

Activity and Selectivity Control in CO₂ Electroreduction to Multicarbon Products over CuO_x Catalysts via Electrolyte Design

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ABSTRACT

CO₂ electroreduction reaction (CO₂RR) to chemicals and fuels is of both fundamental and practical significance since it would lead to a more efficient storage of renewable energy while closing the carbon cycle. Here we report enhanced activity and selectivity for CO₂RR to multicarbon hydrocarbons and alcohols (~69 % Faradaic efficiency and -45.5 mA cm⁻² partial current density for C₂₊ at -1.0 V vs RHE) over O₂-plasma-activated Cu catalysts via electrolyte design. Increasing the size of the alkali metal cations in the electrolyte, in combination with the presence of subsurface oxygen species which favor their adsorption, significantly improved C-C coupling on CuO_x electrodes. The co-existence of Cs⁺ and I⁻ induced drastic restructuring of the CuO_x surface, the formation of shaped particles containing stable CuI species, and a more favorable stabilization of the reaction intermediates and concomitant high C₂₊ selectivity. This work combining both experiment and density functional theory, provides insights into the active sites and reaction mechanism of oxide-derived Cu catalysts for CO₂RR.

KEYWORDS

CO₂ electroreduction, CuO_x catalysts, electrolyte design, cation adsorption, subsurface oxygen

1. INTRODUCTION

The production of chemicals and fuels from the electroreduction of CO₂ (CO₂RR) has attracted great attention, since it can help to close the anthropogenic carbon cycle and contribute to a more efficient storage of renewable energy.¹⁻³ In particular, the generation of multicarbon alcohol and hydrocarbon products (C₂₊) over Cu catalysts is highly desirable in order to access liquid fuels and chemicals with high energy density.⁴⁻⁶ In order to overcome the high overpotential, low C₂₊ selectivity and poor stability of polycrystalline Cu,^{7,8} various catalyst design and preparation strategies, including nanostructuring, oxidation pretreatments, or the synthesis of size- and shape-controlled nanoparticles (NPs), modifying Cu with a second component, have been employed.⁹⁻²⁸

Apart from the structure and electronic properties of the catalysts, the activity and selectivity are also closely related to the composition and nature of the electrolyte. Bicarbonate can facilitate CO₂RR by increasing the CO₂ concentration near the electrode surface through a rapid equilibrium with dissolved CO₂.^{29,30} Adding halides to the bicarbonate electrolyte may further improve CO₂RR by facilitating the stabilization of the carboxyl intermediate.³¹⁻³³ Electrolytes containing larger alkali metal cations resulted in improved C₂₊ formation on metallic Cu foils as well as on Cu(100) and Cu(111) surfaces.³⁴⁻³⁶ The dependence of the product distribution on the cation type was attributed to either a distinct specific adsorption, preferential hydrolysis, or to an electrostatic interaction between solvated cations and adsorbed species in the outer Helmholtz plane (OHP).³⁴⁻³⁷

Plasma activated Cu catalysts have shown vastly improved activity and C₂₊ selectivity, due to their enhanced roughness and the presence of subsurface oxygen and Cu⁺ species during the reaction.^{13,16} Compared to a metallic Cu catalyst, O₂-plasma-oxidized Cu catalysts were found to be much more sensitive to the electrolyte composition, such as the presence of halides.^{31,32} In this work we investigate the synergistic effect of alkali metal cations and halide ions on CO₂RR to multicarbon products over plasma-oxidized Cu catalysts. It has been observed that increasing the cation size significantly improved the activity and C₂₊ selectivity. Density functional theory (DFT) calculations indicate that the more favorable adsorption of larger cations on CuO_x results in the stabilization of CO₂RR intermediates leading to C₂₊ formation. The C₂₊ production was further increased by adding I⁻ to the CsHCO₃ solution, probably due to a significant surface restructuring, improved stability of Cu⁺ species under reaction conditions, and the stronger binding of CO.

2. RESULTS AND DISCUSSION

2.1. Electrolyte-driven nanostructuring. Plasma-activated Cu catalysts were synthesized by treating an electropolished Cu foil (EP) with low-pressure O₂ plasma.¹³ Figures 1 and S1 show scanning electron microscope (SEM) images acquired on O₂-plasma treated Cu foils (O2P2, 20W 2min) after 30 min immersion (without an applied potential) and after 1 h of CO₂RR at -1.0 V vs RHE in the corresponding electrolytes (see sample preparation conditions and electrolyte description in Table S1). The different cations did not obviously change the morphology of the CuO_x foils (O2P2-Li,Na,K,Cs) both, before and after CO₂RR, as well as the amount of oxygen (4-5 at%) detected by energy-dispersive X-ray spectroscopy (EDX) after

CO₂RR (Table S2). However, the presence of CsI induced the formation of Cu_xO_yI_z (x:y:z = 46:12:42 at%) crystals with sizes of 1-3 μm even at open circuit potential. After CO₂RR, shaped Cu_xO_yI_z (x:y:z = 67:6:27 at%) particles with sizes of 0.5-0.8 μm were still present on the surface of O2P2-CsI, surrounded by other rough regions mainly composed of metallic Cu. This is in clear contrast with our previous findings on samples exclusively treated in KI (O2P2-KI),³¹ where shaped particles were not observed after reaction (Figure S1i). The latter suggests that Cs⁺ is able to stabilize CuI species at very negative potentials, which could lead to more Cu⁺ species during the reaction.

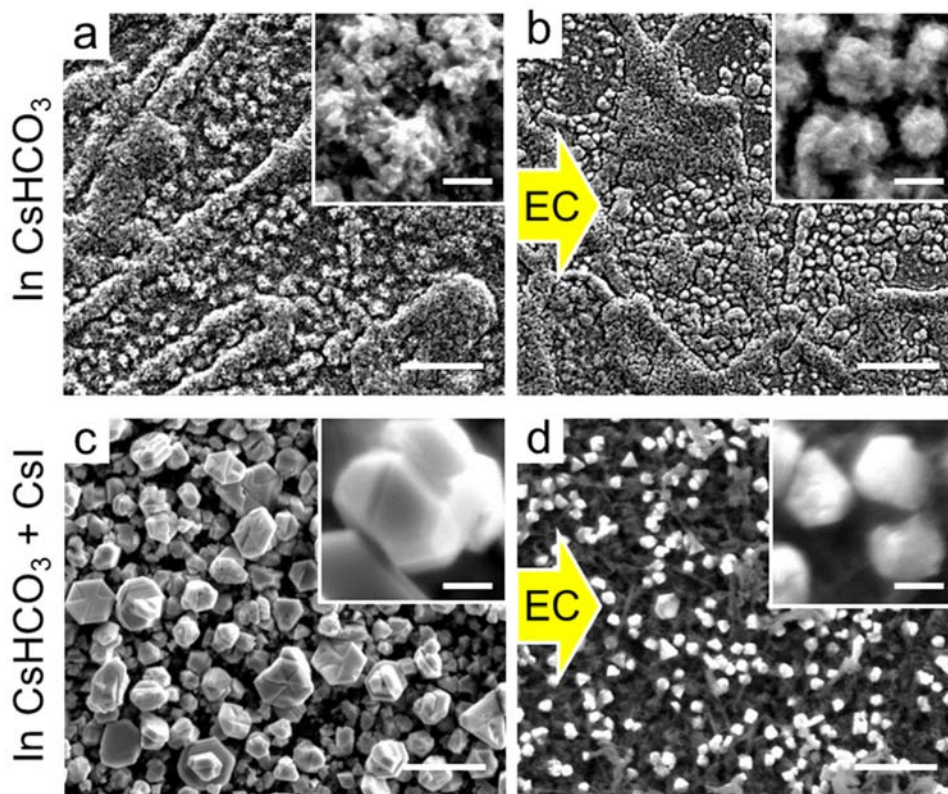


Figure 1. SEM images acquired on O2P2 samples after 30 min immersion in 0.1 M CsHCO₃ (O2P2-Cs, a) and 0.1 M CsHCO₃ + 0.1 M CsI (O2P2-CsI, c) solutions. Images acquired after 1 h

of CO₂RR at -1.0 V vs RHE are also shown (b,d). The scale bars in the main images and inserts are $5\ \mu\text{m}$ and $500\ \text{nm}$, respectively.

In order to understand the binding thermodynamics of the key intermediate CO, temperature programmed desorption (TPD) of CO was conducted. The O₂-plasma treatment conditions strongly affected the surface structure, density and type of defects in the pristine O₂-plasma-activated Cu samples (Figure 2a). Apart from the low temperature desorption feature at $125\ \text{K}$, O2P2 showed two CO desorption features at 172 and $213\ \text{K}$, corresponding to binding energies of 10.8 and $13.5\ \text{kcal mol}^{-1}$ following a first-order Redhead model.³⁸ When compared to the O₂ 100W 10min plasma treated Cu foil (O2P10) and the electropolished Cu foil (EP), the presence of stronger CO binding sites on O2P2, such as defects or low-coordinated sites at stepped facets is evident.¹² Remarkably, the dependence of the CO binding energy on the O₂-plasma treatment conditions directly correlated with the ethylene selectivity.¹³ The CO-binding sites on O2P2 were also investigated before CO₂RR after a sample pre-treatment in different electrolytes (Figure 2b). Although the strongest CO-binding sites observed in the clean O2P2 sample were lost in the O2P2-Cs (missing peaks at 172 and $213\ \text{K}$), such sites are recovered upon subsequent sample restructuring with I⁻ ($228\ \text{K}$ peak for O2P2-KI and O2P2-CsI). This reveals that the shaped-Cu crystals formed on the later samples act as strong CO-binding sites.

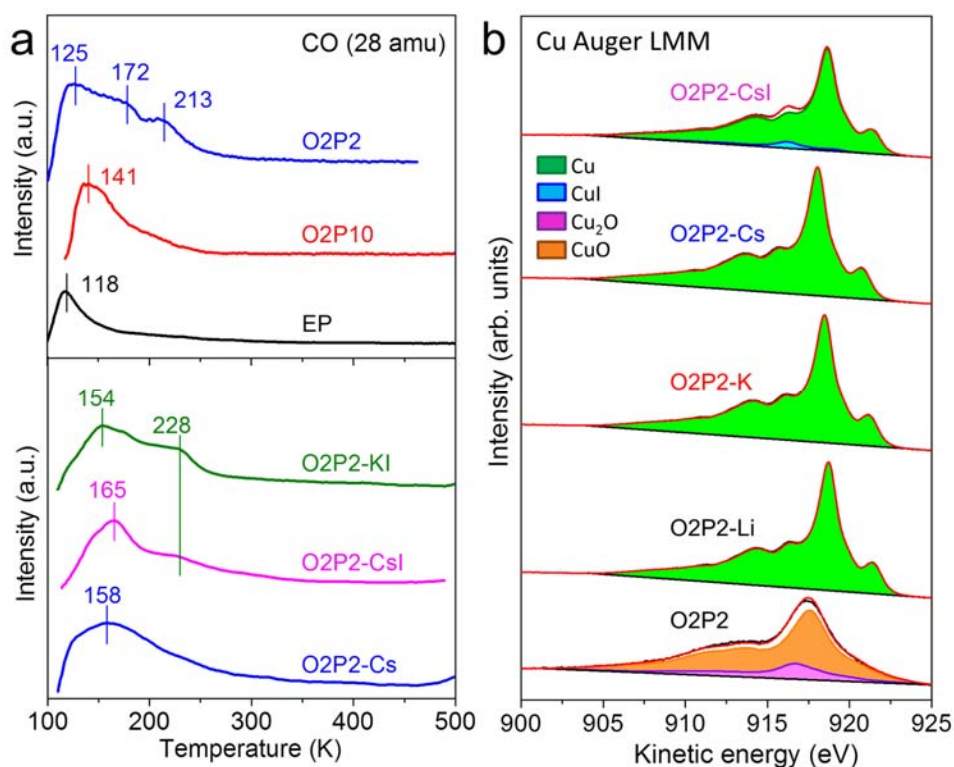


Figure 2. (a) (Top) CO TPD profiles of pristine O₂-plasma-activated (20 W 2 min (O2P2) and 100 W 10 min (O2P10)) Cu foils as well as an electropolished (EP) Cu foil. (Bottom) O2P2 pretreated in different electrolytes containing KI, CsI and Cs. (b) *Quasi in situ* Cu Auger LMM spectra of O2P2 after 1 h of CO₂RR at -1.0 V vs RHE in different electrolytes containing CsI, Cs, K, and Li, as well as the pristine O2P2.

Quasi in situ X-ray photoelectron spectroscopy (XPS) is an efficient surface-sensitive technique to detect the oxidation state of electrocatalysts at different reaction stages without exposure to air.³¹ Consistent with EDX measurements, the surface of the as prepared O2P2 sample was composed by a mixture of Cu₂O and CuO. After the reaction, CuO_x in the O2P2 sample was mostly reduced, with only metallic Cu detected on the surface of samples O2P2-Li, O2P2-Na, O2P2-K, O2P2-Cs, and ~8% Cu⁺ species on O2P2-CsI. By analyzing the I-3d and O-

1s spectra (Figure S2) we confirmed that most of the Cu^+ species detected after CO_2RR exist in the form of CuI . The surface Cu^+ species resistant to reduction under CO_2RR potentials could be stabilized by the adsorbed iodine ions as well as the subsurface oxygen and Cu^+ species^{13,39–43} in the oxide-derived Cu catalysts.

2.2. CO_2 electroreduction performance. The current densities over O_2 -plasma-activated Cu showed a strong dependence on the alkali metal cation size in the order of $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ (Figure 3a), and are much higher than those obtained for electropolished metallic Cu.³⁴ The increased activity on oxidized Cu foils over metallic ones was previously attributed to the increased roughness, defects, and the presence of Cu^+ species or subsurface oxygen species.^{12,13,16,39,42,44–46} Double-layer capacitance measurements (Figure S3) indicated similar roughness of the samples after treatments in distinct MHCO_3 . The activity reported was further corroborated when current densities normalized by the electrochemical surface area (ECSA) were considered,¹² Figure S4. Therefore, the activity difference is not caused by a structural change of the catalysts, but by a chemical effect derived from the nature of the cations. We further optimized the electrolyte by using 0.1 M CsHCO_3 + 0.1 M CsI . The presence of I^- significantly increased the current density, mainly attributed to the strong specific adsorption of I^- and the concomitant increased roughness.^{31,47} Moreover, a higher content of Cu^+ was stabilized during CO_2RR due to the I^- -induced Cu nanostructuring. The increased current density in the presence of $\text{Cs}^+ + \text{I}^-$ over $\text{K}^+ + \text{I}^-$ further verified the stronger promoting effect of larger cations on CO_2RR .

Figures 3b and S5 show the potential-dependent Faradaic efficiencies (FEs) of CO_2RR products. Higher C_2^+ FEs (~69% on O2P2-Cs at -1.0 V vs RHE, Figures 3b and S6) were observed in the presence of Cs^+ , especially on the O2P2-CsI sample at lower overpotentials (see

also C_{2+}/C_1 FE ratio in Figure S7). With increasing the cation size, the partial current densities of C_{2+} products were remarkably increased, while the formation of methane and CO was significantly suppressed (Figures 3c-f and S8), demonstrating that larger cations facilitate C-C coupling versus C_1 pathways (CO desorption or further hydrogenation to methane). The additionally increased C_{2+} production when Cs^+ and I^- were both present in the electrolyte is likely related to the observed stabilization of shaped particles with high amount of Cu^+ species, as well as to the stronger CO binding sites available on the CuO_x foil after $Cs^+ + I^-$ exposure, which have been shown to facilitate C-C coupling (Figure S9).¹² With increasing cation size and the presence of I^- , the competitive H_2 partial current density was also found to increase, while the H_2 FE did not obviously change at more negative potentials and seemed to be independent of the cation size. Therefore, the cation effect on the competitive hydrogen evolution reaction observed here for CuO_x catalysts was different from that observed on metallic Cu.^{34,36} Our O_2 -plasma-activated Cu catalyst, with both, high C_{2+} FE and high partial current density (-45.5 mA cm^{-2} on O2P2-CsI, Figure S10), exhibits superior ability for C_{2+} production compared to previously reported catalysts (Table S3).

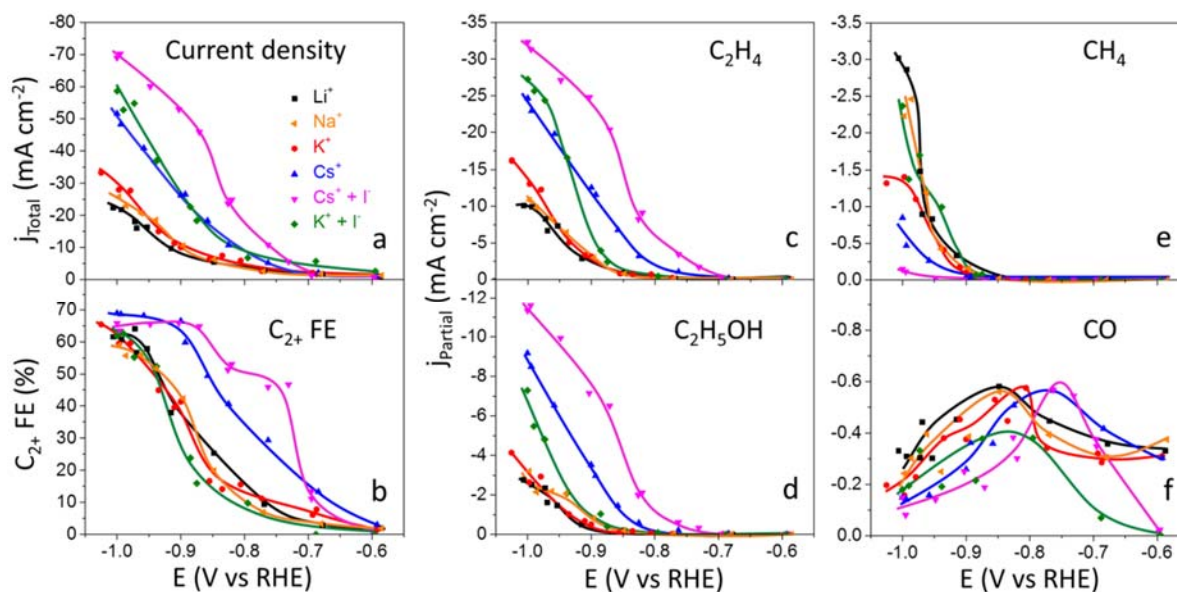


Figure 3. (a) Geometric current densities, (b) total FEs of C_{2+} products, and partial current densities of (c) C_2H_4 , (d) C_2H_5OH , (e) CH_4 and (f) CO as a function of applied potential for O2P2 measured in different electrolytes after 1 h of CO_2RR . Solid lines are guides for the eye.

2.3. The effect of cations on the stability. The effect of alkali metal cation on the stability of the O_2 -plasma-activated Cu catalysts during CO_2RR was studied at -1.0 V vs RHE in 0.1 M $MHCO_3$ solutions, as shown in Figure 4. Ethylene FE of O2P2-Li drastically decreased to $\sim 35\%$ while methane FE increased to $\sim 14\%$ in the first 7 h. Similar trend was also observed on O2P2-Na. However, the deactivation became much slower on O2P2-K and O2P2-Cs. Ethylene FE of both O2P2-K and O2P2-Cs was nearly stable ($>45\%$) in the first 20 h, while methane FE slightly increased to $\sim 6\%$ on O2P2-K and O2P2-Cs. The long-term stability tests indicated the superior effect of larger cations on the stable C_{2+} formation. The slow time-dependent decrease in current density and ethylene/methane FE ratio in all electrolytes are not dominated by the nature of the cations, but are likely due to the sluggish removal of subsurface oxygen species at very negative

potentials for CO₂ reduction as well as to the gradual decrease in the roughness of the sample (roughness factor = 24.7 after 1 h *versus* 11.5 after 30 h in 0.1 M KHCO₃) and associated decrease in the content of strong CO-binding sites in the course of the reaction.

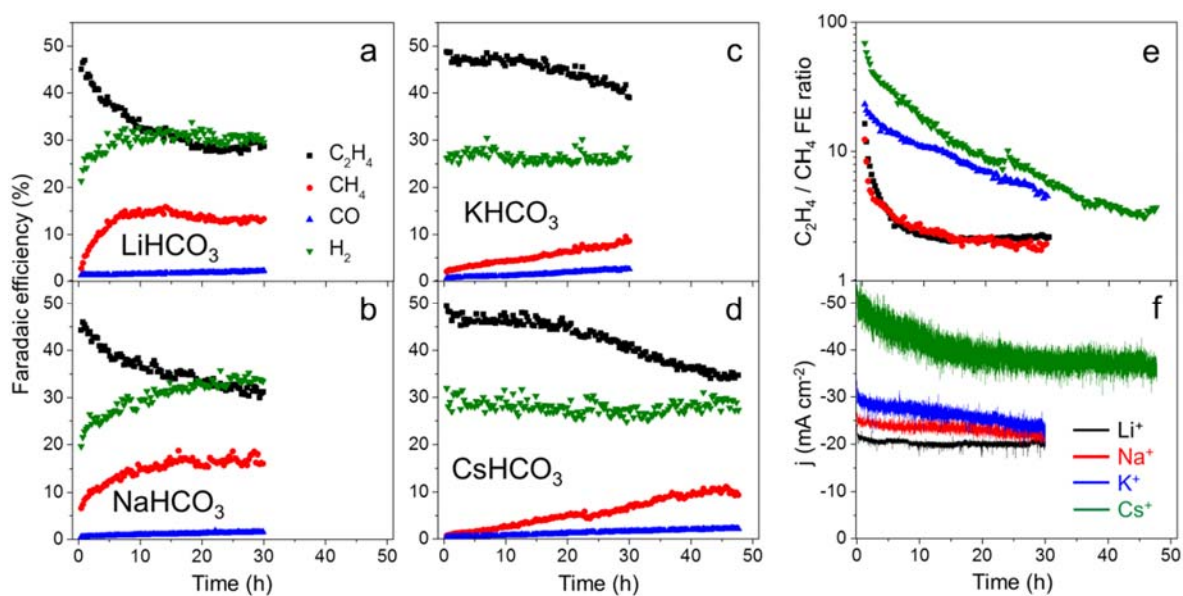


Figure 4. Time-dependent FEs of major gas products at -1.0 V vs RHE in 0.1 M LiHCO₃ (a), 0.1 M NaHCO₃ (b), 0.1 M KHCO₃ (c), and 0.1 M CsHCO₃ (d) solutions. Time-dependent FE ratios of ethylene/methane (e) and current densities (f) in (a-d).

2.4. C-C coupling tuned by specific cation adsorption. DFT calculations were used to examine the specific adsorption of Li, Na, K, and Cs onto Cu(111), Cu(100), and Cu(211) at low (1/9 ML) coverage (Figure 5a). The near-surface region was solvated with 6H₂O* on all three surfaces (forming a water bilayer) to approximate the solvent near the electrode surface (Figure S11). All cations adsorb favorably on Cu(111) and Cu(100) below -1 V_{NHE} and on Cu(211) below -1.5 V_{NHE}, therefore, specific adsorption is favorable at moderate CO₂RR overpotentials.

As the alkali metal cations retain most of their charge on adsorption, the presence of near-surface solvation significantly promotes adsorption (Figure S12). We examined the interaction between the adsorbed cations and reaction intermediates by considering CO*, OCCO*, and OCCOH* intermediates which dictate C₂₊ formation on Cu(100).⁴⁸ We have focused on Cu(100) as it has been shown experimentally to be the most active low-index facet for C₂₊ formation and may dominate the measured selectivity.^{49–52} Figure 4b shows that all the cations promote the formation of CO*, OCCO*, and OCCOH*. The presence of a near-surface electric field, either artificially applied, or due to the presence of a solvated alkali metal cations in the OHP³⁶ or adsorbed on the surface,^{35,48} promotes the formation of polar or highly polarizable intermediates. The formation rate of C₂ products is proportional to the CO* coverage squared, while the C₁ formation rate is only linearly proportional to the CO* coverage. We, therefore, expect that the promotion of CO* adsorption would lead to greater C-C coupling and higher C₂₊ selectivity, further accentuated by promotion of the adsorption strength of the OCCO* and OCCOH* intermediates.

In contrast to what others have found previously with cations only populating the OHP,³⁶ we find that the effect of the specifically adsorbed cations on the formation of CO*, OCCO*, and OCCOH* is dependent on the cation identity. This may be due to their closer position to these intermediates when adsorbed on the surface (average ion-surface distance: 3.6 Å on Cu(100) with 6H₂O*), relative to only occupying the OHP (average ion-surface distance: 5.1 Å on Cu(111)³⁶). The magnitude of the interaction between these cations and the intermediates correlates with the surface normal dipole moment generated on cation specific adsorption (Figure S13), with adsorbed Cs generating the strongest dipole moment and largest interaction with CO*, OCCO*, and OCCOH*. This matches the experimental trend in the C₂₊ formation, where the

more favorable CO* formation in the presence of Cs⁺ results in a higher C₂₊ production rate in the Cs-containing electrolyte at lower overpotentials. Further, the adsorption strength of the cations follows the trend Li < Na < K < Cs on Cu(100), with Cs giving the most favorable adsorption.

The effect of the alkali metal cations on the formation of the intermediates (Figure 5b), was calculated in the absence of near-surface solvation, which we expect to weaken the interaction between the cations and intermediates, but maintain the trend among the cations. Our prior work showed that the presence of alkali metal cations near the electrode surface increased the activation barrier for CO₂ reduction steps which involved the shuttling of protons through water near the electrode surface,⁴⁷ which could hinder formation of C₁ over C₂₊. Further, while we have limited our focus to the effect of the cations on CO*, OCCO*, and OCCOH*, the alkali metal cations, once near the electrode surface, may affect many important intermediates present in the path to C₁ and C₂₊ products, as well as activation barriers between these reaction intermediates (beyond just proton transfer). Therefore, our intent is to only highlight that the cations have an effect on the binding strength of these important intermediates, and that the trend in the effect on CO* adsorption matches the trend in the generation of C₂₊ products. CO* is an important intermediate not only because it is common to both the C₁ and C₂₊ paths, but also because it is a useful descriptor in understanding the binding strength of all carbon containing species which adsorb to the surface through a carbon atom, as their formation energies are known to scale linearly with that of CO*, following a scaling relation.^{53,54} Future work should examine the effect of alkali metal cations on the binding strength of all possible intermediates, as well as on the activation barriers for C-C coupling.

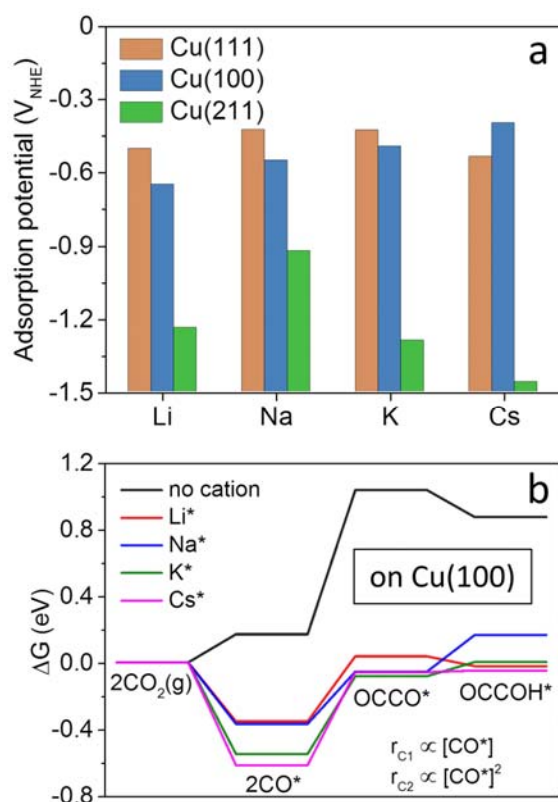


Figure 5. (a) Equilibrium adsorption potential of Li, Na, K, and Cs at 1/9 ML on Cu(111), Cu(100), and Cu(211). Adsorption is calculated from a 1 M solution of the alkali metal cations at 300 K. The near-surface region is solvated with 6 H₂O*. (b) Formation free energy of CO*, OCCO*, and OCCOH* relative to CO₂ (g), H₂ (g), and H₂O (aq) at 1/9 ML on Cu(100) at 1/9 ML on Cu(100) at 300 K. Energies relative to H₂ (g) are equivalent to giving the energy relative to protons and electrons at an electrode potential of 0 V on a RHE scale. The formation energy is calculated in the absence and the presence of Li*, Na*, K*, and Cs* at 1/9 ML.

2.5. The role of subsurface oxygen. DFT calculations were also used to examine the effects of subsurface oxygen present in the copper electrode after plasma-oxidation pretreatment. Figure 6a shows that subsurface oxygen at 2/9 ML (and of generated Cu⁺ species at the electrode

surface) promotes the adsorption of the alkali metal cations to Cu(100) by 0.1-0.3 eV. The promotion of cation adsorption by sub-surface oxygen would increase the cation coverage at any given potential. Figure 6b shows that the presence of subsurface oxygen also accentuates the effect of the cations, significantly promoting CO* formation, beyond that seen for the cations alone (Figure 5b), with Cs* promoting CO* formation the most (by 0.65 eV relative to CO* formation on the bare, non-oxidized, cation-free Cu(100) surface). These results provide indication that subsurface oxygen species can further promote C₂₊ formation. While the particular subsurface oxygen model we used was thermodynamically unstable relative to reduction to form water at CO₂RR potentials, we find that an oxygen-driven reconstruction of Cu(100) also promotes cation adsorption, even in the absence of surface or sub-surface oxygen (Figure S14).⁵⁵

In a recent study, increasing cation size resulted in an increase in the formation of ethylene and ethanol on metallic Cu, with little to no effect on the formation of CO and methane.³⁶ In contrast, on our CuO_x samples, the increased C₂₊ formation correlates with a decrease in the production of CO and methane (Figure 3), suggesting a preferred formation of C₂₊ over C₁. The difference in the C₁ formation is mainly related to the subsurface oxygen and Cu⁺ species in the CuO_x as supported by DFT calculations, as well as the presence of a possible interface between the Cu⁺ and adjacent Cu⁰, which could also promote C-C coupling.^{39,45,56-59}

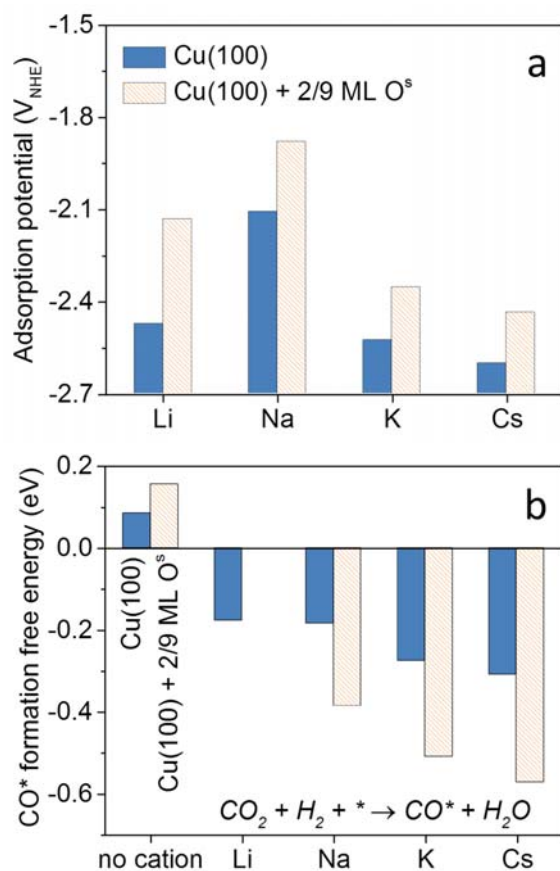


Figure 6: (a) Equilibrium adsorption potential of Li, Na, K, and Cs at 1/9 ML on Cu(100) in the absence and presence of subsurface oxygen (2/9 ML O^s). (b) CO* formation free energy calculated in the absence and presence of Li*, Na*, K*, and Cs* on bare Cu(100) and Cu(100) with 2/9 ML O^s. As subsurface oxygen migrated to the surface in the presence of co-adsorbed Li* and CO*, this data point has been excluded from (b).

2.6. Effect of Adsorbed Iodide. We previously found that iodide remains specifically adsorbed on Cu at small applied overpotentials during CO₂RR and affects the binding of various CO₂RR intermediates. Here we examined theoretically the effect of specifically adsorbed iodide

on alkali metal cation adsorption in the presence of 6 H₂O*. While there is a small effect, in particular, a weakening of the binding of the larger cations (K, Cs) (Figure S15), the complexity of possible interactions between co-adsorbed cation, iodide, and reaction intermediates leaves DFT studies of the collective effects involving iodide (particularly in the presence of Cs) as future work. See additional discussion in the supporting information.

3. CONCLUSIONS

In summary, increasing the alkali metal cation size significantly improved C₂₊ production, with the highest FE of ~69%. The C₂₊ formation was further increased by adding I⁻ to the CsHCO₃ solution (-45.5 mA cm⁻² C₂₊ partial current density), likely due to the presence of shaped particles with high amount of Cu⁺ species during the reaction. DFT calculations show that the specific adsorption of the alkali metal cations is favorable during CO₂RR and that the presence of the adsorbed cations promotes the formation of CO₂RR intermediates (CO*, OCCO*, OCCOH*) that lead to C₂₊ products. The promoting effect is cation specific, with cesium showing the largest promoting effect, consistent with our experimental observation. Our preliminary DFT results indicate that subsurface oxygen, Cu⁺ species, and surface reconstruction introduced by the plasma-oxidation pretreatment lead to a promotion of alkali metal cation adsorption onto Cu surfaces and that subsurface oxygen accentuates the promoting effects of the alkali cations on CO* formation.

4. EXPERIMENTAL AND THEORETICAL METHODS

4.1. Catalyst Synthesis. Commercial Cu foils (Advent Research Materials Ltd., 99.995%) were first cleaned with acetone and ultrapure water (18.2 M Ω) in an ultrasonic bath and then electropolished in phosphoric acid (VWR, 85 wt%) at 3 V versus a titanium foil for 5 min. The electropolished Cu foil was further treated in a plasma etcher (Plasma Prep III, SPI Supplies) at a gas pressure of 400 mTorr of O₂ for the indicated plasma power and time.¹³ The plasma-oxidized Cu foils were pre-treated in different electrolytes for further characterization (see Table S1).

4.2. Scanning Electron Microscopy (SEM) Characterization. The morphology of the O₂-plasma-treated Cu foils was investigated by SEM using a Quanta 200 FEG microscope from FEI with a field emitter as the electron source. The images were acquired in vacuum using a secondary electron (Everhart-Thornley) detector. An acceleration voltage of 10 keV was used. A liquid-N₂-cooled energy-dispersive X-ray spectroscopy (EDX) detector was employed for the elemental analysis of the sample. The error bars in the content of all elements were made on the basis of the EDX spectra from at least six different positions of two identical samples. The samples after the reaction were washed thoroughly with water and transferred immediately to the SEM chamber in order to minimize air exposure. The amount of oxygen resulting from air exposure was negligible and did not affect the elemental analysis results, given that EDX, with a probing depth of ~300 nm at 10 keV, is not surface-sensitive enough.¹⁶

4.3. Quasi in situ X-ray photoelectron spectroscopy (XPS) Characterization. The quasi *in situ* XPS measurements were carried out in an ultrahigh-vacuum (UHV) setup equipped with a non-monochromatic Al X-ray source ($h\nu = 1486.6$ eV) and a hemispherical electron analyzer (Phoibos 100, SPECS GmbH). The Cu 2p_{3/2} peak corresponding to CuO (933.11 eV)⁶⁰ was used

for the energy alignment of the as-prepared plasma-oxidized sample. For the rest of the samples which do not contain any Cu^{2+} species, the peak corresponding to Cu_2O (932.67 eV)⁶⁰ was used instead. The XPS analysis chamber was connected to an *in situ* electrochemical (EC) cell (SPECS GmbH). An Autolab potentiostat (PGSTAT 302N) was used for the electrochemical measurements. The sample transfer from the EC cell to the XPS UHV chamber was performed in vacuum. All XPS spectra were acquired at room temperature. For the deconvolution of the Cu LMM Auger spectra, data acquired in our laboratory from a metallic Cu^0 foil (reduced *in situ* by H_2 plasma), CuI powder from our lab, and CuO and Cu_2O foils from the literature¹⁶ were used as references. The Cu Auger spectra are more sensitive to the presence of Cu^+ species, in particular Cu_xO , in comparison to the O 1s spectra, because the latter are dominated by the contribution of adsorbed species not associated with Cu^+ . They also allow us to distinguish Cu^+ from Cu^0 , which is not the case when evaluating the Cu 2p XPS region.¹⁶

4.4. Temperature Programmed Desorption (TPD) Measurements. The TPD experiments were performed in a stainless-steel UHV chamber equipped with a quadrupole mass spectrometer (UTI 100C). The Cu foil was placed in the sample holder, which consists of a tantalum foil (Alfa Aesar, 99.9%), K-type thermocouple and two tantalum bars (Alfa Aesar, 99.9%). The Cu sample was mounted on a tantalum foil and a K-type thermocouple was welded to the back of the tantalum foil to measure the temperature of the sample holder. The CO gas was in research purity. The doses were reported in Langmuir ($1 \text{ L} = 10^{-6} \text{ Torr}\cdot\text{s}$) and were uncorrected for ion gauge sensitivity. After the sample was cooled down to 100 K, 10 L of CO were dosed into the chamber and CO TPD was carried out with a linear heating rate of 1 K s^{-1} from 100 to 500 K.

The binding energy of CO was calculated using the Redhead equation (assuming first order desorption).³⁸

$$\frac{E_a}{RT_p} + \ln\left(\frac{E_a}{RT_p}\right) = \ln\left(\frac{AT_p}{\beta}\right)$$

A is the pre-exponential factor and assumed to be 10^{13} . E_a is the CO binding energy and R is the ideal gas constant. β is the heating rate and T_p is the peak temperature of CO desorption. Therefore, the CO binding is correlated with the peak temperature of CO desorption.

4.5. Electrochemical Measurements. Electrochemical measurements were carried out in a gas-tight H-cell separated by an anion exchange membrane (Selemion AMV, AGC Inc.). Both, working electrode and counter electrode compartments were filled with 40 mL electrolyte and purged continuously with CO₂ (99.995%, 20 mL min⁻¹). The working electrode compartment was vigorously stirred (1100 rpm). Aqueous 0.1 M LiHCO₃, 0.1 M NaHCO₃, 0.1 M KHCO₃ (Honeywell Fluka, 99.7%), 0.1 M CsHCO₃ (Alfa Aesar, 99.99%), 0.1 M CsHCO₃ + 0.1 M CsI (Alfa Aesar, 99.999%), and 0.1 M KHCO₃ + 0.3 M KI (Sigma-Aldrich, 99%) solutions were used as electrolytes (pH 6.8). A 0.1 M LiHCO₃ solution was prepared by saturating 0.05 M Li₂CO₃ (Sigma-Aldrich, 99.99%) with a flow of pure CO₂ at 1 bar overnight. CsHCO₃ or KHCO₃ was used as a reference and a buffer to avoid significant changes in the pH which could alter the reaction pathway for ethylene/methane formation.³¹ The effect of iodine was studied in 0.1 M CsHCO₃ + 0.1 M CsI or 0.1 M KHCO₃ + 0.3 M KI. All the electrolytes were prepared with ultrapure water and further pre-purified with Chelex 100 Resin (Bio-Rad, 100–200 mesh).⁶¹ The as-received Chelex resin was pre-treated before use with 0.5 M H₂SO₄ (ACS reagent, 95.0–98.0%, Sigma-Aldrich) for 12 h followed by 1 M KOH (99.97%, Sigma-Aldrich) at 60 °C for 24

h, so the Na^+ ions in the pristine resin were replaced by K^+ ions. In the cases of LiHCO_3 and NaHCO_3 , the pristine resin was used. Prior to the measurement, the electrolyte was bubbled with CO_2 for 30 min to remove oxygen in the solution. A platinum gauze (MaTecK, 3600 mesh cm^{-2}) was used as counter electrode and a leak-free $\text{Ag}/\text{AgCl}/3.4 \text{ M KCl}$ electrode (Innovative Instruments, Inc.) as reference electrode. The O_2 -plasma-treated Cu foil was used as working electrode. The effective geometric surface area of the Cu foil is 0.5-4 cm^2 depending on the potential investigated. A fresh sample was measured with a chronoamperometric step for 1 h at each potential, unless stated otherwise. The potentials were controlled with an Autolab potentiostat (PGSTAT 302N). All potentials *versus* Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale and corrected for IR drop as determined by current interrupt. The roughness factors were determined by measuring double-layer capacitance with cyclic voltammetry between 0 and 0.25 V vs RHE, after 1 h of CO_2 electroreduction in different electrolytes at -1.0 V vs RHE .^{16,31} In the case of the 0.1 M $\text{CsHCO}_3 + 0.1 \text{ M CsI}$ and 0.1 M $\text{KHCO}_3 + 0.3 \text{ M KI}$, the samples were transferred to 0.1 M CsHCO_3 and 0.1 M KHCO_3 for the capacitance measurements after 1 h of CO_2 electroreduction at -1.0 V vs RHE and thorough washing with water.

4.6. Product Analysis. The gas products were analyzed by online gas chromatography (GC, Agilent 7890A). Carboxylates (formate and acetate) were analyzed by high-performance liquid chromatography (HPLC, Shimadzu Prominence), while alcohols were analyzed with a liquid GC (Shimadzu 2010 plus). The gas products were analyzed by online gas chromatography (GC, Agilent 7890A) every 17 min. CO , H_2 , and hydrocarbons were separated by different columns (Molecular sieve 13X, HayeSep Q, and Carboxen-1010 PLOT) and quantified by a thermal conductivity detector (TCD) and flame ionization detector (FID). Carboxylates (formate and

acetate) formed during electrolysis were analyzed by high-performance liquid chromatography (HPLC, Shimadzu Prominence), equipped with a NUCLEOGEL SUGAR 810 column and refractive index detector (RID). Alcohols were analyzed with a liquid GC (Shimadzu 2010 plus), equipped with a fused silica capillary column and FID. An aliquot of the electrolyte after reaction was directly injected into the HPLC and liquid GC without further treatment. The reported Faradaic efficiency (FE) and production rate were calculated on the basis of the product distribution and current after 1 h of CO₂ electroreduction at constant potentials.

4.7. Theoretical Calculations. Density functional theory was used to examine the specific adsorption of Li, Na, K, and Cs onto Cu(111), Cu(100), and Cu(211) in the absence and presence of near-surface water. The formation of key CO₂ electroreduction intermediates, including CO*, OCCO*, and OCCOH* was considered on the Cu(100) surface in the absence and presence of co-adsorbed alkali metal cations. We also considered the effect on Cu(100) of sub-surface oxygen and surface reconstruction on alkali metal cation adsorption and CO₂ electroreduction intermediate formation. Co-adsorption of iodide with the alkali metal cations was also examined. The DFT simulations were performed using the Vienna Ab-initio Simulations Package (VASP)⁶²⁻⁶⁴ with a plane wave basis set, the PW91 exchange and correlation functional,⁶⁵ and the Projector Augmented Wave^{66,67} method used to model the core potentials. Calculations were performed in a 3x3 or 2x2 unit cell, with a 5x5x1 or 7x7x1 Monkhorst-Pack mesh,⁶⁸ respectively, used to sample k-space. A 450 eV cutoff energy was used for the plane wave basis set, and the structural optimization was performed until the forces on the atoms were less than 0.02 eV Å⁻¹. Dipole corrections⁶⁹ were included in the surface normal direction (LDIPOL=3, LDIPOL=TRUE). Each surface was comprised of 4-layers of Cu metal atoms, with the bottom two layers frozen at the experimentally measured lattice constant for Cu (3.6 Å). Adsorption was

modeled at 1/9 ML coverage in the 3x3 unit cell or 1/4 ML in the 2x2 unit cell (unless otherwise noted). To examine the effects of subsurface oxygen and surface reconstruction, the most favorable subsurface oxygen absorption sites and missing row reconstructions of Cu(100) generated by oxygen adsorption were taken from Duan et al.⁵⁵ The “DV” missing row structure was replicated in a 2x2 Cu(100) unit cell. The equilibrium adsorption potentials of the alkali metal cations and of iodide were calculated following the methods we have described previously.^{47,70,71} The reaction energies in the absence and presence of the co-adsorbed alkali metal cations for the formation of CO*, OCCO*, and OCCOH* were calculated using DFT energies at 0 K and the computational hydrogen electrode approach, as described previously.⁴⁷

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

Calculations of FE and partial current density, additional SEM images, EDX analysis, XPS data, additional analysis of the electrochemical data, roughness factor measurements, additional theoretical data (PDF)

ACKNOWLEDGMENT

This work was supported by the German Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF) under grants #03SF0523C-“CO2EKAT” and #033RCOO4D-“e-Ethylene”, the Cluster of Excellence RESOLV at RUB (EXC 1069) funded by the Deutsche Forschungsgemeinschaft (DFG), as well as the European Research Council (ERC-725915, OPERANDOCAT). Financial support from the U.S. National Science Foundation (NRT-1449785) and the U.S. Department of Energy (DE-FG02-13ER16381) is also greatly appreciated. This work used the Extreme Science and Engineering Discovery Environment (XSEDE) supported by the U.S. National Science Foundation (ACI-1053575).

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