons and leading to inefficient reaction kinetics, which can lower the Faradaic efficiency and overall product yield. Furthermore, coatings with poor conductivity may lead to the accumulation of charge on the electrode surface, resulting in increased polarization during electrolysis. This effect reduces the effective potential for CO_2 reduction, potentially causing the catalyst to operate at suboptimal conditions. Several strategies can be employed to address this issue, such as incorporating conductive materials (*e.g.*, graphene, carbon nanotubes, or conducting polymers) within the coating structure to improve the overall electron flow while still maintaining the coating's protective and catalytic functions. Moreover, optimizing the thickness and uniformity of the coatings can help reduce resistance while maintaining effective interaction between the catalyst and reactants. Achieving this balance between conductivity and other desirable properties remains one of the most significant challenges in advancing ECR technologies and will require continued research into novel materials and coating techniques.

A critical yet often overlooked challenge in optimizing ionomer-coated catalysts for ECR lies in achieving robust coating-catalyst adhesion while maintaining optimal reaction kinetics. Weak adhesion can lead to coating detachment during prolonged electrochemical

operation, causing performance degradation, decreased efficiency, and even catalyst failure. The dynamic and harsh conditions of electrochemical environments, including fluctuating potentials, electrolyte composition, and potential side reactions, exacerbate this issue, making it difficult to ensure the long-term stability of the coating-catalyst interface. Besided, current efforts are hindered by poorly understood interfacial interactions that lead to delamination, pore blockage, or uneven ionomer/polymer distribution under operational stresses. To address the problem, several strategies can be explored. One approach is surface modification of the catalyst, which can increase the interaction between the catalyst and coating. Techniques such as plasma treatment, functionalization with polar groups, or the application of a primer layer can create a more favorable surface for bonding. Another solution is the incorporation of adhesion-promoting materials, such as conductive polymers, which can form intermediary layers that facilitate a stronger bond between the coating and catalyst. Furthermore, the exploration of more advanced deposition techniques may provide additional coating options that allow for precise control over coating thickness and uniformity, thereby enhancing adhesion strength.

Advanced characterization techniques, particularly in-situ and operando methods, are at the forefront of unraveling the complex interactions between surface coatings and catalysts at the atomic scale [76–78]. The dynamic nature of electrochemical processes means that catalysts and their coatings undergo constant changes, including shifts in electronic states, morphology, and surface structures. Capturing these rapid transformations with sufficient resolution and accuracy remains a significant challenge, especially when considering the need to correlate these changes directly with catalytic performance. Another key challenge remains in integrating multiple complementary techniques to construct a comprehensive picture of the complex interactions between coatings and catalysts, particularly in high-current-density regimes. Machine learning-assisted data analysis could play a pivotal role in deciphering the vast datasets generated by these methods, identifying hidden correlations between coating properties and performance. By bridging the gap between nanoscale characterization and macroscale reactor performance, these advanced techniques will accelerate the rational design of next-generation coatings, engineered not just for optimal initial performance but for sustained operation under industrially relevant conditions.

Looking forward, future work should explore how coating strategies can be combined with optimized cell and reactor architectures and exploring variable operating parameters (pressure, electrolyte composition, *etc.*) under industrially relevant current densities. By doing so, the coating becomes part of an integrated design philosophy that coordinates catalyst activity, mass transport, and reactor operation successful translation of CO_2RR to industrial scale will likely depend on an integrated, system level optimization: combining atomic scale catalyst design with mesoscopic scale engineering and macroscopic reactor design (flow fields, pressure, reactant delivery, cell architecture). Moreover, coating development should embrace multifunctionality: beyond controlling wettability and porosity, next-generation coatings could incorporate features such as selective ion transport layers, hydrophobic hydrophilic hybrid binders or ionomers, and engineered interfaces that influence local pH, reactant concentration, or intermediate stabilization.

Finally, much of the research published in this area is still at the laboratory scale, and the transition to large-scale applications still presents challenges. Future investigations should aim to explore the influence of variables such as pH, applied potential, and electrolyte composition on the nucleation and growth kinetics of these layers, as well as their structural evolution during electrochemical cycling. But most of the coating methodologies explored in contemporary research exhibit a pronounced potential for scalability. This scalability is fundamentally underpinned by the compatibility of these strategies with deposition techniques already established for high-volume production in adjacent technological fields. Techniques including ALD, CVD, and various spray coating methodologies can be engineered to generate uniform, pinhole-free coatings across large-area substrates with exceptional precision. The continued maturation of these deposition methods is anticipated to accelerate the commercial realization of new generation of catalysts for CO_2RR.

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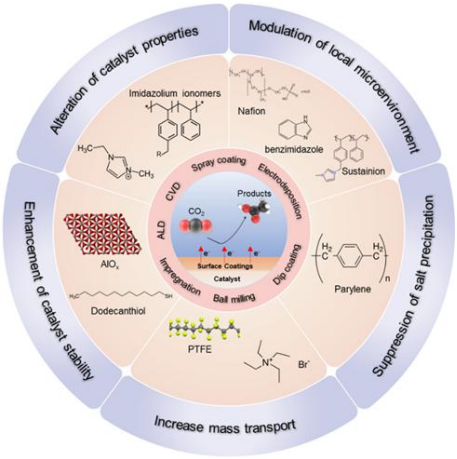
Graphical abstract



Surface coatings as an effective strategy for enhancing catalyst stability, selectivity, and overall reaction efficiency in electrochemical CO_2 reduction.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.