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Review Article

The role of interfacial water in promoting C–C coupling during CO_2 electroreduction

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The electrochemical reduction of CO_2 (CO_2RR) into hydrocarbons and oxygenates presents a promising pathway toward a carbon-neutral energy cycle, but achieving selective product formation remains a challenge. While extensive efforts have focused on catalyst design and electrolyte composition, the role of the interfacial water properties, an often-overlooked parameter, has only recently come under investigation. Water serves as the primary proton donor (in aqueous electrolytes) in the absence of hydronium, which can influence the competition between CO_2RR and the hydrogen evolution reaction (HER). Despite studies dating back to the 1980s demonstrating that electrolyte composition significantly impacts CO_2RR performance, the effects of the electrolyte composition on the interfacial water properties have remained largely unexplored. Recent findings suggest that tuning the interfacial water properties can influence C–C coupling by altering solvation environments and stabilize reaction intermediates. This perspective explores how tuning the interfacial water properties improves C–C coupling, providing a new strategy for improving catalysis.

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Introduction

The electrochemical reduction of CO_2 into chemical fuels and value-added products offers a promising pathway for mitigating anthropogenic carbon emissions, particularly when powered by renewable energy sources [1]. Achieving this transformation at scale is crucial to the broader energy transition and requires the development of electrode interfaces that can drive reactions with both high efficiency and selectivity. Among the most challenging (and interesting) aspects of this process is the formation of multicarbon products, which hold potential as energy-dense fuels and chemical feedstocks [1]. Understanding the mechanisms governing C–C coupling is critical to advancing CO_2RR, as it involves balancing interactions between surface-bound intermediates [2].

While significant progress has been made in designing materials to optimize the intrinsic properties of electrocatalysts, it is increasingly clear that the interfacial microenvironment (the region of electrolyte immediately adjacent to the electrode surface) is also crucial in governing electrocatalytic behavior [3]. This microenvironment dictates reaction outcomes by modulating the solvation structure, influencing pH gradients, and controlling the transport of reactants and ions [3]. A critical, yet often underappreciated, set of variables are the interfacial water properties, which constitute the structure and thermodynamic activity of water (a_w) at the interface [3,4].

Many strategies aimed at tuning the interfacial microenvironment, such as polymer overlayers, surfactants, and porous electrodes, etc., likely modify the interfacial water properties, yet investigations into this are sparse [5–11]. These findings suggest a broader hypothesis: alterations to the interfacial water properties can influence the behavior of intermediates, which can potentially favor C–C coupling [4,12]. This perspective examines how interfacial water properties affect CO_2RR mechanisms and explores strategies to manipulate water properties for improved selectivity.

Direct impact of water activity in tuning CO_2RR

Selectivity in CO_2 electroreduction is governed by the relative surface coverage of key intermediates such as *CO and *H, as well as the availability of vacant sites for bond formation and cleavage. Strategies that shift these surface populations, including promoting *CO accumulation, suppressing *H coverage, or tuning intermediate residence times, can alter the balance between competing pathways such as hydrogen evolution, CO formation, methane production, and C–C coupling. We

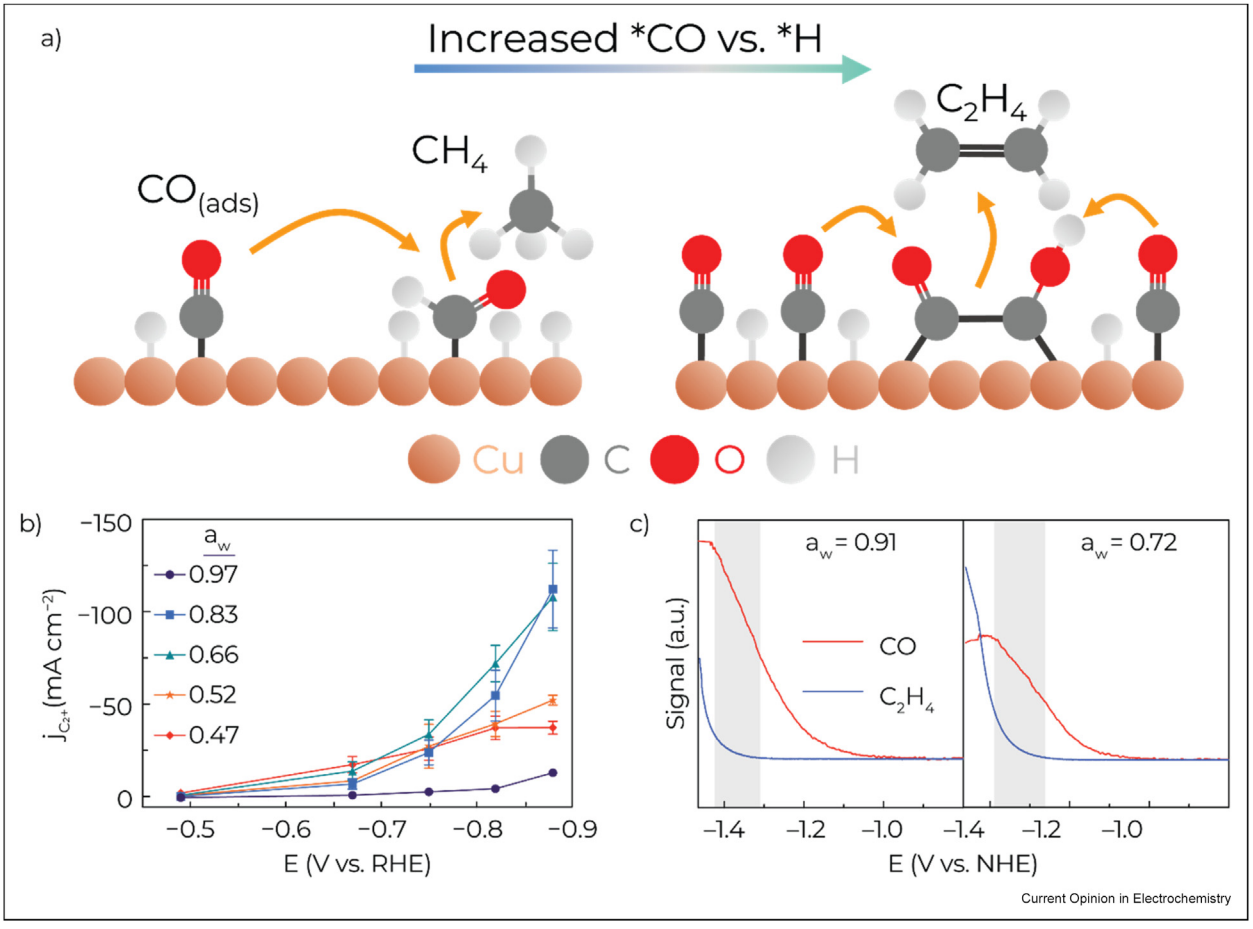
propose that the properties of interfacial water, including its thermodynamic activity (i.e. availability) and hydrogen-bonding structure, play a direct role in modulating these surface coverages.

Since C—C coupling occurs through the reaction of two surface-bound species, its efficiency is tied to the competition between *CO, *H, and vacant sites at the electrode interface [2,13]. It is believed that the C—C coupling step occurs through the Langmuir—Hinshelwood mechanism, in which two surface-adsorbed species react with each other [2]. This mechanism suggests that an optimal balance of *CO, *H, and vacant sites is required for efficient C—C bond formation. For C—C coupling to proceed, the surface must maintain a high coverage of CO (or other related intermediates), while also possessing moderate CO adsorption energy—strong enough to keep CO bound but not so strong that it inhibits further reactivity. Simultaneously, the electrode must also adsorb *H to facilitate hydrogenation steps and contain some fraction of vacant active sites to allow for bond-breaking events, such as C—O cleavage. The competition between *CO, *H, and vacant sites creates a condition that can favor or suppress specific reaction pathways [13]. For example, high H* coverage can steer the reaction toward CH_4 or H_2 formation rather than multicarbon products (Figure 1a) [14]. Conversely, a lack of H* can hinder hydrocarbon production, leading to CO evolution, or in extreme cases $C_2O_4^-$ [15]. Additionally, too much CO can block key sites necessary for further reduction, preventing the transfer of protons, which is required in downstream steps to form hydrocarbons or oxygenates [16].

Water activity directly influences the surface coverage of intermediates by modulating the rate of water dissociation. This relationship is described by the following equation [17]:

$$\log(k') = \log(k_o) - n\log(a_w)$$

Figure 1



(a) Schematic depicting the importance of surface coverage in catalyst selectivity. **(b)** Partial current density for C_{2+} products (PrOH, EtOH, C_2H_4) as a function of potential at various a_w. **(c)** Overlays of the CO (red trace) and C_2H_4 (m/z = 27, blue trace) mass spectrometer signals. The left edge of the gray box is the onset potential of the CO surface peak, and its right edge is the onset potential for C_2H_4.

where k' and k_o are the proton transfer rates in electrolyte solutions and in pure water, respectively, and n denotes the reaction order with respect to water activity (or equivalently, the dependence of the rate on H_2O availability) The decreased water activity arises from two effects: (1) a large fraction of water molecules become structurally confined within the hydration shells of salt ions, and (2) the total molar concentration of water decreases as the salt concentration increases. Together, these effects lower the availability of free H_2O molecules capable of dissociation, thereby suppressing *H formation. This shift can increase the number of vacant surface sites available for CO_2 adsorption, altering the balance of surface-bound species and influence C—C coupling pathways.

Recently we employed highly concentrated $NaClO_4$ electrolytes to tune the bulk water activity between 0.97 and 0.47 [4]. Using this method, we found that restricted water availability (i.e. lower water activity) enhances C—C coupling while suppressing hydrogenation pathways. However, this enhancement is not linear; while moderate reductions in a_w (to values between 0.66 and 0.83) significantly boost C_2+ product formation, further lowering the water activity leads to a decline in catalytic performance (Figure 1b). This resulted in a substantial increase in C_2+ product formation, with a Faradaic efficiency of ≈ 73% at a partial current density of -110 mA/cm^2 when the a_w was optimized to be between 0.66 and 0.83. Electrochemical mass spectrometry revealed that C_2H_4 formation depends on the accumulation of the CO intermediate, where CO and C_2H_4 signals were overlaid to assess their correlation (Figure 1c). The onset of C_2H_4 production consistently occurred when the CO signal reached approximately 50% of its maximum intensity, suggesting that a critical CO surface coverage is required to initiate C—C coupling. This trend was observed across a range of a_w values, supporting the conclusion that lower water activity promotes C—C coupling by increasing CO surface coverage. Taken together, these results demonstrate that water activity serves as a powerful lever to tune the surface coverage of key intermediates and that optimizing these coverages is critical to enhancing C—C coupling efficiency [4].

Our findings suggest that water activity influences the competition between CO hydrogenation and C—C coupling by dictating the local availability of *H and *CO. Additionally, we hypothesize that it may also modulate the solvation and stabilization of key intermediates and influence ion solvation, though this remains to be experimentally verified. In the following section, we examine how a range of strategies, whether intentional or incidental, may influence reactivity through changes in interfacial water dynamics.

Solvation and water structuring effects in C—C coupling

The formation of multicarbon products in CO_2 reduction is (in part) governed by the coverage and configuration of surface-bound CO [18]. Early studies established that a critical CO coverage is required for C—C coupling, with weakly bound atop CO species favoring dimerization [18—21]. While conventional models call attention to the CO adsorption energy, and binding configuration, and interfacial electric field intensity as the primary determinants of selectivity, recent work suggests that the interfacial water structure could influence this process by interacting with key intermediates (e.g. CO, OCCO) via hydrogen bonding, thereby altering their stabilities and coupling rates [4,22—24]. Changes to CO adsorption are largely tied to cation-induced interfacial field effects; however, their role in modulating the interfacial water properties has been largely unexplored [8,25—27].

Although the interfacial water structure remains largely overlooked in mechanistic studies, a few investigations have examined its role in CO_2RR, revealing complex and sometimes contradictory trends. For example, a computational study examined how surface-bound water on a Cu electrode influences the selectivity between hydrocarbon and alcohol products in CO_2RR by serving as a proton donor in electrochemical dehydration steps [28]. This study provided early theoretical evidence that interfacial water structuring can play a role in product selectivity, though its connection to C—C bond formation was not explored.

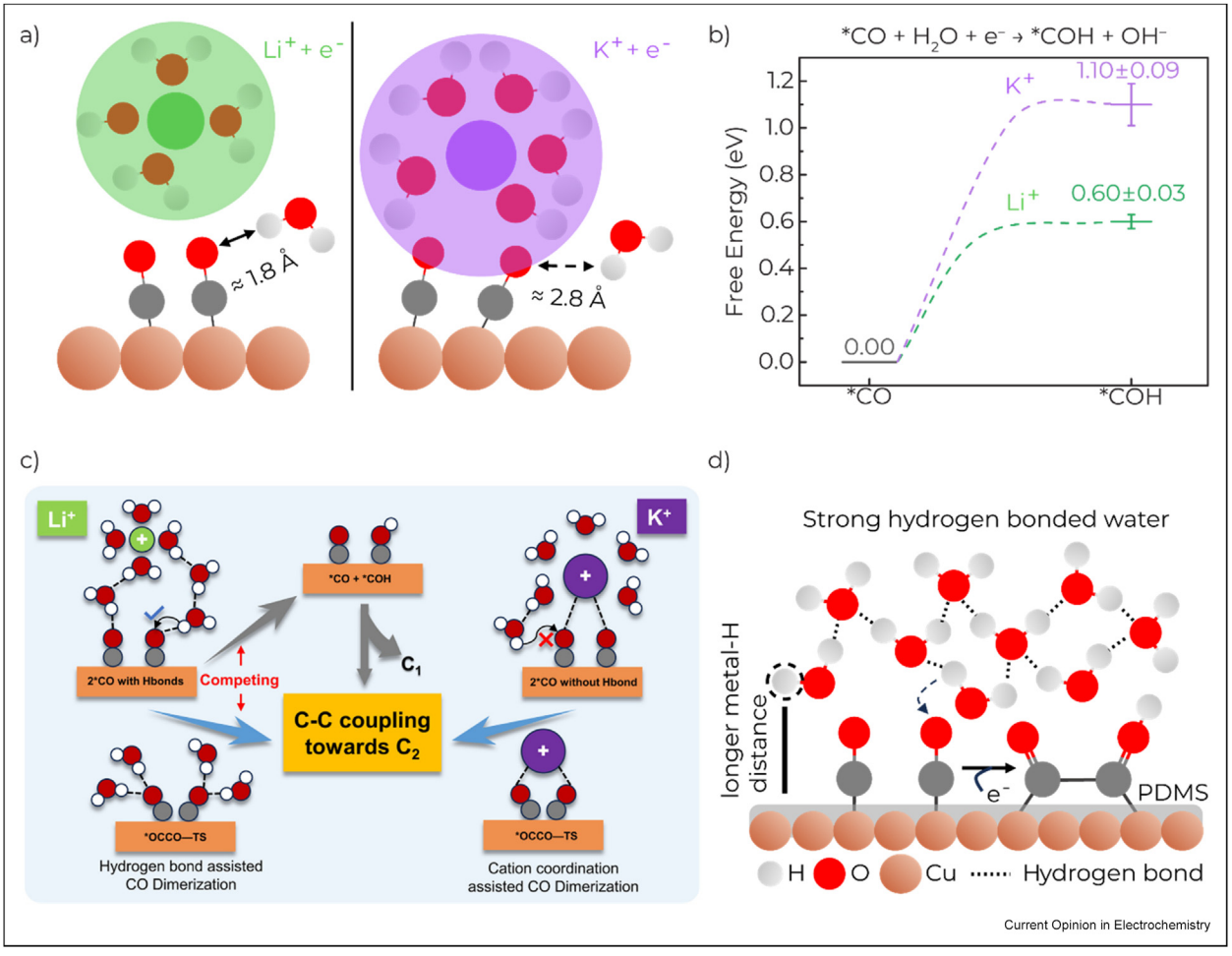
Several studies have demonstrated that larger alkali metal cations enhance C_2 product formation in the order $Li^+ < Na^+ < K^+ < Cs^+$, with the conventional explanation being that these cations stabilize key reaction intermediates via electric field effects or direct coordination with OCCO [8,27]. However, these models neglect how the interfacial water structure is altered by different cations, which could be an important determinant in C—C coupling. A recent computational study revealed that weakly solvated alkali metal cations (K^+) disrupted water's hydrogen bonding network at the interface (relative to Li^+, more strongly hydrated cation), creating a hydrophobic microenvironment that suppresses CO protonation, thereby increasing C—C coupling [12]. This effect is distinct from electrostatic stabilization or coordination, which is typically considered the primary mechanism of cation-induced reaction promotion, and instead suggests that water structuring may play a direct role in modulating reaction pathways. Specifically, the study disentangled three linked contributions to this effect. First, cation-specific interfacial configurations show that K^+ approaches the electrode more closely than Li^+ and disrupts the local orientation and density of water molecules near CO, lowering the probability of hydrogen bonding and thus suppressing protonation steps that lead to C_1 products (Figure 2a and b). Second, solvation by interfacial water alone significantly stabilizes the transition state for OCCO formation, lowering the activation barrier by 0.69 eV compared to vacuum conditions. Third, the presence of

K^+ was shown to lower hydrogen bonding to OCCO in the transition state from ≈3 to ≈1, weakening this stabilization and subtly altering the C–C coupling barrier (Figure 2c).

Interestingly, another experimental study showed an opposite trend when using various quaternary ammonium cations [24]. It was found that hydrogen bonding between interfacial water and CO was positively correlated with C–C coupling efficiency. Using differential electrochemical mass spectrometry (DEMS), they demonstrated that polycrystalline Cu in methyl$_4$N$^+$ and ethyl$_4$N$^+$ electrolytes produced ethylene at −1.29 V vs SHE, while no ethylene was detected with bulkier propyl$_4$N$^+$ and butyl$_4$N$^+$ cations under identical conditions. Surface-enhanced infrared absorption spectroscopy (SEIRAS) revealed that the CO surface coverage remained similar across all cases, but a strong O–D stretch near 2710 cm$^-$, assigned to water molecules hydrogen-bonded to CO_{ads}, was much more prominent in the methyl$_4$N$^+$ and ethyl$_4$N$^+$ cases. The disruption of the water network by the larger cations displaced interfacial water from the CO_{ads} layer and suppressed ethylene production.

While these studies focus on how electrolyte cations alter interfacial hydrogen bonding, similar effects can arise from other modifications to the electrode interface. A recent study using Cu electrodes coated with polydimethylsiloxane (PDMS) induced strong hydrogen bonding at the interface (through hydrophobic effects) which was correlated with enhanced C–C coupling (Figure 2d) [22]. The PDMS-coated Cu(111) surface exhibited ≈ 20% higher selectivity for C_2H_4 compared to bare Cu(111). Ab initio molecular dynamics (AIMD) simulated a much lower relative

Figure 2



(a) Computational schematic showing the cation influence over H_2O and CO interactions. (**b**) Free energy diagram for hydrogenation of CO with Li_+ or K_+ present. (**c**) Schematic showing dominant mechanisms for C–C coupling with either K_+ (purple lines) or Li_+ (green lines) as the cation. Panels **(a–c)** was reprinted (adapted) with permission from Yang et al., JACS **2024**, 146, 5532–5542. Copyright 2024 American Chemical Society. **(d)** Schematic demonstrating influence of a polydimethylsiloxane (PDMS) layer on hydrogen bonding of the interfacial water layer and subsequent promotion. Panel **(d)** was adapted with permission from Wang et al., ACS Catal. **2024**, 14, 3457–3465. Copyright 2024 American Chemical Society.

number of hydrogen bonds (≈10) for the Cu(111)@PDMS compared to ≈ 40 for bare Cu(111), supporting the hypothesis that hydrogen bond disruption can indirectly favor pathways requiring high CO surface coverage.

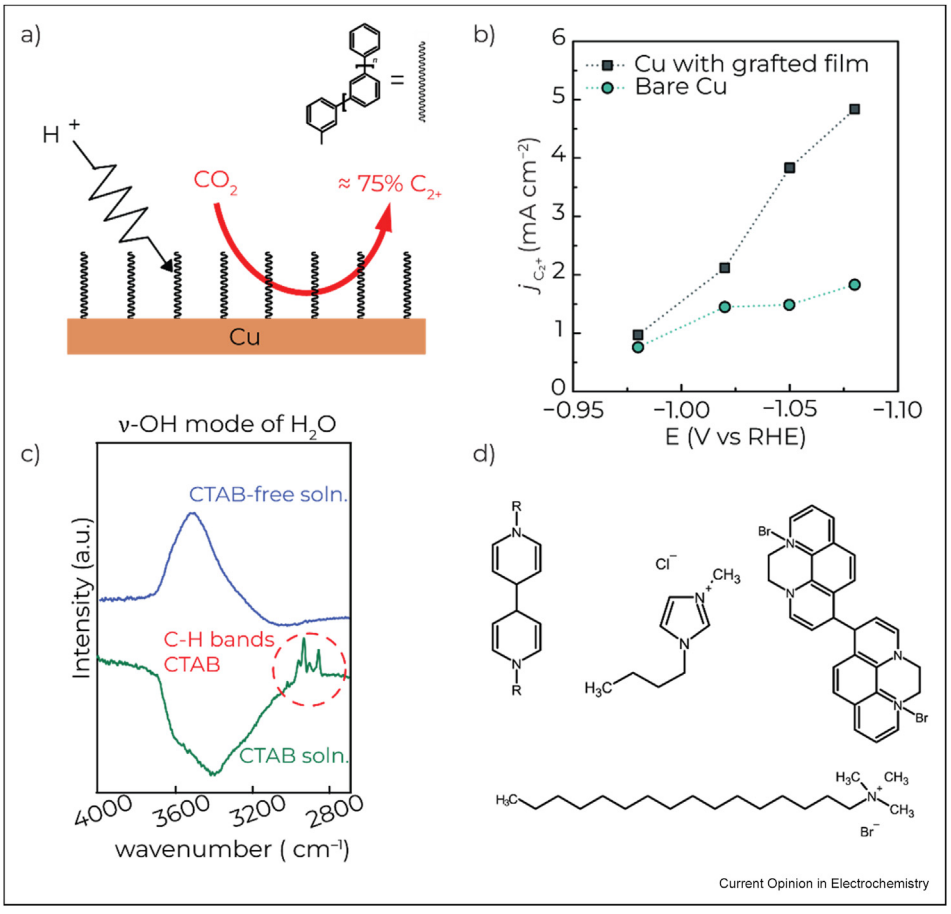
The conflicting trends observed across these studies raise fundamental questions about the precise role of interfacial water structure in C–C coupling. These discrepancies also show that this may be system-dependent, highlighting the need for further investigation into how the local water structuring controls CO_2RR to multicarbon products.

Tuning interfacial micro-environment with additives and polymers

A wide range of strategies centered on modifying the interfacial microenvironment beyond cation control have been explored to improve C_{2+} product formation [3]. These include the use of polymer overlayers/composites, surfactants, ionic liquids, and highly concentrated electrolytes [9,29–36]. While these modifications are often justified by hypotheses related to intermediate stabilization, local pH shifts, or selective site blocking, recent evidence suggests that modification of the interfacial water properties may offer an alternative mechanistic explanation or occur concurrently with the aforementioned effects [4,12].

For example, polymer overlayers, have been reported to enhance C_{2+} selectivity by suppressing hydrogen evolution, restricting proton diffusion, or altering the local pH at the catalyst interface (Figure 3a and b) [30,34,37]. Organic films, such as bipyridine or ionomer coatings, have been suggested to extend the residence time of *CO, stabilize atop-bound CO, or increase the

Figure 3



(a) Schematic depicting the use of aromatic molecules and subsequent **(b)** influence on Cu's CO_2RR to C_{2+} catalytic activity. Adapted with permission from Watkins et al., ACS Energy Lett, **2023**, 8, 189–195. Copyright 2023 American Chemical Society. **(c)** SEIRAS spectra showing suppression of the ν(O–H). Adapted with permission from Zhang et al., J. Phys. Chem. C, **2020**, 11, 5457-5457. Copyright 2020 American Chemical Society. **(d)** Depiction of relevant polymers with hydrophobic moieties that have been employed as modifiers for the CO_2RR. SEIRAS, surface-enhanced infrared absorption spectroscopy.

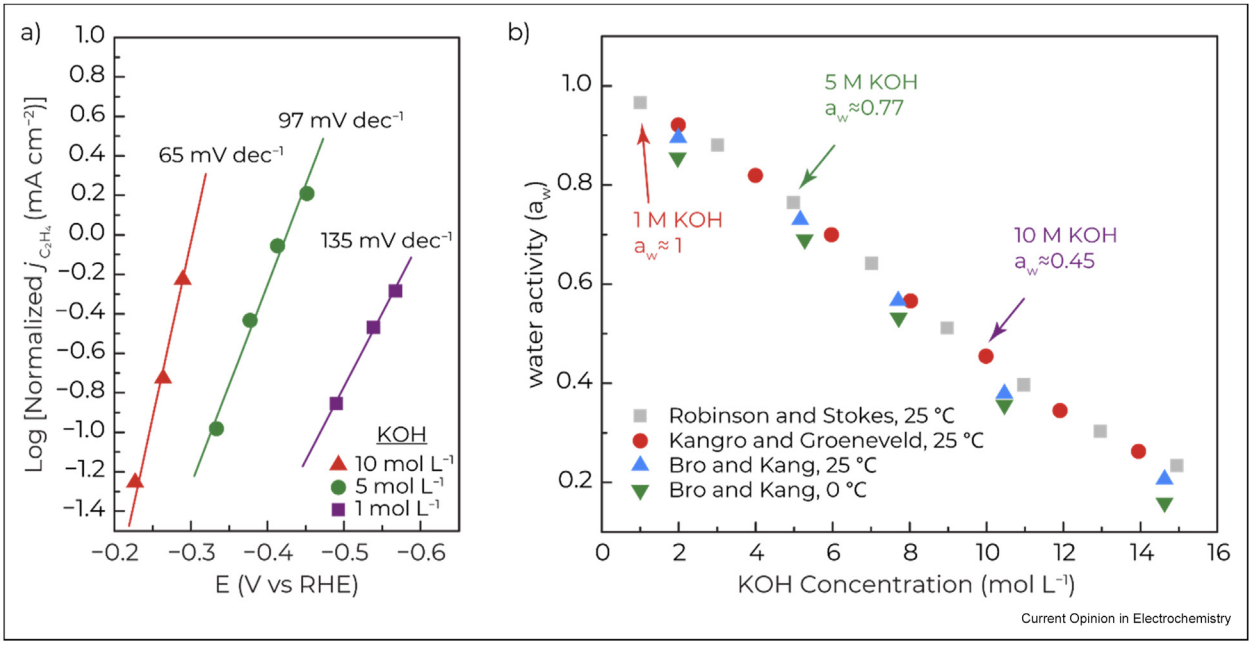
interfacial CO_2 solubility [9,29–35]. Polytetrafluoroethylene (PTFE) incorporation into the catalyst layer was proposed to enhance C–C coupling by repelling liquid electrolyte which enhances the local CO_2 concentration [38]. In many of these cases, the impact on interfacial water activity has not been explicitly investigated, but given that all of these modifiers include hydrophobic moieties, it is likely a contributing factor (Figure 3 c and d).

Altering the electrolyte through the addition of molecular additives has also been leveraged to influence CO_2RR selectivity [39]. Ionic liquids, typically based on imidazolium salts, have been shown to improve C–C coupling on Cu, these systems are often attributed to the stabilization of reaction intermediates such as CO_2^- [40,41]. Molecular additives, like glycine, were suggested to stabilize CHO*, which was proposed to be a key intermediate for C–C coupling [42]. A recent study utilizing imidazolium-based ionic liquids in nonaqueous solvents demonstrated that CO_2 reduction to CO on Ag electrodes proceeds with an apparent activation energy of zero, meaning there's no remaining enthalpic barrier to lower. Consequently, the observed rate enhancement arise solely from increases in the activation entropy, highlighting that even in nonaqueous environments, the interfacial solvent-reorganization dynamics (rather than intermediate stabilization) controls reactivity [43].

Given that many of these additives (e.g. glycine) either present hydrophobic fragments or are known to perturb the hydrogen-bond network of water [44], their ability to reorganize the interfacial solvent layer likely contributes to the observed shifts in selectivity. Indeed, hydrophobic organic modifiers such as cetyltrimethylammonium bromide (CTAB) have been shown to influence CO_2RR selectivity between CO and $HCOO^-$ by altering the interfacial solvation environment, supporting the notion that molecular additives can modulate reaction pathways indirectly through their impact on water structuring [10]. In this study, SEIRAS measurements revealed that CTAB adsorption on Cu electrodes repelled interfacial water at potentials negative of the potential of zero charge, demonstrating that hydrophobic additives perturb the local water structure, which in turn influences catalytic behavior (Figure 3c and d) [7]. However, the extent to which such modifiers can reshape interfacial water structure to drive C–C coupling pathways remains an open question.

In a similar vein, highly concentrated hydroxide solutions (e.g. 10 mol L^{-1} potassium hydroxide [KOH]) were also proposed to promote C–C coupling through

Figure 4



(a) Electrochemical activity for C_2H_4 on Cu in varying concentrations of KOH. From Dinh et al., Science **2018**, 360, 783–787. Reprinted with permission from the American Association for the Advancement of Science. **(b)** Relationship between water activity and KOH concentration. Used with permission of the Electrochemical Society, from the Low-Temperature Activity of Water in Concentrated KOH Solutions, Bro and Kang, 118, **1971**; permission conveyed through Copyright Clearance Center, Inc. KOH, potassium hydroxide.

stabilization of reaction intermediates via a hydroxyl promotion mechanism [36]. However, the bulk water activity of 10 mol L^{-1} KOH is $\approx$ 0.45, reinforcing the idea that altered water microenvironments play a role in tuning CO_2RR performance (Figure 4) [45].

Future directions

Improvements in CO_2RR selectivity on Cu are often attributed to active site modifications or intermediate stabilization; however, diffusional and interfacial effects may play a more significant role [46]. In this context, strategies such as the use of polymer overlayers, surfactants, and ionic liquids, may owe part of their effectiveness to inadvertent modifications of interfacial water properties. Recognizing this shared underlying mechanism reframes these diverse approaches and suggests that water activity and structure can modulate the catalyst performance. Despite this emerging understanding, intentionally tuning interfacial water properties remain a largely untapped strategy for improving C=C coupling in CO_2RR. Few systematic experimental studies have directly examined its role. However, recent findings suggest that interfacial water properties could play a significant role, and many open questions remain. Future work should focus on disentangling the effects of interfacial water structuring and water activity from co-occurring phenomena such as electric field effects and local pH shifts. Addressing this challenge requires systematic investigations using operando spectroscopic techniques (e.g. vibrational sum-frequency generation, SEIRAS, and surface senstive Raman spectroscopy, etc.) and new strategies (such as in-situ scanning probe microscopy) that unambiguously probe water structuring at the interface [47]. Beyond characterization, design strategies incorporating molecular additives or polymer overlays could be intentionally developed to modulate interfacial water activity and structure. However, isolating these effects from other competing influences remains a key challenge. Developing a mechanistic understanding of how interfacial water properties control reaction selectivity will enable the rational design of electrode interfaces that leverage water properties as a functional parameter to optimize CO_2RR toward valuable multicarbon products.

Declaration of competing interest

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.

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Data availability

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

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