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Research Article

Cu(I) Reducibility Controls Ethylene vs Ethanol Selectivity on (100)-Textured Copper during Pulsed CO_2 Reduction

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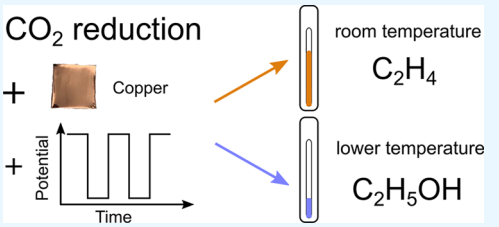
ABSTRACT: The electrochemical CO_2 reduction reaction (CO_2RR) can convert widely available CO_2 into value-added C_2 products, such as ethylene and ethanol. However, low selectivity toward either compound limits the effectiveness of current CO_2RR electrocatalysts. Here, we report the use of pulsed overpotentials to improve the ethylene selectivity to 67% with >75% overall C_2 selectivity on (100)-textured polycrystalline Cu foil. The pulsed CO_2RR can be made selective to either ethylene or ethanol by controlling the reaction temperature. We attribute the enhanced C_2 selectivity to the improved CO dimerization kinetics on the active Cu surface on predominately (100)-textured Cu grains with the reduced hydrogen adsorption coverage during the pulsed CO_2RR. The ethylene vs ethanol selectivity can be explained by the reducibility of the Cu(I) species during the cathodic potential cycle. Our work demonstrates a simple route to improve the ethylene vs ethanol selectivity and identifies Cu(I) as the species responsible for ethanol production.



KEYWORDS: *electrochemical CO_2 reduction, pulsed potential, temperature, ethylene, ethanol*

INTRODUCTION

The electrochemical CO_2 reduction reaction (CO_2RR) has received extensive attention as a solution to the growing demand for sustainably sourced materials and fuels.[1−4] Among the known CO_2RR catalysts, Cu is unique for its ability to produce hydrocarbons and oxygenates,[5−7] in particular, C_2 products such as ethylene (C_2H_4: $2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$) and ethanol ($C_2H_5OH$: $2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$). As these molecules are the important building blocks for key compounds in the chemical industry, the ability to produce these products by using renewable energy has the potential to sustain the global need for materials and chemicals in the 21st century. However, future progress toward the generation of chemical feedstocks derived from the CO_2RR remains impaired by the limited selectivity of C_2 products.

Many strategies have been explored to improve the C_2 selectivity of the Cu electrode, to date, including by tuning the Cu surface facet. Hori et al. investigated the structure sensitivity of Cu and found that the (100) facet was more selective to C_2H_4 (>40%) than the (111) facet (<10%).[8] This selectivity has been attributed to CO_{ad} dimerization (the subscript $_{ad}$ denotes adsorbed species) on the (100) facet.[9−13] This finding has led to the suggestion that increasing the CO_{ad} binding strength on Cu(100)[14] may allow for higher CO_{ad} coverage and consequently improved C_2H_4 selectivity. To this end, strategies for controlling the CO_{ad} interaction with Cu surfaces, for example, by controlling facets, morphology, oxidation states, and dopants have been investigated.[15−18] While these methods have yielded a state-of-the-art C_2 selectivity of >70%, the approaches are often complex and require several synthesis steps. Furthermore, the long-term stability for some of these approaches remains an open challenge.

In comparison to the surface modification methods, the use of pulsed electrochemical potentials has been demonstrated to be a simple and effective way to enhance CO_2RR selectivity,[19−23] especially to C_2 products.[24] We point out the recent work by Aran-Ais et al., which showed that applying a pulsed potential to Cu(100) single crystals could enhance the C_2H_5OH selectivity to 30% and C_2H_4 to 45%, with >75% combined C_{2+} selectivity.[24] This enhancement was attributed to the stabilization of the Cu(I) species which promote C_2H_5OH formation without affecting the C_2H_4 production. While these works have established that the application of a pulsed electrochemical potential can improve the CO_2RR selectivity over the hydrogen evolution reaction (HER) and support C−C coupling, it is still unclear which factor controls the selectivity between C_2H_5OH and C_2H_4 and whether the enhanced C−C coupling can be directed to only one product such as C_2H_4.

In this work, we demonstrate that the factor controlling the selectivity between C_2H_5OH and C_2H_4 is the reduction rate of

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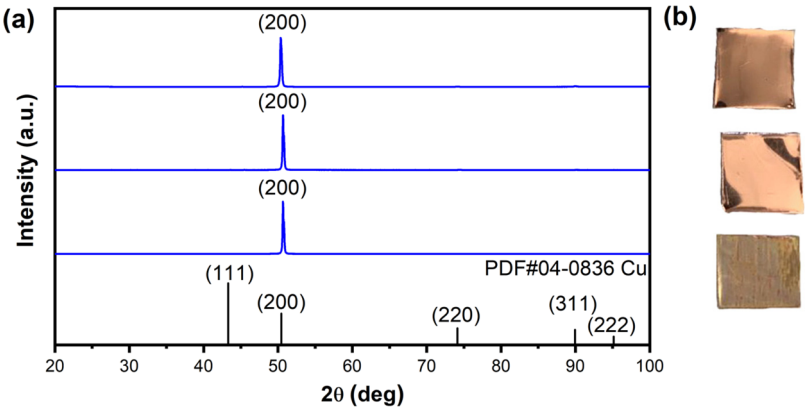

Figure 1. (a) XRD patterns (symmetric out-of-plane scan) and (b) corresponding pictures of unreacted Cu foil, Cu foil after 6 h of the constant potential CO_2RR at −1 V vs RHE, and Cu foil after the 6 h of pulsed potential CO_2RR at E_c = −1 V vs RHE, E_a = 0.6 V vs RHE, with $t_a = t_c$ = 1 s.

the Cu(I) species during the reduction (cathodic) cycle of the pulsed CO_2RR. By controlling the reduction kinetics through temperature control, the C_2H_4 selectivity can be as high as 67% with >75% selectivity toward C_2 products. This C_2 selectivity, which is obtained on a (100)-textured polycrystalline Cu foil under pulsed conditions at 25°C without using any special treatment, is comparable to the state-of-the-art CO_2RR performance.[17] We hypothesize that the transient species formed during the anodic cycle plays a critical role in the selectivity. Thus, the formation of these transient species can be exploited for selectivity control. We found that by tuning the temperature to control the reduction kinetics, C_2H_4 can be favored over C_2H_5OH. When the reducibility of the surface species formed during the anodic cycle is facile, such as when the cell temperature is held at 25°C, the C_2H_4 selectivity is enhanced at the expense of C_2H_5OH. Along the same line of reasoning, by decreasing the temperature to 15 and 5°C, the active species from the anodic cycle persists during the reduction cycle, positively impacting the C_2H_5OH selectivity. The 40% C_2H_5OH selectivity at 5°C is among the highest reported in a buffered, neutral electrolyte.[5,24] The finding that the C_2H_4 vs C_2H_5OH competition corresponds proportionally to the response time of the reduction cycle of the pulsed CO_2RR suggests that the reduction of the surface-oxidized Cu is the factor controlling the C_2 selectivity. Our work has implications on the interpretation of the active species for C_2H_4 vs C_2H_5OH and demonstrates a simple strategy for controlling the selectivity among the C_2 products during the CO_2RR. The combined use of pulsed electrochemical potentials on Cu foils to improve the C_2 selectivity and controlled temperature to tailor the C_2 selectivity presents a possible strategy for future mechanistic investigations and possibly industrial deployment for selective electrosynthesis.

RESULTS AND DISCUSSION

We conducted our CO_2RR experiments in a custom temperature-controlled cell with 0.1 M $KHCO_3$ electrolyte. X-ray diffraction (XRD) shows that our polycrystalline Cu electrodes consist predominantly of (100) facets (Figure 1), which remain robust throughout the CO_2RR experiment. We note that this orientation represents a bulk, out-of-plane value and should not be taken to imply that the surface morphology of the polycrystalline foil has a perfect single-crystal-like (100) orientation. Scanning electron microscopy (SEM) showed that the used Cu foil had a rough surface morphology (*vide infra*). Furthermore, the CO_2RR under the traditionally used constant electrochemical potential yielded a product distribution (Figure S1) consistent with the literature on polycrystalline Cu.[7,25] We performed the pulsed CO_2RR using square wave potentials with symmetric anodic and cathodic pulse intervals ($t_a = t_c$). The anodic potential (E_a) was set to +0.6 V vs RHE for all measurements, while the cathodic potential (E_c) was varied from −0.9 V to −1.15 V vs RHE.

Figure 2 shows the faradaic efficiencies (FEs) of the primary products of the CO_2RR on Cu for 100 ms, 500 ms, and 1 s

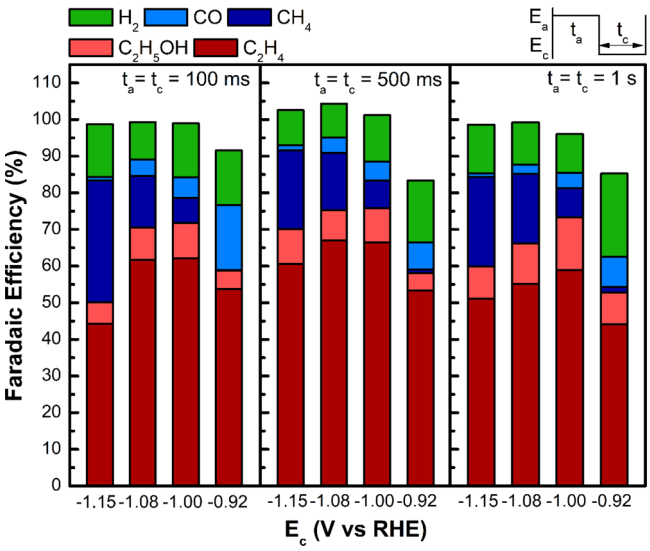

Figure 2. Faradaic efficiencies of the main products of the pulsed CO_2RR on Cu at different E_c values. All data were collected with E_a = 0.6 V vs RHE and $t_a = t_c$ = 100 ms (left), 500 ms (center), and 1 s (right) at 25°C.

pulsed potentials at 25°C. Similar selectivity trends were observed for all three pulse times, suggesting that the effect of the pulse time was minor. There was a slight enhancement in C_2 selectivity for the 500 ms pulse relative to 100 ms or 1 s pulses (Figure 2). At all potentials, C_2H_4 was the major product with 50−67% selectivity at most conditions, while CH_4, H_2, and CO were suppressed to <20, <15, and <10%, respectively (Figure 2). The C_2H_5OH selectivity was ∼10%, resulting in the maximum C_2 selectivity >75% at E_c = −1 V vs RHE, with $t_a = t_c$ = 500 ms. This C_2 selectivity corresponds to

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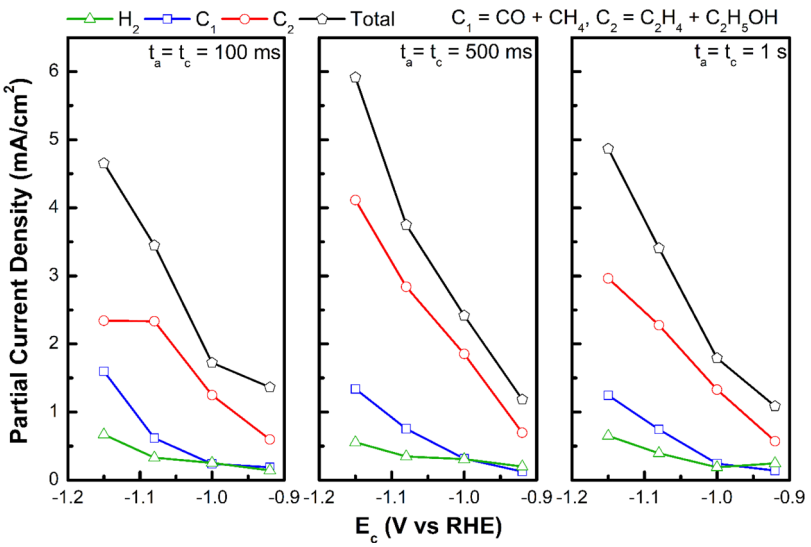

Figure 3. Partial current densities of H_2, C_1, and C_2 products of the CO_2RR on Cu at different E_c values, with E_a = 0.6 V vs RHE, $t_a = t_c$ = 100 ms (left), 500 ms (center), and 1 s (right), at 25°C.

a C_2/C_1 ratio of ∼5.9 (Figure S2), much higher than the literature result (∼1.5) on Cu(100) single crystals under a constant potential.[14] CO production is minimal except at E_c = −0.92 V vs RHE. Interestingly, the total FE also dropped to ∼80−90% at this same potential. This observation may reflect the possible CO oxidation during the anodic potential swing.

We analyzed the partial current densities to investigate whether the activity toward C_2 products was enhanced or the activity toward other products was suppressed (see the Supporting Information for the calculation details). Compared to the previously reported Cu foil with randomly oriented crystal grains,[26] the total CO_2RR current density on (100)-oriented Cu foil was slightly smaller and did not vary significantly with pulse times (Figure 3). However, the partial current density of the C_2 products at −1 V vs RHE increased by 2 × (to ∼2 mA/cm^2 from ∼1 mA/cm^2) with respect to the constant potential situation. The partial current densities of the minor products (H_2 and C_1) decreased to ∼0.6 mA/cm^2 from ∼3 mA/cm^2 in the constant potential report.[25] This observation suggests that pulsed potentials both enhance C_2 generation and suppress other CO_2RR and HER products.

It is important to note that the reported high C_2 selectivity represents the steady state selectivity, which was attained after ∼2 h of the measurement. We chose to report the steady-state performance at the end of a 6 h experiment to ensure consistency of the reporting procedure. The change in the CO_2RR FE in the first 2 h, where the C_2H_4 FE initially increased, provides information on the origin of the C_2 selectivity (Figure S3). We observed a coloration of the electrode surface after the pulsed CO_2RR experiment (Figure 1), indicating a cycle of Cu restructuring or redeposition in the first 2 h of the measurement.[27] This finding is consistent with the inductively coupled plasma mass spectrometry (ICP-MS) work by Speck and Cherevko, which found that Cu can dissolve as early as 0.5 V vs RHE.[28] Interestingly, the cyclic voltammogram stayed approximately the same during this period (Figure S4), suggesting minimal changes in surface roughness (<20% change in the EDLC response) and adsorption features. We therefore believe that the observed C_2 selectivity is not due to the increased surface roughness but rather due to the active surface forming over the (100)-oriented polycrystalline Cu foil. Earlier atomic force microscopy (AFM) investigation on Cu(100) showed that the (100) surface stayed intact during the pulsed CO_2RR through stabilization of the (100) island morphology.[24] Our observation from the cyclic voltammogram showing that the CO_2RR did not significantly change the surface roughness is consistent with the literature's finding. XRD patterns of the polycrystalline Cu foils after a 6 h pulsed potential experiment with E_c = −1 V vs RHE, $t_a = t_c$ = 1 s, as well as a 6 h constant potential experiment with E_c = −1 V vs RHE (Figure 1) show no measurable changes in the facet distribution. We emphasize again that XRD should not be taken as a representative surface model for the Cu foil. SEM shows that the surface Cu foil was rough, even after the CO_2RR (Figure S5). Electron backscatter diffraction (EBSD) showed evidence of (100), (101), and near (112) orientation. However, we were not able to provide a quantitative analysis with the surface roughness of the sample. X-ray photoelectron spectroscopy (XPS) of Cu $2p_{3/2}$ (Figure S6) showed the presence of Cu/Cu_2O (932.6 eV), CuO (933.6 eV), and $Cu(OH)_2$ (935.1 eV). Both samples contain a total of ∼20% CuO plus $Cu(OH)_2$, similar to the amount of CuO and $Cu(OH)_2$ observed for unreacted Cu foil in ambient air.[29] Although we cannot resolve Cu vs Cu_2O due to their overlapping XPS feature, our results suggest that the chemical makeup of the Cu foil did not change going through the constant-potential or pulsed-potential CO_2RR, in agreement with the cyclic voltammogram. Taken together, we hypothesize that the enhanced C−C coupling is due to the active species formed through a series of redox cycles on polycrystalline Cu foil of the preferred (100) orientation. Continuous oxidation and reduction of electrodes under pulsed conditions has been shown to promote the surface CO_{ad} coverage and C−C coupling to ethylene.[27,30,31] This increase in the partial current density of C_2H_4 by ∼3 × in the first 2 h of the experiment (Figure S3) agrees with these observations and suggests that the increased C−C coupling is intrinsic to the changing Cu surface chemistry during pulsed potential application instead of the changing surface area.

Reaction temperature is commonly used to tune selectivity. To understand the enhanced C_2H_4 selectivity under pulsed conditions, we tested the effect of temperature on the pulsed

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CO_2RR at 5 and 15°C using the same experimental parameters. The activation energy for C_2H_4 formation under pulsed conditions was calculated to be 25.98 ± 3.88 kJ/mol (Figure S7) at −1 V vs RHE, which is lower than the C_2H_4 activation energy under constant potential conditions (~35 kJ/mol).[25] This reduced activation energy for C_2H_4 production supports our hypothesis of enhanced C_2H_4 production under pulsed conditions. Under constant potential conditions, the C−C coupling process is limited by the low CO_{ad} coverage, where CO_{ad} must compete against H_{ad} for available Cu sites.[32] Under pulsed potential conditions, we hypothesize that a cycle of oxidizing−reducing potential allows H_{ad} to preferentially desorb. While CO_{ad} can similarly desorb or oxidize at the oxidative potential, we postulate that the kinetics are slower than the H_{ad} desorption. The H_{ad} desorption creates open Cu sites to allow the CO_{ad} coverage to increase relative to H_{ad}, favoring C−C coupling.[27] This effect should simultaneously suppress HER, enhance C−C coupling, and minimize the C_1 product formation, which are the results observed under pulsed potentials.

The critical question is why it is that our C_2H_4 selectivity (>65%) is significantly higher than Aran-Ais et al., whose investigation using a similarly designed experiment showed similar C_2 selectivity (~75%) but with significantly lower C_2H_4 selectivity (~45%).[24] We postulate that the difference could be because most CO_2RR experiments are conducted at room temperature that is closer to 20°C, which is lower than the temperature used in our experiment (25°C). To test this hypothesis, we tested the selectivity at 5 and 15°C for a variety of voltages with E_a = 0.6 V and $t_a = t_c$ = 1 s. In agreement with our hypothesis, we observed a significant temperature dependence of the selectivity between C_2H_4 and C_2H_5OH (Figure 4). At 5°C, C_2H_5OH selectivity is relatively voltage-independent with an FE between 30 and 40%, which is among the highest C_2H_5OH selectivity reported in an H-cell with neutral bicarbonate electrolyte.[5,24] Combined with C_2H_4, the total C_2 selectivity is >60%, which suggests that under pulsed conditions the total C_2 selectivity does not strongly depend on temperature. The results at 15°C support this trend—the selectivity toward C_2 products remains >60%, with C_2H_4 and C_2H_5OH selectivity at values between the 5 and 25°C experiments. We also note that HER selectivity is suppressed to <15% for all potentials at 5 and 15°C (Figure S8), which further strengthens the argument that pulsed voltages suppress HER by decreasing the coverage of H_{ad} on the Cu surface. The amount of formate increases as the overpotential becomes less negative at both temperatures.

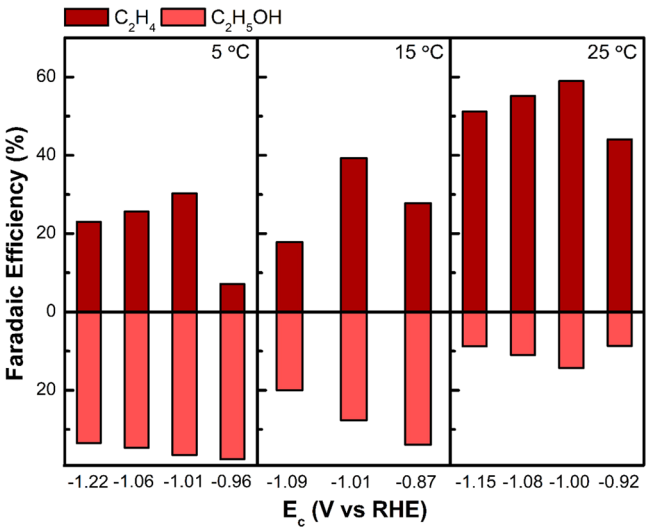

Figure 4. Faradaic efficiencies of ethylene and ethanol for the CO_2RR on Cu at different E_c values, with E_a = 0.6 V vs RHE, $t_a = t_c$ = 1 s, at 5, 15, and 25°C.

Our results demonstrate that the ratio of C_2H_4 to C_2H_5OH is sensitive to reaction temperature, with higher temperatures favoring C_2H_4 and lower temperatures favoring C_2H_5OH. To explain this observation, we consider a shift in the equilibrium between C_2H_4 and C_2H_5OH due to the hydration reaction ($C_2H_{4(g)} + H_2O_{(l)} \rightarrow C_2H_5OH_{(l)}$, $\Delta G^0 = -6$ kJ/mol).[33] If the observed C_2H_5OH selectivity was due to faster C_2H_4 hydration kinetics at higher temperature, the C_2H_4 to C_2H_5OH ratio should move closer to equilibrium at 25°C. However, we observed the opposite result, indicating that the observed effect is not due to the hydration effect, i.e., the observed C_2H_4 vs C_2H_5OH selectivity is a result of catalysis. Cu single-crystal studies attributed the enhancement in the C_2H_4 selectivity to the (100) facets[34] and C_2H_5OH selectivity to the stabilization of Cu(I) under pulsed conditions.[24] These surface Cu(I) species could create an oxophilic surface that stabilizes the adsorbed oxygen that impacts the branching point between the C_2H_4 and C_2H_5OH pathways, i.e., $OHCCH_{2,ad}$.[24] Based on this prior mechanistic proposal, the temperature-dependent C_2H_4 vs C_2H_5OH selectivity observed in our experiments is likely a result of how Cu(I) is stabilized during the pulsed potential, where lower temperature more effectively stabilizes the Cu(I) species.

To understand why Cu(I) is stabilized at lower temperature, we examined the temperature dependence of the current response during the pulsed CO_2RR (Figure S9). Similar to the previous report,[21] we observe a sharp current spike at the beginning of each pulse which decays to a stable current on the ms timescale. We characterize the response time by fitting an exponential function and extracting the time constant, which we found to increase with decreasing temperature (Figure S10). Specifically, the time constant in the reductive cycle (cathodic pulse) was found to be higher at 5°C than at 25°C. We believe that this result indicates the slow kinetics of the reduction of Cu(I) to Cu(0) at low temperature. The similar oxidation and reduction time constants at 25°C indicate that a smaller fraction of residual Cu(I) stays intact during the reductive cycle. Thus, C_2H_4 enhancement is a result of the Cu(I) species being reductively eliminated on the Cu(100) facet, while the higher time constants at low temperature kinetically stabilize Cu(I), effectively allowing the Cu(I) species to facilitate the C_2H_5OH production as has been previously reported.[24] Based on this mechanism, our C_2H_4 enhancement at 25°C compared to the previously reported enhancement in C_2H_5OH on Cu(100) single crystals at room temperature is due to our active control of the reaction temperature at 25°C vs an uncontrolled system that is likely closer to ~20°C. Most importantly, our analysis suggests that the species responsible for C_2H_5OH is Cu(I) while the active sites responsible for C_2H_4 are the reduced Cu facets. Although both Cu(0) and Cu(I) are capable of supporting C−C coupling, the former favors C_2H_4 formation while the latter favors C_2H_5OH.

The details of the exact atomic structure during cycling and its relationship to the C−C coupling remains an open

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question. Polycrystalline surfaces are complicated by the presence of different terminations and structural defects, including grain boundaries and morphologies. In addition to this issue, it is possible that the oxygen atom near the oxidized Cu can migrate into the subsurface. In such situations, the cathodic pulse may not fully reduce the subsurface oxygen since it is kinetically inaccessible, leading to persistent subsurface oxygen species. Several groups have suggested that subsurface oxygen can enhance C_2H_4 selectivity on Cu by increasing the CO_{ad} binding energy which enhances C−C coupling.[35,36] Additionally, Cu(I) may be stabilized by OH_{ad} formed via water electro-oxidation ($H_2O \rightarrow OH_{ad} + H^+ + e^-$), the residue of which could participate in the CO_2RR. Understanding the nature of the oxidized Cu will be essential in understanding and eventually improving the pulsed CO_2RR performance in the future.

CONCLUSIONS

In summary, we report a highly C_2H_4-selective (67%) CO_2RR using square wave potentials on (100)-textured polycrystalline Cu foil with >75% total C_2 selectivity. We show that temperature plays a crucial role in whether the CO_2RR favors ethylene or ethanol with the maximum ethylene production found at 25°C (67%) and the maximum ethanol production found at lower temperature (up to 40%). We attribute the overall enhancement in C_2 selectivity to the reduced H_{ad} coverage, which enhances the CO_{ad} coverage to support C−C coupling during the pulsed CO_2RR. The C_2H_4 selectivity is favored at higher temperature where the cathodic pulse can reduce the majority of Cu(I) to Cu(0). On the other hand, the Cu(I) species persist at a lower temperature, causing the CO_2RR to favor C_2H_5OH. Our results establish a simple method for not only enhancing the CO_2RR selectivity toward the C_2 products but also to tailor the C_2H_4:C_2H_5OH ratio through controlling the reaction temperature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c17668.

Experimental methods; FE of main products of the CO_2RR under constant potentials; the current ratio of C_2/C_1 for the CO_2RR under pulsed potentials; FE and partial current densities of major products of the CO_2RR over time; CV of Cu foil in 0.1 M KOH before and after the CO_2RR; XPS data of Cu foil before and after the CO_2RR; Arrhenius plot of the C_2H_4 partial current density; FE of main products of the CO_2RR under pulsed potentials at 5 and 15°C; pulsed current for 5, 15, and 25°C; and the time constant of cathodic and anodic pulses (PDF)

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Author Contributions

Z.T., E.N., and J.S. conceived the experimental design. Z.T., E.N., and K.E.F. conducted the experiments and analyzed the data. T.H. contributed to the discussion. Z.T. and J.S. prepared the manuscript with help from E.N. and K.E.F. All authors have approved the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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