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Review Article

Recent progress in mechanistic insights into cation effects on electrochemical CO₂ reduction reactions

Xueping Qin, Renata Sechi and Heine Anton Hansen



The impact of cations in the local reaction environment has garnered attention as a crucial factor in tailoring the selectivity of CO₂ reduction, although the mechanism remains under debate. Understanding these cation effects through first-principles computations can facilitate the design of efficient reaction networks and gas diffusion layers in electrolyzers. In this minireview, the latest insights into cation effects on CO₂ reduction reactions are presented, covering aspects such as tuning the interfacial electric field, coordinating reaction intermediates, altering the interfacial water structure, and modulating local CO₂ concentration and pH. Future research directions in this area are also discussed.

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Keywords

Carbon dioxide reduction, Electrochemical interfaces, Cation effects, Density functional theory, Fundamental understanding.

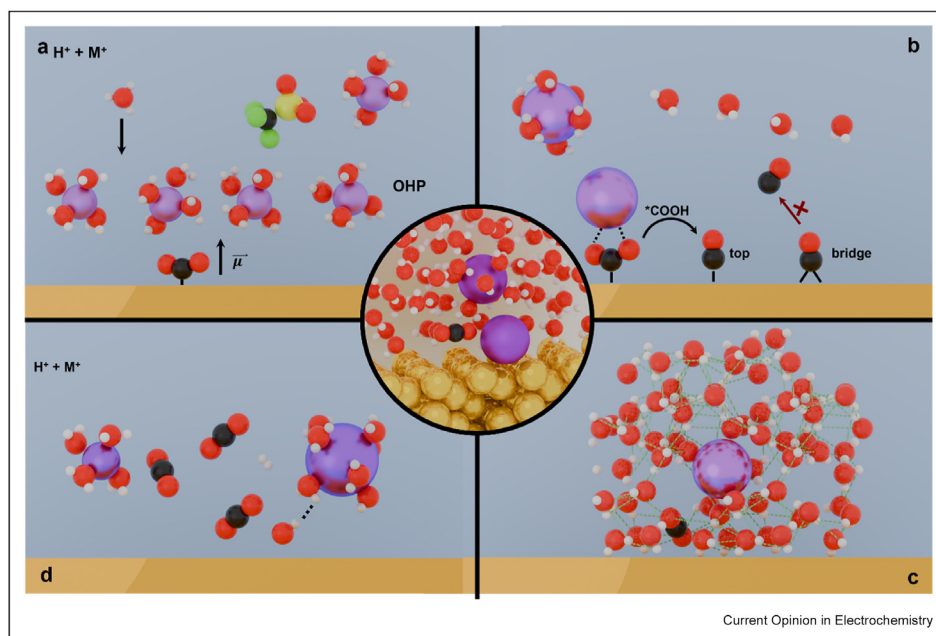
Introduction

The electrochemical carbon dioxide reduction reaction (CO₂RR) is a promising approach to convert the greenhouse gas CO₂ into value-added chemicals and fuels, making it a crucial technology for achieving carbon neutrality. While significant efforts have been made to enhance the activity and selectivity of CO₂RR through catalyst design [1,2], some aspects of the underlying mechanisms remain elusive, particularly regarding the recently recognized cation effects from the local reaction environment in electrolytes [3]. The hydrogen evolution reaction (HER), a competitive side reaction

that affects the selectivity of CO₂RR, has also been reported to be influenced by electrolyte cations [3,4]. Overall, these electrocatalytic reactions, including CO₂RR and HER, occur at electrode–electrolyte interfaces, and alkali metal cations significantly impact reaction kinetics, rates, and Faradaic efficiency through interactions with catalyst surfaces, reactants, intermediates, and products [5].

In the early 1990s, Murata et al. found that simply changing the cation in electrolytes from Li⁺ to Cs⁺ could enhance the activity and selectivity toward C₂₊ products during CO₂RR [6]. Recently, a general trend has emerged in understanding how the size of alkali metal cations influences the reaction rates of CO₂RR [7]. CO₂RR activity increases in the order of Li⁺ < Na⁺ < K⁺ < Cs⁺, correlated with the effective radius of hydrated cations (Li⁺ > Na⁺ > K⁺ > Cs⁺) [8] and their hydration free energies [9]. However, uncertainties remain regarding the exact mechanisms by which these cations affect overall catalytic performance, a hot topic of debate in recent years. Experimentally, *in-situ* characterization techniques such as surface-enhanced infrared absorption spectroscopy (SEIRAS) offer new opportunities to study cation effects from the molecular level in electrocatalytic reactions [10]. For more on this topic, a recent minireview discusses the use of infrared spectroscopy in studying CO₂RR [11]. At the same time, theoretical modeling using density functional theory (DFT) and *ab initio* molecular dynamics (AIMD) simulations can capture interfacial interactions and examine reaction mechanisms [12]. Starting from the early 2000s, AIMD was employed to study the properties of electrode/solution interfaces. For example, it was used for investigating the dehydrogenation of methanol on the Pt(111)/water interface [13], introducing excess electrons to the slab model to apply potentials to the Pt(111)/water interface [14], and later also considering electronic and geometric structures of water bilayers on several transition metal surfaces [15]. Recently, atomic-scale modeling has been widely applied to study CO₂RR, revealing several key mechanisms regarding cation effects, with cation locations in the electric double layer (EDL). In this minireview, we elaborate on four predicted mechanisms demonstrating the cation effects in CO₂RR, as shown in [Figure 1](#): (1) tuning the interfacial electric field, (2) coordinating reaction intermediates, (3) altering the interfacial water

Figure 1



Gold-electrolyte interface (center) and four mechanisms of cation effects on CO₂RR described in this work: (a) tuning the interfacial electric field, (b) coordinating reaction intermediates, (c) altering the interfacial water structure, and (d) modulating local CO₂ concentration and pH. Color code: white (H), red (O), black (C), green (F), yellow (S), orange (Au), violet (alkali metal). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

structure, and (4) modulating local CO₂ concentration and pH.

Tuning the interfacial electric field

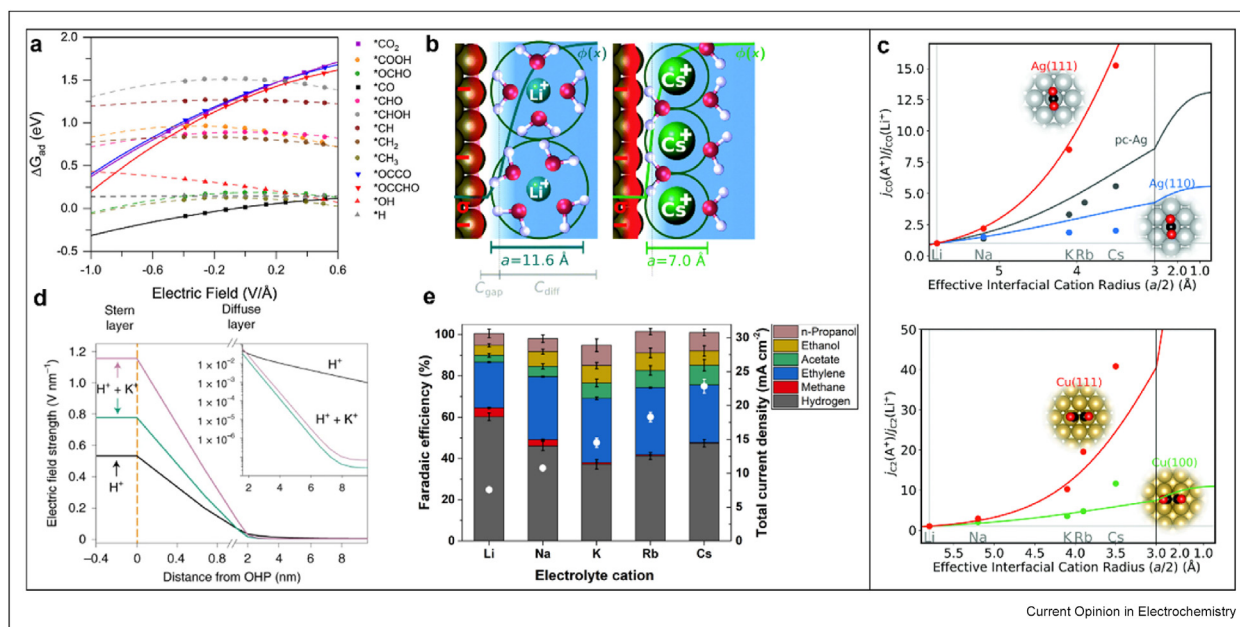
Despite extensive studies on cation effects in CO₂RR, rationalizing specific interactions remains challenging due to the complexity of interfacial structures. Recent advancements in experimental characterizations and theoretical simulations enable researchers to revisit the underlying mechanisms, with the first proposed one involving interfacial electric-field-related interactions [8,16,17].

A pioneering study by Chen et al. showed that cations redistribute the electric field, significantly impacting CO₂RR energetics [18]. Using DFT and experiments, the CO₂-to-CO pathway on Ag(111) was studied, and the cation-induced electric field enhances *CO₂ (* represents an adsorption state) and *COOH adsorption. The dipole moment and polarizability of adsorbates significantly influence electric field effects on CO₂RR [18,19]. At interfaces, the electric field has little effect on the HER since *H has zero dipole moment. However, CO₂RR intermediates like *CO₂, *OCCO, *OCCHO, and *CO, which have considerable dipole moments and polarizability, are strongly affected by the cation-induced electric field (Figure 2a). However, DFT calculations using static ice-like layers showed no systematic trend of the electric field in the

vicinity of *CO with different cations [19]. Instead, trends in activity with different cations were argued to be caused by an increase in concentration of cations at the outer Helmholtz plane (OHP) with increasing cation size.

The cation effect was further elaborated by Ringe et al. [8], who developed a multi-scale continuum modeling approach based on the finite ion-size modified Poisson-Boltzmann model coupled to DFT simulations. It was shown that cations with larger radii concentrate more easily on electrode surfaces due to smaller hydrated cations and weaker repulsive interactions, leading to higher surface charge density and stronger electric fields (Figure 2b). Their model aligns well with experimental trends, demonstrating increased partial current densities for CO on Ag(111) and C₂₊ products on Cu(111) from Li⁺ to Cs⁺ [8] (Figure 2c). Hydrated Cs⁺, with its smaller effective radius, accumulates at the OHP, creating a stronger interfacial electric field that promotes CO₂RR. Another study by Hu et al. proposed that cations modulate the local electric field, improving CO₂RR performance, while concurrently limiting H⁺ migration, which lowers the proton concentration in the OHP, thereby suppressing the HER (Figure 2d) [9]. Besides the electric field, cations exhibit non-electric-field effects on CO₂RR, however, which can also be modulated by the chemical structure and distribution of cations [20] (Figure 2e).

Figure 2



(a) Field effects on various CO₂RR intermediates on Cu(111). Reprinted from Ref. [19]; (b) Origin of cation effects in field-driven electrocatalysis. Reprinted from Ref. [8]; (c) CO partial current density at Ag (top), and partial current density of C₂ products (ethanol and ethylene) at Cu (bottom), at -1 V vs. RHE for different cations normalized to CO and C₂ current density for Li⁺, respectively. Filled circles represent experimental data points, and solid lines are theoretical predictions. Reprinted from Ref. [8]; (d) Electric-field strength profiles over distance from the OHP. Reprinted from Ref. [9]; (e) Reactivity data in CO-saturated 0.1 M alkali metal cation hydroxide at -0.7 V on carbon paper supported Cu microparticles (left axis: Faradaic efficiency, by stacked bars; right axis: total current density, by white dots). Reprinted from Ref. [20].

Coordinating reaction intermediates

In addition to the electric-field effect, cations influence CO₂RR by directly coordinating with reaction intermediates. A joint experiment-theory study by Monteiro *et al.* showed that no CO product could be measured indicating that CO₂RR cannot occur without a trace amount of Cs⁺, as partially desolvated Cs⁺ stabilizes the first CO₂RR intermediate (*CO₂) via short-range electrostatic interactions [21] (Figure 3a). Further research by the same group found that multivalent cations like Ba²⁺ and Nd³⁺ coordinate to *CO₂ steadily, thus stabilizing *CO₂, and enabling barrierless protonation to COOH [4]. Effective CO₂RR requires an interplay between three key parameters influenced by cation acidity: cation stabilization of the *CO₂⁻ or other critical intermediates, suppression of the water reduction activity, and cation accumulation at the OHP [4].

Through AIMD simulations with slow-growth sampling approaches, Qin *et al.* have demonstrated that K⁺ cations can facilitate the initial CO₂ activation step, as well as subsequent proton and electron transfer steps, via direct coordination interactions (Figure 3b) [22,23]. At the same time, cation accumulation at OHP can suppress water dissociation, leading to poor HER activity (Figure 3b) [3,23]. A following systematic theoretical study further demonstrates that the activity and

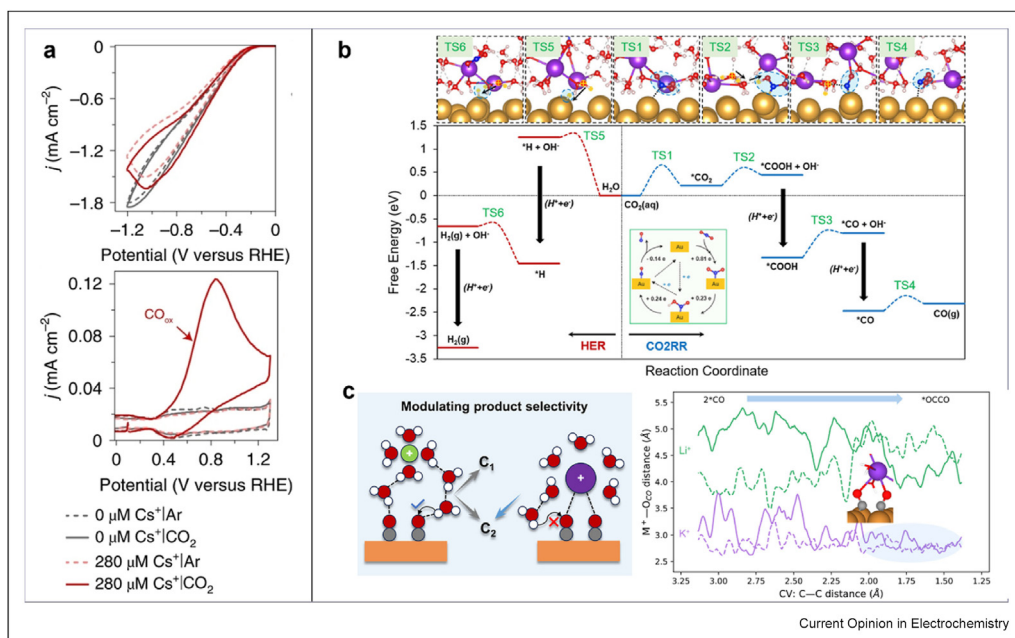
selectivity of interfacial CO₂RR can be modulated by engineering local cation conditions (identity and concentration), which affects the reaction kinetics of both CO₂RR and HER [24].

Due to the short-range coordination interaction between cations and reaction intermediates, cations alter the inner-sphere and outer-sphere mechanisms of the first electron-transfer step in CO₂RR [25]. Using constrained DFT, molecular dynamics, and Marcus theory, it is shown that alkali metal cations facilitate inner-sphere electron transfer, while outer-sphere electron transfer is significantly inhibited with high Marcus barriers and large reorganization energies in the presence of cations in the EDL [25]. Recent simulations also indicate that cations can undergo desolvation and directly stabilize CO₂RR intermediates, such as *CO₂⁻ and *OCCO [26,27]. Additionally, larger cations, compared to smaller ones (e.g., K⁺ vs. Li⁺), can more easily approach the interface through desolvation and coordinate with the *CO+*CO moiety, thereby facilitating efficient C–C coupling in CO₂RR [27] (Figure 3c).

Altering the interfacial water structure

Besides electric field and direct coordination effects, cations can also affect CO₂RR by altering interfacial water structures, impacting the hydrogen bonding

Figure 3



(a) Cathodic scans recorded in argon and CO₂ atmosphere (upper graph) and the subsequent recorded anodic scans performed to oxidize any CO produced (lower graph). Reprinted from Ref. [21]; (b) Complete free energy landscape of CO₂RR and competitive HER at Au–water interfaces with two K cations. Reprinted from Ref. [23]; (c) Schematic representation of the integrated mechanism elucidating the cation-dependent C₂ selectivity through the combination effects of interfacial water molecules and cations (left); Distance of M⁺–O_{Co} along the collective variable (right). Reprinted from Ref. [27].

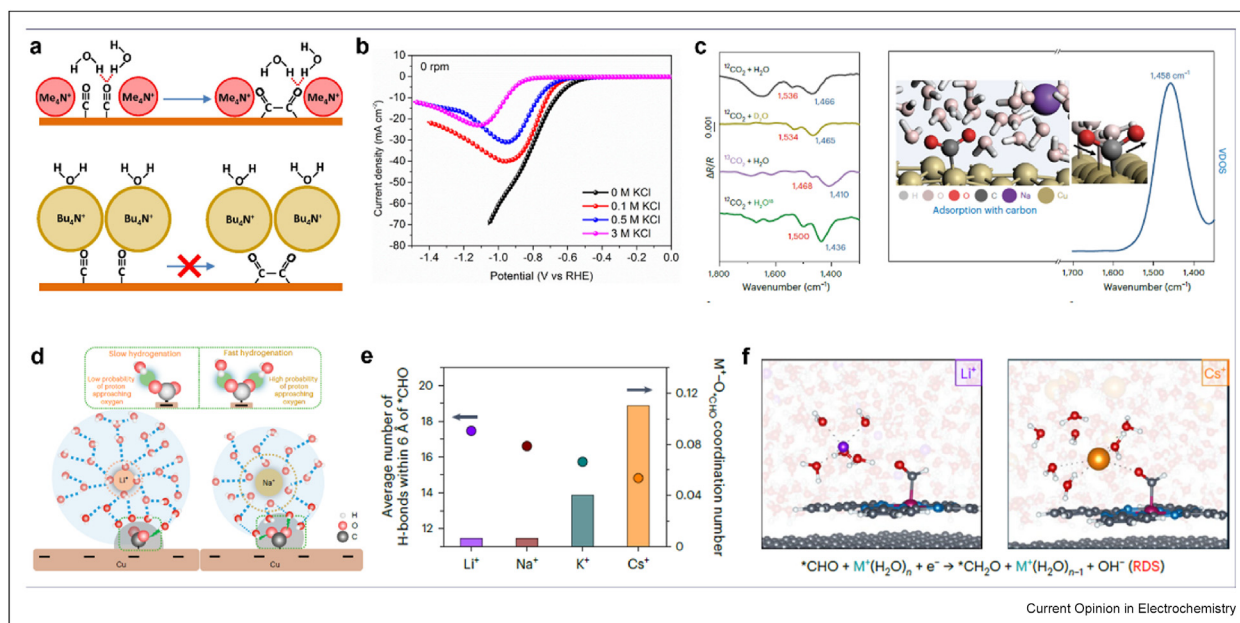
network, proton diffusion pathways, and proton transfer steps. In 2019, Li and co-workers used SEIRAS to show that cation-dependent interfacial electric-fields are too small to explain selectivity changes in CO reductions [5]. Instead, they found that larger cations disrupt hydrogen bonding between surface-adsorbed CO and interfacial water, steering product selectivity (Figure 4a). This study provided critical molecular-level insight into how interactions of surface species with the liquid environment, specifically through hydrogen bonding, control electrocatalytic selectivity [5]. Additionally, cations can impact proton diffusion in acidic electrolytes, inhibiting HER kinetics and enhancing CO₂RR to form formic acid, CO, and multicarbon products [9,28,29]. As evidenced by peaks in linear sweep voltammetry (LSV) curves (Figure 4b), which indicate proton diffusion limitation, the increased K⁺ concentration prevents H⁺ diffusion to surfaces [29].

Very recently, two joint experiment-theory studies further highlighted the essential role of interfacial water structures in cation-enhanced CO₂RR [30,31]. Combining SEIRAS and AIMD simulations on Cu, it was found that Li⁺ enhances CO₂ activation more effectively than larger cations, which is contrary to prevalent viewpoints [30]. As shown in Figure 4c, the isotope-labeled in situ SEIRAS detected the *CO₂ intermediate at approximately ~ 1466 cm⁻¹, which was

further confirmed by the simulated vibrational density of states (VDOS) profile obtained from AIMD simulations. Importantly, both AIMD simulations and spectroscopic features reveal that the rigid water network around Li⁺ hinders proton transfer to *CO₂, while larger cations like Na⁺ promote more flexible water structures, improving hydrogen proximity and thus CO₂RR efficiency (Figure 4d). By combining electrokinetic analyses, kinetic isotope effect studies, and computational work, Yu et al. found that smaller, more acidic alkali metal cations significantly enhance CO₂-to-CH₃OH kinetics, following the trend Li⁺ > Na⁺ > K⁺ > Cs⁺ on a cobalt catalyst, in contrast to the trend for CO on Ag and C₂+ on Cu [31]. Such an activity trend is closely related to the H-bonds around *CHO (Figure 4e). They showed that the cation hydration shell acts as a proton donor in the rate-determining *CHO formation step (RDS), with acidic cations like Li⁺ facilitating proton-coupled electron transfer (Figure 4f). Beyond the known stabilizing effect, this work emphasizes the critical role of cation solvation structure on CO₂RR.

At electrode–electrolyte interfaces, understanding the relationship between water and electric field screening is also essential. It is, however challenging to decouple from the influence of cations on interfacial CO₂RR. The ability of water to screen interfacial fields is expected to be closely related to its capacity to reorient in response

Figure 4



(a) Possible CO_{ads} coupling mechanism on Cu(100) in the presence of methyl₄N⁺, and in the presence of butyl₄N⁺. Reprinted from Ref. [5]; (b) HER LSV curves at 0 rpm for electrochemically-reduced Cu porous nanosheet in 0.05 M H₂SO₄ with different amount of KCl. Reprinted from Ref. [29]; (c) Isotope-edited in situ SEIRAS recorded with D₂O (yellow), ¹³CO₂ (purple) and H₂O (green) (left), and calculated VDOS profiles of the CO₂ adsorbed at Cu(111)/electrolyte interface via the carbon site. Reprinted from Ref. [30]; (d) Schematic presentation of water network around Li⁺ and Na⁺ and its interactions with adsorbed CO₂. Reprinted from Ref. [30]; (e) Cation-dependent average number of H-bonds within 6 Å of *CHO (left y axis) and average coordination number of M⁺-O-CHO at the first peak of the radial distribution function. Reprinted from Ref. [31]; (f) Representative snapshots from MD simulations showing different solvation structures near the cation (Li⁺ and Cs⁺) in proximity of the *CHO intermediate, respectively. Reprinted from Ref. [31]. (For interpretation of the references to color/colour in this figure legend, the reader is referred to the Web version of this article.)

to these fields. It is known from experiment, that the dielectric constant of water is reduced for nano-confined water [32] and in the presence of cations [33], so accurately describing the screening of interfacial fields appears to require a dynamic description of water orientation allowed by MD simulations. A study by Le *et al.* [34] investigated the Helmholtz layer at the Pt(111)/water interfaces at different potentials using AIMD calculations, where the interfaces were electrified by inserting Na⁺ and F⁻ ions next to the surface. A similar setup from constructing the EDL was also used in Ref. [35] for Au(111). The electric field within the water is reduced as the water molecules align their dipoles along the field. For Pt(111), the surface coverage of chemisorbed water increases as the potential shifts from negative to positive; since chemisorbed water induces a significant interface dipole potential, this change in coverage results in a potential shift and a corresponding negative capacitive response [34]. The computational work on Au(111) in Ref. [35], combined with Raman spectroscopy, showed that towards negative potentials, the interfacial water molecules evolve from structurally ‘parallel’ to ‘1-H-down’ and then to ‘2-H-down’. Another recent study [36] on Pt(111)/water interfaces reveals that biasing with (artificially) partially

charged hydrogen atoms leads to a structural response in interfacial water similar to the one with the presence of real explicit ions, supporting the decoupling of water and electrolyte ion responses in double-layer models for low ionic concentrations. The authors of [36] also shows that the electronic polarizability of interfacial water is highly sensitive to its environment, with chemisorbed water coverage affecting work function and capacitance under varying bias conditions, thus agreeing with Refs. [34,35]. It is possible that some of the conflicting cation effects reported on different catalysts stem from different interactions between the catalyst and the electrolyte, which remains to be further investigated.

Modulating local CO₂ concentration and pH

Local pH and CO₂ concentration represent another aspect of CO₂RR that has been primarily explored through experiments. An early experimental study by Hori *et al.* demonstrated that different electrolytes significantly affect CO₂RR selectivity on Cu electrodes by altering the local pH, which depends on electrolyte buffer capacities [37]. The local pH impacts proton availability at the electrode, which in turn affects product selectivity. Afterwards, further studies showed the formation of CH₄ depends on proton concentration,

while the formation of ethylene is not affected by the pH [38,39]. Several studies on Cu single crystals at different pHs [40–42], observed the onset potential for CH₄ depends on pH, which agrees with Hori's studies. However, the relation between ethylene formation and pH dependence is facet dependent. Specifically, the ethylene formation is dependent on pH on Cu(111) facet, while the onset potential for ethylene on Cu(100) was independent of pH, which was relevant to the determination of rate-determining step [43]. While the effect of local pH on rate and selectivity has been discussed as above, the mechanism is still debated for CO₂RR on Cu(100) and Cu (111), especially for C₂₊ products [44–46]. In the following, we specifically focus on the local pH effects related to cations.

In 2016, Singh et al. showed that electrolyte cation size affected CO₂RR on metals via cation hydrolysis near the cathode, thus modifying the local pH and local concentration of dissolved CO₂ [47]. The cathode pH decreased from Li⁺ to Cs⁺, and a reversed trend for cathode CO₂ concentration was observed. Both the local pH and CO₂ concentration contributed to the increased current density as well as higher Faradaic efficiency for CO₂RR over HER on metals when increasing cation size to Cs⁺. Afterwards, an in situ infrared spectroscopy study by Cuesta et al. and a rotating ring-disk electrode assembly designed by Zhang et al. provided strong and direct evidence to Singh's et al.'s hypothesis, where the magnitude of the pH increase at the interface follows the trend Li⁺ > Na⁺ > K⁺ > Cs⁺ [48,49]. However, contradictory to the cation buffering hypothesis, a reversed trend on interfacial CO₂ concentration with different alkali metal cations was proposed by Malkani and co-workers [50]. Based on SEIRAS spectra, the integrated area of the dissolved CO₂ band in 0.25 M alkali metal bicarbonate electrolyte (at -0.8V) decreases by 69 % from Li⁺ to Cs⁺, and the decline in the interfacial CO₂ concentration is more pronounced from Li⁺ to K⁺ than from K⁺ to Cs⁺. Thus, the local CO₂ concentration decreased as the cation size increased. So far, there is no unified conclusion regarding the cation effect on local CO₂ concentration across metal catalysts. The interplay between cation type, local pH, and local CO₂ concentration strongly dictates CO₂RR performance, and there is still a long way for both experiments and theory to fully understand these effects.

Conclusion and outlook

In this minireview, we discussed recent experimental and theoretical advances in the mechanistic understanding of cation effects on CO₂RR. Generally, cations influence CO₂RR kinetics and activity via electric field effects, coordinating interactions, interfacial water structures, and local pH and CO₂ concentrations. However, understanding cation effects at metal-water interfaces remains complex, as it depends on the catalyst, target reaction

pathway, and specific reaction conditions. A unified conclusion has yet to be reached, with even contradictory findings reported for the same reaction systems. While advanced experimental techniques, such as in situ spectroscopy, have provided valuable insights into interfacial dynamics, unifying reaction conditions remains challenging. Therefore, it is increasingly important to extend the capabilities of theoretical simulations through new methods and approaches to better elucidate the fundamental mechanisms at play. Here, we would like to highlight key topics that we believe will be crucial for advancing future research in CO₂RR.

- (1) **New methods for electrode–electrolyte interfaces.** Recently, notable advancements have been made in the methodology development for performing AIMD simulations under constant potentials, enabling, e.g., to simulate non-linear dielectric and ionic responses of the charged interfaces; a widely spread one is VASPsol++ [51]. Additionally, further progress has been achieved in simulating instantaneous charge and potential fluctuations in AIMD simulations [52].
- (2) **Machine learning.** Machine learning (ML) has become quite important for studying CO₂RR, showing a prominent role in accelerating material property computation, catalyst design, testing and ML-aided synthesis [53]. For example, ML has been used as high-throughput virtual screening strategy with a pre-developed ML model and a CO₂RR selectivity map to identify active and selective catalysts for CO₂RR without being limited to a database; the validation of experimental data confirmed the validity of the method [54]. Machine learning interatomic potentials are also a promising approach for simulating CO₂RR. They can be trained on short AIMD simulations, enabling longer (bias) simulations and allowing explorations of the potential energy surface with enhanced computational efficiency [55,56]. We expect the improved sampling statistics enabled by ML-MD will allow detailed simultaneous studies of both the ion-distribution and how this distribution impacts CO₂RR activity and selectivity.

Data availability

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

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors have used chatGPT in order to improve the readability of parts of the manuscript. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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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