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Continuum model to define the chemistry and mass transfer in a bicarbonate electrolyzer

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Abstract

Bicarbonate electrolyzers are devices designed to convert CO₂ captured from point sources or the atmosphere into chemicals and fuels without needing to first isolate pure CO₂ gas. We report here an experimentally-validated model that quantifies the reaction chemistry and mass transfer processes within the catalyst layer and cation exchange membrane layer of a bicarbonate electrolyzer. Our results demonstrate that two distinct chemical microenvironments are key to forming CO at high rates: an acidic membrane layer that promotes *in situ* CO₂ formation, and a basic catalyst layer that suppresses the hydrogen evolution reaction. We show that the rate of CO product formation can be increased by modulating the catalyst and membrane layer properties to increase the rate of *in situ* CO₂ generation and transport to the cathode. These insights serve to inform the design of bicarbonate and BPM-based CO₂ electrolyzers while demonstrating the value of modeling for resolving rate-determining processes in electrochemical systems.

CO₂ electrolyzers can produce carbon-neutral chemicals and fuels using CO₂ from the atmosphere and electricity from wind and solar resources.¹⁻³ To be industrially relevant, CO₂ electrolyzers must achieve high rates of product formation (i.e., current densities >100 mA cm⁻²) and low cell potentials (<3 V) while also efficiently utilizing the CO₂ reactant.^{4, 5} Gaseous CO₂ is often used as the feedstock for pilot-scale CO₂ electrolyzers because of its solubility and mass transfer advantages over CO₂ dissolved in water.⁶⁻⁸ However, isolating pure CO₂ gas from point sources or the atmosphere is costly because a considerable energy penalty (e.g., 50–175 kJ mol⁻¹ CO₂) is required to liberate CO₂ from liquid sorbents used in CO₂ capture processes.⁹⁻¹² These collected CO₂ streams are also not often utilized efficiently in gas-fed CO₂ electrolyzers¹³⁻¹⁶, since often a major fraction of the reacted CO₂ is converted into HCO₃⁻ and CO₃²⁻ [referred to here as (bi)carbonates] upon reacting with OH⁻ produced at the cathode.^{16,17} These issues associated with poor utilization of captured CO₂ gas add cost and complexity when deploying a CO₂ electrolyzer at scale.^{16,18,19}

As a means of addressing the above challenges, we recently demonstrated that HCO₃⁻ solutions (an intermediate in CO₂ capture processes) can be reduced into valuable products (e.g., CO) at high rates using a flow electrolyzer architecture (**Fig. 1a**).²⁰⁻²² The primary benefit of “bicarbonate electrolysis” is that it eliminates the need for CO₂ regeneration, gas handling and compression in upstream CO₂ capture (**Fig. S1**).^{23,24} Central to this technology is a continuous supply of H⁺ to the cathode, which serves to liberate CO₂ from the bicarbonate solution and provide the reactant for CO₂ reduction.^{20,21} This method of using H⁺ to generate CO₂ *in situ* eliminates the carbonation problem discussed above for alkaline CO₂ electrolyzers.^{16,20} High yields for CO (i.e., 40–70%) have therefore been reported for bicarbonate electrolyzers,²¹ and more generally for CO₂ electrolyzers that supply H⁺ to the cathode.^{25,26} Collectively, these features of bicarbonate electrolysis reduce the cost of integrating CO₂ reduction with CO₂ capture by intensifying the process.²³

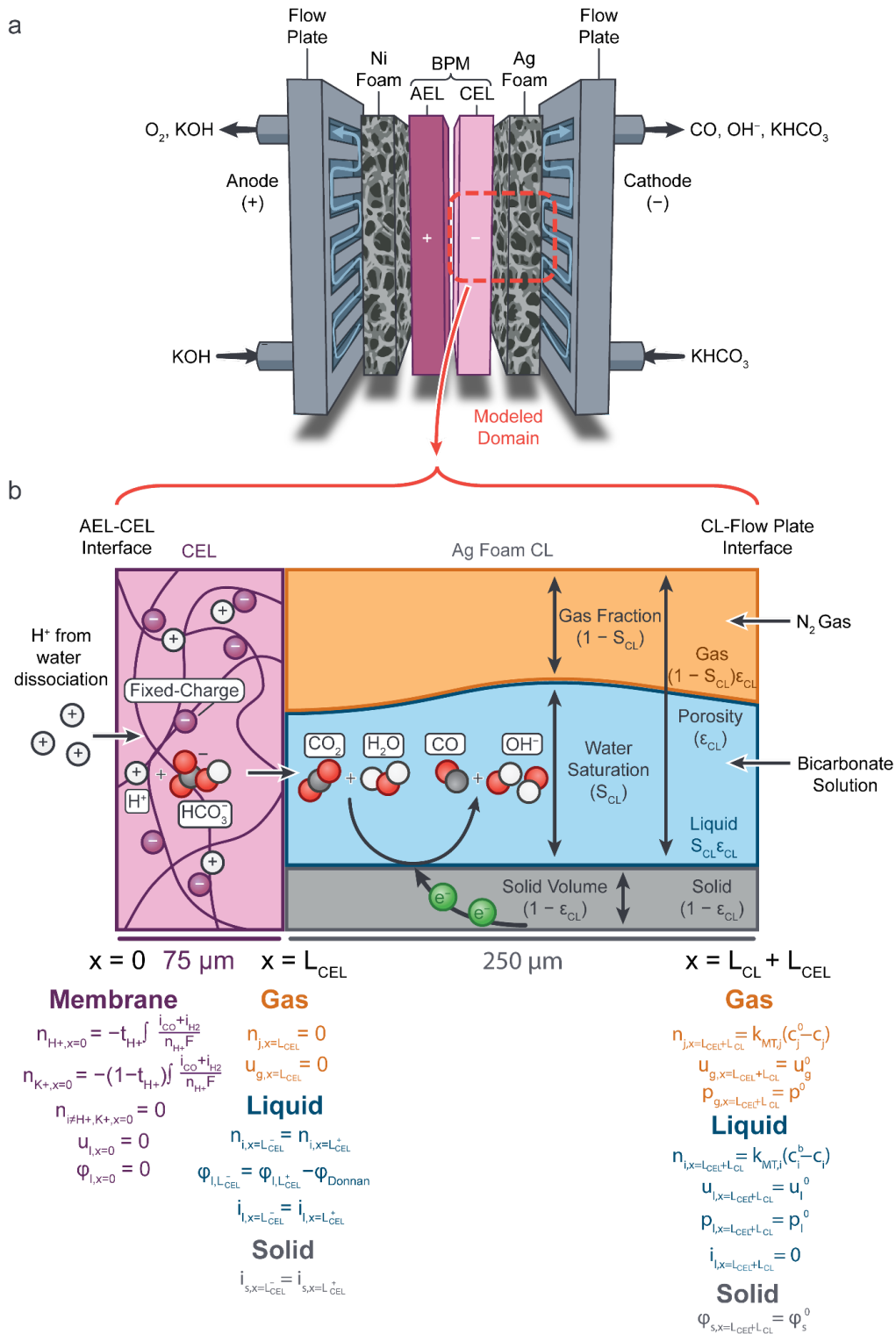
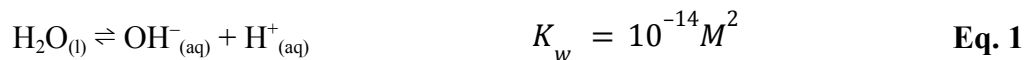
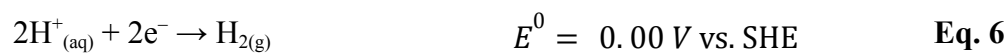


Figure 1: (a) Schematic diagram of a bicarbonate electrolyzer consisting of flow plates, a nickel foam anode, a BPM, and a silver foam cathode. The anode mediates OER and the BPM mediates water dissociation. Sequential reactions occur in the cathode: bicarbonate reacts with protons to form CO_2 *in situ*, which then is subsequently reduced to form CO and OH^- . (b) A representation of the cation exchange layer (CEL) and catalyst layer (CL) and phases (gas, liquid, and solid)

described by the continuum model. Boundary conditions are defined at the AEL/CEL interface ($x = 0$), CEL/CL interface ($x = L_{CEL}$), and at the CL/flow plate interface ($x = L_{CEL} + L_{CL}$).

This study investigates a bicarbonate electrolyzer architecture containing a nickel foam anode, a silver foam cathode, and a BPM (**Fig. 1a**).^{20,27} The BPM consists of an anion exchange layer (AEL) and cation exchange layer (CEL) with a water-dissociation catalyst at their interface.^{20,21,28} Under a reverse bias, water dissociation (**Eq. 1**) occurs at the AEL/CEL interface to supply OH^- to the anode for the oxygen evolution reaction (OER; **Eq. 2**)²⁹ and H^+ to the cathode where it reacts with (bi)carbonates to form CO_2 *in situ* (**Eqs. 3, 4**). The produced CO_2 is then electrochemically reduced into CO at the surface of a silver foam catalyst layer (CL) with OH^- produced as a byproduct (**Eq. 5**).³⁰ In an ideal scenario, these reactions would be perfectly selective and irreversible to enable high CO formation rates. However, several competitive reactions and parasitic processes reduce electrolyzer efficiencies. For example, the hydrogen evolution reaction (**Eq. 6**) competes with CO_2 reduction at the cathode. Furthermore, CO_2 that is formed *in situ* can react with electrochemically-generated OH^- to reform (bi)carbonates (**Eqs. 7, 8**) or remain unreacted in the cathodic product stream. The complex interplays and nonlinearities make it hard to easily understand and resolve the individual processes, and it is therefore challenging to navigate and select electrolyzer design parameters (i.e., material properties, reactor geometries, and operating conditions).





Multiphysics modeling is ideally suited to explore various physical phenomena relevant to CO₂ electrolysis and accelerate the design of optimal reactor architectures.³⁴ However, there are strikingly few CO₂ electrolyzer models, in part due to the numerical challenges associated with coupling highly non-linear transport equations with numerous acid-base and electrochemical reactions. CO₂ reduction models are therefore often developed with simplified reaction or mass transfer kinetics to reduce model complexity.^{35–38} Recently, models have been developed that effectively simulate coupled reaction and mass transfer processes in CO₂ electrolyzers and generally agree with experimental results without the need for empirical parameter fitting.^{32,33,39–42} Using volume-averaged approaches, continuum models can capture the interactions between electrochemistry, acid-base chemistry, and transport phenomena within CO₂ electrolyzers. Importantly, these types of models can inform how electrolyzer design and material properties affect the in-plane transport of ionic species,³² failure mechanisms,³³ and CO₂ reduction product selectivity.⁴⁰ Notwithstanding, the majority of CO₂ reduction models have focused on devices that mediate CO₂ reduction at highly alkaline cathodes and therefore endure significant CO₂ losses to (bi)carbonate formation and transport.^{32,40} The only demonstrated solution to these challenges of low-temperature CO₂ electrolysis is to use an electrolyzer that leverages one or more of the following: (i) a supply of H⁺ to the cathode to neutralize (bi)carbonates^{25,26} or (ii) a CO₂ capture medium as the carbon-bearing feedstock.^{43–45} While these approaches appear to be the most promising way forward, no device-scale models have been developed that simulate the relevant physics in these architectures and compare the results to real experimental data.

We demonstrate here a continuum model for the cathode compartment of a bicarbonate electrolyzer which was validated with electrolyzer experiments (**Fig. 1b**). This model enabled investigation into fundamental relationships between the chemical environment (i.e., pH and CO₂ concentration) in the cathode and the activity and selectivity of CO formation. Importantly, our computational and experimental results demonstrate how H⁺-mediated *in-situ* CO₂ generation improves CO₂ reduction product yields within an electrolyzer.^{25,26} Model insights were used to elucidate membrane and electrode properties that improve performance parameters by modulating mass transport of chemical species within the electrolyzer. In sum, this study provides guidance into the design of future improved architectures based on elucidation of underlying phenomena of the chemical microenvironments.

Results and Discussion

The model was developed to predict bicarbonate electrolyzer performance using parameter values obtained from literature (**Table S1**). The 3-dimensional solid, liquid, and gas phases were represented as homogeneous, 1-dimensional continuums with volume-averaged values for key properties (e.g., porosity, tortuosity, active surface area, and water saturation). Mass transfer was modeled in the through-plane direction because previous reports have shown that the flow channel and porous CL of flow electrolyzers promote relatively uniform mixing in the in-plane direction.^{40,41} The governing equations (based on mass, momentum, and charge conservation) were solved simultaneously to quantify the steady-state concentrations of liquid species (H⁺, OH⁻, K⁺, CO₂, HCO₃⁻, and CO₃²⁻), gas species (CO₂, CO, and N₂) as well as the rates of the CO₂RR (**Eq. 5**), HER (**Eq. 6**), and acid-base reactions (**Eqs. 3, 4 and 7, 8**). The boundary conditions are summarized in **Fig. 2b**.

The model was validated using a bicarbonate electrolyzer architecture that was previously demonstrated to enable high CO formation activity and stability.⁷³ This electrolyzer is composed of flow

plates, a nickel foam anode ($\sim 250 \mu\text{m}$), a BPM, and a silver foam cathode. The silver foam cathode was fabricated by treating silver foam substrates with 30 % (v/v) nitric acid (**Fig. S2**).⁷³ Cross-sectional scanning electron microscopy (SEM) images were used to estimate the silver foam thickness as $250 \mu\text{m}$ (**Fig. S2b** and **Fig. S2d**). Top-view SEM images taken before (**Fig. S2a**) and after (**Fig. S2c**) electrolysis showed no obvious morphological differences.

Electrolysis experiments were performed at constant current densities of 50, 100, 200, and 300 mA cm^{-2} while solutions of 1 M KOH and 3 M KHCO_3 were delivered to the anodic and cathodic flow plates, respectively. Gaseous reaction products formed at the cathode were delivered to the sample loop of a gas chromatograph (GC) using a stream of N_2 gas that was swept through the headspace of the 3 M KHCO_3 reservoir. GC measurements were performed after 5 min of electrolysis to ensure the reaction products had reached saturation concentrations in the catholyte before analysis.²¹ To determine if liquid products were produced, aliquots of the catholyte were collected after 20 min of electrolysis and analyzed using ^1H nuclear magnetic resonance spectroscopy. Each electrolysis experiment was performed in triplicate to determine the FE_{CO} error bars.

Model validation using experimental electrolysis data

The cathodic product stream of the electrolyzer consisted of CO , H_2 , and CO_2 , and no liquid CO_2 reduction products were detected. The FE_{CO} values decreased from $68 \pm 5\%$ to $35 \pm 3\%$ as the current density was incrementally increased from 50 to 300 mA cm^{-2} (**Fig. 2a**) and the experimental CO yields increased from $51 \pm 8\%$ to $74 \pm 6\%$ over the same current density range (**Fig. 2b**). These experimental results agreed remarkably well with the modeling results in terms of partial current densities (**Fig. S3**) and FE_{CO} values (**Fig. 2a**), especially when considering that the model parameters were obtained directly from literature and not fit to the collected experimental data. The model also predicted the experimental

CO yields within experimental error at current densities ranging from 50 to 200 mA cm^{-2} (**Fig. 2b**). However, the predicted and experimental values diverged at 300 mA cm^{-2} . At this high current density, a high rate of OH^- formation increased the pH of the electrolyte in the reservoir (from ~ 8.5 to ~ 9), thereby causing an increase in CO_2 conversion to carbonate as the equilibrium shifted towards CO_3^{2-} over the course of the experiment (**Fig. S4**).²⁰ The model does not account for this higher pH at the CL/flow plate interface and instead uses a constant bulk electrolyte composition (with a pH of 8.5; **Table S2**)⁵² in the mass-flux boundary condition (**Fig. 1b**). We believe this simplification in the model framework is causing the model to underpredict the experimental CO yields. Nonetheless, the simulation exhibits good agreement with the experimental data over a wide range of applied current densities. A higher-dimensional model that accounts for the equilibrium in the flow channel and electrolyte reservoir is needed to predict these values more accurately, but this is beyond the scope of the current work.

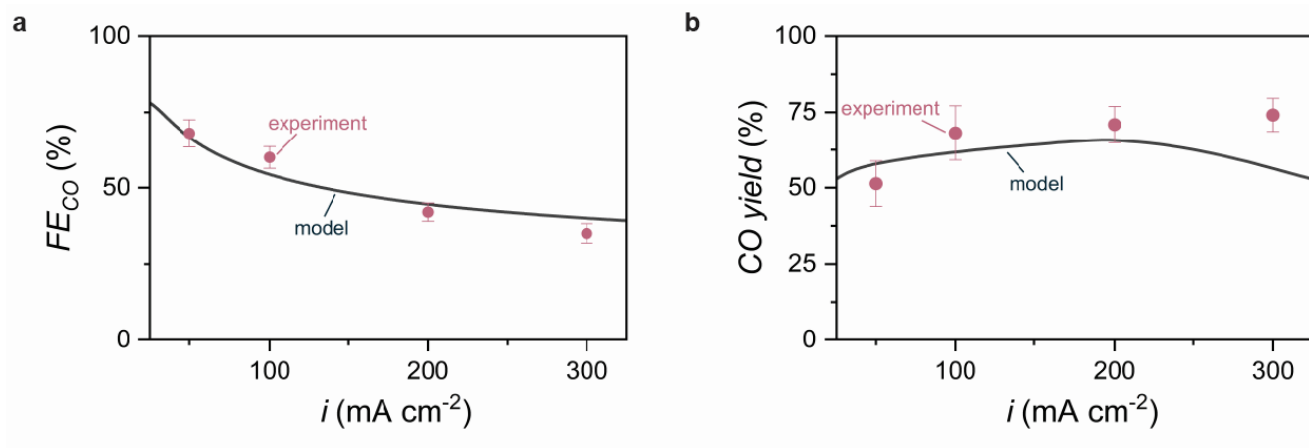


Figure 2: Experimental validation of the cathode model for bicarbonate electrolysis. (a) Experimental (purple circles) and modeled (black lines) data for the (a) FE_{CO} and (b) CO yields as a function of current density. Note that the model was developed using parameters obtained directly from literature without using additional fitting parameters to match the experimental data.

Generation and transport of CO₂

The validated model enables one to investigate the cause for the observed decrease in FE_{CO} values observed at high current densities. We conjectured that the reaction is limited by CO₂ mass transfer and therefore we used the model to track CO₂ generation from bicarbonate and conversion of CO₂ into CO. The model results show that water dissociation within the BPM produces an H⁺ flux that decreases the pH towards the AEL/CEL interface (i.e., at $x = 0$) (**Fig. 3a**). The modeled CO₂ concentration increases within the CEL (**Fig. 3b**) because (bi)carbonates are converted into CO₂ in acidic conditions (**Eq. 3, 4**). As the current density is increased, a proportional increase in the H⁺ flux from the AEL/CEL interface enhances the rate of *in situ* CO₂ generation. Consequently, CO₂ bubbles can be observed nucleating at the CEL/electrolyte interface during electrolysis experiments.²⁰ CO₂ that is produced through this pathway is subsequently reduced or reacted in the CL (**Eq. 5** and **Eq. 8-9**, respectively). These CO₂ consumption processes decrease the steady-state concentrations of CO₂ to < 1 mM throughout the majority of the CL. These results, combined with the experimental observations of decreased FE_{CO} at high current densities, indicate that CO₂ mass transport limits the rate of CO formation in the system.

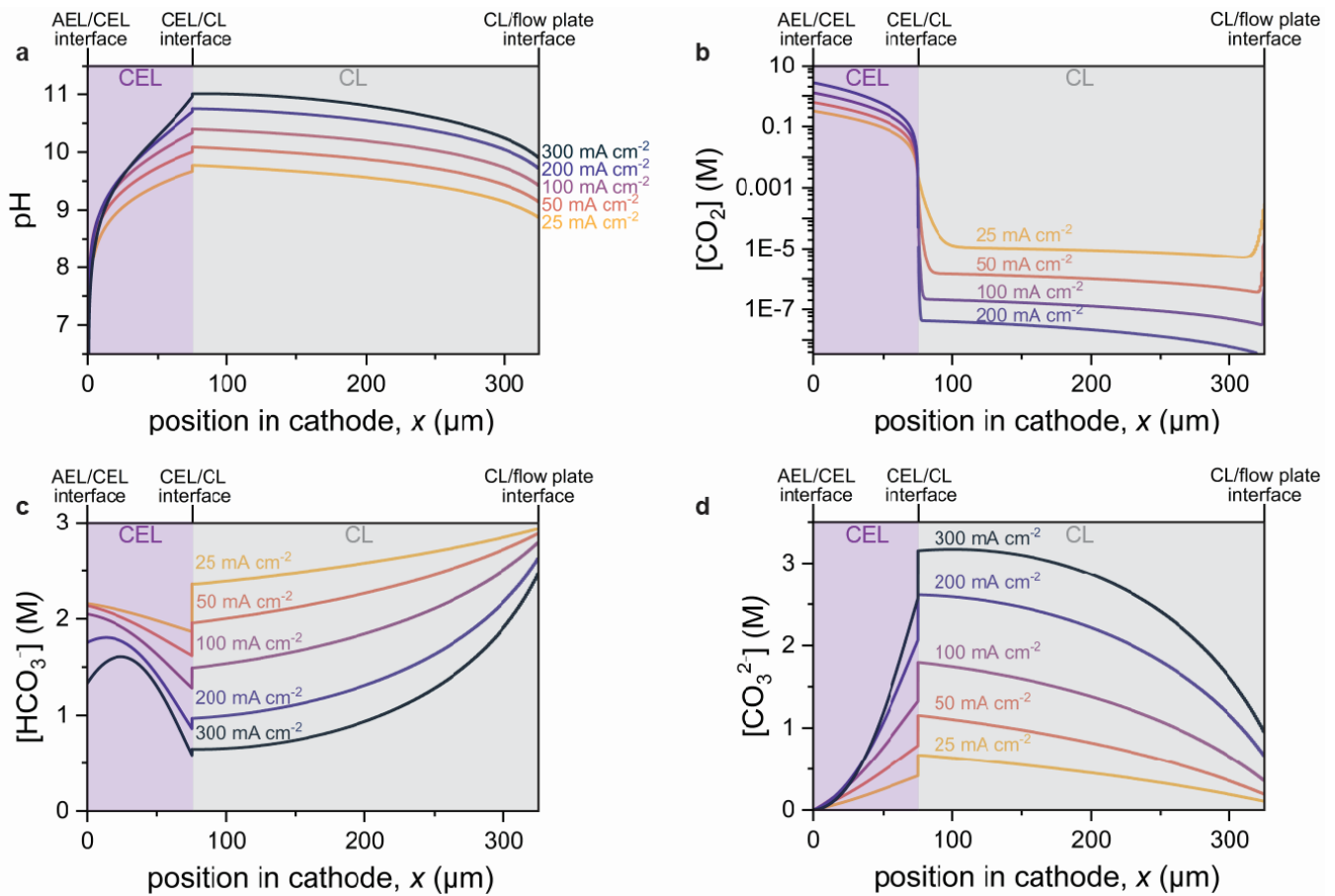


Figure 3: Modeled (a) pH (b) CO₂ (c) HCO₃⁻ and (d) CO₃²⁻ concentrations within the bicarbonate electrolyzer cathode for different applied current densities. Shaded regions indicate the location of the CEL (purple; $x = 0$ to $75 \mu\text{m}$) and CL (grey; $x = 75$ to $325 \mu\text{m}$).

The model demonstrates that the competitive CO₂ generation and consumption processes in the CEL and CL, respectively, cause CO₂ concentration gradients (Fig. 3b) at the CEL/CL interface. These concentration gradients at the CEL/CL interface give rise to CO₂ fluxes of 1.1, 1.8, 2.8, 3.9, and 5.3 mmol m⁻² s⁻¹ towards the CL for current densities of 25, 50, 100, 200, and 300 mA cm⁻², respectively (Fig. S5a). These fluxes constitute the majority of the corresponding modeled CO formation rates (1.0, 1.7, 2.8, 4.6, and 6.2 mmol m⁻² s⁻¹ at the same respective current densities). Consequently, the modeled CO₂ concentration profiles in the CL (Fig. S5b) and CO formation rates (Fig. S5c) are higher near the CEL/CL interface than the rest of the CL. Collectively, these results suggest that regions of the CL closer to the CEL should be more active for CO formation. This conjecture is supported by previous

experiments, which showed that the silver catalyst layers near the BPM had a more significant impact on CO formation rates than the silver catalyst layers added to the backside of the electrode (at the CL/flow plate interface).²¹

The simulated (bi)carbonates concentration profiles are consistent with the modeled pH and CO₂ concentration profiles in terms of the chemical equilibrium (**Fig S4**). As the current density increases, the HCO₃⁻ concentration in the CEL decreases (**Fig. 3c**) because HCO₃⁻ reacts with H⁺ from water dissociation to form CO₂. In the CL, the HCO₃⁻ concentration decreases as the current density increases because electrochemically generated OH⁻ reacts with HCO₃⁻ to form CO₃²⁻. This reaction stoichiometry is also reflected in the modeled CO₃²⁻ concentration profiles in the CL, which increase with increasing current density (**Fig. 3d**). Both the HCO₃⁻ and CO₃²⁻ concentration profiles exhibit a discontinuity at the CEL/CL interface because of Donnan exclusion (i.e., the fixed negative charges in the CEL repel the negatively-charged HCO₃⁻ and CO₃²⁻; **Eq. S7**).⁴⁸ The corresponding electrolyte potential and K⁺ concentration profiles are shown in **Fig. S6**.

These modeling results provide insight into how the dynamic pH-dependent reactions between (bi)carbonates and CO₂ enable CO formation. The HCO₃⁻/CO₂ equilibrium reaction (pKa = 6.31) enables HCO₃⁻ to convert rapidly into CO₂ in the relatively acidic environment within the CEL. At the same time, the HCO₃⁻/CO₃²⁻ equilibrium reaction (pKa = 10.32) enables the pH to rise rapidly within the CL. The high pH in the CL serves to suppress hydrogen evolution, and therefore, enable higher CO product formation rates. These disparate microenvironments in the CEL and CL are essential to a H⁺ flux-mediated CO₂ generation mechanism.^{25,26}

Impact of H⁺ flux and bulk pH on CO formation rates

Without a H⁺ flux to the cathode, the only source of CO₂ in a bicarbonate electrolyzer is the bulk electrolyte, which has a CO₂ concentration of ~8 mM according to the chemical equilibrium.⁵² We modeled how much CO can be formed exclusively from this source of CO₂ by removing the water-dissociation boundary condition at the AEL/CEL interface. Specifically, we reduced the fraction of ionic current associated with H⁺ transport (i.e., the transference number of H⁺, t_{H^+}) at the AEL/CEL interface from 0.9 to 0 (Eq. S5) while increasing the transference number of K⁺ (t_{K^+}) from 0.1 to 1 (Eq. S6). The model results exhibited higher cathodic pH values (Fig. 4a) and lower corresponding CO₂ generation rates without the H⁺ flux. Accordingly, lower FE_{CO} values were observed (Fig. 4b). These modeling results are consistent with our previously-reported experimental data which showed that replacing the BPM with an anion exchange membrane results in lower CO formation rates.²⁰

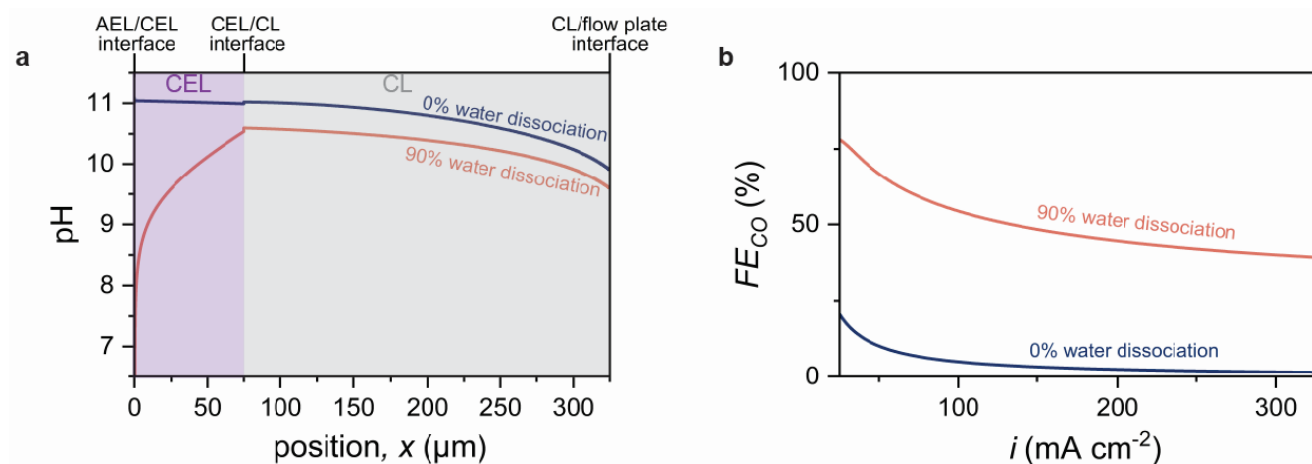


Figure 4: (a) pH profiles and (b) FE_{CO} values for water dissociation rates equal to 0 and 90% of the total charge transport in the liquid phase at the AEL/CEL interface when a total current density of 150 mA cm⁻² is applied. The different water dissociation rates were modeled by toggling the t_{H^+} and t_{K^+} values at the AEL/CEL interface (Eq. 13 and Eq. 14).

The bulk pH of the CO₂ capture solution feedstock is an important parameter for bicarbonate electrolysis because it defines the equilibrium concentrations of CO₂, HCO₃⁻, and CO₃²⁻ in the flow plate (Fig. S4). The impact of this parameter on CO formation was investigated by modulating the bulk

electrolyte concentrations (**Table S2**) in the mass flux boundary conditions at the CL/flow plate interface (**Eq. S39**). A pH regime between 8.5 and 10 was selected to reflect the composition of CO₂ capture solutions used in industry.⁷⁴⁻⁷⁶ The modeling results show that increasing the bulk pH generally decreases the FE_{CO} (**Fig. S7**). A more pronounced effect is observed at low current densities (i.e., <100 mA cm⁻²) because a lower associated H⁺ flux from water dissociation reduces the rate of *in situ* CO₂ generation. At these low current densities, the CO₂ in the bulk electrolyte serves as a primary source of CO₂ for CO₂ reduction.^{52,77,78} Low CO formation rates are therefore observed with higher pH solutions that have lower bulk CO₂ concentrations (**Table S2**). However, at current densities >100 mA cm⁻², the supply of CO₂ from H⁺-mediated CO₂ generation increases and therefore the effect of bulk CO₂ concentration has a less pronounced effect on FE_{CO} (**Fig. S5a**). Notwithstanding, higher pH feedstocks yield lower CO formation rates, even at high current densities, because CO₂ generation from CO₃²⁻ requires twice the H⁺ supply as HCO₃⁻ according to the stoichiometry (**Eq. 3, 4**).

CEL and CL properties predicted by modeling

A primary purpose of developing the model is elucidation and subsequent mitigation of the rate-limiting step that gates CO formation. Our experimental and computational results confirm that CO₂ mass action is limiting because the concentration of CO₂ in the CL is depleted at high current densities (**Fig. 3c**). We therefore computationally investigated CEL and CL material properties that could be independently modulated to increase CO₂ mass transport in order to access higher CO formation rates.

Water dissociation in the BPM provides the H⁺ necessary to generate electrochemically-active CO₂ (**Fig. 4**). From an experimental perspective, the H⁺ flux from water dissociation can be increased by using: (i) an improved water dissociation catalyst;⁵⁹ or (ii) a CEL material composed of an ionomer with a higher concentration of fixed-charge groups [i.e., a higher ion exchange capacity (IEC)] that amplifies

the electric field and hence charge repulsion at the AEL/CEL interface.^{48,61,79} As described earlier, the effect of (i) on the FE_{CO} was investigated by increasing t_{H^+} (Eq. S5) at the AEL/CEL interface, and the modeled FE_{CO} values increased as expected (Fig. S8a). Increased water dissociation activity results in a lower pH near the AEL/CEL interface (Fig. S8b) which increases *in situ* CO₂ formation (Fig. S8c). To investigate (ii), the ionomer IEC was increased from 1 to 3 mmol g⁻¹. The FE_{CO} increased due to inhibited OH⁻ transport at the CL/CEL interface, which caused a pH increase in the CL (Fig. S8d). Therefore, the positive effect of a higher IEC ionomer on FE_{CO} values is two-fold: it decreases the pH in the CEL by enhancing water dissociation and it increases the pH in the CL to suppress hydrogen evolution.

The residence time of H⁺ in the CEL impacts the local pH environments in the cathode, which, in turn, determines the kinetics of *in situ* CO₂ generation and reduction. To quantify the impact of H⁺ residence time on bicarbonate electrolysis, three CEL thicknesses (25, 50, and 75 μm) were simulated and the FE_{CO} values were compared at a constant current density of 150 mA cm⁻² (Fig. S9). The results show that increasing CEL thickness increases the FE_{CO} by modulating ion transport (Fig. S9a). Thicker CELs were found to elongate the H⁺ diffusion path from the AEL/CEL interface to the CEL/CL interface. Consequently, thicker CELs gave rise to higher pH values in the CL because of slower H⁺ transport to the CL (Fig. S9b). These synergistic pH effects enable higher CO₂ concentrations in the CEL (Fig. S9c) and diminished hydrogen evolution in the CL. It is for these reasons that thicker CELs are predicted to achieve higher CO formation rates than thinner CELs. However, thicker CELs increase ohmic resistance (Fig. S9d), and therefore, electrolyzer energy consumption.

The impact of CL thickness and porosity on FE_{CO} was simulated to determine the effect of mass transport rates on the FE_{CO} .^{80,81} The results show that decreasing the CL thickness from 250 to 50 μm increases the FE_{CO} from 48 to 79% at 150 mA cm⁻² (Fig. S10a), which may explain why thinner silver catalyst layers (<10 μm) have enabled FE_{CO} values of ~80% in previous bicarbonate electrolysis

studies.²¹ One of the drivers for this increased performance is the higher concentration of CO₂ in the CEL when using a thin catalyst layer (**Fig. S10b**). This improvement in *in situ* CO₂ generation is due to a shorter diffusion path for (bi)carbonates to transport from the flowplate through the CL to the H⁺ source in the CEL. Higher HCO₃⁻ concentrations are therefore observed in thinner CLs because of faster HCO₃⁻ mass transfer towards the CEL (**Fig. S10c**). Similar to the effect of decreasing CL thickness, increasing CL porosity increases the rate at which (bi)carbonates transport to the CEL (**Fig. S10d**). As above, a faster mass transport rate of (bi)carbonates to the CEL results in more CO₂ formation (**Fig S10e**), which increases the rate of CO₂ reduction (**Fig S10f**). While these results are readily rationalized, it should be noted that a more detailed model which captures flow channel and 3D effects is needed to characterize these parameters fully.^{38,82,83}

Considering the above property-performance relationships, **Fig. 5** shows the cumulative impact of the “improved case” compared to the “basecase”. The improved parameters yield a significant increase in FE_{CO} relative to the basecase across the range of simulated current densities. These observations are a result of elevated CO₂ concentrations in the CEL (**Fig. 5b**), and consequently the CO₂ flux to the CL (**Fig. S11**). As discussed above, the additive and potentially synergistic effects of these improved material properties enables: (i) efficient mass transport through the thin, porous CL; (ii) prolonged residence time for reactive species in the CEL; (iii) suppression of hydrogen evolution in the CL; and (iv) a higher H⁺ concentration in the CEL. The model results serve as benchmarks for future experimental studies to improve the performance of this device and other CO₂ electrolyzers that utilize H⁺-mediated CO₂ generation at the cathode.²⁶

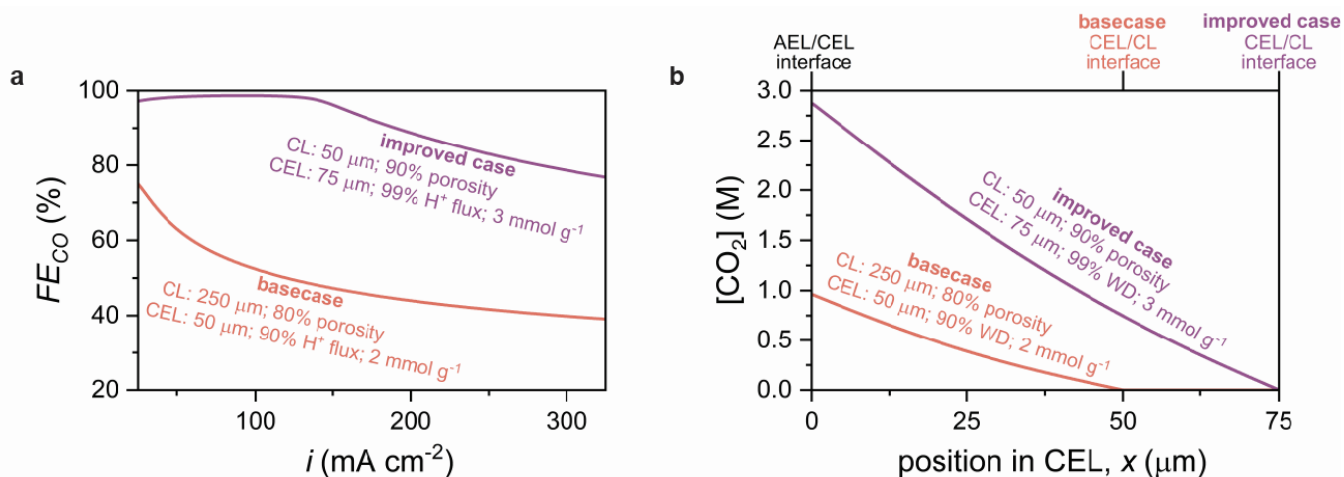


Figure 5: (a) Modeled FE_{CO} values as a function of current density for the improved CEL and CL properties (99% H^+ flux; CEL thickness = 75 μm ; IEC = 3 $mmol g^{-1}$; CL porosity = 0.9; CL thickness = 50 μm) and the basecase properties (90% H^+ flux; CEL thickness = 50 μm ; IEC = 2 $mmol g^{-1}$; CL porosity = 0.8; CL thickness = 250 μm). (b) CO_2 concentration profiles in the CEL for the improved case and the basecase at a constant current density of 150 $mA cm^{-2}$.

Conclusions

We report here an experimentally-validated continuum model for the cathode of a bicarbonate electrolyzer. The model was used to investigate the *in situ* CO_2 generation and reduction mechanism, which eliminates carbonation issues in CO_2 electrolyzers and enables high CO formation rates (>100 $mA cm^{-2}$) from bicarbonate solutions. The results demonstrate the existence of two disparate pH microenvironments associated with this mechanism: an acidic electrolyte/membrane region where H^+ reacts with HCO_3^- to form CO_2 , and an alkaline catalyst layer region that reduces CO_2 to CO and suppresses the competitive hydrogen evolution reaction. A low CO_2 concentration in the catalyst layer slows CO_2 reduction at high current densities, and this mass transfer limitation can be overcome by optimizing material properties. Several model parameters were identified as levers for increasing CO_2 supply rates to the catalyst layer: the rate of water dissociation, the ion exchange capacity and thickness of the membrane, and the thickness and porosity of the catalyst layer. Through modeling and quantifying

the complex pH and CO₂ gradients in CO₂ reduction electrolyzers, one can derive a deeper understanding and help guide the development of materials with enhanced performance.

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Conflicts of Interest

Authors CPB and EWL have filed a patent application for the technology analyzed in this work (U.S. application No. 62/662,391).

Supporting Information

Materials and methods and supplementary data can be found in the Supporting Information

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