Zhang et al. design a bicarbonate electrolyzer to couple carbon dioxide capture with carbon dioxide electroreduction. With careful pH and partial pressure engineering, and the adoption of a cation exchange membrane and intermediate layer, aqueous bicarbonate feedstock is converted into solid formate fuel with a high carbon efficiency.

**Highlights**
- Impacts of CO₂ partial pressure on local pH and carbon efficiency are gauged
- CO₂, bicarbonate, and carbonate equilibrium are key to achieving high carbon efficiency
- Bicarbonate-to-formate electrochemical conversion generates no net acid or base
- Formate is a potential solid fuel for seasonal energy storage

A carbon-efficient bicarbonate electrolyzer

Zhen Zhang,1 Dawei Xi,2 Zhichu Ren,1 and Ju Li1,3,4,*

SUMMARY
Carbon efficiency is one of the most pressing problems of carbon dioxide electroreduction today. While there have been studies on anion exchange membrane electrolyzers with carbon dioxide (gas) and bipolar membrane electrolyzers with bicarbonate (aqueous) feedstocks, both suffer from low carbon efficiency. In anion exchange membrane electrolyzers, this is due to carbonate anion crossover, whereas in bipolar membrane electrolyzers, the exsolution of carbon dioxide (gas) from the bicarbonate solution is the culprit. Here, we first elucidate the root cause of the low carbon efficiency of liquid bicarbonate electrolyzers with thermodynamic calculations and then achieve carbon-efficient carbon dioxide electroreduction by adopting a near-neutral-pH cation exchange membrane, a glass fiber intermediate layer, and carbon dioxide (gas) partial pressure management. We convert highly concentrated bicarbonate solution to solid formate fuel with a yield (carbon efficiency) of greater than 96%. A device test is demonstrated at 100 mA cm⁻² with a full-cell voltage of 3.1 V for over 200 h.

INTRODUCTION
Carbon dioxide electroreduction (CO₂ER) is an attractive strategy of CO₂ utilization for providing various chemicals (HCOOH, CO, C₂H₄, CH₃COOH, C₂H₅OH, etc.) while decreasing atmospheric CO₂ simultaneously. Over the past 40 years, considerable progress has been made in developing numerous types of catalysts to improve the Faradaic efficiency (FE) for CO₂ER relying on a CO₂(gas) feedstock. However, the technology is still far from industrialization because of multiple critical challenges. In particular, carbon efficiency, which is the percentage of CO₂ utilized among the captured, is one of the most basic and pressing issues that impedes the commercialization of CO₂ electrolyzers today. For many traditional anion exchange membrane (AEM) CO₂ electrolyzers, the carbon efficiency is typically below 10%, while a carbon efficiency of over 80% is required for the commercialization of CO₂ER.9

Traditionally, CO₂ capture and CO₂ER have been considered separately. CO₂ captured from dilute sources should be first converted (typically to solid calcium carbonate, CaCO₃), transported, thermally decomposed, and pressurized to become ultra-pure CO₂ gas feedstock (Figure S1). For the prevalent alkaline- or neutral-medium-based aqueous membrane electrode assembly (MEA) electrolyzers, over 50% of the capital cost would come from this solid-state thermal regeneration process which is highly energy intensive. In addition, in the aqueous environment, CO₂ER involves proton-coupled electron transfer (PCET) reactions, locally generating hydroxides (e.g., CO₂ + H₂O + 2e⁻ → CO + 2OH⁻). The OH⁻ ions would have a chance to convert reactive CO₂* into electrochemically inert CO₃²⁻(aq) (2OH⁻ + CO₂ → CO₃²⁻ + H₂O), which is a “trap state” in the catholyte.
a CO₂ MEA electrolyzer with the AEM, HCO₃⁻/CO₃²⁻ ions are the major charge carriers in the electrolyte and would cross over the membrane to the anode side with a high chance of being wasted (Figure S2a). This carbon efficiency loss problem is more detrimental to products with more electrons transferred. For instance, for the 2-electron-transfer reaction of CO production, 2 OH⁻ ions are generated per 1 CO₂ converted, and thus the carbon efficiency loss will be 50%, assuming all OH⁻ → CO₃²⁻ will drift across and get lost. For the 6-electron-transfer reaction of C₂H₅OH production, 6 OH⁻ ions are generated per 1 CO₂ converted, and thus the efficiency loss will be 75% (Table S1). Further, the parasitic hydrogen evolution reaction (HER) also produces OH⁻ (2H₂O + 2e⁻ → H₂ + 2OH⁻), which further lowers the carbon efficiency and FE. Until today, most of the reported CO₂ER research only accounts for the percentage of CO₂ actually converted, but it leaves out the substantial amount of CO₂ unconverted or wasted, which is either lost as crossover CO₃²⁻ or just unreacted and merges into a gaseous mixture with the outlet products. Thus, the combined carbon efficiency and energy efficiency of CO₂ capture and electroreduction, through the traditional route with solid CaCO₃ and ultra-pure gaseous CO₂, is very low.

To address this critical challenge, rather than relying on the CO₂(gas) feedstock, bipolar membrane (BPM) electrolyzers with aqueous bicarbonate HCO₃⁻(aq) input were demonstrated (Figure S2b). In principle, the energy-intensive CO₂ regeneration process could be circumvented. In practice, however, the BPM induces a large overpotential, causing low energy efficiency, and it still suffers from CO₂ escape, low FE, low yield, and low operation lifetime. The carbon efficiency problem is due to the thermodynamically driven CO₂ outgassing from a highly concentrated bicarbonate feedstock. Carbonate ions would be produced spontaneously (2HCO₃⁻ → CO₂(gas) + CO₃²⁻ + H₂O), which suppresses both the FE and carbon efficiency. Here, we note the retention of relatively low pH is crucial, as H⁺(aq) is a promoter of CO₂ER in bicarbonate electrolyzers. H⁺(aq) converts inactive HCO₃⁻ into reactive CO₂. Further, H⁺(aq) balances solution pH, which is crucial to achieving a high carbon efficiency. During operation, reactions that lead to net base production, such as CO production from HCO₃⁻ (full reaction: HCO₃⁻ → CO + ½ O₂ + OH⁻), would pile up deleterious CO₃²⁻(aq) and OH⁻(aq), buffering the feedstock, impeding its further operation. Thereupon, the conversion of bicarbonate is restricted. Consequently, the selectivity of CO₂ER would decline continuously in constant-current mode, as we will show.

RESULTS AND DISCUSSION
Thermodynamic analysis
We first identify the key causes of the carbon efficiency loss in liquid bicarbonate electrolyzers with the Pourbaix diagram (Figure 1A). “No net acid or base production” is essential to maintaining a steady pH and high yield (carbon efficiency). In a bicarbonate electrolyzer, the electrochemical CO₂ER is preceded by in situ CO₂* generation from HCO₃⁻(aq) as follows:

\[ x\text{HCO}_3^-(aq) + x\text{H}^+(aq) \rightarrow x\text{CO}_2 + x\text{H}_2\text{O}(aq) \]  \hspace{1cm} (Equation 1)

\[ x\text{CO}_2 + ze^- + n\text{H}^+(aq) \rightarrow (\text{C}_n\text{H}_{2n+2}\text{O}_{2n+2})^{n^-} + y\text{H}_2\text{O}(aq) \]  \hspace{1cm} (Equation 2)

From the Nernst equation, the slope of the electrochemical reaction above could be expressed as

\[ k = - \frac{nRT}{zF \ln 10}, \]  

where \( n \) and \( z \) are the number of protons and electrons transferred in the reaction, respectively. In particular, for the cation exchange membrane (CEM) configuration with a water anode, \( z \) is also the number
Please cite this article in press as: Zhang et al., A carbon-efficient bicarbonate electrolyzer, Cell Reports Physical Science (2023), https://doi.org/10.1016/j.xcrp.2023.101662
of protons shuttled from the anode side to the cathode side to complete the internal circuit. Therefore, three scenarios can occur:

**Net acid (H⁺) production:**  
\[
z > x + n, \text{or} \ k > - \frac{nRT}{(x + n)}F \ln 10 \tag{Equation 3}
\]

pH intrinsically balanced:  
\[
z = x + n, \text{or} \ k = - \frac{nRT}{(x + n)}F \ln 10 \tag{Equation 4}
\]

**Net base (OH⁻) production:**  
\[
z < x + n, \text{or} \ k < - \frac{nRT}{(x+n)}F \ln 10, \tag{Equation 5}
\]

where \(k\) is the voltage vs. pH slope of a reaction equilibrium line on the Pourbaix diagram.

In particular, for CO₂ER to methane, alcohol, and CO, etc., \(z\) equals \(n\) (which also means \(z < x + n\)), the slope \(k\) is \(- \frac{RT}{F} \ln 10\), and net base would be produced. Thus, these reactions would intrinsically cause the chemical equilibrium to shift toward the “trap state” of CO₂\(^{2-}\) (aq) formation (OH⁻ + HCO₃⁻ → CO₂\(^{2-}\) + H₂O), which is highly electrochemically inert for CO₂ER. Further, the slope of CO₂ER to methane, alcohol, and CO is pH independent because these molecules would not readily shed protons under the operating conditions. However, weak acids such as formic acid (HCOOH) and acetic acid (CH₃COOH) would readily shed protons above a certain pH. Consequently, the slope in the Pourbaix diagram would become less negative. Specifically, we identified that for formate production, \(z = x + n = 2\), and the slope is \(- \frac{RT}{2F} \ln 10\), which indicates the reaction is pH balanced intrinsically, and thus, long-term operation can be maintained. Guided by this general principle of “no pH drift,” we identified formate production to be the target steady-state reaction with CEM, where we should expect a theoretical carbon efficiency of 100%. Indeed, the full-cell reaction thus identified

\[
\text{KHCO₃} \rightarrow \text{KOOCH} + \frac{1}{2} \text{O}_2, \Delta H'_f = 3.13 \text{ eV} \tag{Equation 6}
\]

is analogous to water electrolysis,

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2, \Delta H'_f = 2.96 \text{ eV} \tag{Equation 7}
\]

which is also pH balanced, and thus our metal-formate product KOOCH can be considered “solid hydrogen” fuel that can be produced in steady-pH
configuration. Throughout this work, we demonstrated the electrochemical reactions in device-level MEA electrolyzers (Figure 1B). We employed a CEM, pure bicarbonate feedstock and commercially available tin nanoparticle catalysts.

Although CO$_2$(aq), HCO$_3^-$ (aq), and CO$_3^{2-}$(aq) are often considered to be in the same family, their carbon centers are different in terms of electrophilicity, and thus, the microscopic reaction pathways are different. We believe in order for electroreduction to occur, CO$_2$(aq)/HCO$_3^-$ (aq)/CO$_3^{2-}$(aq) need to be first converted into CO$_2^*$, the surface-adsorbed intermediate at the electrocatalyst/aqueous solution interface before electron transfer from the cathode can occur. Theoretically, using a CEM, the production of formate from pure HCO$_3^-$ (aq) solution would not alter the catholyte pH (Figure 1C). This is because for every formate molecule generated, two protons would be consumed, while exactly two protons would migrate through the CEM. However, if we consume CO$_3^{2-}$(aq) by first combining with 2H$^+$ (aq) to form CO$_2^*$, the generation of each formate molecule would result in the net production of 1 OH$^-$ in the catholyte, thus leading to a carbon efficiency loss of 33% (Figure 1D). The continuous increasing of the concentrations of CO$_3^{2-}$/OH$^-$ triggers a vicious cycle, and the FE/selectivity would plummet drastically, ultimately leading to exclusive HER. Following the net reaction of KHCO$_3$/KOOCH + $\frac{1}{2}$O$_2$, avoiding net acid or base accumulation that ultimately leads to HER is crucial. The question arises as to how to maintain a high concentration of HCO$_3^-$ (aq) while suppressing CO$_3^{2-}$(aq) concentration. And since the maintenance of pH in a specific region to avoid the CO$_3^{2-}$(aq) deep trap is essential, this also calls for a specific initial catholyte pH and CEM.

The concentrations of inorganic carbon species (CO$_2$/HCO$_3^-$/CO$_3^{2-}$) in equilibrium with different atmospheres were computed and plotted against alkalinity, which, as a convention, denotes the concentration of the conserved cations (K$^+$, Na$^+$, Ca$^{2+}$, etc.) in the solution (Figures 1E, 1F, and S3). It is shown that in equilibrium with ambient air where the CO$_2$ partial pressure is 400 ppm (roughly 0.4 mbar), carbonate species dominate: [CO$_3^{2-}$(aq)] $\gg$ [HCO$_3^-$ (aq)] (Figure 1E). This means that a freshly prepared bicarbonate solution would thermodynamically exude CO$_2$ (gas) in contact with normal air, resulting in a mixture of HCO$_3^-$ (aq)/CO$_3^{2-}$ (aq), which suffers enormously from the carbon-efficiency problem stated above and becomes almost inert for CO$_2$ER at some point. This is because CO$_3^{2-}$(aq) is directly inert toward CO$_2$ER and must consume 2H$^+$ (aq) to boost its reactivity. However, when the partial pressure of CO$_2$ in the overhead gas, $P_{CO_2}$, reaches 1 atm and above, bicarbonate dominates in the aqueous phase: [HCO$_3^-$ (aq)] $\gg$ [CO$_3^{2-}$ (aq)] (Figure 1F). This means that the freshly prepared bicarbonate feedstock could be converted into formate with a theoretical yield of ~100% with nearly zero carbon efficiency loss, if in a constant CO$_2$ partial pressure environment of $P_{CO_2} = 1$ atm or higher. No continuous external CO$_2$ gas source is required; only a small quantity of CO$_2$(gas) initially filling up the container headspace would be sufficient.

The key is therefore the maintenance of steady-state H$^+$ (aq) concentration, and this excludes the use of a single AEM in bicarbonate electrolyzers. Instead, we use near-neutral (pH = 5–7, with local pH near the anode being even more acidic) water anolyte and CEM. The advance of our strategy is the maintenance of steady-state acidity throughout the entire process of PCET-based bicarbonate electrolysis, which is achieved by the integration of a low-resistance CEM and the balance of the CO$_2$ dissolution-exsolution equilibrium. Consequently, CO$_2$ (even from dilute sources) could also be absorbed efficiently by hydroxide to form bicarbonate, which could
be directly converted into formate with a yield of >95%, quantified with nuclear magnetic resonance (NMR) (Figures 1G and S4).

At scale, our strategy fits well into the global framework of carbon capture, utilization, and sequestration (CCUS). Various alkali basalt mineral rocks, containing CaO, MgO, SiO2, Na2O, and K2O, were found in abundance on Earth and used for enhanced weathering.25 They are efficient for removing CO2 from the atmosphere and would form carbonates and bicarbonates.25,26 The insoluble components could be separated and buried for carbon sequestration, while the soluble components, containing potassium, sodium, and calcium, etc., with our method, could be converted electrochemically into energy-rich metal-formate fuels (Figure 1G) for seasonal energy storage. A direct formate fuel cell (DFFC) possesses a high volumetric energy density (53g H2 per liter) and high specific energy density (2.13 kWh kg\textsuperscript{−1}, more than 5 times that of the state-of-the-art lithium-ion batteries).

Currently, a state-of-the-art DFFC demonstrated a peak power density of 302 mW cm\textsuperscript{−2}, which is already quite competitive against the standard H2 PEM (proton-exchange membrane) fuel cell (~700 mW cm\textsuperscript{−2}),27 thus opening the door for seasonal or even multi-year storage of the intermittent wind and solar electricity.

Proof of concept

As a proof-of-concept experiment, we intended to first demonstrate that dilute (0.1 M) bicarbonate feedstock can be ~100% converted. We used a freshly prepared 0.1 M KHCO\textsubscript{3} solution and filled the sealed solvent bottle headspace with CO2 gas. There was no external CO2 gas input during the electrolysis. After 7 h of electrolysis, we converted 94.60% of the KHCO\textsubscript{3} to KOOCH (Figures 2A, 2C, and S5). The produced formate concentration is around 94.6 mM, far exceeding the solubility of CO2 (33 mM), and whose absolute quantity is also much greater than the small amount of the overhead CO2 gas. Experimentally, this proved that the formate was converted from aqueous bicarbonate. This conclusion can also be inspected from the law of charge balance in the electrolyte. In our system, the catholyte is KHCO\textsubscript{3}, while the anolyte is pure H2O. Thus, the K\textsuperscript{+} concentration is fixed (There is no obvious volume change of the solution before and after the electrolysis). The catholyte pH before and after the electrolysis ranged from 6 to 7, and thus both the [H\textsuperscript{+}] and [OH\textsuperscript{−}] concentrations are very low compared with K\textsuperscript{+}. Therefore, the positive charge carried by the K\textsuperscript{+} has to be balanced by HCO\textsubscript{2}\textsuperscript{−}, HCO\textsubscript{3}\textsuperscript{−}, and CO\textsubscript{3}\textsuperscript{2−} anions. As the HCO\textsubscript{2}\textsuperscript{−} concentration can be measured with NMR, we can thus know the concentration of HCO\textsubscript{3}\textsuperscript{−} + CO\textsubscript{3}\textsuperscript{2−}. In fact, the concentration of HCO\textsubscript{3}\textsuperscript{−} and CO\textsubscript{3}\textsuperscript{2−} can also be computed from the pH of the solution. This result was quantified and confirmed with both liquid-phase NMR (Figure 3D) and solid-phase X-ray diffraction after evaporation-induced precipitation (Figure 3E). Consequently, the aqueous CO2 feedstock was nearly completely converted into solid formate fuel, with almost 100% carbon efficiency, at ambient pressure and temperature. This also means that CO2 capture can be seamlessly integrated with CO2 electroreduction through the bicarbonate intermediate (in either highly concentrated liquid form, or 2-phase saturated liquid + solid-precipitate form after exceeding the solubility limit) (Figure 1), without going through the energy-consuming CaCO\textsubscript{3} baking and gas compression\textsuperscript{11} processes. We then used a 0.1 M KHCO\textsubscript{3} solution at pH ~ 9 (slightly higher initial pH than fresh solution) to compare. The solution had been aged for 1 day to reach pH 9 and recirculated the catholyte in open-air atmosphere during the electrolysis in the MEA electrolyzer (Figure 2B). Even after 12 h of electrolysis, the yield of formate is only 6%, demonstrating an FE of 0.58%. The pH of the solution was roughly constant before and after the electrolysis, because the CEM configuration ensures pH balance even for exclusive HER.
However, the solution was still unreactive as a mixture of $\text{HCO}_3^-\text{aq}$ and $\text{CO}_3^{2-}\text{aq}$. This highlights the importance of the initial pH for bicarbonate reduction.

Optimizing bicarbonate-to-formate electrolyzer

We further optimized the formate selectivity with cathode/electrolyte interface engineering. A hydrophobic gas diffusion layer carbon substrate would not be favorable for the mass transport of the liquid feedstock, and herein, a plain acid-etched hydrophilic carbon cloth was found to be more efficient, consistent with previous reports (Figure S6). We also found that too strong an acidity at the cathode interface would favor HER. This was supported by comparing the situations of changing the anolyte to be a strong acid ($0.1 \text{M H}_2\text{SO}_4$) and deionized water or by adding an artificial glass fiber buffer layer. Although the use of acids ensured superior ionic conductivity, the FE was below 3% (Figure S7) due to significant $\text{H}^+$ activity at the cathode and $\text{H}_2\text{(gas)}$ evolution. Thus, we used a near-neutral-pH water anolyte and a bicarbonate-impregnated buffer layer between the cathode and CEM. The buffer layer could neutralize protons shuttling directly from the anode side, reducing over-acidity at the cathode/electrolyte surface, thus preventing severe HER.
Please cite this article in press as: Zhang et al., A carbon-efficient bicarbonate electrolyzer, Cell Reports Physical Science (2023), https://doi.org/10.1016/j.xcrp.2023.101662
would be especially important at high current densities when the proton flux is high. In fact, the incorporation of this intermediate buffer layer would enhance the FE from around 50% to over 80% for CO$_2$ER with 3 M bicarbonate. We hypothesize this could be due to the favorable pH gradient induced by the buffer layer. After dissembling the cell, we measured the buffer material to be around 200 $\mu$m thickness. This thickness of layer impregnated with bicarbonate could effectively buffer the pH at the cathode surface, suppressing HER and favoring CO$_2$RR. A similar finding on the effect of buffer thickness was also reported recently.33

Enrichment of K$^+$ (aq) in the vicinity of the catalyst surface could lead to enhanced CO$_2$ER selectivity due to the cation charge effect at the outer Helmholtz layer$^4$,$^{34}$ and increased concentration of the bicarbonate reactant. We first fixed the HCO$_3^-$ (aq) anion concentration to be 0.1 M while varying the K$^+$ (aq) concentration, with the charge balanced by adding Cl$^-$ (aq). There were no significant differences in neutral-pH-solution electrolysis (Figure 3C). We also investigated the impact of anions (including Cl$^-$, I$^-$, SO$_4^{2-}$) on the performance, and we found no obvious change either (Figure S8). Subsequently, we increased both the cation and anion concentrations, and electrolyzed a concentrated (1.0 M) KHCO$_3$ solution, which gave an astonishing 96.67% formate conversion efficiency. It was discovered that the bicarbonate feedstock of higher concentration could sustain a larger current density of 50 mA cm$^{-2}$ until the near complete depletion of inorganic carbon feedstock (Figure 3A). Electrolysis of sodium bicarbonate feedstock in the same conditions led to slightly higher overpotential and lower FE (Figure 3B). With an even more concentrated (3.0 M) KHCO$_3$ solution, our strategy enabled an FE of formate formation of 70.74% at 100 mA cm$^{-2}$ at 25°C (Figures 3D and S9). The MEA electrolyzer with the 3.0 M KHCO$_3$ feedstock could operate at a current density of 100 mA cm$^{-2}$ for over 100 h, yielding over 15 wt % of potassium formate. The yield dropped slightly to an average of over 70% for the prolonged electrolysis test at large current densities (Figure 3E). For comparison, we also performed the electrochemical conversion of bicarbonate to formate in an H-type cell. While we observed similar carbon efficiency and FE compared with the MEA full cell, a lower current density at various potentials was seen (Figure S13).

We first hypothesized that this gradual decrease of carbon efficiency upon long-term testing might be due to the imbalance of CO$_2$ dissolution-exsolution equilibrium, which is triggered by the continuous decrease of CO$_2$ partial pressure with the accumulation of H$_2$ gas in the headspace. As we used aqueous feedstock and the catalyst sites were flooded, we modeled the CO$_2$ exsolution rate from the bulk bicarbonate reservoir with the Hertz-Knudsen equation.$^{35,36}$ Higher current densities led to accelerated CO$_2$ exsolution and the generation of carbonate (Figure S10). This issue may be addressed by incorporating a CO$_2$/H$_2$ separation membrane (e.g., Pd
membrane\textsuperscript{37} to \textit{in situ} remove H\textsubscript{2} or by applying a higher-pressure reaction vessel to enable a higher concentration of dissolved CO\textsubscript{2} (Figures 3F and 3G) or both. Higher temperature results in more CO\textsubscript{2}(g) exsolution, while higher partial pressure results in more CO\textsubscript{2}(g) dissolution. High temperature should also expedite reaction kinetics due to the Arrhenius law if [CO\textsubscript{2}(aq)] is controlled to be the same.

Therefore, we built a customized high-pressure MEA electrolyzer to achieve high yield for concentrated bicarbonate solution (Figure S14). Our setup allowed up to 5 bar of CO\textsubscript{2} partial pressure for a flow electrolyzer. The FE increased to 82.11\% at 5 bar. However, we could not increase the yield above 70\% for a saturated bicarbonate solution. Because the reaction of H\textsuperscript{+} + HCO\textsubscript{3}\textsuperscript{−} → CO\textsubscript{2} + H\textsubscript{2}O has a larger pK\textsubscript{a} (≈6.36) than the formic acid dissociation constant (≈3.75), there should be continuous generation and transport of CO\textsubscript{2}(aq) to the cathode. But still, no reaction is observed beyond a certain formate/bicarbonate ratio at high concentrations. We thus hypothesized this could be due to the poisoning effect of formate on the electrode. At high formate concentrations, the formate anion would compete against the CO\textsubscript{2} for specific adsorption and therefore leads to product inhibition. In the future, catalysts that could withstand formate poisoning at high concentrations should be developed. These catalysts should lead to the production of concentrated pure formate from bicarbonate, thus reducing the liquid separation cost.

In addition to HCO\textsubscript{3}−(aq) feedstock, our CEM electrolyzer may also use high-pressure CO\textsubscript{2}(gas) feedstock directly if it is injected into the headspace. In practice, the use of high-pressure ultra-pure CO\textsubscript{2} gas from CaCO\textsubscript{3} baking is energy intensive. The implication here, nevertheless, is the potential of using high-pressure flue gas directly, which will ensure high CO\textsubscript{2} partial pressure and also lead to high carbon efficiency per our design principle. We envision a steady-state mode of OOCH\textsuperscript{−}(aq) production from high partial pressure CO\textsubscript{2}(gas) into the headspace and alkali-metal hydroxide added to balance the pH, which will enable the continuous production of highly concentrated OOCH\textsuperscript{−}(aq) liquor.

From the highly concentrated OOCH\textsuperscript{−}(aq)-bearing liquor produced, we obtained pure potassium formate (KOOCH) crystals by evaporation-induced precipitation, shown in Figure 1G and verified by X-ray diffraction (XRD) (Figure 2D). Solar evaporation can be implemented efficiently at industrial scale without significant CO\textsubscript{2} footprint.\textsuperscript{38} Solid alkali-metal and alkaline-earth formates (KOOCH, NaOOCH, Ca(OOCH\textsubscript{2}), etc.) are non-toxic, stable, non-corrosive, and suitable for safe, long-term storage, over many years if necessary.\textsuperscript{39,40} In terms of energy density, solid formate fuels are comparable volumetrically to 350-bar hydrogen tanks (Note S1). One just needs to drop such solid salts into water to power a DFFC.\textsuperscript{27} Thus, the combination of high-efficiency bicarbonate-to-formate electrolyzer and DFFC should enable a “solid formate” economy, wherein nations mine volcanic alkali basalt rocks containing ∼10 wt % K\textsubscript{2}O/Na\textsubscript{2}O/CaO and use the soluble components through the presented bicarbonate-formate cycle for long-term fuel generation and storage and the insoluble left-over components (MgO/SiO\textsubscript{2}), after enhanced weathering,\textsuperscript{25} for geological sequestration. The alkali basalt resources on Earth exceed the scale needed for the global energy transition (cycling of 60 Gt year\textsuperscript{-1} CO\textsubscript{2} equivalent) and CO\textsubscript{2} sequestration (103 Gt CO\textsubscript{2}) to mitigate climate change.

**Direct formate fuel cells with produced formate**

As a proof of concept for the “metal formate” economy, we also assembled DFFCs with our own developed catalyst and our own CO\textsubscript{2}ER-produced formate. We prepared a palladium nanoparticle-based catalyst with a facile method of \textit{in situ}
Due to the densely packed nanoparticles, our catalyst exhibited comparable performance as the commercially available catalysts in a DFFC full cell but with 4 times less the palladium loading (Figure S16).

To summarize, from captured liquid bicarbonate or saturated liquid/solid bicarbonate feedstocks, we can produce solid metal formates (crystalized KOOCH, NaOOCH) of high purity with nearly 100% carbon efficiency and decent current density at ambient pressure and temperature (Figure 4). The full-cell reaction achieved is $\Delta H_f^{\circ} (\text{KHCO}_3 + \frac{1}{2}\text{O}_2) = 3.13$ eV, which is highly analogous to water splitting $\Delta H_f^{\circ} (\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2) = 2.96$ eV, with no net acid or base produced; thus the pH of both the catholyte and anolyte compartments are maintained with the use of a single CEM and a buffer layer. The dominance of a high concentration of dissolved bicarbonate over carbonate by maintaining appreciable H$^+$ (aq) is of vital importance to achieving enhanced carbon efficiency and FE of CO$_2$ER, and this could be facilely implemented by near-neutral-pH anolyte, CEM, and CO$_2$ partial pressure management. The direct and complete conversion of highly concentrated bicarbonate liquor in mild conditions is significant to the seamless coupling of carbon dioxide capture and electroreduction. A “formate economy” is envisioned, where metal formates play the role of “solid hydrogen” that are much easier to store over decadal timescales. A DFFC that oxidizes our produced fuel and generates electricity is also demonstrated.

**EXPERIMENTAL PROCEDURES**

**Resource availability**

**Lead contact**

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Ju Li (liju@mit.edu).

**Materials availability**

The materials described in this study, except those obtained from commercial sources or third parties, can be made available upon request.
Data and code availability
Additional data that support the findings of this study are available from the corresponding author upon request.

Materials and methods
Chemicals and materials used for the electrode and electrolyte preparation and electrolyzer assembly, including potassium bicarbonate (≥99.95% trace metals basis), potassium hydroxide (ACS reagent, ≥85%, pellets), potassium chloride (ACS reagent, 99.0%–100.5%), potassium iodide (ACS reagent, >99%), potassium sulfate (ACS reagent, >99%), sulfuric acid (ACS reagent, 95.0%–98.0%), nitric acid (ACS reagent, 70%), multi-walled carbon nanotube (50–90 nm diameter, >95% carbon basis), Nafion 117 ionomer solution (5 wt %), Whatman GF/D microfiber filters (diameter 35 mm), were purchased from Sigma-Aldrich. Carbon substrates including Avcarb 190 carbon paper, Panex carbon cloth, and Aquivion E98-09S CEM (thickness 90 μm) were purchased from Fuel Cell Store. Tin nanoparticles (99.95%, 60–80 nm) were purchased from US Research Nanomaterials. The anode material, IrO2 on carbon paper, was purchased from Dioxide Materials and directly used in the electrolyzer test. Deionized water (18.2 MΩ) was used for the preparation of electrolytes. Carbon substrates purchased from Fuel Cell Store were directly used as hydrophobic carbon substrates. Hydrophilic carbon substrates were obtained by immersion treatment of the carbon substrates in the concentrated nitric acid (70%) overnight (>12 h).

The cathode electrodes were prepared by manually airbrushing precursor solutions on carbon substrates. For the preparation of the Sn (tin) electrodes, tin nanoparticles, multi-walled carbon nanotubes, and Nafion 117 were mixed with a weight ratio of 1:0.2:1 using pure ethanol. Note that the Nafion ionomer is 5 wt %, so that the Sn/Nafion weight ratio is 20:1 rather than 1:1. The loading density for the Sn electrodes was ~4 mg/cm². The buffer layer was prepared by immersing the Whatman glass fiber in the corresponding bicarbonate solution (at the same concentration as the catholyte). The catalyst for DFFCs was prepared by in situ electrodeposition. 100 μL/cm² of palladium chloride solution (50 mM in ethanol) was dropcasted onto carbon strips with a robotic Opentron machine. The carbon was then immersed in a solution of potassium formate (1 M) and potassium hydroxide (1 M). A constant potential of −0.524 V vs. HgO/Hg was applied to the cathode for 5 min.

Flow cell assembly
The MEA flow electrolyzer used was purchased from Dioxide Materials. It was composed of two compartments: anolyte chamber with a titanium anode flow field and catholyte chamber with 904-L stainless-steel flow field. The size of the electrode exposed to the flow field was 5 cm². The buffer layer was clamped between the cathode and the CEM, with the cathode substrate side facing the catholyte flow field and catalyst side facing the buffer layer. The catholyte and anolyte were constantly flowing in and out through silicone tubes connected to peristaltic pumps, both with a constant flow rate of approximately 10 mL/min. The same catholyte/anolyte electrolyte solutions were recirculated in/out of the bulk solutions to form closed loops.

Electrochemical tests
All the electrochemical tests were carried out using an electrochemical workstation of Gamry 3000. Fresh bicarbonate solutions were prepared by dissolving potassium bicarbonate in deionized water and were used immediately. The bicarbonate solutions could also be prepared by sparging CO₂ gas (Airgas, industrial pure) into aged bicarbonate or carbonate solutions to make sure as much as carbonate is converted. Before a typical test, CO₂ gas was sparged to fill the solvent bottle.
to drive away any air. Then the solvent bottle was closed and maintained under a
contant-pressure environment throughout the test. No additional external CO₂
gas source was used in the electrolysis process. In addition, no N₂ gas was sparged
in as the carrier gas. Bicarbonate solutions of various concentrations were used as
the catholyte. Deionized water was typically directly used as the anolyte. There was
no significant difference between using deionized water or slightly acidic water (pH
ranging from 3–5 with sulfuric acid) as the anolyte. The liquid products were tested
with NMR, while the gas products were tested with gas chromatography (GC) in a
separate control test. The CO₂ER performances were typically tested in a flow cell
assembly under the galvanostatic mode. The voltage measured and reported was
the full-cell voltage, and no voltage compensation method was used. For the
DFFC test, the catholyte is a mixture of potassium formate (1.0 M) and potassium
hydroxide (2.0 M), while the anode feeding gas is pure O₂. The DFFC test occurred
at 60°C. For the H cell test, the H-Type Sealed Electrochemical Cell (10/40 mL) was
purchased from Dek Research. An Ag/AgCl electrode was used as the reference
electrode.

Nuclear magnetic resonance tests
The liquid products were analyzed using ¹H NMR spectroscopy (400-MHz, two-
channel Bruker Avance-III HD Nanobay spectrometer) with water suppression.
Dimethyl sulfoxide was used as the internal standard and deuterium oxide (D₂O)
as the lock solvent. The D₂O:H₂O volume ratio was 1:9. A high concentration of
formate solution would be diluted before tests. The FE was calculated using the
equation below:

\[
\text{Faradaic efficiency} (\%) = \frac{N \times F \times n_{\text{product}}}{Q},
\]

(Equation 8)

where \( N \) is the number of electrons transferred, \( F \) is the Faradaic constant, \( n_{\text{product}} \) is
the total moles of products, and \( Q \) the total charge passed. The yield of formate was
calculated below:

\[
\text{Yield} (\%) = \frac{n_{\text{formate}}}{n_0},
\]

(Equation 9)

where \( n_{\text{formate}} \) is the total moles of formate produced, and \( n_0 \) is the concentration of
the starting solution or conservative cation (K⁺).

The standard calibration curve and a typical test result are shown in Figure S4.

Gas chromatography tests
The gaseous products were analyzed using a GC instrument (SRI 8610C, Multiple
Gas Analyzer #5). The instrument was equipped with a thermal conductivity detector
for H₂, O₂, and N₂ analysis, a flame ionization detector (equipped with a methanizer)
for CO, CO₂, and hydrocarbon analysis, two 10-port gas sampling valves, three
columns including a 0.5-meter Hayesepe D column, a 2-meter Hayesepe D column
and a 2-meter Moleseive 5A column, and a 6-channel PeakSimple USB data system.
Argon gas (Airgas, ultra-pure) was used as the carrier gas. The gas products were sparged out with N₂ carrier gas and dried with a custom-made MgSO₄
(Sigma-Aldrich) drying vessel before the GC test. For quantification, each time,
1 mL of gaseous stream was automatically injected into the GC, and the performance
was evaluated as follows:

\[
\text{Faradaic efficiency} (\%) = n \times F \times v \times \frac{c}{(I \times V_m)},
\]

(Equation 10)

where \( n \) is the number of electrons transferred, \( F \) the Faradaic constant, \( v \) the gas
flow rate, \( c \) the concentration (in ppm) of gas product, \( I \) the total current, and \( V_m \)
the molar volume of the gas. The gas flow rate was measured with a mass flow meter at the outlet of the electrolyzer.

The standard calibration and a typical test result are shown in Figures S11 and S12.

**X-ray diffraction**

XRD was conducted on the X-ray diffractometer (Aeris Research edition) using a copper target under a voltage of 40 kV and current of 15 mA. The hygroscopic formate was dried completely before the XRD test.

Computation of the concentrations of inorganic carbon species in the aqueous solution in equilibrium with different atmospheres was performed.

Inorganic carbon species concentration ([IC]) dissolved in the aqueous solution is defined as the following sum:

\[
|IC| = |CO_2|_{(aq)} + [HCO_3^-] + [CO_3^{2-}] 
\]  
(Equation 11)

The equilibrium balance of various inorganic carbon species considered could be evaluated with the following equilibrium equations and constants:

\[
CO_2(aq) \rightleftharpoons CO_2(g), \text{H}_p = \frac{|CO_2|_{(aq)}}{p_{CO_2}} 
\]  
(Equation 12)

\[
CO_2(aq) + H_2O \rightleftharpoons HCO_3^- + OH^-, K_1 = \frac{[HCO_3^-][OH^-]}{|CO_2|_{(aq)}} 
\]  
(Equation 13)

\[
HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}, K_2 = \frac{[H^+][CO_3^{2-}]}{|HCO_3^-|} 
\]  
(Equation 14)

\[
H_2O \rightleftharpoons H^+ + OH^-, K_w = [H^+][OH^-] 
\]  
(Equation 15)

Here, \(H_p\) is the Henry’s constant and could be evaluated as 0.034 M/bar for a dilute salt solution at 1 atm and room temperature, two carbonic acid dissociation constants \(K_1\) and \(K_2\) were evaluated as \(K_1 = 9.6 \times 10^{-7}\) M and \(K_2 = 3.4 \times 10^{-10}\) M at room temperature, respectively, and the water dissociation constant \(K_w\) was 1.0 \(\times\) \(10^{-14}\) M². The partial pressure of CO₂ (\(p_{CO_2}\)) was approximated as 0.4 mbar (or 400 ppm) when the solution was in equilibrium with air or 1 bar when the solvent bottle was filled with pure CO₂, respectively. In an aqueous solution of potassium bicarbonate, the ion charge balance equation could be written as follows:

\[
[K^+] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] 
\]  
(Equation 16)

The alkalinity [A] is defined as the concentration of the conservative ion in the solution, and thus,

\[
[A] = [K^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] 
\]  
(Equation 17)

Where the concentrations of [HCO₃⁻], [CO₃²⁻], [OH⁻], and [H⁺] could all be written as a function of [HCO₃⁻], [CO₃²⁻], or [H⁺] from the equilibrium relations above. Thus, [A] is a function of only one variable. For example, if using the variable [H⁺], we could have the following:

\[
[A] = H_p p_{CO_2} \left( \frac{K_1}{[H^+]} + \frac{2K_1K_2}{[H^+]^2} \right) + K_w \frac{[H^+]}{[H^+]} - [H^+] 
\]  
(Equation 18)
We then used Python to compute and plot the alkalinity or pH as a function of the inorganic carbon species (Figures 1E, 1F, and S3).

**Computation of the decline of aqueous CO₂ concentration as a function of time at different current densities due to partial pressure drop**

As the electrolysis was carried out under the constant-pressure condition, $p_{CO_2}$ would continuously decline while $p_{H_2}$ increases. The Hertz-Knudsen equation could be written in the form:

$$R_{ex,CO_2} = \frac{1}{A} \frac{dN}{dt} = \frac{a \Delta p N_0}{\sqrt{2 \pi MRT}} = a k_{GL} \left[ (CO_2)_{aq} - (CO_2)_{eq} \right]$$  \hspace{1cm} (Equation 19)

Here, $R_{ex,CO_2}$ is the rate of CO₂ dissolution/exsolution from the solution with a unit of mole/time. $R_{ex,CO_2}$ would be negative/positive for CO₂ dissolution/exsolution, respectively. $a$ is the interfacial area with a unit of m². $k_{GL}$ is the gas-to-liquid mass transfer coefficient with a unit of m/s. $V_0$ is the solution volume with a unit of m³.

Reaction kinetics could be considered with the following equations:

$$CO_2(aq) + H_2O \rightleftharpoons HCO_3^- + OH^-, \quad K_1 = \frac{k_1}{k_{-1}}$$  \hspace{1cm} (Equation 20)

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}, \quad K_2 = \frac{k_2}{k_{-2}}$$  \hspace{1cm} (Equation 21)

where $k_n$ and $k_{-n}$ refer to the rate constant of the forward and reverse reaction, respectively. The reactions of OH⁻ with inorganic carbon species were neglected at this point, because the pH was constant and neutral throughout the process. We only approximated the $[CO_2]$ change in the bulk solution due to the partial pressure change. The rate of $[CO_2]$ change could be written as follows:

$$\frac{d[CO_2](aq)}{dt} = - R_{ex,CO_2} + k_{-1} [HCO_3^-] [H^+]$$  \hspace{1cm} (Equation 22)

The results are shown in Figure S10.

**SUPPLEMENTAL INFORMATION**

Supplemental information can be found online at https://doi.org/10.1016/j.xcrp.2023.101662.

**ACKNOWLEDGMENTS**

We extend gratitude to Alexander Quinn for the design of the high-pressure flow electrolyzer with sealed reservoirs for this work. We thank Y. Huang, H. Tang, and A. Abdelhafiz for helpful discussions and S. Miao for graphics design. This work was supported as part of the Hydrogen in Energy and Information Sciences (HEISs), an Energy Frontier Research Center funded by the US Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under award DESC0023450.

**AUTHOR CONTRIBUTIONS**

DECLARATION OF INTERESTS

J.L. and Z.Z. from Massachusetts Institute of Technology filed a provisional patent application for high-yield production of formate salts from bicarbonate using the pressure and pH control method.

Received: July 19, 2023
Revised: September 5, 2023
Accepted: October 5, 2023
Published: October 30, 2023

REFERENCES


Supplemental information

A carbon-efficient bicarbonate electrolyzer

Zhen Zhang, Dawei Xi, Zhichu Ren, and Ju Li
Supplemental Information

Supplementary Note S1

The standard Toyota Mirai hydrogen tanks volume is ~ 122 liters, storing 70 MPa of H$_2$. The density of sodium formate (NaOOCH) is about 1.92 g/cm$^3$. Thus, the mole fraction of H$_2$ and NaOOCH stored in this commercial tank would be 0.80. As fuel cells involving both materials are two-electron-transfer reactions, the volumetric energy density would be around 0.80.
Fig. S1. Two pathways of CO$_2$ER using the CO$_2$ gas feedstock or aqueous bicarbonate feedstock. The decoupling of the carbon capture and CO$_2$ER processes and the demand for a pure CO$_2$ feedstock necessitates an energy-intensive thermal regeneration process.
Fig. S2. (a) Schematic of the traditional anion exchange membrane (AEM) electrolyzer using the CO$_2$ gas feedstock. (b) Schematic of the bipolar membrane (BPM) electrolyzer using the liquid bicarbonate feedstock.
Fig. S3. The concentrations of inorganic carbon (HCO$_3^-$/CO$_3^{2-}$) and pH as a function of alkalinity in equilibrium with a CO$_2$ partial pressure of (C) 0.4 mbar and (D) 1 bar, respectively. Plum and light sky-blue areas correspond to the HCO$_3^-$ and CO$_3^{2-}$ concentration, respectively. This is a magnification of Fig. 2e, f at smaller concentrations.
Fig. S4. Calibration curve of the potassium formate solution quantified with NMR. (a) Plot of peak area ratio as a function of formate concentration. (b) A typical NMR plot showing formate is the only liquid product. The sharp peaks at 2.63 ppm and 8.36 ppm correspond to DMSO and formate, respectively. The broad peak at 4.43 ppm results from water suppression.
**Fig. S5.** The flow field of a 5 cm$^2$ membrane electrode assembly electrolyzer.
Fig. S6. Comparison of different carbon substrates for formate production. Hydrophilic substrates were acid etched to become hydrophilic samples. Avcarb 190 is basic carbon paper, while Panex is carbon cloth. The catholyte used was 0.1 M KHCO₃. The tests were conducted at 25 °C.
Fig. S7. Comparison of electrolysis with an anolyte of strong acid or deionized water. Sulfuric acid was used as the anolyte for the acidic electrolyte, while deionized water was directly used for the neutral electrolyte. The catholyte used was 0.1 M KHCO₃. The tests were conducted at 25 °C.
Fig. S8. Effect of anion on the Faradaic efficiency of bicarbonate conversion to formate at 100 mA/cm² in the MEA cell. The left three columns were performed with 0.1 M KHCO₃+ 0.1 M KX (X = Cl⁻, I⁻, ½ SO₄²⁻). The right three columns were performed with 2.9 M KHCO₃+ 0.1 M KX (X = Cl⁻, I⁻, ½ SO₄²⁻). No significant impact of anion was found in this reaction.
Fig. S9. Electrochemical performance conducted at different temperatures. The catholyte used was 3.0 M KHCO₃. There was no significant difference between the full-cell voltage at these two temperatures, which is contrary to the traditional belief that elevated temperature enhanced performance. The reason should be ascribed to a much fast CO₂ exsolution from the solution at elevated temperatures, which enormously reduced the concentration of active inorganic carbon species in the solution. However, as high temperature increased the solubility of bicarbonate, further efforts could be devoted to applying a high temperature and high-pressure strategy at the same time, which should be promising for further performance enhancement.
Fig. S10. Kinetics of CO₂ exsolution from the aqueous solution with the increase of hydrogen partial pressure at a current density of (a) 20 mA cm⁻² and (b) 100 mA cm⁻². As CO₂ evaporated into the headspace via a flat surface from the bulk solution, we assumed a $a_kG_L$ at an order of magnitude of $10^{-3}$. We assumed a constant faradaic efficiency for hydrogen production as 40%, bicarbonate electrolyte volume of 20 mL, solvent bottle headspace of 20 mL. Dissolved carbon dioxide concentration at equilibrium was around 33 mM, which declined much faster at a larger current density.
**Fig. S11.** Calibration curve of the gas chromatography. We only targeted at hydrogen, oxygen, carbon monoxide, methane, ethane in these experiments.
Fig. S12. A typical GC curve showing that only hydrogen and carbon dioxide were detected. Similar to the calibration plot in fig. S11, the other two peaks in the TCD curve could be ascribed to a change of valve and a second appearance of the hydrogen or air streams due to quantification by different GC columns (there were 3 columns in total), which was confirmed by the manufacturer. CO$_2$ appeared in the outlet because in the control experiments, the system was not closed. Nitrogen gas was constantly sparged in to drive away any gas streams evolved from the solution. However, as we stated in the main text, the system was closed under constant pressure environment for main experiments, which is the key to ensuring a high yield and high carbon efficiency. Nitrogen gas or air atmosphere would lead to an ultra-low CO$_2$ partial pressure, which would kill the reaction very soon.
Fig. S13. Faradaic efficiency for formate production and current density as a function of electrochemical potential in an H cell. Ag/AgCl electrode was used as the reference electrode. We used 3.0 M saturated potassium bicarbonate as the catholyte, Aquivion E98-09S cation exchange membrane, and water as the anolyte.
**Fig. S14.** Customized setup for tests up to 72 psi at MEA level. Two reservoirs were designed for holding the catholyte and anolyte, respectively, in a closed manner.
Fig. S15. Palladium nanoparticle catalyst for direct formate fuel cells, developed by in situ electrodeposition.
Fig. S16. Preliminary results of direct formate fuel cells at MEA level. We obtained comparable results with commercial catalysts, but with much less loading of palladium.
Table S1.
Carbon efficiency and maximum yield for different carbon dioxide electroreduction reactions.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Maximal carbon efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$</td>
<td>0% (would consume CO$_2$)</td>
</tr>
<tr>
<td>CO$_2$ + H$^+$ + 2e$^- \rightarrow$ HCOO$^-$</td>
<td>67%</td>
</tr>
<tr>
<td>CO$_2$ + 2H$^+$ + 2e$^- \rightarrow$ CO + H$_2$O</td>
<td>50%</td>
</tr>
<tr>
<td>2CO$_2$ + 7H$^+$ + 8e$^- \rightarrow$ CH$_3$COO$^- + 2$H$_2$O</td>
<td>36%</td>
</tr>
<tr>
<td>CO$_2$ + 6H$^+$ + 6e$^- \rightarrow$ CH$_3$OH + H$_2$O</td>
<td>25%</td>
</tr>
<tr>
<td>2CO$_2$ + 12H$^+$ + 12e$^- \rightarrow$ C$_2$H$_4 + 4$H$_2$O</td>
<td>25%</td>
</tr>
<tr>
<td>2CO$_2$ + 12H$^+$ + 12e$^- \rightarrow$ C$_2$H$_5$OH + 3$H_2$O</td>
<td>25%</td>
</tr>
<tr>
<td>CO$_2$ + 8H$^+$ + 8e$^- \rightarrow$ CH$_4 + 2$H$_2$O</td>
<td>20%</td>
</tr>
</tbody>
</table>

This chart shows the maximal carbon efficiency for CO$_2$ER with a traditional AEM-based electrolyzer. Aqueous bicarbonate feedstock coupled with a CEM could ensure 100% yield and carbon efficiency for HCOO$^-$ and oxalate production. For other products, CO$_2$ gas coupled with a CEM could ensure a theoretical yield of 100% as well, even though with considerable CO$_2$ regeneration cost with the current technology. Achieving a high yield of other products with liquid bicarbonate feedstock could be possible if an additional proton source could be realized, which would maintain pH balance throughout the entire process, eliminating a need for post liquid-liquid separation.