Low-cost renewable electricity has raised the prospect of using electrochemistry to synthesize fuels and chemicals. CO electrolysis can be used to make valuable multi-carbon products, but previous systems have shown low CO conversion and dilute product streams. Here we describe CO gas diffusion electrolysis cells that make concentrated products at high rates and modest voltages, including a cell that directly outputs a >1 M acetate solution. Our results reveal critical design features for maximizing the efficiency of C₂ electrosynthesis.
SUMMARY
Electrochemical CO conversion is critical for the development of alternative fuel and chemical syntheses. To be efficient, electrosynthesis must make concentrated product streams at high rates with modest potentials, but the combination of these features has not been established for CO or the related CO2 electrolysis. Here we investigate CO electrolysis with gas diffusion electrodes (GDEs) supplied by interdigitated flow fields in electrochemical cells with different ion transport properties. By optimizing gas and ion transport, we show that it is possible to simultaneously achieve high current density, high selectivity, and high single-pass conversion at moderate cell potentials. Using a cell with the GDE directly contacting a Nafion membrane, we demonstrate >100 mA cm$^{-2}$ CO reduction to C2 products and direct production of 1.1 M acetate at a cell potential of 2.4 V over 24 hr. Our results reveal critical design features for maximizing the efficiency of C2 electrosynthesis.

INTRODUCTION
Carbon monoxide reduction on Cu electrodes in aqueous media generates multicarbon (C$_2$+) products of great interest for the production of chemicals from renewable resources including ethylene, ethanol, and acetate.$^{1,2}$ Recently, solid oxide electrolysis cells (SOECs) that split CO$_2$ into O$_2$ and pure CO have been brought to market.$^3$ Combining these systems with CO electrolysis would enable the use of low-carbon electricity to power CO$_2$ conversion to C$_2$+ feedstocks. Furthermore, CO reduction is the rate-limiting step for the direct electrochemical conversion of CO$_2$ to any C$_2$+ product on Cu.$^{4,5}$ A better understanding of CO reduction, particularly in the high current density regime, is important for the development of direct CO$_2$ to C$_2$+ electrolysis cells.

Most studies of CO reduction have been performed with Cu catalysts immersed in CO-saturated aqueous electrolyte solutions.$^{1,2,6-13}$ Although these studies have provided structure-activity insights in the low overpotential regime, the maximum geometric current density that can be achieved in solution-phase CO reduction is on the order of 1 mA cm$^{-2}$ because of the very low solubility of CO ($\sim$1 mM in 1 bar-saturated H$_2$O). By contrast, practical electrolysis cells typically operate at 0.1–1.0 A cm$^{-2}$. Gas diffusion electrodes (GDEs) are designed to overcome solution-phase mass-transport limits by providing hydrophobic channels to deliver gaseous reactants to catalyst particles that are wetted by a thin solid or liquid electrolyte layer. GDEs are used to deliver H$_2$ and O$_2$ to the catalysts in fuel cells and support high current densities in commercial devices. Since O$_2$ and H$_2$ have similarly low solubilities as CO, GDEs are a compelling option for developing CO electrolysis systems.
In addition to current density, energy efficiency is critical for electrochemical synthesis of feedstock chemicals. Typically, the energy efficiency of an electrochemical cell is assessed by comparing the operating voltage (at a specified current density) with the thermodynamic voltage determined by the free energy change of the overall chemical transformation. However, the cell voltage alone is insufficient for determining the true energy efficiency of electrosynthesis. An additional factor is the concentration of the product streams. Dilute streams necessitate energy-intensive downstream separations to purify the products and recover reactant. For gaseous products, the concentration is determined by the single-pass conversion of the gaseous reactant, whereas for liquid products it is determined by the amount of electrolyte that dilutes the product. Thus, an ideal GDE cell used for electrosynthesis will enable high synthesis rates at low cell voltages with high single-pass conversions and minimal electrolyte, producing concentrated product streams.

At present, relatively little is known about how to design GDE cells for efficient CO electrolysis. One early study reported a very high current density of 600 mA cm\(^{-2}\) CO reduction to hydrocarbons and alcohols at an extreme cathode potential (−3.2 V versus normal hydrogen electrode [NHE]) with an unspecified CO flow rate and cathode size.\(^{14}\) A more recent study evaluated CO reduction in a Cu foam GDE in contact with alkaline electrolyte.\(^{15}\) Although up to 50 mA cm\(^{-2}\) CO reduction to ethylene (18% faradaic efficiency [FE]) was obtained at −15°C with this electrode, the use of a high CO flux combined with a small electrode area resulted in a CO conversion of only 0.25% at this current density, which translates into a very dilute product stream. Moreover, to achieve these high current densities, CO gas was forced through the electrode, which blocks the path of ion flow toward the counter electrode and increases cell resistance. Very recently, Jiao and co-workers described CO reduction in a GDE cell with up to 630 mA cm\(^{-2}\) current density for C\(_2\) products and up to 26% single-pass conversion in short electrolyses.\(^{16}\) While this study provides a compelling demonstration of the ability to reduce CO at synthetically useful rates, the cell showed limited stability, with >100 mV voltage increases over 1 hr at 500 mA cm\(^{-2}\) and a propensity for GDE flooding.

Recently there has been much attention given to CO\(_2\) electrolysis using GDEs, both for the production of CO and for C\(_2\) synthesis.\(^{17–22}\) Experimental studies have focused on optimizing current density, cathode overpotential, and, in some cases, total cell potential. Moreover, most studies have performed CO\(_2\) reduction with a GDE contacting a liquid alkaline electrolyte or an anion exchange membrane in order to minimize cathode overpotential. These conditions create a highly alkaline catalyst interface, which can parasitically consume CO\(_2\) by bicarbonate (HCO\(_3^-\)) formation. Bicarbonate can either accumulate in the catholyte (as carbonate) or migrate to the anode and release CO\(_2\) into the O\(_2\) stream. Since one equivalent of HO\(^-\) is formed with every electron transfer in CO\(_2\) reduction with alkaline electrolyte, these processes could consume substantially more CO\(_2\) than what is utilized for product formation and effectively render the electrosynthesis (super)stoichiometric in HO\(^-\). There is a hidden energy cost for producing HO\(^-\) of at least ~400 kJ mol\(^{-1}\).\(^{23}\)

Although GDEs have yielded impressive, industrially relevant CO\(_2\) reduction current densities, the CO\(_2\) conversions calculated from reported reaction conditions are generally low. For CO\(_2\)-to-CO electrolyses that last longer than a few minutes, most conversions are <10% (Table S1).\(^{18,21}\) State-of-the-art reported performance for CO\(_2\)-to-CO reduction with a GDE cell is 190 mA cm\(^{-2}\) with 33% single-pass conversion over a 40-day electrolysis.\(^{20}\) Substantially lower conversions have been obtained for direct CO\(_2\) to C\(_2\) electrolys with GDE cells. A current density of
61 mA cm$^{-2}$ ethylene production was sustained in a 150-hr electrolysis, but the single-pass CO$_2$ conversion was only 0.3%.$^{22}$ In an electrolysis lasting 3 min, 225 mA cm$^{-2}$ combined ethylene and ethanol production was obtained at 7% conversion (22.5% conversion including CO production).$^{17}$ Notably, reported CO$_2$ conversions in GDEs have not exceeded the value expected if CO$_2$ reduction were accompanied by the stoichiometric reaction of CO$_2$ and HO$^-$ generated during electrosynthesis. These results suggest that capture by HO$^-$ is a major contributor to CO$_2$ loss. Most techno-economic analyses of CO$_2$ valorization have not considered the energetic or economic costs of recovering CO$_2$ from carbonate formation or separation from the anodic stream.$^{24,25}$ The energy demand of product separation from dilute streams can greatly exceed the energy content of the product, especially for dilute liquid products.$^{26}$ In principle, operating a GDE cell using a bipolar membrane can prevent loss of CO$_2$ to carbonate formation or migration to the anode. To date, however, only very low CO$_2$ conversions have been obtained in bipolar membrane cells (Table S1).$^{27,28}$

In this study, we investigate CO electrolysis using GDE cells designed to carefully control gas and ion transport. An interdigitated flow field is used to maximize the flux of CO through a carbon-based GDE to a Cu catalyst layer, and three different ion transport configurations are examined. With cells in which the Cu-GDE is in contact with a thin catholyte layer, we show that it is possible to simultaneously achieve high single-pass conversion and high FE for CO reduction over a range of CO flow rates. The current-voltage behavior of the Cu-GDE cathode is independent of the bulk electrolyte pH, which means that the cell voltage is minimized with alkaline electrolyte and an anion transporting membrane. Under operating conditions informed by these insights, we demonstrate >100 mA cm$^{-2}$ and 75% FE for CO reduction with 68% single-pass conversion at a total cell potential of 2.5 V. We also show that it is possible to eliminate the use of a catholyte altogether and produce a highly concentrated liquid product stream. Using a cell design in which a Cu-GDE is directly contacted by a Nafion membrane, we demonstrate >100 mA cm$^{-2}$ CO reduction to C$_2$ products and direct production of a liquid product that is 1.1 M in acetate at a total cell potential of 2.4 V over 24 hr. Our results provide design features for practical CO electrolysis and a foundation for future efforts to address challenges in single-pass conversion for direct CO$_2$ electrolysis.

RESULTS AND DISCUSSION

To prepare the Cu-GDEs, we synthesized the Cu catalyst by NaBH$_4$ reduction of Cu(OAc)$_2$ in 2-ethoxyethanol and suspended it in isopropanol to make a catalyst ink (Figure S1).$^{17}$ The ink was drop dried at a loading of 250 $\mu$g cm$^{-2}$ onto an AvCarb 2230 GDE. The drop-dried catalyst layer was subsequently spray-coated with Nafion 520 dispersion to act as a binder. The GDE is composed of two conductive, hydrophobic carbon materials: a microporous layer (MPL) on top of a carbon fiber mat known as the gas diffusion layer (GDL). The architecture of the Cu-GDE was examined using scanning electron microscopy (SEM) and X-ray tomography. Cross-sectional images revealed that the Cu was confined to a 1- to 2-$\mu$m layer on top of the MPL (Figures 1 and S2). For all of the experiments below, the Cu-GDE was backed by a Ti current collector with a laser-engraved 1-cm$^2$ interdigitated flow field (Figure 1C). The circular footprint of the catalyst covered ~80% of the flow-field area.

We first investigated CO electrolysis using cells in which a Cu-GDE was interfaced with a thin electrolyte layer. The design for configuration 1 is shown in Figure 2A. The catalyst side of the GDE is in contact with a 1 cm x 1 cm x 1.5-mm chamber
containing the electrolyte (the catholyte) where liquid-phase CO reduction products accumulate. The chamber has ports to enable catholyte flow and a port connecting to a Ag/AgCl reference electrode. When CO is flowed into the current collector, it enters the GDL from the flow field and passes through the MPL to reach the Cu catalyst layer at the catholyte interface. Gaseous products and unreacted CO flow out the exit port of the current collector and are analyzed by gas chromatography (GC). The anode side is a membrane electrode assembly (MEA) composed of an IrO2 on carbon (IrO2/C) catalyst layer pressed onto a Nafion membrane. The MEA is backed by a second Ti current collector with a flow field through which humidified N2 is flowed to supply H2O to the anode.

The flow of charges during electrolysis with configuration 1 is depicted in Figure 2B using the 8-electron reduction of CO to ethylene at the Cu-GDE as an example. The flux of HO– ions generated at the Cu-GDE/catholyte interface is balanced by the flux of H3O+ ions through the Nafion membrane generated by H2O oxidation at the anode. In principle, this configuration is compatible with any aqueous catholyte because the H3O+ and HO– ions neutralize each other.

The performance of configuration 1 was first evaluated with 1 M NaOH as the catholyte. Electrolysis was performed with flows of 0.5 standard cubic centimeters per minute (sccm) of CO through the Cu-GDE, 150 μL min⁻¹ of 1 M NaOH through the catholyte chamber, and 10 sccm of humidified N2 through the anode. Tafel data were collected by performing stepped-current chronopotentiometry at current densities ranging from 12 to 144 mA cm⁻². The duration of each step was 9 min, which enabled GC quantification of the gas-phase products and collection of catholyte aliquots for nuclear magnetic resonance (NMR) analysis of the liquid-phase products. The measured potential at each current density showed little variation (±3 mV) over the duration of the step (Figure S3).

Figure 2C shows a Tafel plot of the partial geometric current density for CO reduction to all products (jCO) versus the measured cathode potential, reported versus NHE. The Tafel slope was 121 mV dec⁻¹, and a CO reduction current density of 101 mA cm⁻² was achieved at −1.49 V versus NHE. This current density is nearly two orders of magnitude higher than the diffusion-limited geometric current density for CO in solution-phase electrolyses,6,8,11 demonstrating the benefits of enhanced CO transport with the Cu-GDE. The product distribution versus potential is depicted in Figure 2D, including the H2 produced by competing H2O reduction. The total FE...
for CO reduction ranged from 65% to 76%. Ethylene was the major product overall, and the exclusive gas-phase product except at the most negative potentials, at which small amounts of methane were produced. The remaining CO reduction products were oxygenates including ethanol, acetate, and propanol. Notably, when \( j_{\text{CO}} \) was 101 mA cm\(^{-2}\), 65% of the CO flowing into the cell was converted to reduction products in a single pass. This high single-pass conversion was achieved while maintaining a relatively high total FE for CO reduction. High single-pass conversions obtained with this cell configuration allowed for the production of gas product stream that was 29 vol% ethylene, which to our knowledge is the most concentrated gaseous C\(_2\) product stream that has been generated from CO or CO\(_2\) reduction.

To better understand the factors that control selectivity and CO utilization, we investigated the effects of changing the CO flux. Stepped-current chronopotentiometry was repeated using a lower CO flux of 0.125 sccm (Figure 3A). Under these conditions, a single-pass conversion of 84% and a total CO reduction FE of 73% were
obtained at 48 mA cm\(^{-2}\), which required a potential of \(-1.42\) V. The conversion calculated by quantifying the products was validated by monitoring the CO concentration exiting the cell with and without applied potential (Figure S4). Given that the catalyst-coated portion of the GDE occupies only 80% of the total area of the flow field (Figure 1C), 84% represents essentially quantitative conversion of the CO that comes into contact with the Cu-GDE. As the current was increased beyond the CO reduction mass-transport limit imposed by the 0.125-sccm flux, H\(_2\) evolution necessarily increased, but the single-pass CO conversion remained relatively high. The CO product distribution shifted from exclusively ethylene and oxygenates toward methane at higher current densities. Notably, approximately 60 mV more negative potential was required to attain a total current density of 144 mA cm\(^{-2}\) at 0.125 sccm compared with 0.5 sccm CO flux.

We next performed chronopotentiometry at a fixed current density of 72 mA cm\(^{-2}\) and a fixed total gas flow rate of 0.5 sccm, but with different proportions of CO and N\(_2\) (Figure 3B). With only 5% CO, the single-pass CO conversion was 59%. The dominant CO reduction product under these substrate-starved conditions was methane. As the CO concentration was increased incrementally to 40%, j\(_{\text{CO}}\) increased proportionally and the product distribution shifted to ethylene and oxygenates. The single-pass CO conversions were very similar (70%–77%) for CO concentrations between 10% and 40%. Beyond 40% CO with 0.5 sccm, the CO flux substantially exceeded what is required at the fixed current density of 72 mA cm\(^{-2}\) and as a result j\(_{\text{CO}}\) plateaued. Together, the results in Figure 3 demonstrate that it is possible to simultaneously attain high single-pass conversion and high FE for CO reduction over a range of CO fluxes by matching the current density to the flux. With properly matched current density and flux, ethylene and C\(_2^+\) oxygenates are the only CO reduction products. When the current density substantially exceeds the CO flux, methane becomes a major product and the C\(_3^+\) products are greatly diminished. These changes reflect the higher hydride coverage on the catalyst surface as the proportion of current going toward H\(_2\)O reduction increases, and as a result a lower likelihood of C-C coupling. Water reduction has a greater associated overpotential than CO reduction under these conditions. As the catalyst becomes limited by CO mass-transport H\(_2\)O reduction necessarily increases, resulting in a more negative voltage at the same fixed current density.

To assess the effect of the bulk electrolyte properties, we repeated stepped-current chronopotentiometry using 1 M NaCl instead of 1 M NaOH, with 0.5 sccm CO flux.
Very similar performance was obtained despite the ~7 pH unit difference between these electrolytes. Specifically, $j_{CO}$ showed essentially the same dependence on the potential versus NHE (Figure 2C) and the product distribution showed no substantial change (Figure 2E). The Tafel behavior is consistent with a mechanism in which the rate-determining step is gated by a one-electron transfer to CO$_2$, which may be coupled to a H$^+$ donation from a H$_2$O molecule. At very low concentrations of H$_3$O$^+$ (which is the case in both NaOH and NaCl electrolytes), the rate of this step will depend only on the electron driving force, which is given by a pH-independent reference such as NHE. In this situation, which is usually the case for CO and CO$_2$ reduction catalysts, the cathode overpotential is minimized by operating in alkaline electrolyte because, at a fixed potential versus NHE, the potential versus reversible hydrogen electrode becomes more positive as the pH increases. However, the use of a Nafion MEA anode in configuration 1 results in a high total cell voltage because the anode operates in an acidic environment, which requires more than +1.23 V versus NHE for water oxidation. A plot of $j_{CO}$ versus the total cell potential in configuration 1 is shown in Figure 4C. A $j_{CO}$ of 80 mA cm$^{-2}$ requires 3.4 V.

The high potential of the anode (versus NHE) can be lowered by operating the anodic reaction in an alkaline medium, with the added benefit that inexpensive oxygen evolving catalysts are effective in base. We therefore hypothesized that coupling CO reduction with HO$^-$ oxidation would substantially reduce the total cell voltage. To test this hypothesis we evaluated configuration 2, in which the anode side is composed of an alkaline-doped polybenzimidazole (PBI) membrane in direct contact with an Fe-doped Ni foam anode (Figure 4A). In addition to the catholyte that separates the Cu-GDE and PBI membrane, a second electrolyte (anolyte) is pumped through the Ni foam anode and recirculated (Figure S5).

Chronopotentiometry was performed in configuration 2 using 1 M NaOH for both the catholyte and anolyte and a CO flux of 0.5 sccm. As expected, the Tafel behavior and product distribution of the cathode in configuration 2 was essentially identical to that of configuration 1 (Figures 2D and 4D). However, for a given $j_{CO}$, the cell voltage in configuration 2 was more than 0.8 V lower than in configuration 1 (Figure 4C), which matches the Nernstian shift in the equilibrium potential for O$_2$ evolution in moving from pH 0 (Nafion MEA) to pH 14 (Ni foam in 1 M NaOH). A $j_{CO}$ of 107 mA cm$^{-2}$ required 2.49 V total cell voltage and was achieved with 68% single-pass conversion. When the flow rate was increased to 1 sccm (Figure 4E), $j_{CO}$ reached 168 mA cm$^{-2}$ at a total cell potential of 2.59 V with 56% single-pass conversion and 65% FE. The partial current density for ethylene production, 91 mA cm$^{-2}$, corresponds to a synthesis rate of 424 µmol cm$^{-2}$ h$^{-1}$. The cell performance was reasonably stable in configuration 2, with a ~5% decline in $j_{CO}$ over a 4-hr electrolysis at 144 mA cm$^{-2}$ at 2.45 V (Figure S6).

The use of a liquid catholyte is undesirable for electrosynthesis because it dilutes liquid-phase products and imposes a substantial ion-transfer resistance in the cell. To assess the prospects of gas diffusion CO electrolysis without a catholyte, we prepared cell configuration 3 in which ionic transport is mediated by a Nafion 117 membrane pressed between the Cu-GDE and a porous Ni-coated Ti foam anode (Figure 5A). The cell contains no catholyte chamber or reference electrode, which allows it to be operated at elevated CO pressure. The foam anode sits flush in a recessed pocket in the anode current collector block. During electrolysis, the anolyte is recirculated through the anode to remove O$_2$ and supply electrolyte to the Nafion membrane. The cathode side is the same as in configurations 1 and 2 except that the outflow line is equipped with a trap to collect liquid-phase products. After the
Galvanostatic electrolyses were performed in configuration 3 with 1 M NaOH recirculating through the anode and 4 bar CO flowing at 1.0 sccm through the cathode. The use of 4 bar CO resulted in substantially better stability than 1 bar (Figure S7). Figure 5B shows the product distributions and the total cell voltage for a series of 24 hr electrolyses performed at 24–144 mA cm⁻². As expected, ethylene was the dominant gas-phase product. Remarkably, a highly concentrated liquid-phase product stream was collected from the trap in the gaseous outflow of the cathode. Figure 5C shows the concentration of acetate and alcohols directly obtained from the trap after each 24-hr electrolysis as a function of the galvanostatic current density. With a total current density of 144 mA cm⁻², the cell produced 7.3 mL of a liquid product that was 0.87 M in acetate, 0.07 M in C₂₄ alcohols, and 2.75 M NaOH.
Figure 5C shows that this liquid product concentration can be further increased to 1.1 M acetate if a Nafion 1110 membrane is used in place of the Nafion 117 membrane. Increasing the membrane thickness has no effect on the product selectivity at the same total current density, but does necessitate an additional 40 mV of total cell potential (Figure S8). The thicker Nafion 1110 membrane decreases the volume of water crossing from the anode to the cathode, which increases the liquid product concentration. To our knowledge, the maximum concentration of a liquid C$_2$+ product that has been achieved in previous electrolysis studies is 0.024 M.$^{16}$ The partial current density for acetate that was collected in the liquid trap was 34 mA cm$^{-2}$, corresponding to a synthesis rate of 317 µmol cm$^{-2}$ h$^{-1}$.

The aqueous acetate and HO$^-$ collected from the trap indicates that liquid solutions are transported through the GDE under steady-state electrolysis conditions and...
swept away by the gas flow in the interdigitated flow field (Figure 5D). Excess water is supplied to the Cu-GDE by osmotic drag from the Na⁺ transport through the Nafion. Since the hydrophobic Teflon coating on a carbon GDE is heterogeneous, liquid may be transported through the GDE via hydrophilic channels in the microporous carbon layer. If the exclusive mode of ion transport in configuration 3 were Na⁺ transport from anode to cathode, the resulting concentration of NaOH in the liquid trap should be \( \sim 15 \text{ M} \) at 144 mA cm\(^{-2}\). The much lower \( 2.75 \text{ M} \) concentration observed in the liquid product stream indicates that HO⁻ transport exceeds Na⁺ transport by a \( \sim 3:1 \) ratio during electrolysis, corresponding to a Na⁺ transfer number of 0.25. Although Nafion is typically a highly selective cation-transporting membrane, HO⁻ transport has previously been observed in alkaline electrolytes that are devoid of Cl⁻. For example, Na⁺ transfer numbers as low as 0.3 have been measured for Nafion 120 membranes separating two NaOH solutions. In addition, the selectivity for HO⁻ transport in Nafion during water electrolysis has been shown to increase when Nafion separates an alkaline anolyte from an alkaline catholyte of greater concentration. The combination of these two effects drives the selectivity for hydroxide transport that we observe.

In addition to the products in the trap, smaller amounts of acetate and alcohol products were found in the NaOH anolyte. The amount of products in the anolyte was essentially invariant for electrolyses at 72–144 mA cm\(^{-2}\) and corresponded to \( \sim 9 \text{ mA cm}^{-2} \) of j\(_{CO}\) (Figure 5B), which suggests that the mechanism for product loss to the anolyte is limited by the transport through Nafion at currents greater than 72 mA cm\(^{-2}\). As a result, the loss to the anolyte becomes proportionally less significant as the current increases. Alcohol diffusion across Nafion is well established from fuel cell research. The acetate found in the anolyte may come from either acetate diffusion across the Nafion or ethanol diffusion followed by anodic oxidation to acetate.

Overall, the current-voltage response of configuration 3 is superior to that of configuration 2, with only 2.32 V required to reach 144 mA cm\(^{-2}\) total current. Furthermore, the voltage is more stable in configuration 3, showing an increase of only 13 mV over 24 hr at 144 mA cm\(^{-2}\) (Figure S9). The average single-pass CO conversion at this current density was 43% and the average total FE for CO reduction was 72%. Based on the integration of the H\(_2\) peak in the gas chromatograph, the FE declined by \( \sim 5\% \) over the course of the electrolysis (Figure 5E). Based on the dependence of the cell voltage on the Nafion thickness (Figure S7), the conductivity of the Nafion in configuration 3 was calculated to be 0.022 S cm\(^{-1}\), which is consistent with independent 4-electrode measurements of Nafion conductivity in alkaline electrolytes (Table S8). This value corresponds to an iR loss of 0.11 V at 144 mA cm\(^{-2}\). Given the total cell voltage and the product distribution shown in Figure 5B, the voltage efficiency for CO conversion to ethylene and acetate was calculated to be 24% (see Experimental Procedures). A voltage efficiency of 34% has been reported for CO\(_2\) conversion to ethylene in a GDE cell. However, the volume fraction of ethylene in the product stream was 0.15% in this case, versus 13% for configuration 3. While the exact value will depend on the purification method employed, the energy demand for purifying products that are <1% concentration can exceed the energy requirement of electrosynthesis itself.

Configuration 3 was also evaluated using 1 M HClO\(_4\) instead of 1 M NaOH and an IrO\(_x\) on Ti anode. At a current density of 144 mA cm\(^{-2}\), the cell exhibited a similar total cell voltage but produced H\(_2\) exclusively. Given the cell voltage and the requirement for \( \sim 1.5 \text{ V} \) versus NHE at the anode to sustain acidic H\(_2\)O oxidation,
the cathode is not sufficiently negative (versus NHE) to reduce CO under these conditions.

Sustainable operation in configuration 3 requires recovering the NaOH from the liquid product stream for read addition to the anolyte. Fortunately, sodium acetate is much less soluble than NaOH at 0°C, which provides a simple separation strategy. To test this strategy, we concentrated 3× and cooled to 0°C 6.8 mL of the liquid product that was collected from the electrolysis with Nafion 117 at 144 mA cm⁻², yielding a white crystalline precipitate. Isolation of the solid by a single filtration afforded 0.355 g of material that was 83% sodium acetate hydrate by mass, with NaOH accounting for the mass balance (Figure S12). Thus, the isolated yield from a single precipitation is 47% of the acetate collected in the liquid trap, with no organic impurities. Much higher yields and purities are possible on a larger scale. When the same procedure was repeated with 75 mL of mock liquid product solutions, the yield of precipitated sodium acetate was 80%–85% with 95%–98% purity.

Conclusion
The above results demonstrate that CO electrolysis to C₂ products is a viable electrosynthetic energy storage process. Properly designed GDE cells allow for simultaneous optimization of synthesis rates, FE, and single-pass CO conversion at moderate cell voltages. High single-pass conversion leads to direct production of concentrated gas-phase products. Furthermore, by operating with a CO GDE cathode directly in contact with Nafion, concentrated liquid product streams are transported through the GDE and readily isolated from the gas stream. Since electrochemical conversion of CO₂ into pure CO in high-temperature SOECs is already an established technology, the development of CO GDE electrolysis could allow for efficient electrochemical CO₂-to-C₂ conversion. The cell architectures described here provide a basis for device engineering and scale-up studies. In addition, our results provide a benchmark for studying structure-activity relationships of CO reduction catalysts in the regime of high synthesis rates. The ability to attain high single-pass conversions is a key advantage of CO electrolysis compared with what has been shown for CO₂ electrolysis in GDE cells. Our results therefore motivate an extensive investigation of gas and ion transport properties in CO₂ GDE cells to assess the prospects of improving single-pass conversion for low-temperature CO or C₂ production.

EXPERIMENTAL PROCEDURES
Copper acetate monohydrate (99.99% trace metal basis), sodium borohydride (99.99% trace metal basis), sodium hydroxide (99.99%, semiconductor grade), sodium chloride (99.999% trace metal basis), iridium(III) chloride hydrate (reagent grade), sodium hypophosphite monohydrate, and 2-ethoxyethanol were purchased from Sigma-Aldrich. Titanium foam, Nafion 117, Nafion 212, Nafion 1110, Nafion 520D dispersion, Sigracet 39 BC, and AvCarb 2230 were purchased from the Fuel Cell Store. Boron-doped diamond (BDD) powder was purchased from US NANO. HPLC grade isopropanol was purchased from Fisher Chemicals. Polybenzimidazole sheet (60 µm) was purchased from PBI Performance Plastics. Commercial nickel foam (1.6 mm thick) was purchased from Goodfellow.

Physical Characterization
X-ray tomography measurements where performed with a Zeiss Xradia 520 Versa X-ray CT microscope. Topographical characterization of the flow field and electrodes were made with a Keyence VK-X Series 3D Laser Scanning Confocal Microscope. GDE electrodes where prepared for cross-sectional imaging by first encasing
the electrode in polydimethylsiloxane (PDMS) and applying vacuum during the curing process to drive intercalation and remove bubbles. The PDMS intercalated electrodes where then cleaved with a scalpel. Cross-sectional SEM energy-dispersive X-ray spectroscopy (EDS) images were acquired with an FEI Magellan 400 XHR scanning electron microscope equipped with an XFlash 6j60 SDD EDS detector.

**Cell Construction**

Both anode and cathode current collectors were machined from solid grade 2 titanium metal. The interdigitated flow channels were generated via successive laser engraving with a 100-W Epilog CO2 laser cutter and physical removal of any remaining titanium oxide. All gas connections to the cell were made with Swagelok fittings, and all gas tubing used was 0.062-inch outer diameter and 0.0315-inch inner diameter. Gas flow into the cell was regulated by one or two parallel 0- to 0.5-sccm Alicat mass flow controllers. All gasketing in the cells was laser cut from high-purity high-temperature silicone rubber sheets in either 0.005- or 0.010-inch thickness. The cell body housing the electrolyte chamber (configurations 1 and 2) was 3D printed using a Form Labs 2 SLA 3D printer with the clear FLGPCL02 resin set on medium resolution. All cell configurations were clamped together with a 6-inch-wide Palmgren drill press vice. During assembly, the torque on the lead screw of the vice was set to 50 inch-lb with a torque wrench. A 316 SS gear pump was used for recirculation of the anolyte in configurations 2 and 3. For configurations 1 and 2, a New Era model 1000 syringe pump was used to flow the catholyte through the cell body at a rate of 150 μL min⁻¹.

**Electrochemical Measurements**

A CH Instruments 660D or 670D potentiostat was used for all experiments. Cathode potentials in configurations 1 and 2 were measured versus a Harvard Apparatus LF-2 Ag|AgCl reference electrode, which was connected via PFA Swagelok fitting to the reference port of the cell body. Each experiment was begun with two successive linear sweeps between −1.1 and −1.8 V versus Ag|AgCl to ensure proper functioning of the cell. The linear sweeps were followed by a potentiostatic preconditioning step at −1.1 V versus Ag|AgCl for 60 s, after which an AC impedance spectrum was collected at −1.1 V with frequencies ranging from 1 to 1,000,000 Hz with 10 mV amplitude (Figure S10). The cell was then stepped galvanostatically with one potentiostat and the cathode potentials were measured versus the Ag|AgCl reference electrode. Concurrently, total cell potentials were measured with a second potentiostat. Each galvanostatic step was 9 min in duration. Another impedance measurement was performed at −1.1 V at the end of the current steps to ensure that the impedance of the cell remained constant over the course of the experiment. In the case where configuration 1 was implemented with 1 M NaCl, the cell uncompensated resistance decreased over the course of the electrolysis, possibly because of corrosion and redeposition of catalyst. To account for this drift, we collected impedance measurements at each stepped current and corrected the uncompensated resistance for those values obtained at the corresponding impedance. For experiments using configuration 3, the cell was pressurized to 4 bar CO, except for the experiment at 1 bar. Prior to galvanostatic electrolysis, two linear sweeps were performed (2.15–2.35 V total cell potential, 10 mV s⁻¹ sweep rate) using a single CH Instruments 660D. AC impedance spectra collected at 0 V performed in the absence of any electrochemical cell components (just cell wire leads) yielded an associated wire lead resistance of 0.35 Ω. This contribution to the total cell potentials has been corrected for. All current densities presented are normalized for the geometric footprint of the Cu catalyst layer (0.8 cm²). All pH
measurements were performed using a symPhony sp70p pH meter with a VWR model 582 pH probe. Concentrated alkaline samples were diluted 1:1,000 in H₂O prior to measurement to ensure that the measured pH fell within the range of calibration for the instrument.

To determine the resistance of Nafion 117 when separating sodium hydroxide solutions, we performed four electrode measurements in an H cell: Pt | Ag|AgCl || Nafion 117 || Ag|AgCl | Pt. The Nafion membrane served as the junction between the two halves of the H cell. A series of current steps were imposed upon the two Pt electrodes from 5 to 100 mA cm⁻². The voltage drop across the Nafion was measured by two Ag|AgCl electrodes, which were connected to the cell via Luggin capillaries on opposing sides of the Nafion membrane. The slope of the current versus voltage drop across the Ag|AgCl electrodes yields the resistance experienced between the two electrodes. The effect of electrolyte resistance was corrected for by repeating the experiment in the same setup without the membrane: Pt | Ag|AgCl | Ag|AgCl | Pt.

Gas- and Liquid-Phase Product Quantification

The gas flowing out of the cell was diluted in N₂ to 20 sccm and flowed into the gas-sampling loop of a gas chromatograph (SRI Instruments). A GC run was initiated every 9 min. The gas chromatograph was equipped with a packed MolSieve 13X column and a packed HaySep D column. Ar (Praxair, 99.999%) was used as the carrier gas. A flame ionization detector with methanizer was used to quantify CH₄, C₂H₄, and CO concentration and a thermal conductivity detector was used to quantify H₂ concentration. The products were quantified by comparison of the peak integrals to standard gas mixtures, and the molar quantities were converted to coulombs (C) by multiplying by F, where F is Faraday’s constant and n = 6, 8, and 2 for CH₄, C₂H₄, and H₂, respectively. The charges corresponding to each product were then compared with the charge passed during electrolysis to determine the FE.

Solution-phase products (ethanol [EtOH], acetate [AcO⁻], n-propanol [n-PrOH], and allyl alcohol) were quantified at the end of each experiment using a Varian Inova 600-MHz NMR instrument. A 0.5-mL sample of the electrolyte was mixed with 0.1 mL of D₂O containing 100 parts per million (by mass fraction) DMSO (Sigma-Aldrich, 99.99%) as an internal standard. For NMR quantification in configuration 3, 50 μL of liquid product recovered from the trap was added to 450 μL of D₂O and 100 μL of 100 ppm DMSO standard. The one-dimensional ¹H spectrum was measured with water suppression using a pre-saturation method. The sum of all faradaic efficiencies quantified in this way shows minor fluctuations around 90%–100%. It is assumed that missing current error resides primarily from that of the hydrogen quantification, as this had the largest associated error. Hydrogen currents have been adjusted in the figures to achieve 100% current recovery. Raw quantified hydrogen current densities are given in Tables S2–S6 and faradaic efficiencies are provided in Figure S11.

Electrode Preparation

All Configurations: Cu Cathode GDE

The cathode GDE preparation was uniform across all cell configurations. The cathode GDE was fabricated from an AvCarb 2230 and was laser cut to dimension. The Cu catalyst was synthesized via a previously reported method. Copper(II) acetate monohydrate (0.599 g) was dissolved into 250 mL of 2-ethoxyethanol. This solution was sonicated under Ar for 30 min, after which 20 mL of 30 mM NaBH₄ in H₂O
was added dropwise. The reaction was allowed to stir for 5–10 min under Ar. The suspension of Cu nanoparticles was then filtered and washed with water (3×) and isopropanol (3×), then dried under vacuum and stored in a N₂ glovebox. An ink with a Cu catalyst concentration of 1 mg mL⁻¹ in isopropanol was prepared via bath sonication in a glass vial under Ar. Two hundred microliters of the ink was then drop dried onto an AvCarb 2230 GDE heated to 50°C on a hotplate to yield a catalyst footprint of 0.8 cm², then 3.5 mL of 2.5 wt% Nafion 520D in isopropanol was airbrushed onto the top of the catalyst layer. This spray method yields a patchwork of Nafion globules (Figure S2), which affix the catalyst to the GDE substrate. A 1 × 1-cm PET mask was used to limit the spray area.

**Configuration 1: MEA Anode**

BDD powder (0.5 g) was suspended in isopropanol (1 mg mL⁻¹) containing 1.05 g of dissolved iridium(III) chloride hydrate. This suspension was sonicated for 10 min to ensure homogeneity. Twenty milliliters of 30 mM NaBH₄ in H₂O was added dropwise under stirring. The suspension was then centrifuged and washed with water (3×) and isopropanol (3×). The solids were dried under vacuum to yield at 50 wt% IrOₓ on BDD catalyst nanopowder. An ink was prepared with 2 mg of catalyst in 2 mL of isopropanol containing 10.75 mL of Nafion 520D. This ink was sonicated for 20 min. Two hundred microliters of catalyst ink was drop dried onto a Sigracet 39 BC GDE heated to 50°C on a hotplate. A Nafion 117 membrane, which had been purified, was hot pressed into the GDE with 6.9 kPa of pressure at 130°C for 90 s between two Teflon sheets. This electrode was interfaced with a Ti current collector which had a serpentine flow path machined into it. During electrolysis experiments, humidified N₂ was flowed along the back of the electrode.

**Configuration 2: Ni Foam Anode**

Nickel foam (1.5 mm thick) was laser cut to 12.7 × 12.7 mm and treated according to a previously published method to form a high-surface-area NiFeOOH electrode. The PBI membrane was doped with 6 M NaOH according to previously published methods.

**Configuration 3: Titanium Foam-Supported Ni Anode**

Titanium foam (1.7 mm thick) was laser cut to 12.7 × 12.7 mm. The coupon was the refluxed in 5 mL of 12 M HCl for 1 hr and rinsed with water. The resulting coupon was electroless plated with Ni with a hypophosphite bath. First, the electrode was seeded by immersion in 5 mL of a 35 mM SnCl₂ HCl bath (pH 1) for 1 min. The Ti foam was rinsed off with water and dried before subsequent immersion in a 28 mM PdCl₂ HCl bath (pH 1) for 1 min. The Ti foam was rinsed off with water and blown dry with N₂ gas. It was immediately placed into 5 mL of the Ni plating bath, which consisted of 3.5 g of NH₄Cl, 2 g of NiCl₂ hydrate, 2 g of NaPO₂H₂⋅H₂O, and 1 g of trisodium citrate in 100 mL of DI water. The bath was heated to 80°C on a hotplate for 1 hr. The Ti/Ni foam electrode was then rinsed off and dried, and submerged in 5 mL of 0.37 M Fe(NO₃)₃⋅(H₂O)₉ in DI water. The electrode was allowed to slowly dry in air. Next it was placed into a tube furnace flowing 50 mL min⁻¹ Ar with 500 mg of NaPO₂H₂⋅H₂O upstream from the foam in a quartz weigh boat. The furnace was heated to 450°C for 1 hr. The foam was then cooled under the flow of Ar. The Nafion membrane was purified and then soaked in 1 M NaOH overnight before use.

For the experiment in which 1 M HClO₄ was employed as the anolyte in configuration 3, the Ti coupon was the refluxed in 5 mL of 12 M HCl for 1 hr and rinsed with water. It was then briefly immersed in an aqueous mixture of 0.1 M IrCl₃ and 0.1 M RuCl₃.
coupon was heated to 500°C in a muffle furnace for 30 min. This procedure was repeated five times. Next, 1 mL of 0.1 M IrCl₃ was sprayed via air brush onto one face of the coupon. During the spray deposition the coupon was heated to 80°C on a hotplate. The coupon was again heated to 500°C for 1 hr in a muffle furnace. This resulted in a Ti DSA coated in IrOₓ on one face. A Nafton 117 membrane was used as purified and the cell was pressurized to 4 bar CO and galvanostated at 144 mA cm⁻². The recorded total cell potential was 2.24 V.

Method of Calculating Voltage Efficiency
The voltage efficiency (Veff) for the production of ethylene and acetate was calculated for configuration 3 using the following equation:

\[ V_{\text{eff}} = \left( \frac{E_{C_{2}H_{4}\text{ thermo}} \times FC_{2}H_{4}}{100} \right) + \left( \frac{E_{\text{acetate thermo}} \times \text{FE}_{\text{acetate}}}{100} \right) \]

where \( E_{C_{2}H_{4}\text{ thermo}} = 1.06 \) V is the thermodynamic cell potential for ethylene; \( E_{\text{acetate thermo}} = 0.776 \) V is the thermodynamic cell potential for acetate; \( E_{\text{cell}} = 2.32 \) V is the measured cell voltage; \( FE_{C_{2}H_{4}} = 35.3\% \) is the faradaic efficiency for ethylene; \( FE_{\text{acetate}} = 23.7\% \) is the faradaic efficiency for acetate in the liquid trap only.

Method of Purification for Electro-Synthesized Sodium Acetate
Liquid product (6.8 mL) resulting from electrolysis at 144 mA cm⁻² in configuration 3 was concentrated under vacuum to 2 mL. This concentrated product was cooled to 0°C in an ice bath. A fleck of sodium acetate was added to initiate crystallization. The product was allowed to crystallize at 0°C for 20 min. The crystalline slurry was then filtered over a medium-porosity glass frit and compacted to aid removal of any excess NaOH liquid from the crystalline product. The resulting crystalline product was dried under vacuum at 70°C to yield 0.355 g (47% yield) of acetate hydrate material with 83% purity. The remaining mass balance was NaOH. With the same procedure repeated on a larger scale (75 mL) using mock liquid product solutions, the yield was 80%–85% with 95%–98% purity.

SUPPLEMENTAL INFORMATION
Supplemental Information includes 14 figures and 8 tables and can be found with this article online at https://doi.org/10.1016/j.joule.2018.10.007.

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AUTHOR CONTRIBUTIONS
M.W.K. and T.R.V. conceived the project. D.S.R. and T.R.V. designed and fabricated the cells. D.S.R. performed the experiments. M.W.K. and D.S.R. wrote the original draft. All authors contributed to interpreting the data and editing the manuscript.

DECLARATION OF INTERESTS
The authors have filed a provisional patent application for production of concentrated product streams using some of the cell designs described here.
REFERENCES


Supplemental Information

Carbon Monoxide Gas Diffusion Electrolysis
that Produces Concentrated C₂ Products
with High Single-Pass Conversion

Donald S. Ripatti, Thomas R. Veltman, and Matthew W. Kanan
Supplemental Information
Figure S1: TEM images of the Cu catalyst. a) Low and b), c) High magnification images.
Figure S2: Additional characterization of the GDE cathode via microscopy and profilometry. a) SEM cross sectional image of the GDE with EDS elemental mapping showing copper, fluorine and carbon. b) Black and white optical image of copper catalyst face of GDE. Image shows Nafion patchwork on the surface. c) Confocal laser microscope topological map of as-purchased Avcarb 2230 GDE substrate. Roughness calculated with Keyence Sdr roughness method. d) Confocal laser microscope topological map of catalyst layer on Avcarb 2230 prior to Nafion spray deposition.
Figure S3: Potential traces obtained during Tafel collection for Configurations 1 and 2 with 1 M NaOH electrolyte and 0.5 sccm CO flow. Galvanostatic steps of 12, 24, 48, 72, 96, 144 mA cm$^{-2}$ were applied to the cell. **a)** Configuration 1 cathode potential vs time. **b)** Configuration 2 cathode potential vs time. **c)** Configuration 2 total cell potential vs time.
**Figure S4:** Additional Configuration 1 data with 1 M NaOH electrolyte. 

**a)** Graph of on-line GC data monitoring the CO concentration exiting the cell. The flow rate of CO into the cell was 0.125 sccm. At first the cell is off, then is turned on (galvanostatic at 48 mA cm\(^{-2}\)) and then off again. This data corroborates the calculated utilization derived in **Figure 3b** from the analogous data point in the main text. 

**b)** Percent selectivity \((100 \times \frac{j_{\text{specific}}}{j_{\text{CO}}})\) as a function of the volume fraction of CO in N\(_2\) at a fixed current (144 mA cm\(^{-2}\)) and gas flow rate into the cell. 

**c)** Tafel data with the partial current densities and corresponding voltages collected with a flow rate of 0.250 sccm CO into the cell. The calculated percentage single pass utilization numbers are represented with the thin green bars to the right of each current step.
Figure S5: Opposing view of cell Configuration 2. The Ni foam anode sits flush in a pocket machined into the Ti anode current collector. Anolyte is recirculated through the Ni foam to remove O₂ bubbles formed from hydroxide oxidation. This same anode configuration is employed in cell Configuration 3, with a Ni-coated Ti foam serving as the anode.
Figure S6: Stability data for Configuration 2 in 1 M NaOH galvanostated at 144 mA cm$^{-2}$ and a CO flow rate of 1 sccm. a) Partial current densities vs time. Dashed line corresponds to the sum of current going towards CO reduction, $j_{\text{CO}}$. b) Total cell voltage vs time. $j_{\text{CO}}$ is relatively stable over the course of the electrolysis, although the selectivity for the individual CO reduction products shifts. The selectivity for acetate increases while the selectivity for alcohols and ethylene decreases. Methane begins to grow in as a product after the first hour of electrolysis. The total cell potential rises 70 mV over the course of 4 h with an average potential of 2.45 V. The cell maintained a single pass utilization of 42%.
Figure S7: Electrolysis in Configuration 3 with 1 bar CO. Measurements were performed at galvanostatic current density of 144 mA cm$^{-2}$ with 1 sccm CO over 24 h using Nafion 117 membrane. a) Average partial current densities and average total cell potential over 24 h. b) Faradaic efficiency for gaseous products and total cell voltage vs time. The faradaic efficiencies were determined by on-line GC analysis.
Figure S8: The effect of varying the thickness of the Nafion Membrane in Configuration 3. Measurements were performed at a galvanostatic current density of 144 mA cm\(^{-2}\) over 24 h with 4 bar CO at 1 sccm. Nafion 212, 117 and 1110 were used, with thicknesses of 51 µm, 183 µm, and 254 µm, respectively. a) Partial current densities vs membrane thickness. Corresponding total cell voltages are displayed above each electrolysis. b) Concentration of liquid products obtained in the trap vs membrane thickness. c) Na\(^+\) transfer number vs membrane thickness. The transfer number is calculated from the total charge passed and the amount of Na\(^+\) obtained in the liquid trap.
Figure S9: Additional data on for cell Configuration 3. Measurements were performed with 4 bar CO at 1 sccm using Nafion 117. a) Total cell voltage vs time at different galvanostatic current densities. b) The volume of liquid product obtained in the trap after 24 h of electrolysis vs current density.
**Figure S10:** Impedance spectroscopy of Configuration 1 with 1 M NaOH. The cell was potentiostated at the indicated voltage for 5 min prior to each impedance spectra acquisition. Voltages presented are vs NHE. 

**a)** Zoom-in showing the non-faradaic high-frequency impedance loop. This loop shows no appreciable dependence on potential. The uncompensated resistance at constant current is taken as the series sum of $R_1$ and $R_2$. 

**b)** Zoom-out of the impedance spectra depicting both impedance loops. $R_3$ shows clear potential-dependent behavior and is taken to be the charge transfer resistance. The second impedance loop shows non-ideal capacitive behavior, which is best modeled as a Constant Phase Element (CPE) and likely arises from the porous nature of the GDE electrode. Such a model yields an error of fit on the order of ~5% when using CHI software’s impedance modeling package.
Figure S11: Faradaic efficiencies using Configurations 1, 2 and 3. All data are from experiments using 1 M NaOH electrolyte. a) Configuration 1 faradaic efficiency vs measured cathode potential with 0.5 sccm CO. b) Configuration 2 faradaic efficiency vs measured cathode potential with 1 sccm CO. c) Configuration 3 faradaic efficiency vs measured total cell potential with 4 bar CO at 1 sccm using Nafion 117 membrane.
Figure S12: $^1$H NMR in D$_2$O of solid crystalline product obtained from 24 h electrolysis in cell Configuration 3 at 144 mA cm$^{-2}$. 
Figure S13: Representative $^1$H NMR of catholyte collected from Configuration 2 with 1 M NaOH electrolyte. Inset shows the full acetate peak relative to the DMSO standard.
Figure S14: Representative $^1$H NMR of liquid product obtained from Configuration 3. Inset shows the full acetate peak relative to the DMSO standard.
Sample Calculation of CO₂ Conversion

\[
\left( \frac{mC}{s \ cm^2} \right) \left( \frac{1 \ C}{1000 \ mC} \right) \left( \frac{mol \ e^-}{96485 \ C} \right) \left( \frac{1 \ mol \ ethene}{12 \ mol \ e^-} \right) \left( \frac{2 \ mol \ CO_2}{1 \ mol \ ethene} \right) \left( \frac{22.4 \ L}{1 \ mol \ CO_2} \right) \left( \frac{1000 \ mL}{1 \ L} \right) \left( \frac{60 \ s}{1 \ min} \right) \left( 1 \ cm^2 \ geometric \right) = ml \ min^{-1} \ CO_2 \ consumed \ by \ device \ for \ ethene \ synthesis
\]

\[
100 \times \left( \frac{ml \ min^{-1} \ CO_2 \ consumed}{ml \ min^{-1} \ CO_2 \ flowed \ in} \right) = \% \ CO_2 \ conversion \ to \ ethene
\]

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Table S1: Literature CO₂ reduction GDE data and calculated single pass conversions.
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**Table S2:** Tabulated Tafel data from Configuration 1 operating with 1 M NaOH electrolyte and 0.5 sccm CO.
| Total E | E vs NHE | \( \text{mA cm}^{-2} \) | \( \text{H}_2 \) | \( \text{CH}_4 \) | \( \text{C}_2\text{H}_4 \) | \( \text{Allyl Alcohol} \) | \( \text{Propanol} \) | \( \text{Ethanol} \) | \( \text{Acetate} \) | \( \text{Methanol} \) | Total Conversion % | Conversion % |
|--------|---------|------------------|-----|-----|------|----------------|-------|-------|-------|------|---------|----------------|--------|
| 2.95   | -1.33   | 4.55             | 4.24| 0.0 | 1.24 | 1.05          | 0.15  | 0.0   | 0.0   | 0.0  | 93.6    | 4.0            |
| 3.04   | -1.38   | 7.52             | 10.30| 0.60| 2.66 | 2.12          | 0.54  | 0.0   | 0.0   | 0.0  | 98.9    | 9.8            |
| 3.20   | -1.42   | 11.37            | 22.98| 0.99| 4.03 | 4.63          | 2.00  | 0.0   | 0.0   | 0.0  | 95.8    | 21.4           |
| 3.31   | -1.45   | 13.68            | 35.64| 1.40| 4.62 | 7.31          | 4.35  | 0.08  | 0.0   | 0.0  | 93.6    | 33.6           |
| 3.44   | -1.46   | 16.25            | 47.94| 1.81| 5.37 | 11.74         | 8.14  | 0.12  | 0.0   | 0.0  | 97.3    | 49.0           |
| 3.72   | -1.49   | 34.90            | 67.24| 1.18| 3.36 | 15.06         | 11.77 | 0.10  | 0.0   | 0.0  | 98.0    | 66.7           |

**Table S3:** Tabulated Tafel data from Configuration 1 operating with 1 M NaCl electrolyte and 0.5 sccm CO.
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<th>Propanol</th>
<th>Ethanol</th>
<th>Acetate</th>
<th>Methanol</th>
<th>Total %</th>
<th>Conversion %</th>
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<td>3.90</td>
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<td>1.13</td>
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<td>4.0</td>
<td></td>
<td></td>
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<td>1.16</td>
<td>4.44</td>
<td>7.34</td>
<td>3.58</td>
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<td>21.42</td>
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<td>10.46</td>
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<td>68.1</td>
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</table>

**Table S4:** Tabulated Tafel data from Configuration 2 operating with 1 M NaOH electrolyte and 0.5 sccm CO.
<table>
<thead>
<tr>
<th>Total Cell E</th>
<th>E vs NHE</th>
<th>mA cm$^{-2}$</th>
<th>H$_2$</th>
<th>CH$_4$</th>
<th>C$_2$H$_4$</th>
<th>Allyl Alcohol</th>
<th>Propanol</th>
<th>Ethanol</th>
<th>Acetate</th>
<th>Methanol</th>
<th>Total %</th>
<th>Conversion %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.0</td>
<td>10.94</td>
<td>0.0</td>
<td>1.86</td>
<td>2.11</td>
<td>0.71</td>
<td>0.0</td>
<td>82.4</td>
<td>4.7</td>
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<td>7.39</td>
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<td>90.78</td>
<td>1.41</td>
<td>5.95</td>
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</table>

**Table S5:** Tabulated Tafel data from Configuration 2 operating with 1 M NaOH electrolyte and 1.0 sccm CO.
<table>
<thead>
<tr>
<th>Total Cell E V</th>
<th>H₂</th>
<th>CH₄</th>
<th>C₃H₄</th>
<th>Allyl Alcohol</th>
<th>Propanol</th>
<th>Ethanol</th>
<th>Acetate</th>
<th>Acetate anolyte</th>
<th>Propanol anolyte</th>
<th>Ethanol anolyte</th>
<th>Total</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
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<td>16.18</td>
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<td>0.03</td>
<td>0.06</td>
<td>0.02</td>
<td>0.39</td>
<td>1.58</td>
<td>0.00</td>
<td>1.15</td>
<td>100</td>
<td>3.4</td>
</tr>
<tr>
<td>2.27</td>
<td>22.52</td>
<td>1.27</td>
<td>23.00</td>
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<td>0.99</td>
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</tr>
</tbody>
</table>

**Table S6:** Tabulated data from Configuration 3 operating with 1 M NaOH anolyte and 1.0 sccm CO at 4 bar. Values averaged over 24 h of operation.
<table>
<thead>
<tr>
<th>Total Cell E (V)</th>
<th>j_{tot} (mA cm^{-2})</th>
<th>Acetate (mol L^{-1})</th>
<th>Ethanol (mol L^{-1})</th>
<th>Propanol (mol L^{-1})</th>
<th>Allyl alcohol (mol L^{-1})</th>
<th>pH</th>
<th>Transfer number</th>
<th>Na^{+} (mol L^{-1})</th>
</tr>
</thead>
<tbody>
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<td>0.002</td>
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<td>2.27</td>
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<td>0.613</td>
<td>0.021</td>
<td>0.006</td>
<td>0.005</td>
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</tbody>
</table>

**Table S7**: Liquid product composition resulting from Configuration 3 operating with 1 M NaOH anolyte and 1.0 sccm CO at 4 bar after 24 hours of operation.
<table>
<thead>
<tr>
<th>mS cm⁻¹</th>
<th>1 M HClO₄</th>
<th>1 M NaOH</th>
<th>2 M NaOH</th>
<th>4 M NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>82.0</td>
<td>14.6</td>
<td>16.5</td>
<td>22.0</td>
</tr>
</tbody>
</table>

**Table S8:** 4 electrode H-cell Pt | Ag|AgCl ||Nafion 117|| Ag|AgCl | Pt measurements of Nafion 117 membrane conductivity when separating various electrolytes.
References