Electrochemical acetate production from high-pressure gaseous and liquid CO_2

Jiachen Li[1,2], Yun Kuang[1], Xiao Zhang[1], Wei-Hsuan Hung[1,3], Ching-Yu Chiang[4], Guanzhou Zhu[1], Gan Chen[2,5], Feifei Wang[1,6], Peng Liang[1], Hongjie Dai[1]*

Affiliations:

[1] Department of Chemistry and Bio-X, Stanford University, Stanford, CA 94305, USA.

[2] Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA.

[3] Institute of Materials Science and Engineering, National Central University, Taoyuan 32001, Taiwan.

[4] National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan.

[5] Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA.

[6] Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China.

*Correspondence to: hdai@stanford.edu.

Abstract

Electro-reduction of CO_2 (CO_2RR) to high-value chemicals is important to environmental and energy landscapes, with one of the challenges being direct and efficient acetate production. Here we show a $Cu(OH)_2$ derived Cu/CuO_x catalyst achieving 87% Faradaic efficiency (FE) of CO_2RR to acetate in KOH electrolytes with borate additives under 58 atm $CO_2(g)$. Dynamic electrolytic speciation reveals high concentrations of dissolved $CO_2(aq)$ and low of proton donor HCO_3^- as the key to acetate. In-situ Raman spectroscopy suggests O-bound bidentate intermediate $*OC^{\bullet}O*$ formed on Cu(I) under high pressures as the acetate precursor. Introducing $CO_2(l)$ to the interface between $CO_2(g)$ and electrolyte by melting $CO_2(s)$ further increases $[CO_2(aq)]$ and boosts acetate partial current density to 86 mA/cm^2 with 71% FE. A Cu^{2+} cross-linked alginate coating layer on cathode surface drastically enhances the durability of Cu/CuO_x catalyst during 20 h reaction, affording a potassium acetate yield of 30 $mg \cdot h^{-1} \cdot cm^{-2}$ directly from CO_2RR.

Introduction

Closing the carbon cycle by CO_2 capture and conversion to useful fuels and chemicals through electro-reduction could help mitigate the challenging energy and environmental problems. Among the various high-value long-chain (C_2+) CO_2RR products[1,2], production of ethylene has been particularly successful on copper-based electrocatalysis[3-5] in aqueous electrolytes and has been guided by high-throughput catalyst screening algorithms[6,7]. In contrast, acetate, another important C_2 industrial feedstock[8], was mostly a minor product[1,2,9] with limited mechanistic understandings[9-13]. Non-metal[10], precious metal[14,15] and covalent organic framework (COF)[16] based catalysts, as well as novel bacteria based approaches[17,18] have been used for acetate production but usually with low partial current densities (Supplementary Table 1). In non-aqueous electrolyte systems such as methanol, acetic acid was generated by the reaction between $CO_2^{\bullet-}$ intermediate and the solvent[19-21], but also with very limited yields (Supplementary Table 2). Electro-reduction of CO (CORR) to acetate coupled with anodic electro-oxidation of water and crossover ethanol[22,23] reached 10^2 mA/cm^2 level acetate partial current densities[24,25] (Supplementary Table 3), but with < ~ 10% energy efficiencies for overall CO_2-CO-acetate conversion[23,26]. Currently, industrial acetate production is based on methanol carbonylation using organometallic catalysts and halide-based promoters at high temperature and pressure conditions[27,28]. Efficient electro-catalytic synthesis of acetate directly from CO_2 has been appealing but formidable.

As a heterogeneous process, CO_2RR is complex and depends not only on the catalyst but also on electrolyte composition[29] and concentration of dissolved $CO_2(aq)$, the electro-active species[30,31]. We previously showed the importance of high > 45 atm $CO_2(g)$ partial pressure to increase dissolved $CO_2(aq)$ concentration to > 1 M level in a $KHCO_3$ electrolyte[32], leading to an initially surprising result of CO_2RR to nearly pure formate production (98.2% peak FE at 5.7 mA/cm^2 partial current density, and 55.0% FE at 34.1 mA/cm^2 peak partial current density) on a copper-based catalyst[33]. This was rationalized by that only at such high $CO_2(aq)$ concentrations were abundant $*OC^{\bullet}O*$ intermediate[34,35] formed with favorable kinetics[36,37] on the coordinately unsaturated Cu(I) sites (Cu^{+}_{CUS}) through Cu-O linkages on Cu_2O (111) facet[32,33,38], opening the pathway of $*OC^{\bullet}O*$ protonation by electrolytic HCO_3^- ions[39,40] for the dominant production of formate.

Here by applying 58 atm $CO_2(g)$ over electrolytes, we achieved efficient CO_2RR with up to 87.3% acetate FE and up to 86.3 mA/cm^2 partial current density on a Cu/CuO_x catalyst, obtaining acetate as the dominant CO_2RR product at high partial current densities on copper-based electrocatalysts in aqueous systems. Dynamic Fourier-transform infrared (FTIR) and Raman spectroscopies together with electrochemical pH monitoring revealed high $CO_2(aq)$ and low proton donor (HCO_3^- and H^+) concentrations in the electrolytes as key parameters for high acetate selectivity over hydrogen evolution (HER) or other C_1 and C_2 products on catalyst surface. High-pressure in-situ Raman spectroscopy suggested the O-bound bidentate intermediate $*OC^{\bullet}O*$ on active Cu(I) sites as the precursor to acetate. By introducing a liquid CO_2 layer over the electrolyte to further increase $CO_2(aq)$ concentration, we obtained a high 71.7% acetate FE at 86.3 mA/cm^2 partial current density. Also important was a novel alginate coating layer on the cathode, affording drastic catalyst stabilization and efficient CO_2RR-to-acetate production over 20 h for ~ 51.7% acetate FE at 65.4 mA/cm^2 partial current density with a high potassium acetate yield of 30 $mg \cdot h^{-1} \cdot cm^{-2}$.

Results

CO_2RR under high pressure conditions

We synthesized $Cu(OH)_2$ nanowires on Cu foil by applying 5 Hz alternating square-wave (SW) potentials of -0.75 and 0 V vs. saturated calomel electrode (SCE) in a basic KCl solution (Supplementary Figure 1, see Methods for details). Cyclic voltammetry (CV) suggested the formation of $Cu(OH)_2$ on Cu foil by repeated oxidation at 0 V and mild reduction at -0.75 V[41] during SW treatment, with the foil color changing from red to light green (Figure 1a). Grazing incidence X-ray diffraction (GIXRD) confirmed abundant $Cu(OH)_2$ formation on Cu (Figure 1b), and based on Scherrer equation[42], the crystalline domains in the material were < 20 nm (Supplementary Figure 1, see Supplementary Methods for details). Scanning electron microscopy (SEM) showed fiber-like structures on the foil after SW treatment (Figure 1c), and high-resolution transmission electron microscopy (HRTEM) revealed that each fiber was comprised of parallel bundles of ~ 10 - 40 nm wide nanowires (Figure 1d) with high porosity (Figure 1e). This hierarchical and porous structure was attributed to Cl^- and OH^- promoted Cu etching/corrosion[4,43] (Supplementary Figure 1), leading to a ~ 10.4 times higher electrochemical surface area (ECSA) of this SW-$Cu(OH)_2$/Cu electrode than the original Cu foil (Supplementary Figure 1, see Methods for details).

Pairing SW-$Cu(OH)_2$/Cu with Ni anode and Ag/AgCl reference electrode, we performed CO_2RR under 58 atm CO_2(*g*) partial pressure in a high-pressure electrolyzer[33] with Nafion membrane separating the catholyte and anolyte (Figure 2a, see Methods for details). A basic 6 M KOH solution was employed as the electrolyte with 0.8 M H_3BO_3 added to accelerate CO_2(*g*) dissolution[44,45] (named as solution B with B standing for basic, initial pH = 14.3 tested by a home-designed electrochemical pH measurement method based on Zn redox[33,46] shown in Supplementary Figure 2, see Supplementary Methods for details). For 1 h CO_2RR under a constant reduction potential of -1.3 V vs. Ag/AgCl (-0.39 vs. reversible hydrogen electrode, RHE) initiated after equilibrating the electrolyte under 58 atm CO_2(*g*) for 1 h (Figure 2b), we observed a high acetate FE of 87.3% at 5.1 mA/cm^2 partial current density (Figure 2c). More negative potentials led to decreases in acetate FE and increases in reduction current, resulting in a maximum acetate partial current density of 39.2 mA/cm^2 at -1.7 V vs. Ag/AgCl (-0.91 V vs. RHE) with 52.5% FE (Figure 2d and Supplementary Figure 3). This corresponded to a potassium acetate yield of 17.9 $mg\cdot h^{-1}\cdot cm^{-2}$, exceeding all previous copper-based CO_2RR-to-acetate production (Supplementary Table 1). In-situ Raman spectroscopy revealed that SW-$Cu(OH)_2$/Cu was continuously reduced to lower Cu valences with decreased Cu^{2+} species over time at -0.91 V vs. RHE (1.4 V more negative than Cu^{2+} to Cu^{+} reduction potential[47]) under 58 atm (Supplementary Figure 3, see Methods for details). Quantitative analysis based on X-ray photoelectron spectroscopy (XPS) suggested Cu(I) and Cu(0) species dominated after the first 5 min of CO_2RR (Supplementary Figure 4, see Supplementary Methods for details). Since our reactions typically lasted 1 - 20 h >> 5 min, it was the $Cu(OH)_2$ derived Cu(0)/Cu(I) sites on cathode surface acting as effective electrocatalysts during high pressure CO_2RR.

By investigating various electrolytes, we found that CO_2RR in an acidic 1 M KCl + 0.03 M $KHCO_3$ solution under 58 atm CO_2(g) (named as solution A with A standing for acidic, initial pH = 4.6, see Methods for details) also afforded a high 61.1% acetate FE at -1.8 V vs. Ag/AgCl (-1.46 V vs. RHE) with a considerable 25.8 mA/cm^2 partial current density (Supplementary Figure 3). For electrolyte A vs. B the pH (initially 4.6 vs. 14.3) and CO_2(*aq*) concentration [1.27 vs. 0.48 M after 1 h equilibrating under 58 atm CO_2(*g*) measured by micro-IR[32], see Methods for details] were quite different, yet CO_2RR in both electrolytes afforded high acetate FEs. Clearly, electrolyte pH or $[CO_2(aq)]$ was not the sole determining factor of acetate selectivity for CO_2RR.

For 1 h CO_2RR at -1.46 V vs. RHE under 58 atm, increasing $KHCO_3$ in the 1 M KCl electrolyte from 0 to 0.03 M significantly improved acetate FE from 24.5% to 61.1% and suppressed HER FE from 42.5% to 9.4% (Supplementary Figure 3), accompanied by pH increase from 3.1 to 4.6. However, further increasing bicarbonate to 0.1 M (pH = 6.7) in 1 M KCl resulted in acetate FE dropping to 18.0% and formate FE jumping to 47.0% (Supplementary Figure 3). More extreme was that in a pure 0.5 M $KHCO_3$ solution, CO_2RR with the same catalyst produced dominantly formate instead of acetate, with 71.6% formate FE at -0.91 V vs. RHE and 53.2% at -1.46 V vs. RHE respectively (Supplementary Figure 3), similar to our previous finding of dominant formate productions using a $Cu_2O(111)$-rich catalyst in 0.5 M $KHCO_3$ under 58 atm $CO_2(g)$[32,33]. These results clearly showed a negative effect of higher HCO_3^- concentration to CO_2RR selectivity towards acetate. A plausible explanation was that HCO_3^- could act as efficient proton donors[39,40] to protonate $*OC^{\bullet}O*$ intermediates, preventing C-C coupling and hijacking CO_2RR to formate production.

In electrolyte B (6 M KOH + 0.8 M H_3BO_3), the solution pH, $CO_2(aq)$, CO_3^{2-}, and HCO_3^- concentrations evolved over equilibrating time after applying 58 atm $CO_2(g)$ were monitored by electrochemical pH measurement, micro-IR spectroscopy of $CO_2(aq)$ quantification[32], and home-designed plasmon enhanced Raman spectroscopy of CO_3^{2-} and HCO_3^- quantification[48,49] (Supplementary Figure 5, see Methods for details). When the equilibrating time prior to starting CO_2RR increased from 1 to 2, 3, 5, and 10 h, we observed pH lowering accompanied by $[CO_2(aq)]$, $[CO_3^{2-}]$, and $[HCO_3^-]$ increasing (bicarbonate increased from < 0.01 to 0.78 M, Fig. S13), and the CO_2RR acetate FE decreased from 52.5% to 8.3% while formate increased from 10.5% to 43.6% for 1 h reactions at -0.91 V vs. RHE (Figure 3a and Supplementary Figure 6). Thus, similar to the acidic electrolyte cases, CO_2RR in basic electrolytes with higher $[HCO_3^-]$ also favored formate over acetate.

We noticed that with catalyst states to be similar (Supplementary Figure 7), efficient productions of acetate in drastically different electrolyte A and B shared a common characteristic of high $[CO_2(aq)]/[HCO_3^-]$ ratios > ~ 10 (Supplementary Figure 6). The $[CO_2(aq)]/[HCO_3^-]$ ratio appeared to be a useful indicator for CO_2RR selectivity to acetate in mildly acidic to highly basic electrolytes (pH = 4.6 ~ 13.7, Figure 3b). When electrolyte pH was below ~ 3 in acidic electrolytes (Supplementary Figure 3 and 6), H^+ could become the dominant proton donor over HCO_3^-[39], leading to substantial H_2 evolution. We arrived at an important conclusion that a high ratio between dissolved $CO_2(aq)$ and proton donor concentration was key to efficient C-C coupling for acetate formation by CO_2RR on Cu/CuO_x electrocatalysts.

In electrolyte B under different $CO_2(g)$ partial pressures, for 1 h CO_2RR performed at -0.91 V vs. RHE after 1 h equilibrating under 58, 45, 30 and 15 atm $CO_2(g)$, we observed decreasing acetate FE from 52.5% to 15.9% and increasing ethanol FEs from 17.8% to 34.5% (Figure 3c and Supplementary Figure 6), suggesting that for conditions of similarly high $[CO_2(aq)]/[HCO_3^-]$ ratios of 10^2 level (Supplementary Figure 6), CO_2RR selectivity shifts from acetate to ethanol with decreasing $CO_2(aq)$ concentration. A similar trend was also observed for 1 h CO_2RR at -1.46 V vs. RHE in acidic electrolyte A (Figure 3d and Supplementary Figure 6). Hence, in addition to the positive correlation between acetate/formate FE ratio and $[CO_2(aq)]/[HCO_3^-]$, we also observed a positive correlation between acetate/ethanol FE ratio and $[CO_2(aq)]$ (Figure 3d).

Acetate formation *via* a bidentate *OC•O* pathway

To investigate the CO_2RR mechanistic pathway to acetate on our Cu/CuO_x catalyst, we performed in-situ Raman spectroscopy of the species formed on cathode during CO_2RR in a custom-built high-pressure cell under 1, 15, 30, 45, and 58 atm respectively (Figure 4a, see Methods for details) at -0.91 V vs. RHE in solution B. Focusing 532 nm laser on the electrocatalyst surface, we observed obvious CO_2 vibration signals[50] at ~ 1291 and 1392 cm^{-1} when the $CO_2(g)$ pressure increasing above 30 atm (Figure 4b), due to increasing $CO_2(aq)$ (> 0.21 M, Figure 3c) on the catalyst surface. Importantly, we observed obvious doublet peaks at ~ 1455 and 1478 cm^{-1} when $CO_2(g)$ pressure was over 45 atm at -0.91 V vs. RHE (Figure 4c). The doublet peaks disappeared upon removing the reduction potential, accompanied by a significant increase in the CO_2 peaks (Figure 4d) due to halting of $CO_2(aq)$ consumption at the catalyst surface by CO_2RR. We assigned the doublet peaks to symmetric C-O stretching vibration ν of the O-bound bidentate intermediate[51,52] *OC•O* that can evolve into the acetate precursor α_{2a} (Figure 4e). Correspondingly, the O-C-O deformation vibration δ[51-53] was also identified at ~ 721 cm^{-1} (Supplementary Figure 3). We found that C-O stretching in acetate ion was indeed in the similar ~ 1300 - 1500 cm^{-1} range, consistent with previous work[53-55] (Supplementary Figure 7).

In our previous studies[32,33], we have shown that a Cu_2O (111)-rich catalyst enabled > 98% CO_2RR-to-formate FEs under 58 atm $CO_2(g)$, since the > 1 M high $[CO_2(aq)]$ resulted in competitive CO_2 adsorption on $Cu^{+}{}_{CUS}$ sites (configuration α, Figure 4e) over water [adsorption energy = -61.9 vs. -54.0 kJ/mol on Cu_2O (111)] to afford abundant $*OC^{\bullet}O*$ intermediate *via* Cu-O linkages (configuration α_1, Figure 4e)[38], and the resulting $*OC^{\bullet}O*$ could be rapidly protonated to form formate (configuration α_{2b}, Figure 4e)[35,38]. With the current SW-$Cu(OH)_2$/Cu electrode in 0.5 M $KHCO_3$ under 58 atm $CO_2(g)$, we again observed dominant formate FEs (Figure 5a and Supplementary Figure 3). In contrast, switching from $KHCO_3$ to solution A, solution B, and 0.25 M K_2SO_4 solution with much lower $[HCO_3^-]$ under the otherwise identical CO_2RR conditions led to dominant acetate production over formate (Figure 2c, 5a, and Supplementary Figure 3). Since the current catalyst was also comprised of mixed Cu(I)/Cu(0) species under CO_2RR potentials (Supplementary Figure 3, 4, and 7), the efficient acetate productions in solution A, solution B, and K_2SO_4 were attributed to $*OC^{\bullet}O*$ formed on active Cu(I) sites coupling with a second one-carbon species/intermediate under proton deficient conditions, resulting in C-C coupling for the formation of acetate (Figure 4e). The second one-carbon species/intermediate coupling with $*OC^{\bullet}O*$ on Cu(I) sites could be CO_2 molecule[10,13] or other $*CO_xH_y$ intermediates such as $*CH_3$ and $*CH{=}O$ formed on nearby active Cu(0) sites[9,12,13,52]. Such C-C coupling outcompeted against $*OC^{\bullet}O*$ protonation for formate production under conditions of higher $[CO_2(aq)]/[HCO_3^-]$, resulting in higher acetate/formate FE ratios (Figure 3b). At lowered pressures with reduced $[CO_2(aq)]$, the CO_2RR pathway to $*OC^{\bullet}O*$ and acetate gave way to the Cu(0)-*CO pathways (Figure 4e), leading to increased ethanol as the main product as observed experimentally (Figure 3c, 3d, and Supplementary Figure 6).

Previous studies mostly focused on acetate formation on copper-based catalysts by CO electroreduction[23,25], not by direct CO_2RR. A popular CORR pathway involved absorbed *CO and their dimerization to form the ketene intermediate $*CH_2{=}C{=}O$[13,25,56]. However, we observed neither *CO (~ 280, 350, and 2100 cm^{-1}) nor $*CH_2{=}C{=}O$ (~ 1960 cm^{-1}) signals[50,57] in our in-situ Raman spectroscopy under high pressures up to 58 atm, and no appreciable CO production was observed in any of our electrolytes (acidic, basic or near neutral) used for high-pressure CO_2RR. The $[HCO_3^-]$-dependent competition between formate and acetate production also lacked an explanation by the ketene pathway. Further, in the acidic solution A (initial pH = 4.6) we also observed high CO_2RR-to-acetate FEs (Supplementary Figure 3), which was inconsistent with the ketene pathway to acetate requiring high OH^- availabilities[56]. These argued against the tandem pathway of CO_2-CO-ketene-acetate during high pressure CO_2RR.

The formation of ethanol or hydrocarbons in CO_2RR involved C-C coupling of two neighboring $*CO_xH_y$ intermediates on Cu(0) sites (configuration β_2, Figure 4e) *via* various pathways[1,58,59]. In electrolyte B, as $[CO_2(aq)]$ decreased from 0.48 M at 58 atm $CO_2(g)$ partial pressure to 0.12 M at 15 atm, we observed decreasing acetate FEs from 52.5% to 15.9% and increasing ethanol FEs from 17.8% to 34.5% (Figure 3c and Supplementary Figure 6). The adsorption of CO_2 on active Cu(0) sites *via* Cu-C linkage (configuration β, Figure 4e) shows lower Gibbs free energy gains[38,60] than its adsorption on Cu(I) *via* Cu-O linkage (configuration α, Figure 4e), so that at low $[CO_2(aq)]$ conditions, configuration β energetically dominates over α. Thus, during CO_2RR under lower pressures, few $*OC^{\bullet}O*$ were formed on Cu(I) sites for the carboxylate pathways, giving methane, ethylene, or ethanol as the dominant product (Figure 5a, Supplementary Figure 3 and 6) through protonation or dimerization of $*CO_xH_y$ on Cu(0) sites in proton-rich or proton-deficient electrolytes, respectively. In contrast, for high pressure conditions with high $[CO_2(aq)]$, configuration α increased to significant degrees to form abundant $*OC^{\bullet}O*$, affording higher acetate selectivity over ethanol and hydrocarbons, and leading to acetate/ethanol FE ratio positively correlating to $[CO_2(aq)]$ (Figure 3d).

Summarizing all the 1 h CO_2RR results of SW-$Cu(OH)_2$/Cu in various electrolytes including KCl + $KHCO_3$, KOH + H_3BO_3, $KHCO_3$, and K_2SO_4 under 1 - 58 atm $CO_2(g)$ partial pressures, we found that the dominant reduction product shifted from hydrocarbons to alcohols and then to carboxylates when $[CO_2(aq)]$ increased from $\sim 10^{-2}$ to 10^0 M, while the C_1 vs. C_2 selectivity shifted to the C_2 direction with higher $CO_2(aq)$ and lower HCO_3^- concentrations (Figure 5b). The resulting two-dimensional map of CO_2RR selectivity vs. $[CO_2(aq)]$ and vs. $[CO_2(aq)]/[HCO_3^-]$ on Cu/CuO_x catalyst (Figure 5b) corroborated the selectivity trends observed by other researchers, such as CO_2RR under higher CO_2 pressure shifting from producing ethylene to ethanol[61], from hydrocarbons to formic acid[62], and from methane to ethylene[63]. Also, lower electrolyte HCO_3^- concentration shifted CO_2RR from producing methane to C-C coupling for ethylene formation[63] (Supplementary Table 4). Such a systematic pathway map could shed light to disentangling the complex intercorrelated CO_2RR mechanisms and facilitate further rational design of electroreduction systems toward any desired product.

Optimized acetate production by introducing $CO_2(l)$ and alginate coating

In our sealed CO_2RR system the maximum $CO_2(g)$ pressure is 58 atm at room temperature due to phase equilibrium[64] (Figure 6a). By melting dry ice under 58 atm $CO_2(g)$ in the sealed high-pressure electrolyzer, we introduced a $CO_2(l)$ layer over the aqueous electrolyte B, which was visualized through the window of a high-pressure optical cell (Figure 6a and Supplementary Figure 7, see Methods for details). The measured $[CO_2(aq)]$ in electrolyte B under 58 atm $CO_2(g) + CO_2(l)$ was ~ 1.4 times higher than that under 58 atm CO_2(g) at ~ 3 mm beneath the electrolyte interface (Figure 6b, see Methods for details). We then conducted 1 h CO_2RR at -1.7 V vs. Ag/AgCl in solution B after 30 min equilibrating under 58 atm $CO_2(g) + CO_2(l)$, with SW-$Cu(OH)_2$/Cu bent to L-shape in order to parallel its end to the interface of $CO_2(l)$ and electrolyte interface (Supplementary Figure 7, see Methods for details). With this cathodic configuration paired to a high performance NiFe-HC anode for efficient long-term oxygen evolution reaction (OER) at high currents[33,65], we increased acetate FE from 52.5% under 58 atm $CO_2(g)$ (Figure 2c) to 71.1% under 58 atm $CO_2(g) + CO_2(l)$, accompanied by a much higher partial current density of 86.3 mA/cm^2 (Supplementary Figure 7). Note that CO_2RR was done in aqueous electrolytes under $CO_2(g)$ + $CO_2(l)$ at room temperature, which differed from CO_2RR in supercritical conditions[61,66] for which > 31.1 ^{o}C were required (Figure 6a).

Lastly, we developed a sodium alginate (SA) coating layer on our cathode (to obtain SA-SW-$Cu(OH)_2$/Cu) capable of enhancing the cathode durability for efficient CO_2RR to acetate (Supplementary Figure 8, see Methods for details). Through the 20 h reduction at -1.7 V vs. Ag/AgCl in solution B under 58 atm $CO_2(g) + CO_2(l)$, the SA-SW-$Cu(OH)_2$/Cu afforded 51.7% acetate FE at a high 65.4 mA/cm^2 partial current density (Figure 6c and Supplementary Figure 8) with a potassium acetate yield of 30 $mg \cdot h^{-1} \cdot cm^{-2}$ from direct CO_2RR. Comparing with SW-$Cu(OH)_2$/Cu without a SA coating, SA-SW-$Cu(OH)_2$/Cu showed significantly prolonged CO_2RR efficiency to acetate over time, and the concentration of dissolved Cu^{2+} species in catholyte largely decreased with a much lighter blue color after 20 h (Supplementary Figure 8). As observed previously[4,67], Cu^{2+} species were generated from the Cu/CuO_x cathode even at reduction potentials due to trace oxygen in the system (possibly coming from anodic OER despite the introduction of oxygen absorber in the electrolyzer, see Methods for details), which caused cathode corrosion over long term CO_2RR. This stability issue was circumvented with the SA coating layer since alginate was well-known to cross-link by divalent ions like Cu^{2+} to form a gel-like network[68,69] (Figure 6d), slowing down copper dissolution and thus protecting the cathode degradation. Interestingly, we observed pronounced K 2p signals in the XPS spectra of SA-SW-$Cu(OH)_2$/Cu after long-term CO_2RR (Supplementary Figure 8), suggesting cation exchange of K^+ with the initial Na^+ ions in the alginate layer. The thickness of this alginate layer was estimated to be < 42 nm by XPS with Ar ion sputtering. Quantitative analysis of the Cu 2p features and $L_3M_{4,5}M_{4,5}$ auger peaks showed obviously higher Cu oxidation states on the cathodes with alginate protection (Figure 6e and Supplementary Figure 8), indicating a slowdown of Cu dissolution that stabilized the active sites needed for efficient CO_2RR-to-acetate conversion.

Conclusions

In summary, we opened a highly efficient electrochemical CO_2RR-to-acetate production pathway on a $Cu(OH)_2$ derived Cu/CuO_x catalyst under 58 atm $CO_2(g)$ and further under liquid $CO_2(l)$. The concentrations of dissolved $CO_2(aq)$ and HCO_3^- were revealed to be important parameters for determining CO_2RR selectivity. In-situ Raman spectroscopy supported the mechanism of $^*OC^{\bullet}O^*$ on Cu(I) sites coupling with a second one-carbon species/intermediate to form the acetate precursor. This high-pressure CO_2RR system led to dominant acetate production from CO_2RR on copper-based electrocatalysts. The fundamental insight and high yield/efficiency acetate production could facilitate further optimizations of CO_2RR towards specific products.

Methods

Preparation of SW-Cu(OH)$_2$/Cu and SA-SW-Cu(OH)$_2$/Cu electrodes. Firstly, a constant oxidation current of 5 mA/cm^2 was applied on a Cu foil (99.999%, 0.5 * 4 cm^2, Thermo Fisher Scientific) with graphite as the counter electrode in an electrolyte consisting of 0.375 M NaOH, 0.236 M Na_2CO_3, and 0.066 M Na_2SiO_3. After 15 min of oxidation, the foil was transferred into 25% w/w H_2SO_4 and soaked for 2 hours to remove the surface oxidation layer, following by washing with ultrapure water three times before usage. A typical square-wave redox cycling was conducted in an H-type glass cell (Supplementary Figure 1) with two electrolyte zones separated by a 180 μm thick Nafion 117 membrane (Chemours, DuPont). The electrolyte contained 1 M KOH or 0.5 M KCl + 1 M KOH, with a saturated calomel electrode (SCE) used as the reference electrode and graphite rod used as the counter electrode. In order to prepare SW-Cu(OH)$_2$/Cu, the oxidation and reduction potentials were set to be 0 V and -0.75 V vs. SCE using a CH Instrument 760E electrochemical workstation, with an alternating frequency of 5 Hz and a total cycling time of 0.5 hours (Supplementary Figure 1). As-prepared SW-Cu(OH)$_2$/Cu electrode was rinsed by ultrapure water and stored in vacuum before CO_2RR. To prepare SA-SW-Cu(OH)$_2$/Cu, 50 mg alginic acid sodium salt (Sigma-Aldrich) was dissolved in to 10 mL 1:1 v/v ethanol + H_2O solution, and SW-Cu(OH)$_2$/Cu was immersed in the fresh solution for 10 min. After immersion, the electrode was rinsed by ultrapure water and dried in vacuum for the following steps.

Material characterizations. Synchrotron-based grazing incidence x-ray diffraction (GIXRD) was performed on BL13A of Taiwan Light Source (TLS) at National Synchrotron Radiation Research Center (NSRRC), Taiwan, with a monochromatic x-ray of wavelength 1.02174 Å collimated to a spot size of 500 * 500 um^2, and θ/2θ normal scan performed by eight-circle diffractometer. Scanning electron microscopy (SEM) was performed on JEOL JSM6335 Field Emission Scanning Electron Microscope operating at 20 kV. High-resolution transmission electron microscopy (HRTEM) was performed on FEI Tecnai G2 F20 X-TWIN Transmission Electron Microscope using a carbon coated Cu mesh grid for holding the nanowire samples collected by ultrasonicating the SW-Cu(OH)$_2$/Cu electrode. X-ray photoelectron spectroscopy (XPS) was performed on PHI 5000 VersaProbe system using micro-focus (25 W, 100 μm), with Al Kα (1486.6 eV) as the radiation source, and all the binding energy values were calibrated with C1s peak (284.6 eV). X-ray diffraction (XRD) was performed on Rigaku Smart Lab 9 kW system at a scan speed of 2 degree/min from 5° to 100°. Inductively coupled plasma mass spectrometry (ICP-MS) was performed on Thermo Scientific XSeries 2 ICPMS system. Raman spectroscopy was performed on Horiba Jobin Yvon Raman Spectroscopy, with a plasmonic gold[70] (pGOLD) substrate for signal enhancement if necessary. Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet iS50 FTIR Spectrometer. Ultraviolet-visible spectroscopy (UV-Vis) was performed on Agilent Cary 6000i Spectrophotometer.

Electrochemical surface area (ECSA) measurement of as-prepared electrodes. ECSA measurements of the as-prepared SW-$Cu(OH)_2$/Cu and Cu foil electrodes were conducted in an H-type glass cell with SCE as the reference electrode and graphite rod as the counter electrode. In a 0.5 M $KHCO_3$ solution, a 20 mV potential window around the open circuit potential (OCP) of the three-electrode system was used for cyclic voltammetry (CV) measurement at scan rates of 100, 250, 500, 750, and 1000 mV/s to obtain a series of parallelogram shaped CV profiles that revealed the pure capacitance performance of the system without any reduction-oxidation reaction (Supplementary Figure 1). The average difference between the charging and discharging current densities Δj was correlated to the corresponding scan rate, resulting in linear regressions with high determination coefficients R^2 (Supplementary Figure 1). Thus, the ECSA ratio between two working electrodes was derivable from their linear regression slopes.

Setup of the high-pressure electrolysis system. We previously reported a home-designed three-electrode high-pressure electrolyzer[33] with a polytetrafluoroethylene (PTFE) reactor in a stainless-steel shell that allowed CO_2RR under high pressure conditions (Figure 2a). The catholyte and anolyte was separated by a Nafion 117 membrane, with oxygen absorber (Oxy-Sorb 300 cc packet) introduced in the shared gas phase to remove O_2 and prevent the competing oxygen reduction reaction (ORR)[71]. After reaction, the gaseous products were quantified by SRI MG#5 gas chromatography (GC), and the liquid products were diluted by deuterium oxide (D_2O) and quantified by Varian Inova 600 MHz nuclear magnetic resonance (NMR) spectroscopy under a solvent suppression mode.

Three-electrode CO_2RR measurements under high pressure $CO_2(g)$ and 1 atm $CO_2(g)$ bubbling conditions. Before testing the CO_2RR performance of as-prepared electrodes, we applied a constant current of 0.1 mA between two graphite rod electrodes for 12 h to remove possible metal ions dissolved in electrolyte B, $KHCO_3$, and K_2SO_4 solutions. For electrolytes containing KCl, Chelex 100 resins (Bio-Rad, regenerated with 1 M HCl and 1 M KOH) were used to remove possible impurities. After purification, the electrolytes were kept under high pressure conditions for 1 to 10 h to equilibrate with the gas phase. High pressure CO_2RR was conducted using KCl saturated Ag/AgCl electrode as reference electrode and Ni foam as anode in the high pressure electrolyzer (Figure 2a) with a typical resistance of ~ 3 Ω between the cathode and reference, and constant reduction potentials applied for 1 h before sample collection. For comparison, 1 atm CO_2RR were conducted in an H-type glass cell under 30 sccm $CO_2(g)$ bubbling with a 0.5 h equilibration time before the 1 h reactions. A typical resistance between the cathode and reference was ~ 1 Ω. The cathodic headspace of H cell was connected with GC for online analysis of gaseous products. Unless otherwise mentioned, 0.5 M $KHCO_3$ solution were used as the anolyte for 1 atm and high pressure CO_2RR conditions.

CO_2RR product analysis. We quantified the gas products including hydrogen, carbon monoxide, methane, and ethylene by GC. After high pressure reactions, the gas samples were collected in gas sampling bags and injected into GC after calibrating by standard gas mixtures (1% w/w and 0.5% w/w of hydrogen, oxygen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, and acetylene, in nitrogen). For common 1 atm CO_2RR measurements, the cathodic headspace of H cell was directly connected to GC with a flow rate of 30 sccm, and the online analysis of gas component repeated every 20 min. For both high pressure and 1 atm CO_2RR measurements, one-dimensional ^{1}H NMR spectroscopy was performed under water suppression mode for product analysis after samples diluted by 10% v/v D_2O and the inner reference dimethyl sulfoxide (DMSO). Standard solutions of potassium formate, potassium acetate, ethanol, and n-propanol were prepared for deriving NMR calibration curves.

Dynamic electrochemical measurements of solution pH under high pressures. In order to track the pH evolution in electrolytes used for high pressure CO_2RR, we developed an electrochemical method based on the reduction-oxidation reactions of zinc[33,46] (Supplementary Figure 2). A typical electrochemical pH measurement was performed in the high pressure electrolyzer with a zinc foil working electrode paired with a KCl saturated Ag/AgCl reference electrode and a Ni foam counter electrode. After a desired equilibrating time under specific $CO_2(g)$ partial pressures, CV profiles were recorded at a 20 mV/s scan rate, and the onset interconversion potential Φ between Zn(0) and Zn(II) species was derived from the tangent lines of Zn(0) oxidation peaks and Zn(II) reduction peaks on the CV profile (Supplementary Figure 2). Then the solution pH became derivable from Φ combining with concentration of an inorganic carbon species CO_3^{2-} or HCO_3^- based on Nernst equation. This electrochemical pH measurement is applicable to solutions with pH > 6.5.

High-pressure in-situ Raman spectroscopy. We set up a high pressure Raman spectroscopy (Figure 4a) for the in-situ monitoring of SW-$Cu(OH)_2$/Cu catalyst and surface intermediates during CO_2RR. A 10 mL PTFE cell was equipped with a Pt wire counter electrode and Ag/AgCl reference electrode. The cell was set in a stainless steel shell that sustained high pressures up to 100 atm, with a 3 mm sapphire window allowing optical measurements. For a typical high-pressure in-situ Raman spectroscopy measurement, 0.3 * 0.3 cm^2 SW-$Cu(OH)_2$/Cu electrode was stick onto the working electrode substrate by double sided copper tape, and solution B after 1 h equilibration under corresponding pressures was injected into the cell. After sealing the stainless steel shell, high pressures were applied from a CO_2 cylinder, then the reduction potential was applied from the potentiostat. A typical resistance between the cathode and reference was ~ 5 Ω. Raman spectra were obtained on Horiba Jobin Yvon Raman Spectrometer equipped with a PilotPC 500 Laser Diode Controller, a Spectra-Physics Laser Exciter, and a Mitutoyo 50* M Plan APO NIR Objective of a 2.0 cm long working distance enabling the focusing of 532 nm laser onto the electrode surface.

Enhanced Raman spectroscopy for dynamic quantification of CO_3^{2-} and HCO_3^- ions in the electrolytes. Raman spectroscopy was previously employed to characterize the inorganic carbon species HCO_3^- and CO_3^{2-} in solutions, but with limited sensitivities especially for the HCO_3^- ion[48,49]. A nanostructured plasmonic gold (pGOLD) thin film[70] on a borosilicate glass disc (customized by Nirmidas Biotech, Inc.) to serve as the substrate for a plasmon enhanced Raman spectroscopy. The pGOLD substrate showed isolated gold islands of 50 - 200 nm in size patching together on the glass surface according to SEM, with gaps of 10 - 50 nm between the islands (Supplementary Figure 5). The Raman spectra were obtained on Horiba Jobin Yvon Raman Spectrometer equipped with a PilotPC 500 Laser Diode Controller, a Spectra-Physics Laser Exciter, and a Mitutoyo 50*

M Plan APO NIR Objective of a 2.0 cm long working distance enabling the focusing of 532 nm laser onto the pGOLD substrate.

Dropping HCl titrated 2 M K_2CO_3 (pH = 10.0) onto the pGOLD substrate for an enhanced Raman measurement, we observed two prominent peaks at 1015 and 1065 cm^{-1}, corresponding to the stretching of C-OH bond in HCO_3^- and C-O bond in CO_3^{2-} respectively[72,73] (Supplementary Figure 5). Compared to common Raman measurements on a polycrystalline gold foil substrate, pGOLD afforded significantly larger peak areas of ~ 8 times for both the two species (Supplementary Figure 5). However, this enhancement effect was orders of magnitude lower than that for molecules absorbed on plasmonic substrates[74], a rationale of which was that liquid phase Raman spectra on the pGOLD substrate detected the entire volume of solution under the laser focus, unlike typical surface enhanced Raman scattering (SERS) solely detecting the densely packed molecules on the hot spots of a plasmonic substrate. In the laser focal volume of the solution, enhancement of Raman scattering decays in power law of d^{-10} where d refers to the distance from Raman active species to the plasmonic surface[75].

Calibration curves for CO_3^{2-} and HCO_3^- quantification. To obtain Raman calibration curves for quantifying HCO_3^- and CO_3^{2-} ions in the solutions, we prepared 50 mL 2.0 M K_2CO_3 solution and stepwise titrated it using diluted HCl, with the solution pH dynamically monitored by a pH meter. At desired pH points, 50 μL aqueous samples were transferred into our previously reported optical cell[32] (Supplementary Figure 5) equipped with a 3 mm thick quartz disc window pairing with the pGOLD substrate, and the cell thickness was adjusted to be $d = 103.0$ μm. Using the 532 nm laser, Raman measurements were recorded during solution pH decreasing from the original 13.3 to the final 8.0, with 30 scan cycles at a laser exposure time of 10 s at each point. The integrated Raman peak areas of HCO_3^- and CO_3^{2-} were normalized by the corresponding peak areas at pH = 10.0 to avoid laser power fluctuations and minimize other unexpected deviations. Correlating the normalized peak areas with calculated CO_3^{2-} and HCO_3^- concentrations at different pH values resulted in two calibration curves with high linearities (Supplementary Figure 5). This pGOLD enhanced Raman spectroscopy detected down to ~ 10 mM for HCO_3^- and ~ 1 mM for CO_3^{2-} based on a standard deviation analysis of its sensitivity at 532 nm.

Dynamic Raman quantification of CO_3^{2-} and HCO_3^- in electrolytes under high pressures. With a 3 mm thick quartz disc window pairing to the pGOLD substrate in our previously reported high pressure optical cell[32], the cell thickness was adjusted to 50 μm before 5 mL of fresh electrolyte transferring to the solution reservoir connected with the optical cell (Supplementary Figure 5). And with the reservoir screwed and sealed, valve V_1 connected to CO_2 cylinder and V_2 closed, 15 - 58 atm $CO_2(g)$ was applied to the headspace of the reservoir. After equilibrating for a desired time, we opened V_2 to sample the optical cell, and adjusted the 532 nm laser beam under microscope mode to focus on the pGOLD substrate. Raman spectrum for each sample was recorded over 10 - 30 scan cycles in 30 s. For switching to the next sample, we closed V_2 and opened V_3 to have the cell and channels flushed by the new liquid sample in reservoir, then closed V_3 and opened V_2 to inject the new sample and recorded new spectra. Dilute HCl acidified 2 M K_2CO_3 solution (pH = 10.0) was measured before each experiment and used as a standard solution for peak normalization. CO_3^{2-} and HCO_3^- concentrations were then derived from their calibration curves, respectively.

Dynamic micro-IR quantification of dissolved $CO_2(aq)$ in electrolytes under high pressures. The concentration of dissolved $CO_2(aq)$ in various electrolytes was measured by an in-situ micro-IR technique that we previously reported[32]. The stainless steel cell frame was screwed tightly with O-rings onto the windows to ensure good sealing under high pressures. The transmission FTIR spectra were conducted on a Nicolet iS50 FTIR Spectrometer. After 1 - 2 mL fresh electrolyte transferring into the sample reservoir connecting to the 0.5 - 6 μm thick optical cell equipped with 3 - 6 mm thick CaF_2 windows, we kept valve V_2 opened, V_3 closed, and V_1 connected to the CO_2 cylinder, and applied 15 to 58 atm $CO_2(g)$ to the reservoir with a gas-liquid interphase area of ~ 1.5 cm^2. IR spectra were recorded after desired equilibrating time periods at a resolution of 0.96 cm^{-1}. By integrating the obtained $CO_2(aq)$ IR absorption peak at 2343 cm^{-1}, dissolved $CO_2(aq)$ concentration was derivable from its molar extinction coefficient[32] $\varepsilon = 1.74 * 10^4\ M^{-1}\cdot cm^{-2}$.

Preparation of NiFe-HC anode for efficient OER. For electrochemical synthesis of NiFe-HC anode that we previously reported as an efficient OER catalyst[33,65], a Ni-Fe alloy foam of Ni : Fe = 2 : 8 was used as the working electrode and coupled with a Pt mesh counter electrode. With an 80 °C oil bath, a 0.25 A/cm^2 constant oxidation current was applied onto the two electrodes for 16 h in 0.1 M $KHCO_3$ solution. After the electrochemical oxidation, as-prepared NiFe-HC electrode was rinsed by water and ready to be used as anode after drying in vacuum.

Three-electrode CO_2RR measurements under high pressure CO_2(*g*) + CO_2(*l*). Previously we obtained a reciprocal correlation between CO_2(*g*) partial pressure and dissolved CO_2(*aq*) concentration in various solutions[32]. The maximum CO_2(*g*) pressure is measured to be 58 atm at 23 °C (Figure 5a), limiting the further improvement of dissolved CO_2(*aq*) concentration in the electrolytes. We came up with a novel method to further increase CO_2(*aq*) by introducing CO_2(*s*) into the system. During a common 58 atm CO_2RR process, we added 20 g dry ice into our high pressure chamber in a container hanging above the electrolytes, and put the whole electrolyzer into a 30 °C water bath. Then we immediately sealed the high pressure electrolyzer and applied 58 atm CO_2(*g*). We kept tracking the electrolyte temperature using a thermocouple during the dry ice melting. The temperature typically recovered to ~ 23 °C within 30 min, upon which we removed the water bath and started 1 to 20 h CO_2RR. Since the addition of CO_2(*s*) into the high pressure system afforded a liquid CO_2 layer on the aqueous electrolyte that could lead to concentration gradients of dissolved CO_2(*aq*) in the electrolyte, we bent the SW-$Cu(OH)_2$/Cu or SA-SW-$Cu(OH)_2$/Cu foil to L shape, making the foil parallel to the CO_2(*l*) and electrolyte interface with an immersion depth ~ 3 mm in the aqueous phase (Supplementary Figure 7). To reduce the circuit resistance, 4 * 1 cm^2 carbon paper 29 AA (Fuel Cell Store) was clipped together with the L-shape electrodes for a better conductivity. A typical resistance between the cathode and reference was ~ 3 Ω. A 50 μm thick Nafion 212 membrane (Chemours, DuPont) and NiFe-HC anode were used in these conditions. When the reactions were over, we released the pressure and opened the electrolyzer as normal, and there was no dry ice remained.

In order to directly observe the CO_2(*l*) layer on the electrolyte upon melting of CO_2(*s*), we equipped our high pressure optical cell with an extra dry ice reservoir controlled by valve V_4 (Supplementary Figure 7). With 3 mL fresh electrolyte transferring into the solution reservoir connected to the 50 μm thick optical cell equipped with 6 mm thick borosilicate glass windows, we kept V_1 and V_2 open while V_3 and V_4 closed. After 2 g CO_2(*s*) adding to the dry ice reservoir, 58 atm CO_2(*g*) was applied to the whole system through V_1, then V_4 was open and V_1 was closed. The stainless steel dry ice reservoir contacted directly with air through a large area for heat transfer, making CO_2(*s*) inside quickly melt and a thin ~ 3 mm CO_2(*l*) quickly become observable in the optical window in 2 min (Figure 6a). By recording the IR absorption of surface solution B under this 58 atm $CO_2(g)$ + $CO_2(l)$ condition after 0.5 h equilibrating, we noticed a ~ 1.4 times increasement of $CO_2(aq)$ concentration ~ 3 mm beneath the interface compared with 1 h equilibrating under 58 atm $CO_2(g)$ without $CO_2(l)$ (Figure 6b).

Data Availability: All data supporting the findings of this study are available in the article and Supplementary Information, or available from the authors upon request.

Code Availability: All the MATLAB codes supporting the findings of this study are available in Supplementary Information.

Acknowledgments: The authors thank Jinyu Guo, Yunha Jung, and Dr. Huaxin Gong for their warm help. This work was supported by Deng Family Gift Fund and Stanford Bits & Watts Program. Part of this work was performed at Stanford Nano Shared Facilities (SNSF), supported by National Science Foundation under award ECCS-2026822.

Author Contributions: H.D. and J.L. designed the study. J.L., Y.K., X.Z., W.H., C.C., G.Z., G.C., and P.L. performed material synthesis and characterizations. J.L., Y.K., X.Z., F.W., and P.L. performed electrochemical and spectroscopic experiments. J.L. performed calculations and derivations. J.L. and H.D. prepared the manuscript. All authors participated in data analysis and result discussions.

Competing Interests: The authors declare that they have no competing interest.

Figure Legends/Captions

Figure 1. Synthesis and characterization of SW-$Cu(OH)_2$/Cu. a, CV profile of pure Cu foil in 0.5 M KCl + 1 M KOH, scanning from 0.5 to -1.0 V vs. SCE at 1 mV/s. With the $Cu(OH)_2$ oxidation peak occurring at -0.225 V and reduction peak occurring at -0.902 V, the 9000 cycles of SW redox treatment between 0 and -0.75 V in 30 min led to $Cu(OH)_2$ accumulation on Cu surface. Images on the right showed the color change of Cu foil from red to light green after 0.5 h SW treatment. **b,** GIXRD pattern of as-prepared SW-$Cu(OH)_2$/Cu, revealing multiple $Cu(OH)_2$ crystal facets formed on the electrode surface during SW treatment. **c,** SEM image of as-prepared SW-$Cu(OH)_2$/Cu, showing abundant fiber-like structures on the electrode surface with lengths in micron scale. **d,** HRTEM image of a single fiber on electrode surface, suggesting formation of the fiber by parallel bundles of ~ 10 – 40 nm thin nanowires. **e,** Zoom-in image of a single nanowire with crystal defects highlighted by dashed lines, indicating the high porosity of electrode after SW treatment leading to an increasing surface area (Supplementary Figure 1).

Figure 2. CO_2RR of SW-$Cu(OH)_2$/Cu under 58 atm CO_2(*g*). a, A simplified schematic of high pressure CO_2RR electrolyzer. With catholyte and anolyte separated by a Nafion membrane, the shared gas phase was kept at high CO_2(*g*) partial pressures up to 58 atm to achieve high CO_2(*aq*) concentration. Oxygen absorber was employed to absorb O_2 generated by OER on the anode. **b,** Geometric current density profile of SW-$Cu(OH)_2$/Cu during 1 h CO_2RR in electrolyte B (6 M KOH + 0.8 M H_3BO_3) at -1.7 V vs. Ag/AgCl under 58 atm. The electrolyte was equilibrating for 1 h before CO_2RR. **c,** 1 h CO_2RR of SW-$Cu(OH)_2$/Cu in electrolyte B at -1.3 to -1.9 V vs. Ag/AgCl under 58 atm, with 87.3% maximum acetate FE achieved at -1.3 V. At more negative reduction potentials, acetate FE significantly decreased with increasing HER. Error bars were obtained from three parallel experiments. Data were presented as mean values +/- SD. **d,** Partial current densities of acetate and C_2+ products for 1 h CO_2RR of SW-$Cu(OH)_2$/Cu at -1.3 to -1.9 V vs. Ag/AgCl under 58 atm. Maximum acetate and C_2+ partial current densities of 39.2 and 55.6 mA/cm^2 were reached at -1.7 V, respectively. Error bars were obtained from three parallel experiments. Data were presented as mean values +/- SD.

Figure 3. CO_2RR selectivity between formate, acetate, and ethanol. a, For 1 h CO_2RR at -0.91 V vs. RHE in solution B equilibrating after 1 to 10 h under 58 atm CO_2(*g*), acetate FE and partial current density decreased with decreasing [CO_2(*aq*)]/[HCO_3^-] ratios at extending equilibration times. In contrast, formate FE and partial current density increased with the decreasing [CO_2(*aq*)]/[HCO_3^-] ratios. Error bars were obtained from three parallel measurements. Data were presented as mean values +/- SD. **b,** A positive correlation between acetate/formate FE ratio and [CO_2(*aq*)]/[HCO_3^-] ratio was observed in mild acidic to basic CO_2RR conditions, indicating high

[$CO_2(aq)$]/[HCO_3^-] as a key to selective acetate production over formate. Dashed line was drawn to guide the eye. Error bars were obtained from three parallel experiments. Data were presented as mean values +/- SD. **c,** For 1 h CO_2RR at -0.91 V vs. RHE in solution B equilibrating after 1 h under 15 to 58 atm $CO_2(g)$, acetate FE and partial current density increased with increasing [$CO_2(aq)$] due to elevating $CO_2(g)$ partial pressure. In contrast, ethanol FE and partial current density decreased with increasing [$CO_2(aq)$]. Error bars were obtained from three parallel measurements. Data were presented as mean values +/- SD. **d,** A positive correlation between acetate/ethanol FE ratio and [$CO_2(aq)$] was observed in both solution A and B, indicating [$CO_2(aq)$] as a key to selective acetate production over ethanol at high [$CO_2(aq)$]/[HCO_3^-] conditions. Dashed line was drawn to guide the eye. Error bars were obtained from three parallel experiments. Data were presented as mean values +/- SD.

Figure 4. CO_2RR mechanism on a Cu/CuO_x catalyst explored by in-situ Raman spectroscopy. a, A top-view photo and side-view schematic of the high-pressure in-situ Raman spectroscopy. A three-electrode electrochemical cell was equipped with a stainless steel shell with a sapphire window, allowing in-situ Raman measurement during high-pressure CO_2RR. **b,** High-pressure in-situ Raman spectroscopy for CO_2RR on SW-$Cu(OH)_2$/Cu at -0.91 V vs. RHE in solution B under elevating $CO_2(g)$ partial pressures. With pressure increasing to 30 atm, pronounced CO_2 peaks at ~ 1291 and 1392 cm^{-1} started to appear, suggesting the abundance of $CO_2(aq)$ at high pressures. And with pressure increasing to 45 atm, doublet peaks started to be observed at ~ 1455 and 1478 cm^{-1}, which were assigned to symmetric C-O stretching vibration ν of the O-bound bidentate intermediate $*OC^{\bullet}O*$ (configuration α_1). **c,** Zoom-in Raman spectrum of the C-O stretching vibration under 58 atm. The peaks were fitted to Cauchy-Lorentz distributions with $R^2 = 0.98$. **d,** Raman spectroscopy on the SW-$Cu(OH)_2$/Cu electrode in solution B under 58 atm $CO_2(g)$ without applying a reduction potential. When the -0.91 V vs. RHE was removed, the α_1 ν peaks vanished and CO_2 peaks significantly increased, suggesting the pause of CO_2RR. **e,** A simplified schematic of CO_2RR mechanism in producing formate, acetate, ethanol, and hydrocarbons. On a mixed Cu/CuO_x catalyst surface, CO_2 adsorption on active Cu(I) sites *via* Cu-O linkage resulted in configuration α, and adsorption on active Cu(0) sites *via* Cu-C linkage resulted in configuration β. Electro-reduction of α resulted in $*OC^{\bullet}O*$, while electro-reduction of β resulted in *CO (configuration β_1). As the precursor of carboxylate group, α_1 protonation resulted in the formation of formate, and α_1 coupling with a second one-carbon species/intermediate (such as CO_2, $*CH_3$, and *CH=O) resulted eventually in the formation of acetate. Alternatively, electro-reduction and protonation of β_1 resulted in $*CO_xH_y$ on Cu(0) sites (configuration β_2). Methane was formed by the thorough electro-reduction and protonation of isolating β_2, while ethylene and ethanol were formed by C-C coupling of neighboring β_2, followed by further electroreduction, protonation, and inner molecular rearrangements.

Figure 5. CO_2RR selectivity trend on a Cu(I)/Cu(0) catalyst. a, 1 h CO_2RR performance of SW-$Cu(OH)_2$/Cu in solution A, 0.25 M K_2SO_4, and 0.5 M $KHCO_3$ at -1.46 V vs. RHE under 1 atm $CO_2(g)$ bubbling condition and 58 atm high pressure condition, revealing the huge influence of reaction condition to CO_2RR selectivity. CO_2RR started 0.5 h after $CO_2(g)$ applied because of their much quicker equilibration than the basic electrolytes. Error bars were obtained from three parallel experiments. Data were presented as mean values +/- SD. **b,** CO_2RR selectivity of SW-$Cu(OH)_2$/Cu at various conditions. A reduction potential of -1.46 V vs. RHE was applied for mild acidic and near neutral electrolytes (KCl + $KHCO_3$, $KHCO_3$, K_2SO_4), and -0.91 V vs. RHE for basic electrolytes KOH + H_3BO_3. With measured $[CO_2(aq)]$ increasing from ~ 10^{-2} to 10^{0} M level, dominant CO_2RR product (FE significantly higher than other products) shifted from hydrocarbons to alcohol then to carboxylates. And with measured $[CO_2(aq)]/[HCO_3^-]$ ratio increasing from ~ 10^{-1} to 10^{2} level, dominant CO_2RR product shifted from C_1 to C_2.

Figure 6. Boosting CO_2RR performance by introducing $CO_2(l)$. a, CO_2 phase diagram and phase transition. CO_2 gas-liquid equilibrium pressure at 23 °C was measured to be 58 atm. By introducing dry ice under 58 atm $CO_2(g)$, a thin $CO_2(l)$ layer was observed between the electrolyte B and gas phase upon $CO_2(s)$ melting in the high pressure optical cell (Supplementary Figure 7). **b,** Micro-IR measurement of $[CO_2(aq)]$ in solution B after 1 h equilibrating under 58 atm $CO_2(g)$ without $CO_2(l)$ and 0.5 h equilibrating with $CO_2(l)$. Integration of $CO_2(aq)$ absorption peak at 2343 cm^{-1} revealed ~ 1.4 times $[CO_2(aq)]$ increase in the electrolyte. **c,** 20 h CO_2RR of L-shape SA-SW-$Cu(OH)_2$/Cu at -1.7 V vs. Ag/AgCl in solution B under 58 atm $CO_2(g)$ + $CO_2(l)$. As prepared SW-$Cu(OH)_2$/Cu was immersed in sodium alginate solution to coat an alginate layer on the surface (see Methods for details). The cathode was bent to L shape in order to parallel its end to the interface of $CO_2(l)$ and aqueous catholyte. Paring with a NiFe-HC anode, 51.7% acetate FE was achieved at 65.4 mA/cm^2 partial current density for 20 h CO_2RR, with a 30 $mg{\cdot}h^{-1}{\cdot}cm^{-2}$ potassium acetate yield. Error bars were obtained from three parallel experiments. Data were presented as mean values +/- SD. **d,** A schematic of alginate chains passively crosslinked by Cu^{2+} species from the catalyst surface. Cu^{2+} ion interacted with GG blocks in the alginate chains, leading to an egg-box configuration that linked the chains and formed a protection layer on the catalyst surface. **e,** Quantitative analysis of Cu valence evolution on the catalyst surface. During CO_2RR at -1.7 V vs. Ag/AgCl in solution B, Cu species were continuously reduced to lower valences. And with the catalyst coated by an alginate protection layer, the reduction of Cu was largely prolonged, enabling the efficient production of acetate during 20 h long-term reaction.

References

1 S. Nitopi *et al.* Progress and Perspectives of Electrochemical CO_2 Reduction on Copper in Aqueous Electrolyte. *Chem. Rev.* **119**, 7610-7672 (2019).

2 K. P. Kuhl, E. R. Cave, D. N. Abram & T. F. Jaramillo. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy Environ. Sci.* **5**, 7050-7059 (2012).

3 C. T. Dinh *et al.* CO_2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science.* **360**, 783-787 (2018).

4 X. Zhang *et al.* Selective and High Current CO_2 Electro-Reduction to Multicarbon Products in Near-Neutral KCl Electrolytes. *J. Am. Chem. Soc.* **143**, 3245-3255 (2021).

5 S. Y. Lee *et al.* Mixed Copper States in Anodized Cu Electrocatalyst for Stable and Selective Ethylene Production from CO_2 Reduction. *J. Am. Chem. Soc.* **140**, 8681-8689 (2018).

6 M. Zhong *et al.* Accelerated discovery of CO_2 electrocatalysts using active machine learning. *Nature.* **581**, 178-183 (2020).

7 Y. Guo *et al.* Machine-Learning-Guided Discovery and Optimization of Additives in Preparing Cu Catalysts for CO_2 Reduction. *J. Am. Chem. Soc.* **143**, 5755-5762 (2021).

8 A. W. Budiman *et al.* Review of Acetic Acid Synthesis from Various Feedstocks Through Different Catalytic Processes. *Catal. Surv. from Asia.* **20**, 173-193 (2016).

9 Q. Zhu *et al.* Carbon dioxide electroreduction to C_2 products over copper-cuprous oxide derived from electrosynthesized copper complex. *Nat. Commun.* **10**, 3851 (2019).

10 Y. Liu, S. Chen, X. Quan & H. Yu. Efficient Electrochemical Reduction of Carbon Dioxide to Acetate on Nitrogen-Doped Nanodiamond. *J. Am. Chem. Soc.* **137**, 11631-11636 (2015).

11 Y. Wang *et al.* CO_2 reduction to acetate in mixtures of ultrasmall $(Cu)_n$,$(Ag)_m$ bimetallic nanoparticles. *Proc. Natl. Acad. Sci. U.S.A.* **115**, 278-283 (2018).

12 C. Genovese, C. Ampelli, S. Perathoner & G. Centi. Mechanism of C–C bond formation in the electrocatalytic reduction of CO_2 to acetic acid. A challenging reaction to use renewable energy with chemistry. *Green Chem.* **19**, 2406-2415 (2017).

13 H. Wang *et al.* CO_2 electrolysis toward acetate: A review. *Curr. Opin. Electrochem.* **39**, 101253 (2023).

14 C. Li, B. Zha & J. Li. A $SiW_{11}Mn$-assisted indium electrocatalyst for carbon dioxide reduction into formate and acetate. *J. CO_2 Util.* **38**, 299-305 (2020).

15 B. Zha, C. Li & J. Li. Efficient electrochemical reduction of CO_2 into formate and acetate in polyoxometalate catholyte with indium catalyst. *J. Catal.* **382**, 69-76 (2020).

16 X. F. Qiu *et al.* A Stable and Conductive Covalent Organic Framework with Isolated Active Sites for Highly Selective Electroreduction of Carbon Dioxide to Acetate. *Angew. Chem.* **61**, e202206470 (2022).

17 S. Cestellos-Blanco, H. Zhang, J. M. Kim, Y. X. Shen & P. Yang. Photosynthetic semiconductor biohybrids for solar-driven biocatalysis. *Nat. Catal.* **3**, 245-255 (2020).

18 J. Kim, S. Cestellos-Blanco, Y. X. Shen, R. Cai & P. Yang. Enhancing Biohybrid CO_2 to Multicarbon Reduction via Adapted Whole-Cell Catalysts. *Nano Lett.* **22**, 5503-5509 (2022).

19 T. Saeki, K. Hashimoto, N. Kimura, K. Omata & A. Fujishima. Electrochemical reduction of CO_2 with high current density in a CO_2 + methanol medium II. CO formation promoted by tetrabutylammonium cation. *J. Electroanal. Chem.* **390**, 77-82 (1995).

20 R. Aydin & F. Köleli. Electrochemical reduction of CO_2 on a polyaniline electrode under ambient conditions and at high pressure in methanol. *J. Electroanal. Chem.* **535**, 107-112 (2002).

21 R. Aydin & F. Köleli. Electrocatalytic conversion of CO_2 on a polypyrrole electrode under high pressure in methanol. *Synth. Met.* **144**, 75-80 (2004).

22 D. S. Ripatti, T. R. Veltman & M. W. Kanan. Carbon Monoxide Gas Diffusion Electrolysis that Produces Concentrated C_2 Products with High Single-Pass Conversion. *Joule.* **3**, 240-256 (2019).

23 S. Overa *et al.* Enhancing acetate selectivity by coupling anodic oxidation to carbon monoxide electroreduction. *Nat. Catal.* **5**, 738-745 (2022).

24 P. Zhu *et al.* Direct and continuous generation of pure acetic acid solutions via electrocatalytic carbon monoxide reduction. *Proc. Natl. Acad. Sci. U.S.A.* **118**, e2010868118 (2021).

25 W. Luc *et al.* Two-dimensional copper nanosheets for electrochemical reduction of carbon monoxide to acetate. *Nat. Catal.* **2**, 423-430 (2019).

26 J. Choi *et al.* Energy efficient electrochemical reduction of CO_2 to CO using a three-dimensional porphyrin/graphene hydrogel. *Energy Environ. Sci.* **12**, 747-755 (2019).

27 P. M. Maitlis, A. Haynes, G. J. Sunley & M. J. Howard. Methanol carbonylation revisited: thirty years on. *J. Chem. Soc., Dalton Trans.* **11**, 2187-2196 (1996).

28 J. Qi *et al.* Selective Methanol Carbonylation to Acetic Acid on Heterogeneous Atomically Dispersed ReO_4/SiO_2 Catalysts. *J. Am. Chem. Soc.* **142**, 14178-14189 (2020).

29 M. Konig, J. Vaes, E. Klemm & D. Pant. Solvents and Supporting Electrolytes in the Electrocatalytic Reduction of CO_2. *iScience.* **19**, 135-160 (2019).

30 T. Möller *et al.* The product selectivity zones in gas diffusion electrodes during the electrocatalytic reduction of CO_2. *Energy Environ. Sci.* **14**, 5995-6006 (2021).

31 Y. C. Tan, K. B. Lee, H. Song & J. Oh. Modulating local CO_2 concentration as a general strategy for enhancing C-C coupling in CO_2 electroreduction. *Joule.* **4**, 1104-1120 (2020).

32 J. Li, J. Guo & H. Dai. Probing dissolved $CO_2(aq)$ in aqueous solutions for CO_2 electroreduciton and storage. *Sci. Adv.* **8**, eabo0399 (2022).

33 J. Li *et al.* Electroreduction of CO_2 to formate on a copper-based electrocatalyst at high pressures with high energy conversion efficiency. *J. Am. Chem. Soc.* **142**, 7276-7282 (2020).

34 S. Zhao *et al.* Advances in Sn-Based Catalysts for Electrochemical CO_2 Reduction. *Nano-Micro Lett.* **11**, 62 (2019).

35 J. T. Feaster *et al.* Understanding Selectivity for the Electrochemical Reduction of Carbon Dioxide to Formic Acid and Carbon Monoxide on Metal Electrodes. *ACS Catal.* **7**, 4822-4827 (2017).

36 C. I. Shaughnessy *et al.* Intensified Electrocatalytic CO_2 Conversion in Pressure-Tunable CO_2-Expanded Electrolytes. *ChemSusChem.* **12**, 3761-3768 (2019).

37 C. I. Shaughnessy *et al.* Insights into pressure tunable reaction rates for electrochemical reduction of CO_2 in organic electrolytes. *Green Chem.* **22**, 2434-2442 (2020).

38 A. K. Mishra & N. H. De Leeuw. Mechanistic insights into the Cu(I) oxide-catalyzed conversion of CO_2 to fuels and chemicals: A DFT approach. *J. CO_2 Util.* **15**, 96-106 (2016).

39 G. Marcandalli, A. Goyal & M. T. M. Koper. Electrolyte Effects on the Faradaic Efficiency of CO_2 Reduction to CO on a Gold Electrode. *ACS Catal.* **11**, 4936-4945 (2021).

40 Y. Chen, C. W. Li & M. W. Kanan. Aqueous CO_2 reduction at very low overpotential on oxide-derived Au nanoparticles. *J. Am. Chem. Soc.* **134**, 19969-19972 (2012).

41 S. D. Giri & A. Sarkar. Electrochemical Study of Bulk and Monolayer Copper in Alkaline Solution. *J. Electrochem. Soc.* **163**, H252-H259 (2016).

42 J. I. Langford & A. J. C. Wilson. Seherrer after Sixty Years: A Survey and Some New Results in the Determination of Crystallite Size. *J. Appl. Crystallogr.* **11**, 102-113 (1978).

43 A. T. Baker. The Ligand Field Spectra of Copper(II) Complexes. *J. Chem. Educ.* **75**, 98-99 (1998).

44 D. Guo *et al.* Borate-catalyzed carbon dioxide hydration via the carbonic anhydrase mechanism. *Environ. Sci. Technol.* **45**, 4802-4807 (2011).

45 G. Hu *et al.* Carbon dioxide absorption into promoted potassium carbonate solutions: a review. *Int. J. Greenh. Gas Control.* **53**, 28-40 (2016).

46 P. Delahay. Potential-pH Diagram of Zinc and Its Applications to the Study of Zinc Corrosion. *J. Electrochem. Soc.* **98**, 101-105 (1951).

47 W. M. Haynes, D. R. Lide & T. J. Bruno. *CRC Handbook of Chemistry and Physics*. 95th edn, pp. 5-81 (CRC Press, 2014).

48 X. Lu *et al.* In-situ observation of the pH gradient near the gas diffusion electrode of CO_2 reduction in alkaline electrolyte. *J. Am. Chem. Soc.* **142**, 15438-15444 (2020).

49 M. K. Wong, A. M. Shariff & M. A. Bustam. Raman spectroscopic study on the equilibrium of carbon dioxide in aqueous monoethanolamine. *RSC Adv.* **6**, 10816-10823 (2016).

50 W. Akemann & A. Otto. The effect of atomic scale surface disorder on bonding and activation of adsorbates: vibrational properties of CO and CO_2 on copper. *Surf. Sci.* **287**, 104-109 (1993).

51 W. Shan *et al.* In Situ Surface-Enhanced Raman Spectroscopic Evidence on the Origin of Selectivity in CO_2 Electrocatalytic Reduction. *ACS Nano.* **14**, 11363-11372 (2020).

52 D. Bohra *et al.* Lateral Adsorbate Interactions Inhibit $HCOO^-$ while Promoting CO Selectivity for CO_2 Electrocatalysis on Silver. *Angew. Chem.* **58**, 1345-1349 (2019).

53 R. L. Frost & J. T. Kloprogge. Raman spectroscopy of the acetates of sodium, potassium and magnesium at liquid nitrogen temperature. *J. Mol. Struct.* **526**, 131-141 (2000).

54 M. San Andrés, J. M. De La Roja, V. G. Baonza & N. Sancho. Verdigris pigment: a mixture of compounds. Input from Raman spectroscopy. *J. Raman Spectrosc.* **41**, 1468-1476 (2010).

55 J. Buse, V. Otero & M. Melo. New Insights into Synthetic Copper Greens: The Search for Specific Signatures by Raman and Infrared Spectroscopy for Their Characterization in Medieval Artworks. *Heritage.* **2**, 1614-1629 (2019).

56 H. H. Heenen *et al.* The mechanism for acetate formation in electrochemical $CO_{(2)}$ reduction on Cu: selectivity with potential, pH, and nanostructuring. *Energy Environ. Sci.* **15**, 3878-3990 (2022).

57 F. Shao *et al.* In situ spectroelectrochemical probing of CO redox landscape on copper single-crystal surfaces. *Proc. Natl. Acad. Sci. U.S.A.* **119**, e2118166119 (2022).

58 Y. Hori, R. Takahashi, Y. Yoshinami & A. Murata. Electrochemical Reduction of CO at a Copper Electrode. *J. Phys. Chem. B* **101**, 7075-7081 (1997).

59 L. R. L. Ting *et al.* Enhancing CO_2 Electroreduction to Ethanol on Copper–Silver Composites by Opening an Alternative Catalytic Pathway. *ACS Catal.* **10**, 4059-4069 (2020).

60 M. Favaro *et al.* Subsurface oxide plays a critical role in CO_2 activation by Cu(111) surfaces to form chemisorbed CO_2, the first step in reduction of CO_2. *Proc. Natl. Acad. Sci. U.S.A.* **114**, 6706-6711 (2017).

61 R. Qiu *et al.* Enhanced electroreduction of CO_2 to ethanol via enriched intermediates at high CO_2 pressures. *Green Chem.* **25**, 684-691 (2023).

62 K. Hara, A. Tsuneto, A. Kudo & T. Sakata. Electrochemical reduction of CO_2 on a Cu electrode under high pressure: Factors that Determine the Product Selectivity. *J. Electrochem. Soc.* **141**, 2097-2103 (1994).

63 R. Kas, R. Kortlever, H. Yılmaz, M. T. M. Koper & G. Mul. Manipulating the Hydrocarbon Selectivity of Copper Nanoparticles in CO_2 Electroreduction by Process Conditions. *ChemElectroChem.* **2**, 354-358 (2015).

64 C. Coquelet *et al.* Transport of CO_2: Presentation of New Thermophysical Property Measurements and Phase Diagrams. *Energy Procedia.* **114**, 6844-6859 (2017).

65 Y. Meng *et al.* Highly active oxygen evolution integrated with efficient CO_2 to CO electroreduction. *Proc. Natl. Acad. Sci. U.S.A.* **116**, 23915-23922 (2019).

66 O. Melchaeva *et al.* Electrochemical Reduction of Protic Supercritical CO_2 on Copper Electrodes. *ChemSusChem.* **10**, 3660-3670 (2017).

67 F. D. Speck & S. Cherevko. Electrochemical copper dissolution: A benchmark for stable CO_2 reduction on copper electrocatalysts. *Electrochem. Commun.* **115**, 106739 (2020).

68 D. Cozzi, P. G. Desideri & L. Lepri. The Mechanism of Ion Exchange with Alginic Acid. *J. Chromatogr.* **40**, 130-137 (1969).

69 M. Urbanova *et al.* Interaction Pathways and Structure-Chemical Transformations of Alginate Gels in Physiological Environments. *Biomacromolecules.* **20**, 4158-4170 (2019).

70 B. Zhang, R. B. Kumar, H. Dai & B. J. Feldman. A plasmonic chip for biomarker discovery and diagnosis of type 1 diabetes. *Nat. Med.* **20**, 948-953 (2014).

71 L. R. Braga, C. I. G. L. Sarantópoulos, L. Peres & J. W. B. Braga. Evaluation of absorption kinetics of oxygen scavenger sachets using response surface methodology. *Packag. Technol. Sci.* **23**, 351-361 (2010).

72 W. W. Rudolph, G. Irmer & E. Konigsberger. Speciation studies in aqueous HCO_3^- - CO_3^{2-} solutions. A combined Raman spectroscopic and thermodynamic study. *Dalton Trans.* **7**, 900-908 (2008).

73 A. R. Davis & B. G. Oliver. A vibrational-spectroscopic study of the species present in the CO_2-H_2O system. *J. Solut. Chem.* **1**, 329-339 (1972).

74 P. L. Stiles, J. A. Dieringer, N. C. Shah & R. P. Van Duyne. Surface-enhanced Raman spectroscopy. *Annu. Rev. Anal. Chem.* **1**, 601-626 (2008).

75 J. P. Camden, J. A. Dieringer, J. Zhao & R. P. Van Duyne. Controlled Plasmonic Nanostructures for Surface-Enhanced Spectroscopy and Sensing. *Acc. Chem. Res.* **41**, 1653-1661 (2008).