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Hydroxide is not a promoter of C₂₊ products formation in electrochemical reduction of CO on Copper

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Abstract: Highly alkaline electrolytes have been shown to improve the formation rate of C_{2+} products in the electrochemical reduction of carbon dioxide (CO₂) and carbon monoxide (CO) on copper surface, with the assumption that higher OH concentrations promote the C-C coupling chemistry. In this work, we demonstrate that higher concentrations of cations (Na⁺), rather than OH, exert the main promotional effect on the production of C_{2+} products by systematically varying the concentration of Na⁺ and OH at identical absolute electrode potential. The impact of the nature and the concentration of cations on the electrochemical reduction of CO is supported by experiments in which a fraction or all of Na⁺ is chelated by a crown ether. Chelation of Na⁺ leads to drastic decrease in the formation rate of C_{2+} products. The promotional effect of OH determined at the same potential on the reversible hydrogen electrode scale is likely caused by larger overpotentials at higher electrolyte pH.

Introduction

The electroreduction of CO₂ to energy-dense products in aqueous solution is an attractive strategy to store the intermittent renewable electricity in a sustainable fashion^[1]. A near-neutral electrolyte is typically employed to conduct CO₂ electrolysis because (a) CO₂ reacts with alkaline solution, and (b) many active catalysts are thermodynamically not stable in acidic environment^[2]. However, the use of near-neutral electrolyte poses great challenges in achieving high energy efficiency in commercial CO2 electrolyzers (e.g., in a membrane electrode assembly configuration) due to the current lack of a highperformance membrane and anode material, i.e., electrocatalyst for the oxygen evolution reaction (OER), at neutral pH^[3]. The microfluidic flow cell developed by Kenis' group^[4], as well as more recent advancements reported by others^[5], enables the usage of alkaline electrolyte for CO₂ electrolysis, in which the gas-phase CO₂ is not directly purged into the electrolyte but is in contact with the electrolyte at the catalyst surface, i.e., tripe-phase-boundary^{[4a,} ^{5b, 6]}. This configuration effectively extends the pH range of the electrolyte for CO₂ electrolysis and also greatly enhances the reaction rate by improving the mass transport^[4-5].

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Adapting this flow cell configuration, a recent study reports that the C₂ product formation in CO₂ electrolysis using Cu catalyst can be significantly improved by using a more concentrated alkaline electrolyte^[5a]. A similar phenomenon is also observed in the electroreduction of CO^[7], a reduction reaction that is believed to share the same pathway as CO₂ electroreduction after CO₂ is converted to the surface adsorbed CO (CO_{ads})^[8]. While these results seem to suggest a quite feasible way to promote CO2 electroreduction towards more valuable products, i.e., to increase the electrolyte pH, major inconsistencies exist between this hypothesis and the current mechanistic understanding of the formation of C2+ products^[8e, 9]. As revealed by recent experimental and computational investigations, the rate determining step (RDS) of C2+ product formation is the dimerization of two COads through Langmuir-Hinshelwood process which does not include a proton transfer^[9a, 9b]. Thus, the C₂₊ product formation rate is not expected to show such a strong dependence on the electrolyte pH.

The increase of alkaline electrolyte concentration does not merely increase the concentration of hydroxide, but also the concentration of the balancing cations, which also could impact the electrode-mediated reactions. Although the cation effect in electrocatalysis has been reported recently^[10], molecular pathways through which cations exert impact remain debated. According to the classical Gouy-Chapman-Stern (GCS) model, cations reside at the outer Helmholtz plane (OHP) and the diffuse layer^[11]. Thus, a higher cation concentration of cations in the electrolyte could increase the density of cations at the OHP, which may induce a stronger electrostatic field at the interface^[10a, 10d]. Strong field has recently been proposed to stabilize the key intermediate of CO₂ electroreduction and lower the energy barrier of C₂ products formation^[10d]. However, recent work from Koper and co-workers show, at least in a specific case, the strength of electrostatic field does not change with the concentration of protons^[12]. Thus, the classical picture could be too simplistic to describe the complexity of the electrochemical interface. In addition, the formation rate of C₂₊ products at different electrolyte pH should be compared at potentials referenced to the standard hydrogen electrode (SHE) instead of the reversible hydrogen electrode (RHE) because the RDS does not include any proton transfer^[8e, 9]. Otherwise the reactions performed at a higher electrolyte pH are actually subjected to a larger overpotential by $\Delta pH \times 59 \text{ mV}$ at room temperature, i.e., 2.3kT ΔpH , which would lead to an increase in the reaction rate. Thus, systematic investigations are highly desired to deconvolute the influence of the electrolyte pH, the concentration of cations and the reference scale with which overpotentials are calculated on the formation rate of C₂₊ products in CO₂ electroreduction.

Mechanistic studies of CO_2 electroreduction in an aqueous electrolyte is challenging because the multitude of chemical equilibria among CO_2 , hydroxide, bicarbonate and carbonate

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make the isolation of roles of any specific ion in the reaction difficult and in many cases lead to contradictory conclusions^[13]. The electrochemical CO reduction reaction (CORR) is more straightforward because CO does not participate in any electrolyte reactions. The CORR is generally believed to share the same reaction pathways and the RDS as the electroreduction CO₂ reduction reaction (CO₂RR) on Cu surfaces^[8], making it a more appropriate probe reaction for mechanistic investigations. Using polycrystalline Cu foil electrodes, Wang et al. performed reactivity studies of CORR with an electrolyte pH of 7 and 13, respectively, and reported that the onset potentials for C_{2+} products were similar^[8c]. To rationalize these experimental data, Liu et al. performed computational studies using a microkinetic model to obtain further insights into the formation of C₂ products^[8d]. However, the experimental results could be convoluted by the sluggish mass-transport in their system due to the low solubility of CO (~ 1 mM), making the kinetic analysis different than those obtained in systems without mass-transport limitations^[9a, 9b]. Herein, we use our recently developed polycrystalline Cu electrode that employs a gas diffusion mechanism in a standard three-electrode H-cell^[9b] to systematically investigate the C₂₊ product formation in (a) electrolytes with an equal amount of hydroxide and different amounts of cations and (b) electrolyte with different amounts of hydroxide and an equal amount of cations at both the RHE and the SHE scales. We demonstrate that the increase in concentration of Na⁺, rather than OH⁻, promotes the formation rate of C2+ products when the CORR is conducted at the same absolute potential.

Results and Discussion

Differentiating the Impact from Hydroxide and Cation on CORR. Reactivity studies based on the linear sweep voltammetry (LSV) curves (Supporting Information, Figure S3) and chronoamperometry measurements on the RHE scale show that the CORR rate increases with the Na⁺ concentration and the alkalinity of electrolytes. The CORR rate on micron-size Cu particles supported on carbon paper at -0.7 V_{RHE} increases almost linearly with the concentration of NaOH in the electrolyte from 0.1 to 0.5 M, and then more gradually when the NaOH concentration increases to 1 M (blue trace in Figure 1; Supporting Information, Figure S4). An approximately 3-fold increase in the total current density for the CORR (*j*CORR) is observed as NaOH concentration is increased from 0.1 M to 1 M. The change in the resistance of the electrolyte at different ion strengths has been accounted for in the reactivity studies. This is consistent with several literature reports that CORR is more favored at higher electrolyte pH^[7, 8d]. To isolate the impact of the concentration of Na⁺ on the CORR, reactivity studies are also performed on the same catalyst and potential in 0.1 M NaOH + (x-0.1) M NaClO₄ electrolyte (x = 0.1, 0.25, 0.5, 0.75, 1; Supporting Information, Figure S5). NaClO₄ is selected for matching the cation concentration because the CIO4anion does not change the electrolyte pH and is known not to adsorb on the electrode surface^[13a, 14]. Further, the high solubility of NaClO₄ in water (17.1 M at room temperature) affords a wide range of Na⁺ concentration. *j*corr increases roughly linearly with the concentration of Na⁺ from 0.1 to 1 M at the same pH of 13.1. However, the increase (ca. 2-fold) is less drastic than its counterpart in pure NaOH electrolytes. Importantly, j_{CORR} is consistently lower in the less alkaline electrolyte with the same Na⁺ concentration, which again appears to indicate the positive effect of the higher OH⁻ concentration on the CORR performance.



Figure 1. CO electroreduction in various electrolytes. Partial current density of the CORR in a series of *x* M NaOH electrolyte (x = 0.1, 0.25, 0.5, 0.75, 1) and 0.1 M NaOH + (x - 0.1) M NaClO₄ electrolyte at -0.7 V_{RHE}. The error bars represent the standard deviation from at least three independent measurements.

Comparing the rate of C₂₊ products in the CORR at the same absolute potential, i.e., on the SHE scale, reveals that the concentration of Na⁺, rather than OH⁻, plays the dominant role in promoting the reactivity. At -0.7 V_{RHE} , the formation rates for all $C_{2^{+}}$ products are clearly enhanced by the higher Na^{+} concentration when x increases from 0 to 0.9 in 0.1 M NaOH + xM NaClO₄ (Figure 2 a), indicating a promotional effect of the cation. Again, the increase is more pronounced in 1 M NaOH than that in 0.1 M NaOH + 0.9 M NaClO₄, which seems to imply that the cation concentration is not solely responsible for the increase of the formation rate of C2+ products in more concentrated alkaline electrolytes. Recent reports have shown that the rate determining step (RDS) is the formation of C2+ products is the C-C coupling of adsorbed CO on Cu,^[9a, 9b] which is independent of the H⁺ or OH⁻ concentration. Thus, the choice of comparing the cation effect in the formation of C2+ product in the CORR at different pH with the identical potential on the RHE scale is not justified, because the driving force in the C-C coupling chemistry is the absolute potential of the electrode. Strikingly, formation rates for all C2+ products are nearly identical at the same absolute potential (-1.47 V vs. SHE) with 1 M of Na⁺ regardless of the OH⁻ concentration in the electrolyte (Figure 2 a). Similar results are obtained at intermediate concentrations of NaClO₄, i.e., x = 0.1 and 0.4, in the NaOH + xM NaClO₄ electrolyte when comparing with the pure NaOH electrolyte with the identical Na⁺ concentration (Supporting



Figure 2. CO electroreduction potential at SHE scale. Partial current densities of $C_{2^{+}}$ products, including ethylene, acetate, ethanol, acetate and n-propanol. a) Comparison of CO electroreduction conducted in 0.1 M NaOH, 0.1 M NaOH + 0.9 M NaClO₄ and 1 M NaOH, respectively. The reference potentials are chosen to be the same in RHE scale (-0.7 V_{RHE}) and SHE scale (-1.47 V_{SHE}), separately. b) Hydroxide ion concentration dependence with a fixed 1.0 M cation concentration at -1.5 V_{SHE}. The error bars represent the standard deviation from at least three independent measurements.

Information, Figures S6 and S7). These results strongly indicate that the improvement of C_{2+} product formation in concentrated alkaline electrolytes could be largely, if not completely, attributed to the high concentration of cations rather than OH⁻.

To confirm the decisive role of the Na⁺ concentration in the formation of C₂₊ products, reactivity studies are conducted at the identical Na⁺ concentration (1 M) while systematically varying the OH⁻ concentration in a series of xM NaOH + (1-x)M NaClO₄ electrolytes (x = 0.1, 0.25, 0.5, 0.75, and 1) . At -1.5 V_{SHE}, all C₂₊ products exhibit nearly identical formation rates as the electrolyte [OH⁻] is increased from 0.1 to 1 M (Figure 2 b; Supporting Information, Figure S8), which provides further evidence that hydroxide has a very weak, if at all, promotional effect on the formation of C₂₊ products in the CORR. In contrast, the formation rates of methane and hydrogen do increase quite substantially with the increase of either Na⁺ or OH⁻ concentration (Figure 3). The RDS of CH₄ formation the has been confirmed to

uncompensated electrolytes (Figure 3 a-c).

Impact of Cation Chelation by Crown Ether on CORR. The impact of Na⁺ on the formation of C₂₊ products in the CORR is further highlighted by its systematic removal through chelation with a crown ether while maintaining the OH- concentration in the electrolyte. 15-Crown-5 is a crown ether known to effectively and completely chelate an equimolar Na⁺ to form a bulky organic cation^[17], referred to as C-Na⁺ in this work, which is employed to change the nature of the cation in the electrolyte (Figure 4 a). jcorr in 1 M NaOH at -1.53 V_{SHE} (or -0.7 V_{RHE}) decreases substantially with the increase of the fraction of Na⁺ in the electrolyte chelated to C-Na⁺, from 16.6 mA/cm² without adding any crown ether to 4.1 mA/cm² with all Na⁺ chelated to C-Na⁺ (Figure 4 b). Further, the FE for C₂₊ products decreases from 62.3 % to 31.3 % with the increasing fraction of Na⁺ chelated. It is worth noting that the potential on neither the SHE or the RHE does not change when the increasing amount crown introduced to the electrolyte, as the OH⁻ concentration is not affected by the



Figure 3. pH dependence of CH₄ and H₂ formation rate. Partial current densities of hydrogen and methane production in 0.1 M NaOH, 0.1 M NaOH + x M NaClO₄ and 0.1 + x M NaOH electrolyte (x = 0.9 a), 0.4 b) and 0.1 c)) at -0.7 V_{RHE}. The error bars represent the standard deviation from at least three independent measurements.

be the hydrogenation of CO_{ads} by H_{ads} through a Langmuir– Hinshelwood type mechanism^[9a, 9b], and thus rate comparison at chelation. This demonstrates that the nature of cations could have a major impact on the reactivity and selectivity for electrode

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at

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NaOH

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different

the identical potential on the

electrolyte pH. The promotion

of CH₄ and H₂ production is likely due to the increase of hydrogen binding energy (HBE) at higher electrolyte $pH^{[15]}$. The increased binding

of Hads on Cu surface can

improve the energy barrier of

the RDS of CH4 formation and

provide more optimal HBE for

HER^[16]. At -0.7 V_{RHE} , the

electrolyte shows a clearly

higher CH₄ formation rate

than those in both cation

scale

RHE

appropriate

concentrated

compensated



Figure 4. Cation chelation with crown ether. a) A schematic shows the decrease of cations in OHP due to the chelation of 15-Crown-5. IHP and OHP represent inner Helmholtz plane and outer Helmholtz plane, respectively. b) CO electroreduction current densities and Faradaic efficiencies compared at 1 M NaOH electrolyte chelated with different amount of 15-Crown-5 at -0.7 VRHE/-1.53 VSHE. c) CO electroreduction current densities and Faradaic efficiencies compared in 0.5 M NaOH and in 1 M NaOH chelated with 0.5 M 15-Crown-5 at -1.53 V_{SHE}. The error bars represent the standard deviation from at least two independent measurements.

surface mediated reactions. This is consistent with previous reports showing that different alkali metal cations lead to significantly different rates and product distributions in CO₂RR^{[10b,} ^{10d]}. C-Na⁺ is much bulkier than Na⁺, and thus not expect to get as close to the electrode surface as Na⁺. This is confirmed by the reduced Stark tuning rate of the adsorbed CO on polycrystalline Cu from 34 cm⁻¹/V in 0.1 M NaOH to 25 cm⁻¹/V in 0.1 M C-NaOH determined with attenuated total reflectance surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) (Supporting Information, Figure S9). A lower Stark tuning rate within the Gouy-Chapman-Stern (GCS) model suggests that the distance between the outer Helmholtz plane (OHP) and the electrode surface is larger, presumably due to the larger cation size of C-Na⁺ as compared to Na+[18]. It is worth noting that the presence of 0.5 M of C-Na⁺ in the presence of 0.5 M of free Na⁺ still exerts a major impact on the reactions occurring on the electrode surface (Figure 4 c), with *j*corr being only roughly half as much in 1 M NaOH with 50% of Na⁺ chelated into C-Na⁺ as in 0.5 M NaOH (Figure 4 c). The FE for C_{2+} products is also lower than the latter by 20.6 %. This suggests the bulkier C-Na⁺ still have access to and impact the surface mediated reactions.

Potential Pathways for Cations to Affect Surface Mediated CORR. Although multiple mechanisms through with cations could influence the electrode surface mediated reactions have been proposed in the literature, results presented in this work highlight the drastic impact and complexity of the cation effect in electrocatalysis. Site blocking during specific adsorption of ions

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has been demonstrated by anions^[11, 19], but no direct experimental evidence has been reported for specific cation adsorption^[11, 19-20]. Janik and Koper claimed specific adsorption of alkali cations on Pt in the potential range relevant for the underpotential deposited H based on indirect evidence from cyclic voltammetric and computational

investigations^[21]. However, cation specific adsorption is unlikely in the present case. Na⁺ should be preferred in the specific adsorption, if it occurs at all, over C-Na⁺ due to its bulkiness. Thus, no change in the CORR rate and product distribution are expected with C-Na⁺ in addition to Na⁺ if specific adsorption is responsible for the cation effect. This is in contradiction to the data presented in Figure 4 c. We note that the lack of specific adsorption of C-Na⁺ is confirmed by the lack of Stark tuning of any bands Manuscr cepted

associated with the crown ether (Supporting Information, Figure S10). Another commonly invoked mechanism to explain the cation effect is modification of the interfacial electric field due to the different cation sizes^[10a, 10d, 18]. However, we do not observe any detectable change in the Stark tuning rate in adsorbed CO on Cu in the Na⁺ concentration range of 0.1 to 1 M (30-33 cm⁻¹/V; Supporting Information, Figure S11). The lack of change in the Stark tuning rate of adsorbed CO on Pt at different pH values, i.e., H⁺ concentrations, has been reported recently by Koper and coworkers^[12]. This is likely because that the concentration of cations in neither the bulk nor the diffuse layer has any significant impact on the Helmholtz capacitance, as suggested by a recent computational study^[10a]. The average electric field between the OHP and the electrode surface within the framework of the GCS model does not change appreciably in the Na⁺ concentration range investigated in this work, and thus cannot explain the enhanced production of C2+ products in the CORR at higher Na+ concentrations. Modified local electric field, as suggested by Bell and coworkers^[10a, 10d], at higher cation concentrations could lead to higher densities of "hot spots" that favor the formation of C2+ products. Another possibility is that interfacial water structure is modified at higher concentrations of cations^[18, 22], which could facilitate the C-C coupling pathway by better solvating the transition state complex. We stress that these speculative rationalizations of the cation effect highlight the gap in the molecular level understanding how the nature and concentration of cations impact surface-mediated electrocatalytic reactions. 4

Conclusion

By comparing the formation rate of C_{2+} products in two sets of CORR experiments in electrolytes containing (a) an identical concentration of OH⁻ and varying concentrations of Na⁺; and (b) varying concentrations of OH- and an identical concentration of Na⁺ by controlling the electrode potential at both the RHE and the SHE scales, we show that higher concentrations of Na⁺, rather than that of OH^{-} , promote the formation of C_{2+} products in the CORR on Cu. Although this conclusion goes against a common assumption made in the CO2RR and CORR community, it is reasonable upon close consideration and in light of recent mechanistic insights. The identification of the coupling of two adsorbed CO as the RDS entails the overpotential should be referenced to the absolute potential, rather than on the RHE scale. Concentrations cations and anions (OH-) in the same type of electrolyte are always varied together. Thus, the modified reactivity results at different electrolyte concentrations could be attributed to either the effect of cations or anions, unless experiments, such as those described in this work, are specifically designed to delineate the effect of cations and anions.

It should be noted that highly alkaline electrolytes could be beneficial in improving the performance of CO_2 or COelectroreduction at the device level due to engineering considerations, because the current ion-exchange membrane and OER catalysts favor alkaline over neutral conditions. In addition, higher pH environment could reduce the required voltage in full cell operations because the equilibrium potential of the OER would shift to less positive values but the C-C coupling chemistry will be unaffected.

Experimental Section

Methods: Details of experimental methods are provided in the Supporting Information.

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Conflict of interest

The authors declare no conflict of interest

Keywords: CO₂ reduction • copper • electrochemistry • energy conversion • solar fuels

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RESEARCH ARTICLE

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The nature and concentrations of cations have drastic impact on the electroreduction of CO. The experimental measurements by systematically varying the concentration of Na⁺ and OH⁻ revealed that higher concentrations of cations (Na⁺), rather than OH⁻, exert the main promotional effect on the production of C²⁺ products at identical absolute electrode potential.



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Hydroxide is not a promoter of C_{2+} products formation in electrochemical reduction of CO on Copper