Electrolytic Conversion of Bicarbonate into CO in a Flow Cell

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Summary

Electrochemical CO$_2$ reduction offers a method to use renewable electricity to convert CO$_2$ into CO and other carbon-based chemical building blocks. While nearly all studies rely on a CO$_2$ feed, we show herein that aqueous HCO$_3^-$ solutions can also be electrochemically converted into CO gas at meaningful rates in a flow cell. We achieved this result in a flow cell containing a bipolar membrane (BPM) and a silver nanoparticle catalyst on a porous carbon support. Electrolysis upon a N$_2$-saturated 3.0-M KHCO$_3$ electrolyte solution yields CO with a faradaic efficiency (F.E.$_{CO}$) of 81% at 25 mA cm$^{-2}$ and 37% at 100 mA cm$^{-2}$. This output is comparable to the analogous experiment where the electrolyte is saturated with gaseous CO$_2$ (faradaic efficiency for CO is 78% at 25 mA cm$^{-2}$ and 35% at 100 mA cm$^{-2}$). The H$^+$ flux from the BPM is critical to this chemistry in that it reacts with the HCO$_3^-$ feed to generate CO$_2$, which is then reduced to CO at the gas diffusion electrode. These results are important in that they show that the addition of gaseous CO$_2$ to HCO$_3^-$ electrolytes is not necessary in order to obtain reduced carbon products with a flow cell architecture. This process offers a means of using electrolysis to bypass the thermally-intensive step of extracting CO$_2$ from HCO$_3^-$ solutions generated in carbon capture schemes.

Keywords

electrolysis; flow cell; bicarbonate; carbon dioxide; carbon monoxide; carbon capture and utilization
Introduction

A number of different cell configurations have been proposed in an effort to reach the high current densities and product selectivities that would be required by a commercial CO₂ electrolyzer, yet there is no low-temperature CO₂ electrolyzer available to the market.¹⁻⁷ The majority of cell configurations supply CO₂ to the cathode of the electrochemical cell as a saturated solution in a supporting aqueous electrolyte.¹,²,⁷ There are also many examples where gaseous CO₂ is delivered directly to the electrode without a liquid medium.⁸⁻¹² A challenge with CO₂-fed liquid systems is that bubbling gaseous CO₂ into the electrolyte reaches a saturated [CO₂] of ~0.033 M at ambient temperature and pressure prior to and during electrolysis. This saturation point fundamentally limits the maximum current density that can be achieved for CO₂ reduction in the bulk liquid phase.¹³ Furthermore, the addition of CO₂ to the electrolyte causes a lowering in pH resulting in conditions that favour the competing hydrogen evolution reaction (HER) instead of the CO₂ reduction reaction (CO₂RR).¹⁴⁻¹⁶ These characteristics of CO₂-saturated electrolyte systems provide the impetus to explore alternative pathways for accessing electrolytically-reduced carbon products at high current densities.

A system capable of efficiently utilizing bicarbonate (HCO₃⁻) as a source of carbon to form electrochemical products is compelling because the maximum carbon concentration in a saturated aqueous solution of KHCO₃ (~3.3 M) is greater than for saturated CO₂ (33 mM). The ability to convert HCO₃⁻ in solution to a reduced carbon product would also provide an opportunity to avoid electrolyte acidification caused by the addition of gaseous CO₂. However, very few examples of systems capable of these electrochemical transformations currently exist. A study by Hori in 1983 showed that formate could be produced from the electrochemical reduction of a 1.0-M NaHCO₃ solution without a CO₂ supply in an H-cell architecture containing a mercury catalyst, but with a partial current density for formate (J_{formate}) of <1 mA cm⁻².¹⁷ Kanan and coworkers reported in 2015 that a palladium catalyst in an H-cell was able to reduce 2.8-M KHCO₃ into formate without a CO₂ feed at J_{formate} = 3.2 mA cm² (c.f. 6.1 mA cm² in a CO₂-fed HCO₃⁻ solution). To our knowledge, these results set the benchmark for electrochemical HCO₃⁻ conversion to a reduced carbon product in a system without supply of CO₂.¹⁴ All other reports of HCO₃⁻ reduction
chemistry show lower current densities and faradaic efficiencies compared to CO$_2$-fed systems. Moreover, formate is the only product that has been reported from the reduction of HCO$_3^-$ without a CO$_2$ feed, thus the electrochemical reduction of HCO$_3^-$ into CO without a CO$_2$ supply is not currently known.

Our program has an interest in developing flow cells that mediate CO$_2$RR at high current densities.\textsuperscript{10} Our previous studies have shown that a membrane reactor architecture with a BPM separating the cathode and the anode gas diffusion layers is effective at mediating CO$_2$RR with CO$_2$ delivered either as a gas\textsuperscript{8} or as dissolved in aqueous electrolyte.\textsuperscript{9} While a gaseous CO$_2$ feed enables higher current densities,\textsuperscript{10,18,19} there are practical advantages to delivering liquid rather than gas to the reactor.\textsuperscript{10} However, realizing high current densities with a liquid feed is challenging because of the low solubility limits of CO$_2$.

Recognizing that the BPM delivers H$^+$ to the cathode, we became intrigued by the possibility that the high H$^+$ flux at the BPM could react with HCO$_3^-$ to form a high local concentration of CO$_2$ that would be available for electrochemical reduction at the catalyst,\textsuperscript{20,21} and without the need for an external supply of CO$_2$.

Following this line of inquiry, we built an electrochemical flow reactor\textsuperscript{8,9} to electrochemically reduce KHCO$_3$ solutions without the need to supply the electrolyte with gaseous CO$_2$. We demonstrate herein a 3.0-M KHCO$_3$ electrolyte yeilds a F.E.$\textsubscript{CO}$ of 81\% at 25 mA cm$^{-2}$ that is comparable with a system wherein the electrolyte is saturated with CO$_2$ gas (F.E.$\textsubscript{CO}$ = 78\%). This experiment provides the following unique observations: (i) a carbon product other than formate as the product of electrochemical reduction performed upon a HCO$_3^-$ solution; (ii) comparable electrolytic activity measured for HCO$_3^-$ electrolytes with and without saturation from a gaseous CO$_2$ feed; (iii) the electrochemical conversion of HCO$_3^-$ solutions in a continuous flow reactor; and (iv) that the BPM in flow cell enhances the conversion of HCO$_3^-$ to CO through a CO$_2$ mediated pathway. These results illuminate an alternative way to electrolytically form carbon-based products derived from CO$_2$. This methodology also presents a new opportunity for air capture schemes because electrolysis could potentially bypass the energy-intensive thermal extraction of CO$_2$ gas from HCO$_3^-$ solutions.\textsuperscript{22}
Results and discussion

A two-electrode liquid flow-cell electrochemical reactor was used for our electrochemistry experiments (Figure 1). The flow cell was built in-house and consists of housing, gaskets, anode and cathode flow-field plates and a membrane electrode assembly (MEA). The anode and cathode housings are made from stainless steel and serve to deliver liquid electrolyte to the anode and cathode. The titanium cathode flow plate and stainless steel anode flow plate sandwich the 4-cm² MEA. The anode (316 stainless steel) and cathode (grade 2 titanium) flow-field plates (active areas = 4 cm²) contain serpentine channels 1.5 mm wide and 1.5 mm deep with 1-mm ribs. The MEA consists of a nickel foam anode (2.5 × 2.5 cm²), a BPM (3 × 3 cm²), and a silver nanoparticle-coated porous carbon support as the cathode (2.5 x 2.5 cm²). The entire assembly is sandwiched between the two stainless housings fastened with 8 bolts. The silver-coated carbon cloth cathode was prepared by spray coating carbon cloth (CeTech) with a mixture of commercially-available silver nanopowder and Nafion™ solution. The anode feed was 1.0-M KOH delivered at 50 mL min⁻¹ and the cathode feed was an aqueous solution of either 3.0-M K₂CO₃ or 3.0-M KHCO₃ delivered at 50 mL min⁻¹ continuously purged through the head space with either N₂ or sparged with CO₂ gas at a rate of 160 sccm. Cyclic voltammetry measurements of the two-electrode flow cell were collected over the -1.5 to -3.5 V range (reported as the cell potential). Faradaic efficiencies for CO production were measured at constant cathodic current densities of 25, 50, 75 and 100 mA cm⁻². pH measurements were obtained by diverting ~10 mL of catholyte flowing through the peristaltic pump into a glass vial from which the pH was measured. Gas chromatography (GC) analysis of the gaseous headspace at the electrolyzer outlet showed CO, CO₂, and H₂ as the only detectable products. The cathode solution was analyzed by ¹H NMR after electrolysis and no liquid products were detected. F.E. for CO is reported with the remainder of the electrochemical products confirmed as H₂. Further description of the setup and full cell dimensions are included in the Supplementary Information (Figure S1). Control experiments were also applied using an analogous flow cell architecture with an anion exchange membrane (AEM) in place of the BPM.
Figure 1. Experimental setup of (a) electrochemical flow cell experiment (b) an expanded view of the flow cell, and (c) dimensions of the cathode & anode flowplates. Nickel foam (anode) and silver deposited on a porous carbon support (cathode) were separated by a BPM. 1.0-M KOH electrolyte was circulated through the stainless flow plate and oxidized into O$_2$ gas at the anode. Either KHCO$_3$ or K$_2$CO$_3$ electrolyte solutions with CO$_2$ sparged in or with N$_2$ purged through the headspace were circulated through the titanium flow plate and reduced into CO at the cathode. The cathodic products were analyzed by gas chromatography (GC). Electrolyte flows were driven by peristaltic pumps at 50 mL min$^{-1}$. Gas flows (N$_2$ or CO$_2$) were set at 160 sccm. All dimension in (d) are in cm.

Electrolysis of HCO$_3^-$ solutions produce CO

The flow cell setup described above was used to test the electrochemical production of CO during electrolysis of two 3.0-M KHCO$_3$ solution systems: (i) KHCO$_3$ reservoir sparged with CO$_2$; and (ii) N$_2$
purged through the headspaces of the KHCO₃ reservoirs. Cyclic voltammograms (CVs) were collected between potentials of -1.0 and -3.5 V (Figure 2a) in a two-electrode flow cell, and F.E.₃ value were measured between current densities of 25 and 100 mA cm⁻² in 25-mA cm⁻² increments (Figure 2b). The viability of the flow cell towards CO₂ reduction was confirmed by results from the CO₂-saturated 3.0-M KHCO₃ solution (Figure 2, black): The CV exhibits a sharp rise in current density at -2.5 V and a current density of 90 mA cm⁻² at -3.5 V was measured. The moderate F.E.₃ of 78% exhibited at low current densities (25 mA cm⁻²) is further reduced at higher current densities (e.g., 35% at 100 mA cm⁻²). These results are consistent with previous reports of CO₂-to-CO reduction in liquid-fed flow cells.⁹,²³,²⁴

Having validated the CO₂RR activity of our flow cell, we then investigated the electrochemical reduction of HCO₃⁻ in the absence of a CO₂ supply. CVs collected over the -1.0 to -3.5 V cell potential range show similar reductive sweep profiles to the CO₂-saturated solution (Figure 2a). Peak current density of 100 mA cm⁻² was measured for the KHCO₃ solution in the absence of CO₂ supply. Electrochemical reduction of N₂-saturated 3.0-M KHCO₃ solution showed a F.E.₃ of 81% at a current density of 25 mA cm⁻², and 37% at 100 mA cm⁻² (Figure 2b, orange). These results represent the first observations of the production of CO from a HCO₃⁻ solution in the absence of a gaseous CO₂ feed, and the first example of producing a reduced carbon product other than formate from HCO₃⁻. We note that the difference in F.E.₃ for the N₂-saturated 3.0-M KHCO₃ solution with the analogous CO₂-saturated solution is <2% at every current density between 25 and 100 mA cm⁻². Electrochemical reduction of the N₂-saturated 3.0-M K₂CO₃ solution was also performed following similar procedures and showed a F.E.₃ of 4.0% at 20 mA cm⁻², and 1.0% at 100 mA cm⁻² (Figure S2). The relatively low F.E.₃ for the CO₂⁻ solution confirms that CO₂⁻ is not electrochemically active.
Figure 2. Electrochemical reduction of KHCO$_3$ solutions sparged with CO$_2$(g) (black) and N$_2$(g) (orange) in an electrolyzer flow cell containing a BPM show nearly identical behavior: (a) CVs recorded over the -1.5 and -3.5 V range at a scan rate of 100 mV s$^{-1}$ in a 3.0-M KHCO$_3$ solution; (b) F.E$_{CO}$ measured at constant current densities between 25 and 100 mA cm$^{-2}$ in a 3.0-M KHCO$_3$ solution; (c) $J_{CO}$ as a function of [KHCO$_3$]. Cathode: silver deposited on porous carbon support; anode: nickel foam; catholyte: KHCO$_3$; anolyte: 1.0-M KOH. $J_{CO}$ values were measured at a constant cell potential at 3.0 V in a series of KHCO$_3$ solutions prepared with different HCO$_3^-$ concentrations saturated with CO$_2$ or N$_2$. 
The dependence of $F.E_{CO}$ on $[\text{HCO}_3^-]$ was investigated by measuring the partial current densities for CO ($J_{CO}$) at a constant cell potential of 3.0 V for a series of N$_2$-saturated and CO$_2$-saturated KHCO$_3$ solutions prepared with HCO$_3$ concentrations ranging from 0.5 M to 3.0 M (Figure 2c). The results show that increasing $[\text{KHCO}_3]$ increases the $J_{CO}$ from 13 mA cm$^{-2}$ at 0.5 M to 25 mA cm$^{-2}$ at 3.0 M. The same solutions bubbled with CO$_2$ show a similar (but less pronounced) increase in $J_{CO}$ from 19 mA cm$^{-2}$ at 0.5-M KHCO$_3$ to 26 mA cm$^{-2}$ at 3.0-M KHCO$_3$. The $F.E_{CO}$ and total current densities for each electrolyte are provided in Figure S3. The $J_{CO}$ for solutions with <2 M of KHCO$_3$ (where most CO$_2$RR studies are performed) were significantly greater in each case for the CO$_2$-fed electrolytes. The N$_2$-saturated solution yields $J_{CO}$ values comparable with those measured for the CO$_2$-saturated solution at $[\text{KHCO}_3] > 2.5$ M. An increase in $J_{CO}$ values with increasing $[\text{HCO}_3^-]$ (for both the N$_2$-saturated and the CO$_2$-saturated solutions) is consistent with HCO$_3^-$ enhancing the rate of the electrochemical reduction of CO$_2$ through a rapid exchange with CO$_2$ or suppression of HER with increasing electrolyte pH.$^{14}$

**Defining the reactions in the flow cell**

Resolving the electrochemically active species in the flow reactor is made challenging by the closed reaction vessel and the dynamic acid-base equilibria that defines the relative concentrations of CO$_2$, HCO$_3^-$, and CO$_3^{2-}$. We therefore designed a set of experiments to confirm that the amount of CO produced from a HCO$_3^-$ stream is governed by three key processes: (i) an acid/base equilibrium of HCO$_3^-$ with protons supplied by the BPM to form CO$_2$ and H$_2$O at the membrane-solution interface; (ii) the reduction of this *in-situ* generated CO$_2$ to CO and OH$^-$; and (iii) the *in-situ* generated OH$^-$ increasing the bulk pH to favor CO$_3^{2-}$ formation, which inhibits CO production (Figure 3a). We operated a flow cell with either a BPM or an AEM at 100 mA cm$^{-2}$ for 2 hours and measured $F.E_{CO}$ while tracking the concentration of CO$_2$(g) leaving the flow cell ([CO$_2$]$_{outlet}$) and the pH of the bulk catholyte solutions (Figure 3a). We also operated the flow cell containing the BPM, but while circulating KHCO$_3$ without an applied potential (denoted BPM/no electrolysis). These experiments showed that the [CO$_2$]$_{outlet}$ decreased over time with both the BPM and
AEM, and that the \([\text{CO}_2]_{\text{outlet}}\) measured with the BPM system is higher than that measured for the AEM and BPM/no electrolysis (Figure 4a). The formation of \(\text{CO}_2\) on the cathodic side of the BPM membrane was confirmed by an independent experiment with an H-cell, where operation at 20 mA cm\(^{-2}\) produced enough \(\text{CO}_2\) to exceed the solubility limit of \(\text{CO}_2\) (Figure 4d). We also observed a correlation of \(\text{F.E.}_\text{CO}\) to \([\text{CO}_2]_{\text{outlet}}\) for both the BPM and AEM (Figure 4c), where \(\text{F.E.}_\text{CO}\) decreases with \([\text{CO}_2]_{\text{outlet}}\) as a function of time. Finally, the pH of the catholyte increased as a function of time for all three experiments (Figure 4b), where electrolysis accelerated the change in alkalinity.

These collective experimental results support the cathodic reaction chemistry listed in Figure 3b. The higher \([\text{CO}_2]_{\text{outlet}}\) measured with the BPM than with the AEM is consistent with the BPM supplying a flux of \(\text{H}^+\) that is available for reaction with \(\text{HCO}_3^-\) to form \(\text{CO}_2\) (Figure 3b). This conclusion is further supported by the higher \([\text{CO}_2]_{\text{outlet}}\) measured when the flow cell with the BPM is subjected to electrolysis (and thus creating a higher \([\text{H}^+]\) at the cathode) relative to the experiment without an applied potential. We interpret the linear relationship that exists between \(\text{F.E.}_\text{CO}\) and the \([\text{CO}_2]_{\text{outlet}}\) for both membranes as an indication that \(\text{CO}_2\) is the electrochemically active species; i.e., a higher amount of \(\text{CO}_2\) available enables more \(\text{CO}\) to be generated through \(\text{CO}_2\text{RR}\) at the catalyst. This correlation is also consistent with the BPM yielding a higher local \(\text{CO}_2\) concentration at the catalyst.
Figure 3. a) Schematic representation of the dominant chemical and electrochemical reactions occurring in the flow cell containing a BPM: Reaction of H⁺ with HCO₃⁻ to form CO₂ at the membrane interface, and the electrochemical reduction of CO₂ at the catalyst to form CO and OH⁻. b) Summary of the reaction chemistry at the membrane and catalyst surfaces and in the bulk solutions in the cathode reaction compartment when a BPM and AEM are used. The most reactive H⁺ donors (orange) and electrochemically active species (green) that dominate reactivity are highlighted. The reactions indicated in light grey are not expected to govern the reaction chemistry.
Figure 4. Temporal change in (a) [CO$_2$]$_{\text{outlet}}$ and (b) pH during electrolysis of 3.0 M KHCO$_3$ at 100 mA cm$^{-2}$ with a BPM (orange) or AEM (blue). A control experiment, BPM/no electrolysis (grey), was recorded in a flow cell containing a BPM with the circulation of catholyte without an applied potential. (c) F.E.$\text{CO}_2$ as a function of [CO$_2$]$_{\text{outlet}}$ during the 2-h electrolysis of a 3.0-M KHCO$_3$ solution at 100 mA cm$^{-2}$ with a BPM (orange) and an AEM (blue). The ~20% difference in F.E.$\text{CO}_2$ values at the same [CO$_2$]$_{\text{outlet}}$ is attributed to the difference in pKa values of the indicated H$^+$ donors in the BPM and AEM flow cells. The headspace was purged with a 160 mL/min N$_2$ stream for all experiments. (d) Image of an H-cell where a BPM separates a silver-coated carbon gas diffusion electrode in the cathodic compartment and a Pt mesh anode in the anodic compartment. The formation of CO$_2$ bubbles during the electrolysis of HCO$_3^-$ at a current density of 20 mA cm$^{-2}$ confirm enough CO$_2$ is produced to exceed the solubility limits of CO$_2$ in aqueous media.

The ~20-% higher F.E.$\text{CO}_2$ values obtained with the BPM relative to the AEM at the same [CO$_2$]$_{\text{outlet}}$ (e.g., 10,000 ppm) also point to differences in H$^+$ donors available at the CO$_2$RR electrocatalyst surfaces.
Considering that the H⁺ donors available with the BPM are HCO₃⁻, H⁺, and H₂O (Figure 3b), we can assume HCO₃⁻ to be the most active H⁺ donor because the pKa of 10.3 is lower than that of H₂O (pKₐ = 14.0), and the high pH would diminish the role of H⁺. The protons delivered by the BPM would also facilitate the conversion of CO₃²⁻ into HCO₃⁻, which could then be converted to CO₂ through acid/base equilibria. In the case where the AEM is used, the build up of OH⁻ would deplete HCO₃⁻ near the membrane surface leaving H₂O as the sole H⁺ donor for CO₂RR (Figure 3b). On this basis, we conclude that a higher concentration of H⁺ donors provided by the BPM than the AEM is responsible for the 20-% difference in F.E.-CO at a constant [CO₂]_{outlet}.

Finally, we are able to rationalize the observed increase in pH of the KHCO₃ catholyte solution during electrolysis with both the BPM and AEM systems to be a consequence of OH⁻ being generated from both HER and CO₂RR at the catalyst (Figure 4c). In accordance with previous models,²⁷,²⁸ this increase in pH would decrease F.E.-CO over the course of our electrolysis experiments where the catholyte solutions are not recycled. The higher F.E.-CO values could indeed be recovered by replenishing the catholyte with KHCO₃ (Figure S4). An additional advantage over the AEM is that the BPM suppresses the increase of the pH of the catholyte during electrolysis (thereby slowing the shift in the equilibrium of carbon species in solution towards catalytically inactive CO₃²⁻; Figures S5-S6) by delivering protons to react with CO₃²⁻ to form HCO₃⁻.

This collection of experiments point to the conversion of HCO₃⁻ to CO being enabled by: (i) an acidic region at the membrane interface; and (ii) a basic region at the catalyst. The acidic membrane interface enables CO₃²⁻ to be converted into HCO₃⁻, and HCO₃⁻ to be converted into catalytically active CO₂(g). The basic pH region at the catalyst layer arises from CO₂RR chemistry that generates OH⁻ concomitant with CO production. An important outcome of this study is the demonstration that the BPM can deliver a local concentration of CO₂ to the catalyst that exceeds the solubility limits of CO₂ in aqueous media. The ability for the membrane to enable a high concentration of CO₂ at the basic catalyst layer offers a strategy for realizing higher CO₂RR current densities from aqueous feedstocks. This HCO₃⁻ reduction system also offers the additional advantage of not requiring a CO₂ feed that would acidify the reaction.
Conclusions

We demonstrate that HCO$_3^-$ can be reduced to CO in a flow cell containing a BPM without a supply of CO$_2$ gas to the electrolyte. The observation that a 3.0-M KHCO$_3$ system without a CO$_2$ feed yields a comparable faradaic efficiency for CO with a similar system with a CO$_2$-fed solution was not expected given that it is widely assumed that a CO$_2$ feed is necessary for CO production. The BPM plays a critical role in this reaction chemistry by delivering a H$^+$ flux to the cathode that converts HCO$_3^-$ (and CO$_3^{2-}$) into catalytically active CO$_2$. An important feature of this flow reactor is that the *in-situ* generation of CO$_2$ provides a higher concentration of CO$_2$ at the catalyst surface than the solubility limits of CO$_2$ in aqueous media. This finding offers new opportunities for realizing high current densities with a liquid feed. This work also demonstrates that carbon products other than formate can be generated from HCO$_3^-$ solutions, thereby presenting new opportunities for carbon capture and utilization schemes.

Experimental Procedures

Materials:

KHCO$_3$ (99%) and K$_2$CO$_3$ (99%) were purchased from Alfa Aesar. Ag nanopowder (trace metal basis, 99%) and Nafion 117 solution (5 wt%, in a mixture of lower aliphatic alcohols and water) were purchased from Sigma Aldrich. Carbon cloth was purchased from the Fuel Cell Store and cut into desired dimensions with a blade. Nickel foam gas diffusion electrode material was purchased from MTI. BPM (Fumasep FBM) were purchased from FuMA-tech and stored in 1M NaCl Solution.

Electrode preparation:
The cathode catalyst ink was prepared by mixing 52 mg of silver nanopowder, 500 µL of DI water, 500 µL of isopropyl alcohol and 70 µl Nafion 117 solution. The catalyst ink was then spray-coated on a 4-cm² area of carbon cloth and dried under a gentle air stream. Kapton tape (McMaster-Carr) was used as a mask during the deposition process to avoid catalyst being deposited outside the active area of the carbon cloth. The catalyst loading was determined to be 100-120 counts per second by X-Ray fluorescence analysis.

**Electrochemical measurement and product analysis:**

A CH instruments 660D with a picoamp booster was used for all experiments. Electrochemical measurements were made with a two-electrode system with Ni foam as the anode and Ag spray-coated on carbon cloth as the cathode. The anode electrolyte was 1000 mL of 1 M KOH solution delivered by a peristaltic pump at 50 mL/min. The cathode electrolyte was 125 mL of 3 M K₂CO₃ or 0.5 ~ 3 M KHCO₃ with 0.02 M ethylenediaminetetraacetic acid (EDTA, 99%, Sigma Aldrich) added to remove impurities. The head space of the catholyte solution was purged with N₂ (Praxair, 99.9%) or CO₂ (Praxair, 99.9%) gas at 160 sccm in a sealed flask with an outlet into the flow cell. The catholyte solution was delivered by another peristaltic pump at 50 mL/min into the flow cell electrolyzer, which was then vented back into the flask. Fresh electrolyte was used for each set of experiment. Samples of the gas headspace in the flask were delivered into a gas chromatograph (GC, Perkin Elmer). The GC was equipped with a packed MolSieve 5A column and a packed HayeSepD column. Argon (Praxair, 99.999%) was used as the carrier gas. A flame ionization detector (FID) equipped with a methanizer was used to quantify CO and CO₂ concentrations and a thermal conductivity detector (TCD) was used to quantify H₂ concentrations. Control experiments with a two-compartment H-cell were performed wherein the anode (platinum mesh) and cathode (Ag-coated carbon cloth) compartments contained 30 mL of 1 M KOH and 30 mL of 3.0-M KHCO₃, respectively, separated by a BPM.

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Declaration of Interests: The authors declare no competing financial interests.

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