



Review

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ABSTRACT

Electrochemical CO₂ reduction (eCO₂RR) to high-value chemicals and fuels, especially oxygenates and long-chain hydrocarbons, are of great interest for industrial applications, as well as offering a feasible strategy to reach the global goal of net-zero carbon emissions. Over the past few decades, research efforts have been focused on the development of both the rational design of electrocatalysts and electrolyzer systems, along with understanding the underlying mechanisms behind the electrolyte environment (e.g., cations, anions, and pH effects) on eCO₂RR. In this review, we summarize recent progress on investigating the intriguing cation effect which steer the challenging eCO₂RR toward the desirable directions. Although several hypotheses have been proposed but no consensus has been reached on the underlying mechanism of cation effects toward the eCO₂RR. We overview the complex nature of cation effect to modify the electrode and electrolyte interface for converting CO₂ efficiently to the target products based both on the latest experimental and computational findings, and provide our viewpoint of future directions and possible strategies in this topic for further improving the eCO₂RR performance.

Introduction

Motivation for CO₂ recycling

With the rapid economic development in the past few centuries, the carbon cycle has been gradually disrupted by the increased combustion of fossil fuels since industrial revolution. According to the International Energy Agency 2021 (atmospheric CO₂ concentration $\approx$ 417 ppm), the anthropogenic CO₂ emission is approximately 36.3 gigatons (Gt), while the total global CO₂ fixation amount ($\approx$ 200 megatons (Mt)) by green plants and autotrophic organisms per year is less than 6 % of the aforementioned emission amount [1,2]. It has been predicted that about 500 gigatons of CO₂ will be produced from 2010 to 2060 as fossil fuels will still be a major source of energy for the future [3,4]. Excessive CO₂ emission has caused severe environmental issues like global warming and polar ice caps melting and hence sea level rising [1,4]. Therefore, the development of CO₂ utilization technology is a top priority to achieve zero-carbon emissions for the society of the twenty-first century. The first step for decarbonization is to capture CO₂, which has been commercialized since 1950s as a pretreatment for cryogenic

air separation [5–7]. Then the captured CO₂ has been previously considered to pump deep underground and dissolve in the mid-depth ocean for long-term storage. However, the possibility of leakage and massive energy consumption prevents these strategies from being realized [8–10]. The electrochemical conversion of CO₂ into value-added chemical feedstocks offers a better method to turn waste CO₂ emissions into valuable products, as well as closing the carbon loop [11–13].

Thermodynamics and economics of eCO₂RR

CO₂ is a thermodynamically stable molecule wherein the C atom is attached to each O atom by a double bond with high dissociation energy of around 750 kJ mol⁻¹ [14]. Therefore, the activation of CO₂ molecules has been regarded as the initial step of eCO₂RR. As the first electron transfer to form the CO₂^{•-} radical intermediate has a very negative redox potential (−1.9 V vs NHE), the activation of CO₂ is difficult. However, the utilization of electrocatalysts will stabilize the CO₂^{•-} radical by forming chemical bonds between the active sites on the electrocatalysts and CO₂ molecules to bend the linear structure of CO₂ and hence weaken the C=O double bond, resulting in a less

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Table 1
Half reaction of eCO₂RR for possible process with equilibrium potentials.

Reactions	E^0 / [V vs RHE]
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}(\text{l})$	-0.19
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}$	-0.10
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO}(\text{l}) + \text{H}_2\text{O}$	-0.06
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH}(\text{l}) + \text{H}_2\text{O}$	0.03
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}$	0.17
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4(\text{g}) + 4\text{H}_2\text{O}$	0.08
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g}) + 3\text{H}_2\text{O}$	0.09
$2\text{CO}_2 + 14\text{H}^+ + 14\text{e}^- \rightarrow \text{C}_2\text{H}_6(\text{g}) + 4\text{H}_2\text{O}$	0.14
$2\text{CO}_2 + 18\text{H}^+ + 18\text{e}^- \rightarrow \text{C}_3\text{H}_7\text{OH}(\text{l}) + 5\text{H}_2\text{O}$	0.10

negative redox potential [15,16]. The $\text{CO}_2^{\cdot -}$ radical is generally considered to bound to the active sites of electrocatalysts through three potential coordination structure: 1) the C atom in CO_2 molecules can act as a Lewis acid to receive electrons from Lewis base centers like oxide ions to form carbonate-like species; 2) The oxygen atoms in CO_2 molecules can donate lone pairs of electrons to the surficial Lewis acid center; 3) A mixed coordination structure on the surface of electrocatalysts can be formed with the C atom and O atoms in CO_2 molecules acting as electron acceptors and donors, respectively [17]. After initial activation by the electrocatalysts, the eCO₂RR undergo a multiple proton-coupled electron transfer (PCET) process, which generally involves two-, four-, six-, eight- and twelve-electron reaction pathways to form different desirable products, such as CO, HCOOH, CH₄, CH₃OH, and C₂H₄ [18]. Table 1 summarized the potential products of eCO₂RR and their corresponding standard potentials calculated through the Gibbs free energy of reaction with gas-phase thermochemistry data and Henry's Law data for aqueous products from NIST [12,19].

Most recent research has been contributed to the above fundamental understanding of reaction mechanisms and electrocatalysts designing, while other works have contributed to the development of lab-scale CO₂ electrolyzer system [20–24]. Nevertheless, limited efforts have been conducted to understand the feasibility of eCO₂RR for generating value-added chemicals and fuels on a techno-economic basis, as well as the essential role of eCO₂RR played in the future to mitigate the energy shortage caused by the fossil fuels depletion. Although the production of long-chain carbon products from reductive coupling of CO₂ is more favorable for the current chemical fuel infrastructure, it comes at massive energy cost, which makes only certain products economically viable if considering the energy efficiency and products selectivity [25]. As suggested in Fig. 1 from Bushuyev et al., even though the

gravimetric and volumetric energy density increase with carbon chain length, the energy density decreases when normalized to the transferred electron number, which suggests that higher energy efficiency must be achieved for producing longer-chain carbon molecules to obtain similar overall energy storage capacity comparing with shorter-chain molecules production [25].

Among all the simple and small molecules produced from eCO₂RR, C₂ products like ethylene and ethanol have a larger global market sizes, up to US\$230 billion and US\$75 billion, respectively, comparing to C₁ products, such as CO (US\$ 3 billion) and HCOOH (US\$ 6 billion) [26]. However, a recent techno-economic analysis (TEA) shows that the production costs of CO and HCOOH are around US\$ 0.44 and 0.59 kg⁻¹, respectively, competitive with conventional processes, whereas the production costs of C₂H₄ and C₂H₅OH are US\$ 2.50 and 2.06 kg⁻¹, which is not economically feasible at the present electricity price [26]. Fortunately, with the fast development of photovoltaic and wind energy, the decreasing cost of photovoltaic electricity (~US\$ 0.03 kWh⁻¹) and wind electricity (~US\$ 0.02 kWh⁻¹) price makes the utilization of eCO₂RR technologies increasingly feasible for commercial applications [27–29]. And it has been estimated that an increase in energy efficiency to ~50 % and a decrease in renewable electricity price to US\$ 0.01 kWh⁻¹ would make C₂ products production economically viable [26].

Challenges and opportunities of CO₂ utilization

Although the fast development of water electrolyzer and fuel cell industries, as well as the mature chlorine alkali industry, provide a reasonable road map for the commercialization of eCO₂RR. However, there are still challenges existed in both fundamental research and industrialization of eCO₂RR technology. Firstly, the infrastructure of the overall system for electrolysis needs to be further enhanced, including both the performance and durability of the electrode and the ion-exchange membrane, as well as the architectural efficiency of the electrolytic cell [30,31]. Secondly, further optimizing the performance of the electrocatalysts is another priority. So far, unlike Pb, Hg, Tl, In, Sn, Cd, and Bi metals produce mainly formate, Au, Ag, Zn, Pd, and Ga metals produce mainly carbon monoxide, Ni, Fe, Pt, and Ti metals reduce little amount of CO₂ while reduce primarily H₂O to H₂, Cu stands out as a unique electrocatalysts which generating hydrocarbons, aldehydes, and alcohols [12,32]. These current state-of-the-art electrocatalysts still have some inevitable problems. For instance, the current density of the eCO₂RR can rarely reach the ideal industrial A cm⁻² level. Moreover, the low Faradaic Efficiency (FE) to high-value C₂+ products will significantly increase the costs of subsequent products

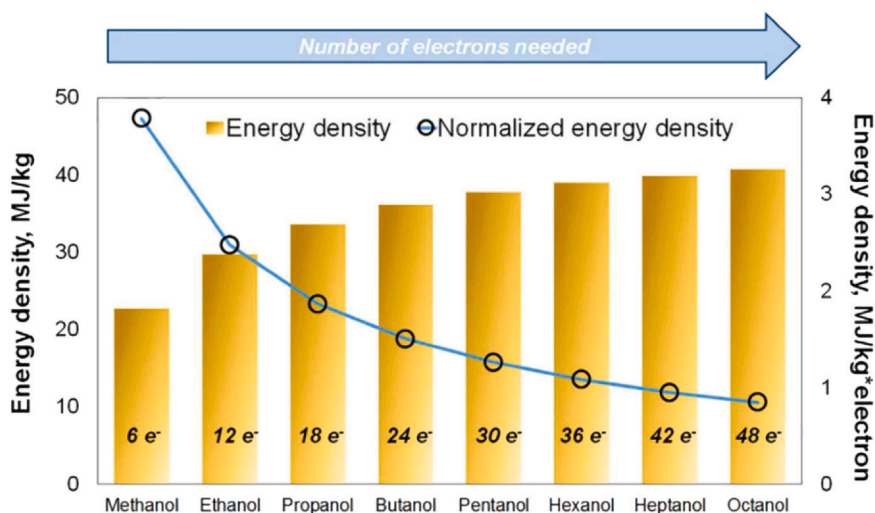


Fig. 1. Comparison of energy density and normalized energy density of unbranched alcohols. Reprinted with permissions from Bushuyev et al. [25].

separation and purification processes. Even worse, the competing electrochemical reactions, such as hydrogen evolution reaction (HER), will further decrease the selectivity of eCO₂RR into high-value carbonaceous products. Thirdly, as the optimal condition to electrocatalyze CO₂ reduction is in near neutral or basic electrolytes with a pH higher than 7, CO₂ would convert into (bi) carbonate according to the equations as follows:



These conversion along with the low solubility of CO₂ in aqueous electrolytes (~33 mM) results in a critical depletion in CO₂ concentration near the electrode surface [33,34].

Understanding the cation effects in eCO₂RR

While many great efforts have been dedicated in designing novel electrocatalysts and membrane systems to improve the overall performance (i.e., faradaic efficiency, energy efficiency, stability and selectivity) of eCO₂RR, they have typically focused on the catalyst and system design strategies and rarely discussed the local environment near the electrode-electrolyte interface, which is also essential in determining the catalytical performance of eCO₂RR according to most recent studies. We note that the cation identity in the electrolyte significantly affects the reaction rates and selectivity of eCO₂RR. Therefore, in order to make a suitable choice of electrolyte, it is crucial to understand how the cations distribute in the electric double layer (EDL) and their critical effect on eCO₂RR. The Gouy-Chapman-Stern (GCS) model describes the EDL structure between the electrode and the electrolyte [35]. As shown in Fig. 2, an EDL forms to neutralize the charge of the biased electrode in the electrolyte [36]. The EDL structure consists of an Inner Helmholtz Plane (IHP), in which ions are specifically adsorbed on the electrode, an Outer Helmholtz Plane (OHP), where ions are not chemisorbed but surrounded by solvent molecules (i.e. are solvated), and a diffuse layer extends from the OHP to the bulk of the solution (ions in the diffuse layer are disorderly arranged).

Cations in the EDL have been reported to play an essential role in a series of important electrochemical reactions including the HER, hydrogen oxidation reaction (HOR), and oxygen reduction reaction (ORR), and so on [37–41]. In this review, we summarize the most recent works on cation effects in eCO₂RR and introduce both the direct experimental cation effects reflecting the FE and current density, and theoretical calculations which can further investigate the insights into

cations on the EDL including the effect of cations on the applied potential and the interfacial electric field. Cations were classified into alkali metal cations, cationic surfactants, and multivalent cations. In each section, we overview a few important factors which affect the cation distribution in the EDL: applied electrode potential and actual electrode potential near the surface (i.e., potential at the OHP), electrode properties, pH, and the chemical characteristics of cations in the electrolyte. This review is aimed at providing our perspective of future directions for further development on this research area and potential strategies for enhancing the eCO₂RR performance through electrolyte optimization.

Alkali metal cations

The alkali metal cations effect in enhancing the eCO₂RR activity and selectivity toward the target products was first reported by Paik et al., who found the overpotential for eCO₂RR toward HCOOH decreased when changing Li⁺-containing electrolyte to Na⁺ or tetraethylammonium-containing electrolytes [42]. Hori and Murata then observed that the faradaic efficiency of C₂₊ products increased on polycrystalline Cu while the selectivity for the HER decreased from Li⁺ to Cs⁺ [43]. Since then a series of research on cation-enhancing eCO₂RR performance has been reported on Ag, Au, Pb, Sn, and Cu [44–48]. Hori and Murata firstly proposed in their work that the cation specific adsorption change the potential profile in the EDL based on Frumkin's theory [49]. However, this theory of cation adsorption on transition metal electrodes is not applicable as the equilibrium potentials calculated by Mills et al. are ranging from −2.63 V vs NHE for Li⁺ to −2.44 V vs NHE for Cs⁺ for specific cation adsorption on Ag electrode [50], greater than the operating potentials of eCO₂RR. Another old opinion for alkali metal cation effect for eCO₂RR is the possible steric hindrance to affect OHP potential due to the variation of cation size and has been investigated in a previous study using a modified Poisson-Boltzmann equation, which suggests the variation of hydrated cation size has a negligible effect on the OHP potential for an applied potential > −1 V vs RHE [51].

In contrast to the above theory for explaining the cation effects during eCO₂RR, a second theory proposed by Singh et al. postulates that cations can affect the eCO₂RR by buffering the interfacial pH to maintain a correspondingly high CO₂ concentration [52]. It is noted that the pH near the cathode for conducting the eCO₂RR rises as the applied cell voltage increases, which will significantly reduce the amount of dissolved CO₂ presented as molecular CO₂ in the vicinity of the cathode and increase the concentration of HCO₃[−] and CO₃^{2−}, hence lead to a reduced selectivity for producing C₂₊ hydrocarbons and an increased selectivity for H₂ and CH₄ production [43,53]. In this cation hydrolysis theory, although alkali cations do not undergo hydrolysis in the bulk, the hydration shell of larger cations such as Cs⁺ experience a stronger electric field than smaller cations, which decreases their pK_a of hydrolysis and results in a more neutral interfacial pH [13], as suggested in the schematic in Fig. 3.

Moreover, Table 2 shows the calculated pK_a values of hydrolysis for different alkali cations in the bulk electrolyte and in the vicinity of Ag or Cu electrode surfaces at −1 V vs. RHE [52], which suggests that the pK_a of cation hydrolysis decreases with increasing cation size near the cathode surface as a result of the increased electrostatic interaction between H atoms of the H₂O molecules in the hydration shell of cations and the cathode. The pK_a of cation hydrolysis are hence increased monotonically with increasing the separation distances (< 1 nm) between the cathode and the cation. Furthermore, they also point out that the fact for the pK_a of cation hydrolysis in the vicinity of the Ag electrode always smaller than that near the Cu electrode is due to the higher specific capacitance and therefore the charge density on the Ag electrode surface. Fig. 4 shows their calculated pH and CO₂ concentration over the Ag and Cu cathode at −1 V vs. RHE, in agreement with the trend predicted in their pK_a value for cation hydrolysis given in Table 2 [52].

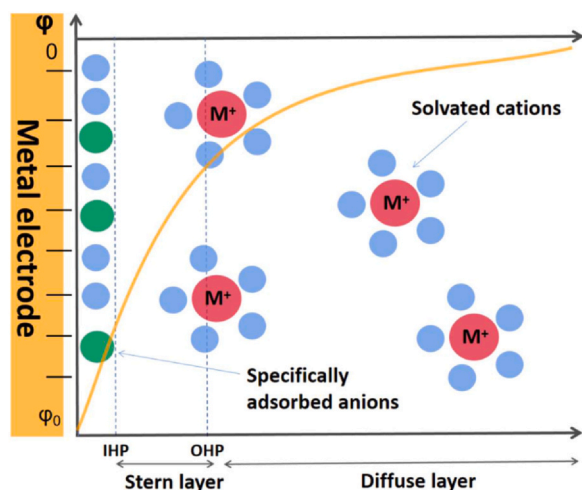


Fig. 2. Schematic illustration of the electric double layer structure in the Gouy-Chapman-Stern model. The red, green, and blue spheres represent cations, anions, and solvent molecules, respectively.

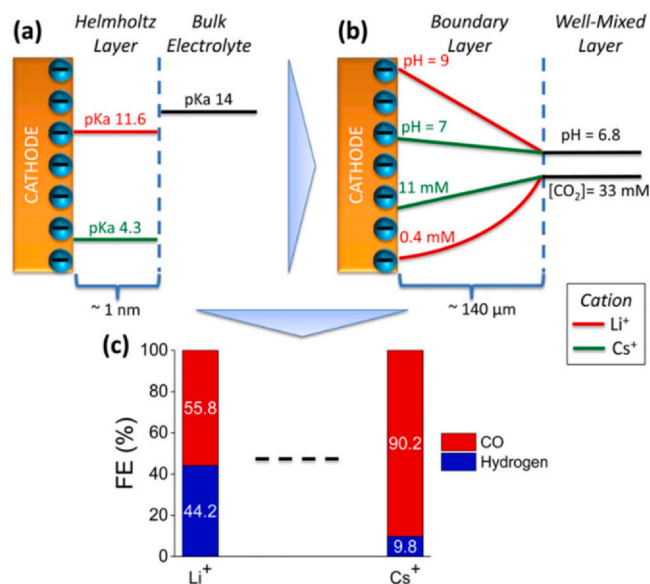


Fig. 3. (a) Schematic illustration of cation hydrolysis effect on the eCO₂RR over Ag. (a) pK_a of hydrolysis of hydrated Li⁺ and Cs⁺ inside the Helmholtz layer and in the bulk electrolyte and (b) distribution of pH and CO₂ concentration in the boundary layer. Hydrated Cs⁺ would maintain the pH close to 7 and increase the CO₂ concentration while hydrated Li⁺ does not buffer the cathode and leads to a decreased CO₂ concentration to 0.4 mM. (c) FE for H₂ decreases and CO increases with increasing cation size due to a decrease in polarization. Reprinted with permission from Singh et al. [52].

Table 2

pK_a of Hydrolysis of Cations in the Bulk Electrolyte and near Ag and Cu Cathodes at -1 V vs RHE^a.

Cation	Cation size (pm)	pK _a		
		In bulk electrolyte	Near Ag cathode	Near Cu cathode
Li ⁺	69	13.6	11.64	13.16
Na ⁺	102	14.2	10.26	11.44
K ⁺	138	14.5	7.95	8.49
Rb ⁺	149	14.6	6.97	7.23
Cs ⁺	170	14.7	4.31	4.32

^aThe pK_a of hydrolysis increases linearly with the distance between the cation and the cathode. The minimum and maximum value of pK_a occurs at the cathode and a separation distance greater than ~1 nm. Reprinted with permission from Singh et al [52].

Ayemoba et al. experimentally tested this pH buffering hypothesis through probing the pH at the Au electrode/electrolyte interface with ATR-SEIRAS and confirmed that the magnitude of the pH increase at the interface agrees with Singh's hypothesis. Moreover, they also point out that the effect of pH buffering was overestimated by Singh et al., especially for larger cations [54].

However, Malkani et al. showed contradictory observations that the increased cation size will decrease the interfacial CO₂ concentration on Au surface using ATR-SEIRAS. Their combined spectroscopic and electrochemical results suggest that the concentration of interfacial CO₂ is dependent on the CO₂ consumption rate via reduction or reaction with the OH⁻ produced at the electrode, rather than the cation buffering theory [55].

Considering the presence of cations can affect the eCO₂RR at adequately low applied potential with minimized mass transport limitations and undetermined local environments of electrode, there should exist some other mechanisms about the cation effects. The third theory suggests that alkali metal cations near the electrode surface will induce high electric fields of ~ -1 V/Å around the ion and extend roughly 5 Å

from the solvated cations center and outside this region decay to zero [56,57], as shown in Fig. 5a in the simulated electric field distribution of K⁺ in contact with CO₂ molecules through DFT calculations and microdynamic modeling by Chen et al. [56]. Basically, larger cation sizes are believed to cause weaker interfacial electric field with the EDL at a given potential below the potential of zero charge (PZC) since larger cation center cannot approach to the electrode as close as smaller cations, according to the GCS double layer model. This phenomenon has been demonstrated by both Roth et al. [58] and a more recent work by Li et al. [59]. They used tetraalkylammonium cations with different alkyl chain length to determine the Stark tuning rate, which represents the electric field strength, of linearly bonded CO on Pt and Cu electrode. Although they found the Stark tuning rate decreases with increasing the alkyl chain length of the cations (i.e., cation size) [58,59], it should be noted that this correlation between electric field strength and cation sizes was obtained from the experiments which used hydrophobic tetraalkylammonium ions with weakly bound hydration shell [60]. Therefore, if we consider hydrated alkali cations including Li⁺, Na⁺, K⁺, and Cs⁺, the size of which are analyzed to be 2.1, 2.4, 2.7, and 3.13 Å [61], respectively, Li⁺ is supposed to induce the strongest interfacial electric field in the double layer. However, this hypothesis is exactly contrary to a previous reported operando Raman studies in which the stark tuning rate of linearly bound CO on polycrystalline Cu film electrode increases in the order of Li⁺ < Na⁺ < K⁺ < Rb⁺ ≈ Cs⁺ [62]. This obvious contradiction emphasizes the importance of considering the hydration shell of cations rather than barely hydrated cation size, especially for monovalent cations with more concentrated charges, such as Li⁺ and Na⁺, which have longer range influence on neighboring water molecules and are thus likely to have more than one layer of water molecules in the hydration shells [62,63]. Therefore, the hydration shells size decreases in the order of Li⁺ > Na⁺ > K⁺ > Rb⁺ ≈ Cs⁺. A more recent molecular dynamics simulation by Monteiro et al. suggests that the cations with small hydration shells, such as Cs⁺, accumulate easier at the OHP and therefore induce stronger interfacial electric field [64], as schematically illustrated in Fig. 5b by Pan et al [60]. Another spectroscopy work by Gunathunge et al. provide further evidence for this electric field theory which found that the adsorbed CO molecules experience a larger interfacial electric field by observing the peak frequencies of C≡O stretch band decrease with increasing the cation size [65], as shown in Fig. 5c. And it should also be noted that since the peak frequencies are dependent linearly on applied potential with similar slopes in all cases, this peak frequencies changes should be ascribed to the interfacial electric field changes rather than coverage effects [66].

Moreover, the presence of these cation size dependent electric fields can significantly affect the adsorption energy of CO₂ to CO reaction intermediates such as *CO₂ and *COOH on Ag or Sn surface [56,67], as well as other C₂₊ product intermediates such as *OCCO on Cu surface [57,67–69]. The interaction energy between a uniform electric field and an adsorbate is given as follows:

$$E = E_0 + \mu\epsilon - \frac{\alpha\epsilon^2}{2} \quad (3)$$

Where E_0 represent the adsorption energy without an electric field and E represent the adsorption energy in an electric field; α and μ are the polarizability and intrinsic dipole moments for the adsorbate, respectively; and ϵ represents the electric field.

As schematically illustrated in Fig. 6a from Resasco et al. [67], the accumulation of alkali cations in the OHP will induce a dipole field to stabilize the adsorption of surficial reaction intermediates that have dipole moments. They calculated the field effects on various eCO₂RR intermediates on Cu (111) facet (Fig. 6b) according to Eq. 3 and summarized the calculated polarizabilities and dipole moments of possible adsorbates in Table 3, which suggested that adsorbates with positive μ such as *CO₂, *CO, and *OCCO are stabilized, while adsorbates with negative μ like *COOH and *CHOH are destabilized. However, for other

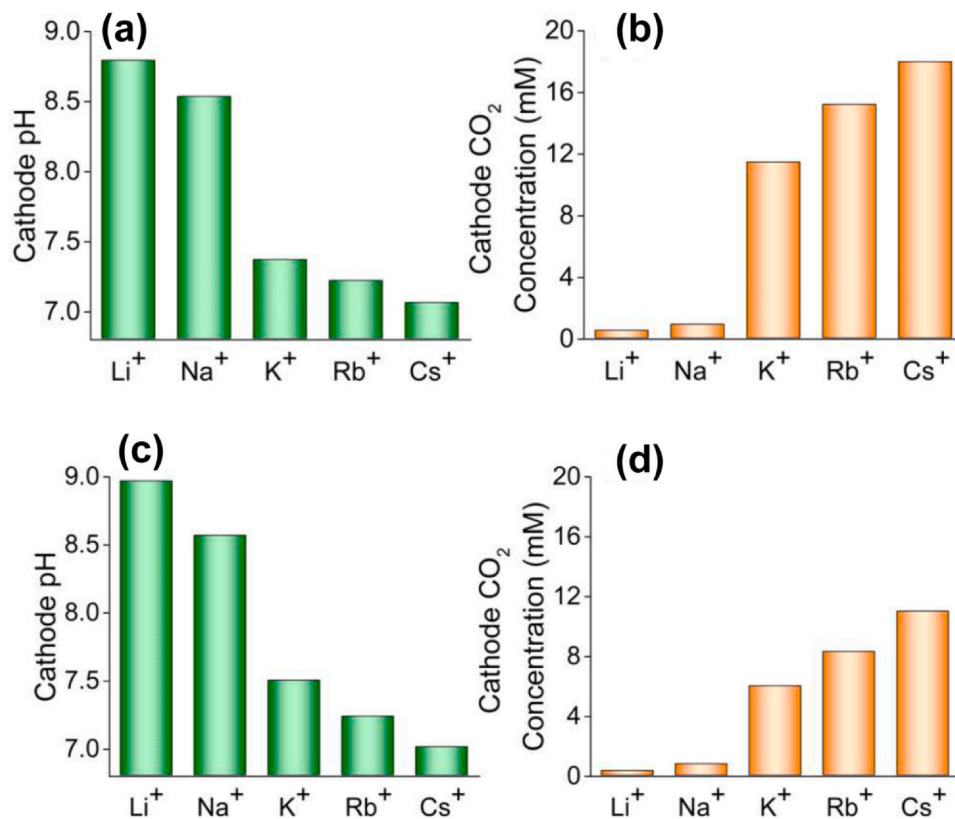


Fig. 4. Calculated values of (a) cathode pH, (b) cathode CO₂ concentration over Cu, and Calculated values of (c) cathode pH, (d) cathode CO₂ concentration over Ag at -1 V vs RHE in CO₂-saturated 0.1 M M HCO₃ (M = Li, Na, K, Rb, Cs) electrolyte. Reprinted with permission from Singh et al. [52].

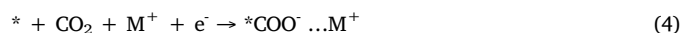
intermediates without significant value of dipole moment such as ^{*}H and ^{*}CHO, the effect of this dipole field is negligible. Their experimental observations that the partial current densities for CO, H₂ and CH₄ maintained stable while the partial current densities for HCOOH, C₂H₅OH and C₂H₄ increased with increasing the cation size further support this field-dipole theory.

However, since the field-dipole theory alone can not explain the experimentally found trend with cation size, Resasco et al. further revealed through their calculations that larger hydrated cations are more energetically favored at the OHP than smaller ones, which was confirmed by their experiments showing that only a small percentage of larger cations is needed to significantly affect the intrinsic rates of certain products formation [67]. Additionally, except for the commonly studied transition metal catalysts like Cu, a more recent work from Vijay et al. suggests that metal single-atom and N-doped graphene electrode possess larger dipole moments for ^{*}CO₂, which will result in stronger stabilization of adsorbates for a given electric field during eCO₂RR [70].

Although the field-dipole theory proposed an explicit mechanism of how cation stabilize intermediates with large dipole moments in medium range, their impact on the cation-coupled electron transfer (CCET) or PCET process is more complicated. Therefore, research efforts in the past few years have contributed to investigate the impact of short-range interaction between the partially dehydrated cations and negatively charged eCO₂RR intermediates through forming coordinated cation-CO₂ complexes [64,71,72]. For instance, as suggested from the AIMD simulations in Fig. 7a by Monteiro et al., alkali metals bind to the O atom in CO₂ resulted in the average cation-CO₂ coordination numbers $N_{M^+-O(CO_2)}$ of 0.1 ± 0.3 , 0.9 ± 0.2 , 0.9 ± 0.4 , 1.3 ± 0.5 for Li⁺, Na⁺, K⁺, and Cs⁺, respectively [72]. Such coordinated cation-CO₂ complexes show negligible impacts on the H₂O molecule numbers in the hydration shell of cation but are believed to allow the stabilization of the CO₂⁻ intermediate by ~ 0.5 eV and enhance the electron transfer

from the catalytic active site to the CO₂ unit [72]. Another AIMD simulations from Liu et al. revealed the dynamic coordination structures between the water/OCCO and cations [71]. Their results showed that two oxygen atoms in OCCO intermediate can appear at the same time in the first hydration shell of larger cations such as Cs⁺, which means larger cations can interact with two CO molecules simultaneously to promote the formation of the C-C bond and hence facilitate the further CO₂ conversion to C₂ products [71].

Beyond affecting the products selectivity, such coordinated cation-CO₂ complexes are also known to influence the reaction rate [46,64,73]. As presented by Shin et al. [73], the CCET step can significantly affect the production rates of CO and C₂H₄ while opposite trend for the PCET-related CH₄ formation was found on Cu electrode. For instance, the CCET of CO formation from CO₂ can be represented as Eq. 4:



According to the Butler-Volmer equations as follows:

$$j_{co} = nFkP_{CO_2}C_{M^+}e^{-\alpha_c F(E - E_{(reaction)}^{0'})/RT} \quad (5)$$

Where n and k are the number of electrons and rate constant involved in the CO₂-to-CO conversion reaction, respectively, and P_{CO_2} represents the CO₂ partial pressure. $E_{(reaction)}^{0'}$ is the formal reduction potential of the elementary step reaction of Eq. 4. α_c is the cathodic charge transfer coefficient, and F , R , and T are the Faraday constant, gas constant and temperature, respectively.

The reaction rate of CO formation can be thus determined by the interfacial cation concentration C_{M^+} . As proposed by Shin et al. that the excess cations at the EDL is to screen the electrode surface charge included in the CCET step, C_{M^+} is therefore assumed to be equal or proportional to the cation-dependent electrode surface charge density $|\sigma|$ [74], which can be estimated through integrating differential capacitance (C_{diff}) from the E_{PZC} using the equation as follows: [75].

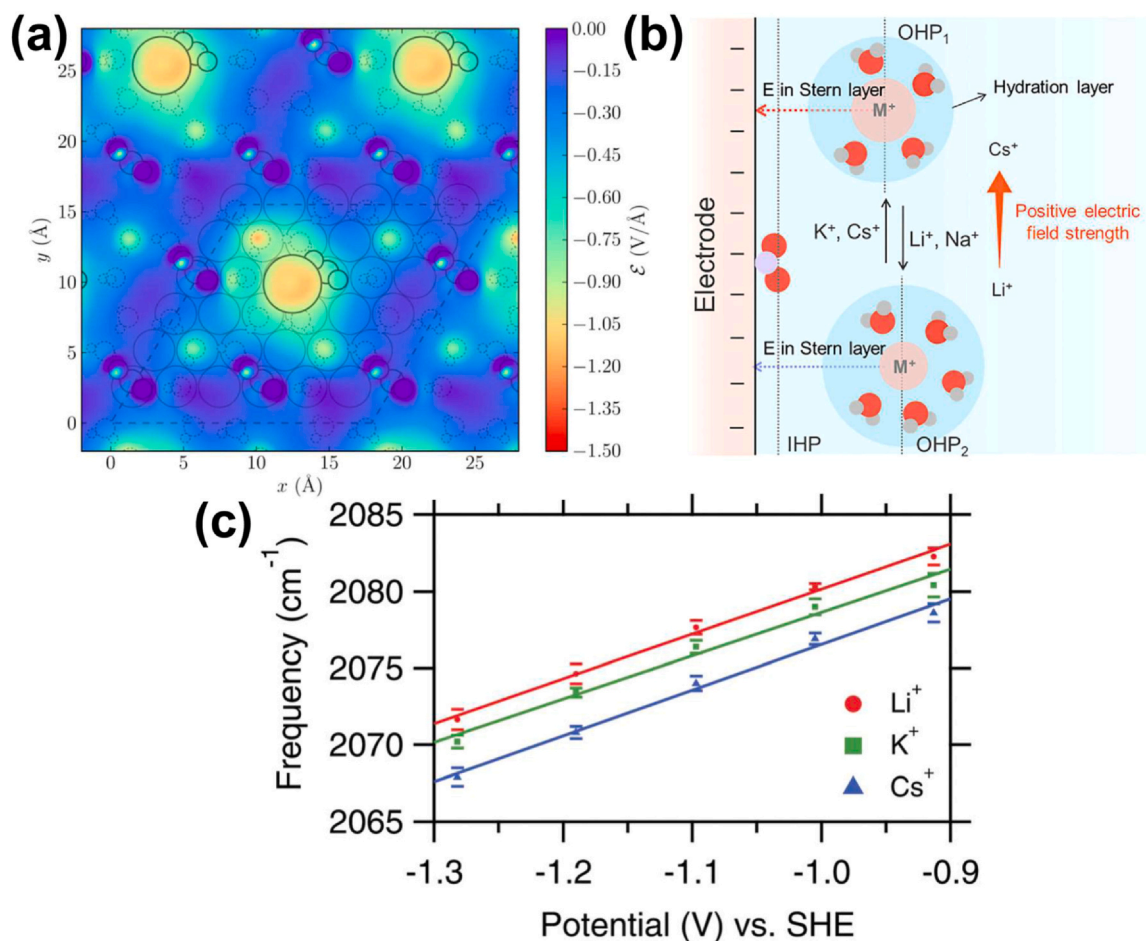


Fig. 5. (a) Electric field distribution of K^+ in contact with CO_2 . K^+ (large circles) and CO_2 in its vicinity are outlined in black for emphasis. Reprinted with permission from Chen et al. [56]. (b) Schematic of cations changing the electric field within the GCS double layer. Reprinted with permission from Pan et al. [60]. (c) Peak frequencies of the C=O stretch band of linearly-bonded CO decreased on polycrystalline Cu electrode as a function of applied potential in CO-saturated 0.1 M cations-containing electrolyte, suggesting larger interfacial electric fields with increasing cation size. Reprinted with permission from Gunathunge et al. [65].

$$|\sigma| = \left| \int_{E_{PZC}}^{E'} C_{diff} dE \right| \quad (6)$$

As shown in Fig. 7b and c, the linear correlation curves of the first-order kinetics of j_{CO} and $j_{\text{C}_2\text{H}_4}$ on $|\sigma|$ suggest the existence of CCET step on CO and C_2H_4 formation [73]. Similar observation has been found on alkali cations in the work of Ringe et al., where weakly hydrated cations are calculated to be more concentrated at the OHP in their continuum electrolyte model and therefore induce higher surface charge density to favor CO formation [76].

Except for the CCET step, the influence of PCET is more complicated as the Volmer step of HER ($\text{H}_2\text{O} + \text{e}^- + * \rightarrow * \text{H} + \text{OH}^-$) can serve as a proton donor to facilitate CO_2 protonation. In fact, the trend between cation effect and HER activity is determined by the electrode identity [77] and the mass transport [74]. For instance on Au and Ag surfaces under alkaline conditions, larger hydrated alkali cations accumulated at the OHP may enhance the HER activity through facilitate the Volmer step from Li^+ to Cs^+ at low overpotentials [74,78]. For some other metal electrode surfaces that interact relatively weaker with H than Pt, but are also active for eCO_2RR such as Cu, the partial current density of

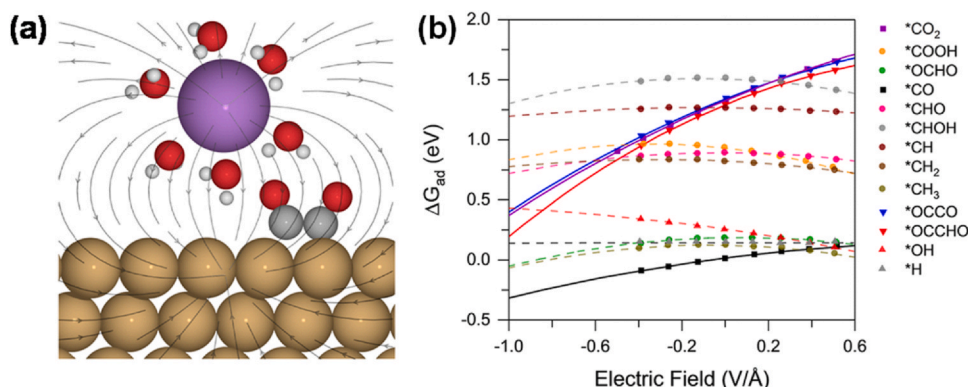


Fig. 6. (a) Schematic representation of electrostatic interactions between solvated cations present at the OHP and adsorbed intermediates having large dipole moments. (b) Field effects on various eCO_2RR intermediates on Cu (111). The curves are fit to Eq. 3 and the corresponding polarizability α and dipole moment μ of the adsorbates are given in Table 3. Reprinted with permission from Resasco et al. [67].

Table 3

Calculated Dipole Moments and Polarizabilities of Adsorbates on Cu (111) based on equation 3^a.

adsorbate	μ (e Å)	α (e Å ² /V)
*CO ₂	0.76	0.40
*COOH	-0.19	0.60
*OCHO	0.04	0.42
*CO	0.23	0.22
*CHO	0.00	0.36
*OCCP	0.66	0.54
*OCCHO	0.75	0.74
*CHOH	-0.05	0.52
*CH	-0.02	0.18
*CH ₂	-0.08	0.26
*CH ₃	-0.03	0.44
*OH	-0.26	0.14
*H	0.00	0.00

^a Adapted with permission from Resasco et al [67].

H₂ production increases slightly from Li⁺ to Cs⁺ while electrochemical CO₂ to C₂ products activity shows much greater enhancement [79]. Moreover, research efforts have also been focused on the impact of the

alkali cation hydration shell on the transfer kinetics of proton-electron, including either the structure or the polarization of H₂O molecules [80,81], and the intermolecular interactions between the reaction intermediates and the H₂O molecules in the hydration shell [82], which suggest that the hydrated structures of cations can also impact the PCET kinetics of eCO₂RR.

Cationic surfactant

Except for alkali cations, amphiphilic surfactants, which are consisted of long alkyl chain with a polar headgroup, have also been investigated to enhance the eCO₂RR performance and significantly suppress the competing HER [83–88]. Although the suppression of HER activity in the presence of cationic surfactants is still debatable, current hypotheses are mainly focused on the effects on the activation energy of H₂O dissociation and the displacement of interfacial H₂O molecules to decrease the concentration of protic sources [84,87]. As suggested in both experimental and computational results by Ummireddi et al., the presence of tetraethylammonium (TEA⁺) cation in the electrolyte will decrease the activation energy for H₂O dissociation and enhance the HER activity on Fe and Ni, while opposite trend was found on Cu and Ag [87]. Furthermore, they also found that the

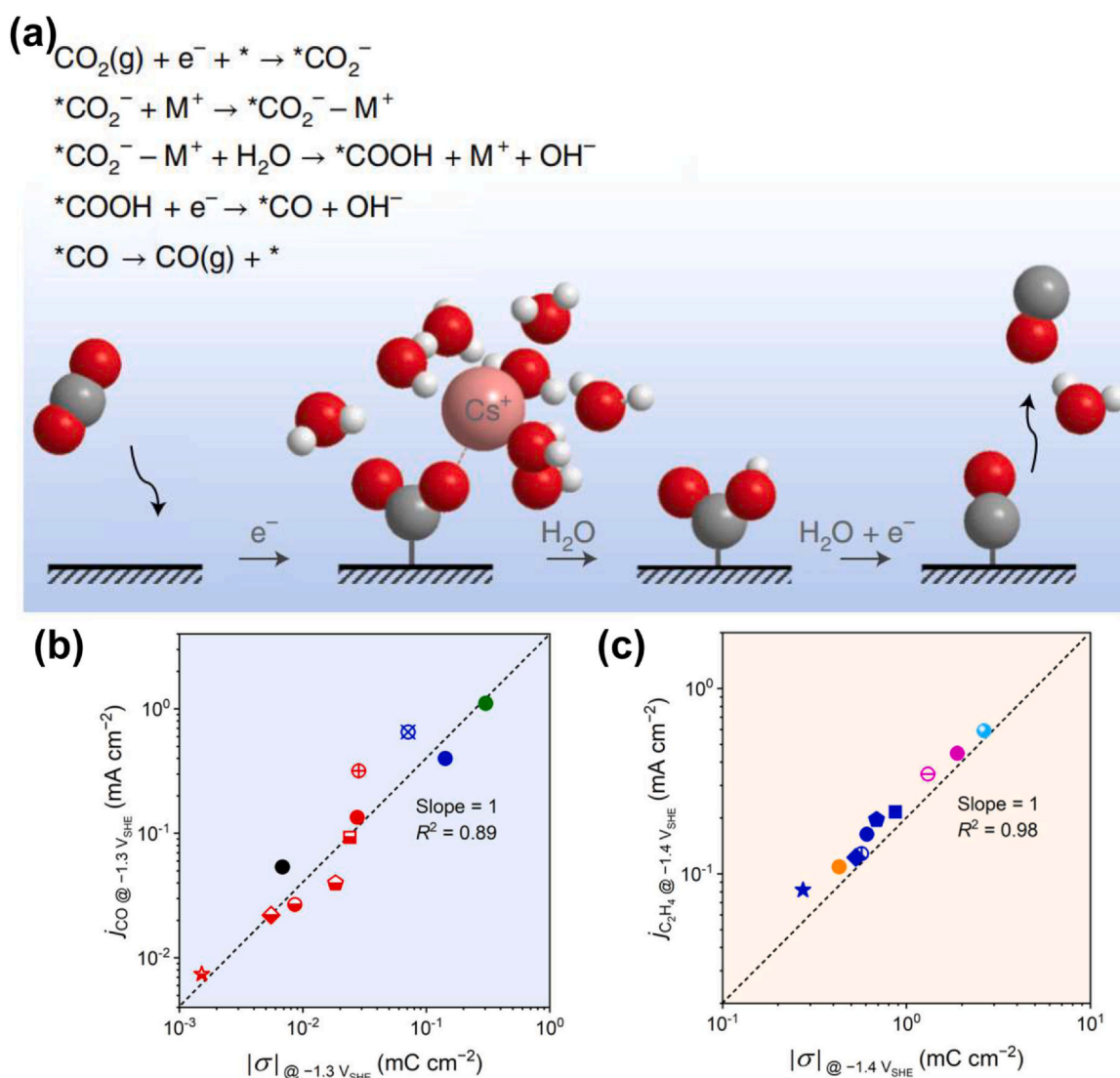


Fig. 7. (a) Schematic representation of the coordination of the cation with negatively charged CO₂⁻ intermediate together with a proposed reaction mechanism. Reprinted with permission from Monteiro et al. [72]. Correlation plots of (a) j_{CO} on the Ag electrode at $-1.3 \text{ V}_{\text{SHE}}$ for CO₂ to CO formation and (c) $j_{\text{C}_2\text{H}_4}$ on the Cu electrode at $-1.4 \text{ V}_{\text{SHE}}$ for CO₂ to C₂H₄ formation with surface charge density $|\sigma|$ gathered with various M⁺ identities. Reprinted with permission from Shin et al. [73].

increased $^*\text{COO}^-$ binding energy is crucial to enhance the eCO_2RR activity and selectivity on metals which bound $^*\text{COO}^-$ too weakly (e.g. Cu and Ag) [87]. In another HER suppression model proposed by Zhang and Banerjee et al., the HER suppression was found to be enhanced via the reorganization and displacement of interfacial H_2O molecules in the presence of cetyltrimethylammonium bromide (CTAB) in the EDL. The bleach of the O-H stretching mode ($\nu\text{-OH}$) and HOH bending mode (δ_{HOH}) of H_2O in their SEIRAS results confirmed the reduced concentration of interfacial H_2O , which is most likely driven by hydrophobic and steric effects from the alkyl chain of CTAB [89]. The authors further focused on the interaction between CTAB and different alkali cations to study their synergistic impact on the eCO_2RR . They found that the eCO_2RR selectivity (CO , CH_4 and C_2H_4) in the presence of CTAB are almost independent with respect to Li^+ , Na^+ , and K^+ , however, Cs^+ defy this trend and showed high HCOO^- selectivity. The evolution of EDL under electrocatalytic conditions was tracked by EIS measurements in this work. As suggested by a previous study of Banerjee et al. [83], the measured double layer capacitance, C_{dl} , are always smaller in the presence of CTAB compared to additive-free experiments as the presence of surfactant will decrease the local dielectric constant via adding long hydrocarbon tails to the double layer. However, in this work, the decline of C_{dl} is notably less steep in Cs^+ electrolyte compared to that of Li^+ while the C_{dl} are almost the same for both the Li^+ and Cs^+ electrolyte without CTAB, which strongly support the hypothesis that hydrated Li^+ , Na^+ , and K^+ can be displaced by CTA^+ easier than Cs^+ , as Cs^+ tend to form a more compact layer to compete with CTA^+ at the interface, as schematically illustrated in Fig. 8a. The synergistic effects of Cs^+ induced field and the hydrophobicity of

CTA^+ to hinder the CO dimerization pathway to C_2H_4 are proposed to be the reason for unusually high HCOO^- production [84]. Similar impeding effect has also been previously reported by Li et al. where they found the presence of tetrabutylammonium will disrupt the interfacial H bonding and hinder the diffusion of local proton sources for CO dimerization pathway to C_2H_4 [59].

Unlike the above works which add the cationic surfactant in the electrolyte, another strategy to utilize cationic surfactant to enhance the eCO_2RR performance is to directly decorate the surfactant on metal catalysts [90,92], as shown in Fig. 8b. The long hydrocarbon chains not only supply multiple aerophilic tunnels to promote CO_2 transportation but also impede the accessible proton from approaching the catalyst surface due to electrostatic repulsion. It was found that Cu nanowires with Cetyltrimethylammonium (CTAC) showed the highest selectivity toward HCOOH . The 16-carbon linear chain of CTAC was able to form bilayer assembly structure on Cu nanowires, which is essential to capture and facilitate the diffusion of CO_2 molecules to achieve higher accumulation at the electrode/electrolyte interface [90]. Besides, the long linear chain is energetically favoring the stabilization of OCHO^* , a typical intermediate for the formation of HCOOH [90]. Moreover, the molecular dynamics simulations in this work suggest that surfactant, such as tetraoctylammonium chloride (TTAC), with branched chains tend to aggregate to form spherical micelles, which could not be adsorbed on the Cu surface but increase the selectivity of CO [90]. Other research has also been focused on the intermolecular interactions between the reaction intermediates and the H_2O molecules in the

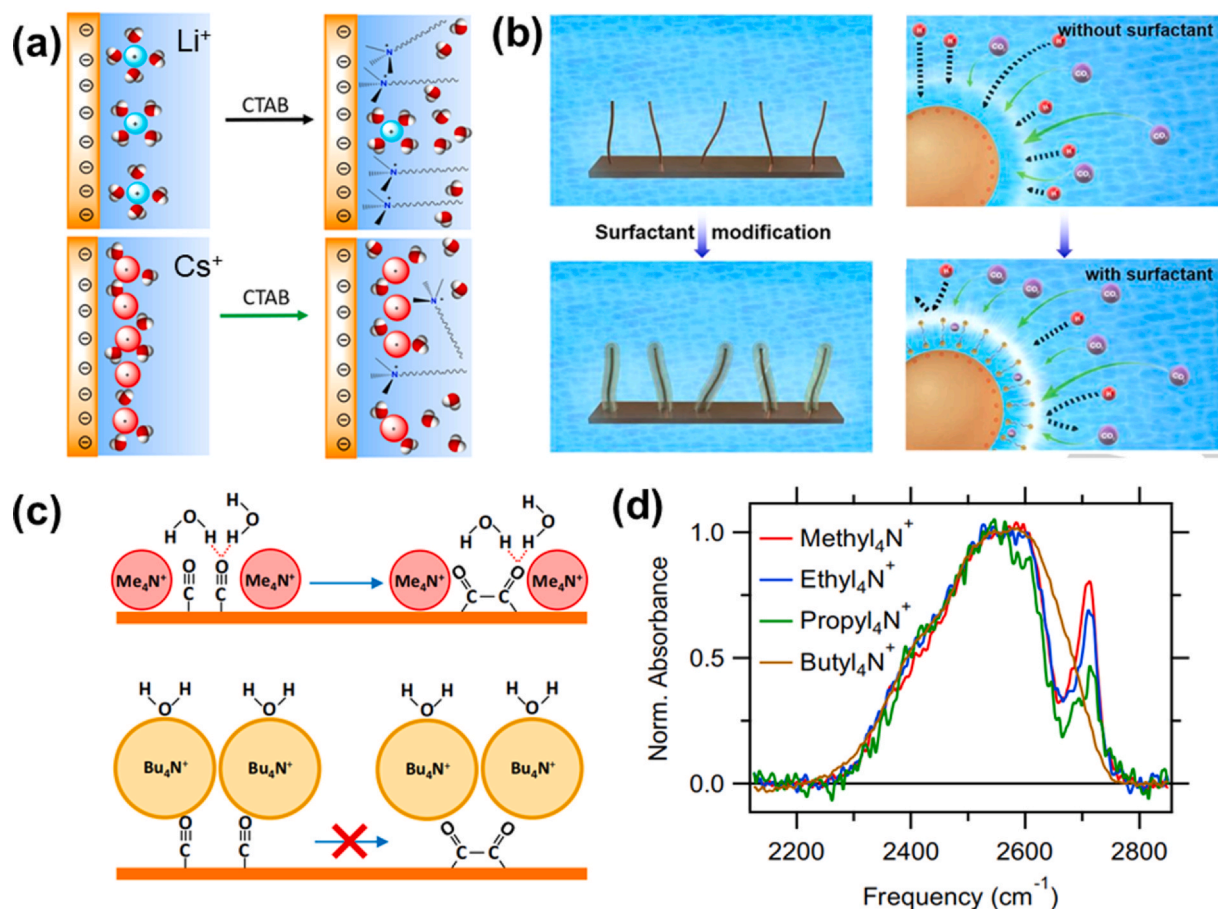


Fig. 8. (a) Proposed model for interfacial CTA^+ accumulation in Li^+ and Cs^+ -containing electrolytes. Reprinted with permission from Banerjee et al. [84]. (b) Schematic of quaternary ammonium cation surfactant modification on a Cu nanowire array electrode surface and schematics showing the transportation of the CO_2 and H^+ from bulk electrolyte to electrode surfaces on pristine Cu NW and surfactant modified Cu NW. Reprinted with permission from Zhong et al. [90]. (c) Possible CO coupling mechanism on Cu(100), as proposed by Bagger et al. [91], which shows interfacial waters are available to stabilize the CO dimer by hydrogen bonding in the presence of small alkyl ammonium cations while the formation of CO dimer is blocked due to the displacement of the interfacial water by the large hydrophobic cations. (d) Normalized O-D stretch spectra recorded at a potential of -1.02 V in the presence of different cations. Reprinted with permission from Li et al. [59].

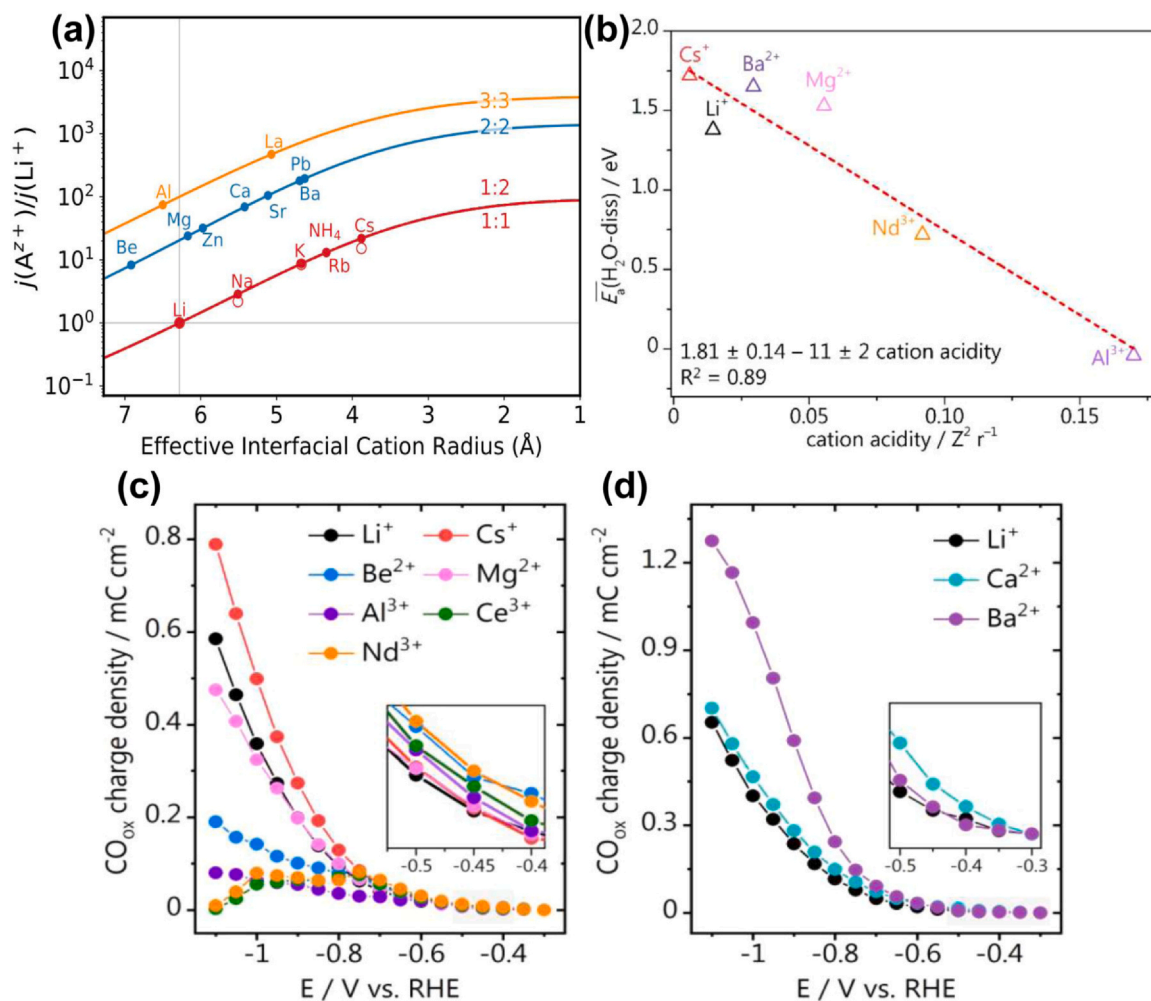


Fig. 9. (a) Prediction of cation effects on the electrocatalytic CO₂ reduction on Ag (111) at -1 V vs. RHE using the determined interfacial ion size correlation for hydrated ions with the ionic crystal radius. The figure depicts the predicted CO partial current density for 0.1 M A_xB electrolytes having a cation: anion charge ratio of $z: z_x$ as a function of the effective interfacial cation size relative to Li⁺ as a cation. Reprinted with permission from Ringe et al. [76]. (b) Activation barrier for water dissociation vs cation acidity, calculated as the average of the values for 2 and 3 H₂O molecules in the cation solvation shell. This process is barrierless for Al³⁺. Amount of CO produced probed via consecutive cathodic/anodic voltammetry at pH = 3 in (c) 0.1 M Li₂SO₄ + 1 mM Mⁿ⁺ electrolytes with Mⁿ⁺ = Li⁺, Cs⁺, Be²⁺, Mg²⁺, Al³⁺, Nd³⁺, Ce³⁺ and (d) 0.2 M LiClO₄ + 2 mM Mⁿ⁺ with Mⁿ⁺ = Ca²⁺, Ba²⁺. Reprinted with permission from Monteiro et al. [64].

hydration shell of cationic surfactant. For instance, as proposed schematically in Fig. 8c by Li et al. [59], CO dimerization is hindered by the presence of large cations through displacing the H₂O layer on top of surface-adsorbed CO, which has been predicted by a previous computational work that H bonding of interfacial H₂O molecules to the stabilization of CO dimer to its terminal oxygens is essential [91]. Their SEIRAS results in Fig. 8d shows that a prominent band could be found on top of the broad O-D stretch band at around 2710 cm^{-1} in the presence of two small cations while this band is completely absent in large butyl₄N⁺-containing electrolyte, further supporting their hypothesis that the intermolecular interaction between CO_{ad} and interfacial H₂O is disrupted in the presence of larger cations [59].

Multivalent cations

In addition to the alkali cations and cationic surfactant, the utilization of electrolyte containing multivalent cations is particularly interested in eCO₂RR as such electrolyte are much cheaper than the commonly used alkali metal cation containing electrolyte, though only few papers have reported insights on the use of multivalent cations-based electrolytes [64,76,93–96]. For instance, the eCO₂RR rate over a CuSnPb alloy electrode in La³⁺ containing electrolyte was reported to be two-times higher than that of Na⁺ at the same potential, and the

promotion effect was ascribed to the additional stabilization of the CO₂^{•−} anion radical in the RDS [95]. Moreover, the FEs of CH₃OH in this work increased from 17.8 % in Al³⁺ to 35.7 % in La³⁺. The FEs of CH₃CHO, which ranged between 1.8 % and 7.3 % in the other electrolyte, showed up to 17.6 % in the presence of Zr⁴⁺ [95]. Besides, Hussain et al. applied ab initio molecular dynamics to show that the size of multivalent cations can not only determine the location of the outer Helmholtz plane but also influence the polarizability and polarization of adsorbed CO and electronic density accumulation on the O atom of the adsorbed CO affecting its adsorption energy [94]. Their combined IR spectroscopic data also suggests that the size of the multivalent cations will result in a cation-dependent degree of H bonding of interfacial H₂O with adsorbed CO, which will also affect the eCO₂RR mechanism [94]. Waegle et al. investigated the effects of multivalent cations on the eCO₂RR performance in their theoretical work by quantitatively analyzing the cation specific adsorption or quasi-specific adsorption, as well as the corresponding impacts on the structure of the bulk and interfacial H₂O [96]. However, such theoretical studies would need to be supported with more experimental observations that a comprehensive trend can thus be confirmed.

Another DFT calculations in Fig. 9a by Ringe et al. also theoretically predicted that the existence of multivalent cations such as Be²⁺, Al³⁺, Ba²⁺, and La³⁺ should show two orders of magnitude higher activity

toward CO than Cs^+ on Ag (111) electrodes at -1 V vs RHE, as the larger charge of these multivalent cations would induce more intense interfacial electric field [76]. Additionally, not as previously observed for alkali cations, a more recent work by Monteiro et al. emphasized the importance of carefully considering the effects of multivalent cations on the competing H_2O reduction, which is the main branch of HER occurring at high overpotentials and was always disregarded by the DFT predictions [64]. As shown in Fig. 9b, they observed that the activation barrier for water dissociation showed a strong correlation with the cation acidity (Z^2/r , square root of the charge over the ionic radius), with weakly hydrated trivalent cations leading to the highest activity. Therefore, their eCO_2RR results (Fig. 9c and d) on polycrystalline Au electrode at $\text{pH} = 3$ in multivalent cations-containing electrolyte showed the highest absolute activity for CO formation in the presence of Cs^+ while trivalent species such as Al^{3+} and Nd^{3+} displayed the least activity for CO generation, seemingly contradictory to the predictions obtained in the research of Ringe et al. Accordingly, even though there might be any promotional effect of these trivalent cations on the eCO_2RR , they actually favor even more the H_2 production [64]. Although the above works have partially or theoretically verified the possibility of accelerating the activity and selectivity of eCO_2RR with the utilization of multivalent cations, the main disadvantages which limit the application of multivalent cations were aroused from their low solubility and possible formation of oxide and/or hydroxide deposit to block active sites under neutral and alkaline conditions [64,93,97]. Future research efforts in this area could focus on further optimization of the complex eCO_2RR mechanism in the presence of multivalent cations and also the application of multivalent cations in strong acidic media to carry out the eCO_2RR at industrially relevant current densities [98,99].

Conclusions and future outlook

Coupling eCO_2RR with a renewable energy source such as wind and solar to produce value-added fuels and chemicals is a promising strategy to mitigate the environmental issues caused by excessive CO_2 emission and energy shortage aroused by fossil fuels depletion. In this review, we summarized the cation identity including alkali metal cations, cationic surfactant, and multivalent cations, to modify the electrode-electrolyte interface in the EDL, which influence both the selectivity and activity of the electrochemical reduction of CO_2 in the following ways:

- (1) Control the pH gradient near the electrode and hence the local CO_2 concentration by buffering the interfacial pH.
- (2) Establish and modify the interfacial electric field to stabilize certain reaction intermediates with large dipole moment.
- (3) Determine the HER activity through tuning the H^+ concentration near the electrode via electrostatic interactions.

We note that the above hypotheses are proposed mainly from the current research on alkali metal cations. Multivalent cations have not been extensively studied, possibly due to their limited applications under neutral and alkaline conditions. For cationic surfactant, although there are more relevant research works have been reported than multivalent cations, however, due to their larger size and more complex hydration structure that increased the cost of theoretical calculations, the development of corresponding explanations for the origin of their activity is still slow. Therefore, we emphasize the importance of further deepening the understanding on the mechanisms of different types of cations that promoting the eCO_2RR . Besides, current theories are based mainly on computational predictions which are not adequately evidenced experimentally. For instance, the aforementioned medium-range field-dipole theory can be confirmed indirectly with the help of advanced operando Raman and ATR-SEIRAS spectra and conventional electrochemical methods [94,100,101], while the short-range cation-

CO_2 coordination is more challenging to characterize as it requires much higher spatial and temporal resolution. Therefore, we emphasize the importance of further advancing the characterization methods to provide more experimental evidence supporting the cation promotion effects, while simultaneously optimizing the existing models within considering the synergy of intrinsic microkinetics, mass transport limitations, and homogeneous reactions to rationalize various experimentally observed trends.

Moreover, Future research efforts may focus more on acidic eCO_2RR , as the conversion of CO_2 into (bi)carbonate in alkaline media is inevitable and hence consumes higher energy than that is stored by eCO_2RR to continuously regenerate the (bi)carbonate into CO_2 in order to maintain stable performance [102–104]. Although steady-state CO_2 electrolysis is possible in near-neutral media, CO_2 is still consumed by the OH^- anions produced by the eCO_2RR , and the (bi)carbonate is protonated near the anode to regenerate CO_2 which results in low carbon efficiency [105,106]. Therefore, although efficient eCO_2RR in acidic electrolyte is challenging as the competing HER is generally more facile than the eCO_2RR , it is still worth to put more research efforts into acidic systems, especially within the presence of cations. It has been reported that CO_2 electroreduction to CO was viable in mildly acid with mixed $\text{HClO}_4/\text{NaClO}_4$ and K_2HPO_4 electrolytes [107,108], or in strongly acid with mixed $\text{H}_3\text{PO}_4/\text{KCl}$ solutions [109]. For instance, Bondué et al. point out that the proton reduction can be efficiently suppressed in acidic media through increasing the formation rate of CO/OH^- from eCO_2RR to compensate the mass transfer of protons to the electrode surface [107]. Huang et al. demonstrate that the presence of K^+ in strong acid can trigger CO_2 activation under a proton-depletion local environment and hence suppresses the HER from water reduction [109]. Moreover, a very recent work of Gu et al. reveals that the presence of alkali cations in the double layer can lower the concentration of H_3O^+ ions in the OHP through shielding the electric field in the diffusion layer and thus suppressing the migration of H_3O^+ ions towards the electrode, as well as strengthen the electric field and stabilize the key intermediates in CO_2 reduction [98]. Although the cation-induced pH gradients in acidic eCO_2RR reactor is inevitable which leads to high cell voltages, Monteiro et al. point out that eCO_2RR can still be carried out at considerably lower cell potentials through careful choice of cations in the electrolyte, resulting in a reduction of up to 30 % in process energy costs in direct comparison with neutral media. Specifically, considering an electricity price of $\text{US\$ } 0.03\text{ kWh}^{-1}$, running the reaction in CsSO_4 at $\text{pH } 4$ instead of KHCO_3 (at 200 mA cm^{-2}) could lead to saving $\text{US\$ } 1343$ per ton of CO produced [99]. In order to further lower the cell voltages and hence the cost of acidic eCO_2RR , future research efforts may focus on increasing the operating temperature or using electrooxidation of organic compound to replace the sluggish OER.

Furthermore, as discussed above, cation promotion effects also influence the electrochemical CO reduction (eCORR) to produce hydrocarbons, methanol, and C_{2+} oxygenates, and it seems eCORR is more promising than eCO_2RR as there is no carbonate formation and hence low pH gradients exist in alkaline medium.

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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