Electrocatalytic CO₂ reduction (CO₂R) offers renewable energy storage in the form of fuels and chemicals, realizing carbon utilization to mitigate anthropogenic CO₂ emissions. McCallum et al. report a computational model, coupled with machine learning, to efficiently explore the broad parameter space of CO₂R to multi-carbon products in a membrane electrode assembly.
Reducing the crossover of carbonate and liquid products during carbon dioxide electroreduction

Christopher McCallum,1 Christine M. Gabardo,1 Colin P. O’Brien,1 Jonathan P. Edwards,1 Joshua Wicks,2 Yi Xu,1 Edward H. Sargent,2 and David Sinton1,3,*

SUMMARY
Membrane electrode assembly (MEA) electrolyzers can perform stable, high-rate carbon dioxide (CO₂) electroreduction for renewable fuels and chemicals, thereby realizing effective carbon utilization to mitigate anthropogenic CO₂ emissions. Here, we present a numerical, multiphysics model, computationally intensified 60-fold with a machine learning analysis of computational and experimental data, to address the most urgent systems challenges in CO₂ MEA electrolyzers: mitigating carbonate and liquid product crossover to increase CO₂ utilization and energy efficiency. We explore the effect of varying the applied potential, CO₂ partial pressure, ion-exchange membrane thickness, membrane porosity, and membrane charge on these three metrics. By selectively tuning these physical system parameters, we identify conditions that realize negligible CO₂ reactant loss, a 2-fold enhancement in CO₂ utilization, and a 2-fold decrease in Nernstian overpotential, corresponding to a multi-carbon, full-cell energy efficiency of 21%. These results may direct future MEA system designs and motivate thin anion-exchange membrane structures.

INTRODUCTION
The renewably powered electrocatalytic reduction of carbon dioxide (CO₂) promises seasonal energy storage and a means to produce low-carbon fuels.1–5 The most significant operating costs (80%–95%) of this approach are those of the reactant CO₂ and electricity inputs.7 Commercial deployment of CO₂ reduction (CO₂R) will, therefore, require the near-complete utilization of reactant CO₂, with high energy efficiency. Realizing these two criteria simultaneously presents a significant challenge when operating an electrolyzer at industrially relevant current densities (>100 mA cm⁻²).6–8 Although CO₂ can be reduced to a multitude of products, multi-carbon (C₂) products are particularly desirable because of their high value, energy density, and large existing markets. Copper (Cu) catalysts show high CO₂R selectivity toward ethylene (C₂H₄) and ethanol (EtOH),5,9–12 motivating further investigation of these electrocatalytic systems.

Gas diffusion electrodes (GDEs) improve reactant gas availability at the catalyst, thereby enabling higher current density capability.13–16 Traditional H-cells have largely been replaced by flow-type electrolyzers using GDEs. Compared with other flow-type electrolyzers, higher CO₂ utilization and operational stability have been realized through membrane electrode assemblies (MEAs), wherein an ion-selective membrane is in direct contact against the cathodic GDE.17,18,19–28 The choice of membrane polarity (e.g., cation or anion selective) has major implications for the
selectivity of CO$_2$R.$^{22}$ Anion exchange membranes (AEMs) yield a highly alkaline local cathode environment, thus supporting conditions that are favorable for CO$_2$R to multi-carbon products at high efficiency.$^{14,23}$

Traditional AEM-based MEAs suffer from liquid product crossover, in which liquid cathode products (e.g., EtOH) readily pass through the membrane, requiring high-cost separation from the anolyte.$^{29}$ Bipolar and cation exchange membrane (CEM) MEAs can decrease liquid product crossover, but the acidic environment afforded by the membrane enhances the hydrogen evolution reaction (HER) and decreases CO$_2$R selectivity.$^{30}$ Recent experimental studies have exploited novel MEA system designs to enhance liquid product concentration and address the crossover issue: some have tuned system conditions to increase EtOH extraction from the cathode, whereas others have added an additional separation/concentration channel between the cathode and anode compartments.$^{24,25,31}$ Although these MEA systems show promise for the efficient production of multi-carbon liquid products, major advancements are needed to attain concentrated products at high energy efficiency.$^{31,32}$

Single-pass CO$_2$ utilization in MEA systems remains low, on the order of 30%.$^{25}$ The rest of the supplied CO$_2$ exits the cathode gas stream with the gas products or crosses through the MEA to the anode. The latter route of CO$_2$ loss—and the primary source of energy and carbon losses in CO$_2$R—is due to the formation of carbonate (CO$_3^{2-}$), which results from the reaction of CO$_2$ with the high-concentration OH$^-$/CO$_3^{2-}$ at the cathode.$^{33}$ Formed CO$_3^{2-}$ and bicarbonate (HCO$_3^-$) ions migrate under the applied cell electric field through the AEM and are then reacted back to CO$_2$ in the locally acidic environment of the anode. The evolved CO$_2$, as much as 70% of the total reacted CO$_2$, exits the system with the anolyte, mixing with oxygen (O$_2$) produced during the anodic O$_2$ evolution reaction (OER).$^{34}$ Although it is possible to separate the CO$_2$ from this mixture for reuse, the added separation drives up costs and reduces overall efficiency.$^{35}$ To mitigate CO$_2$ crossover, systems have been developed that couple alkaline ionomers in the cathode layer with a CEM between the cathode and the anode.$^{27}$ This approach eliminated CO$_2$ crossover but suffered from low selectivity (<15%) for CO$_2$R. Other approaches have removed the liquid anolyte entirely, instead, relying on a humidified gas stream to show greater CO$_2$ utilization and lower CO$_3^{2-}$ formation relative to the electrolyte systems.$^{24,28,31,36–38}$ In these configurations, water availability—as a reactant for CO$_2$R and to hydrate the AEM—is a concern, especially at high current densities.

Recent computational modeling of an MEA for CO$_2$ to carbon monoxide (CO)$^{36}$ and C$_2$$_+$ production$^{39}$ has highlighted the benefits of MEAs and revealed a catalyst-layer non-uniformity in product selectivity, which informs design parameters for enhanced C$_2$$_+$ energy efficiency. Modeling also allows for an efficient exploration of a broad parameter space, beyond that accessible or feasible with an experimental campaign. The computational expense of modeling can be further decreased by employing machine learning to choose the optimal simulations to perform, reducing the parameter combinations to be tested (from thousands if all combinations are tested to tens when chosen selectively) and the data dimensionality.$^{5,7,40–42}$ This coupling enables enhanced understanding and investigation of experimental work.

In this work, we model CO$_2$R to multi-carbon products with the aim of increasing reactant utilization and energy efficiency via mitigating CO$_2$ and product crossover. We simulate an MEA with mass-transport considerations in addition to electrochemical and acid-base equilibria reactions for Cu-based cathodic reactions of CO$_2$R and
HER. The anodic OER occurs at an iridium oxide (IrO₂) anode in KHCO₃ electrolyte. We model the full cell, including the anolyte, to account for all reactions across the width of the porous anode, rather than assuming zero thickness. By modulating the physical-system parameters, such as CO₂ partial pressure, current density, and membrane properties, we show that carbonate formation can be mitigated substantially. Further, by fine-tuning the system properties via machine learning, we show increased CO₂ utilization and CO₂R energy efficiency, as well as decreased EtOH crossover to the anolyte.

RESULTS AND DISCUSSION

Multiphysics model

The system was modeled as a one-dimensional electrochemical cell for the reduction of CO₂ and the oxidation of H₂O at 1 atm (except where noted) and 20°C in 0.1 M KHCO₃ anolyte with an AEM between the cathode and the anode (Figure 1). Building upon recent MEA modeling work, this model considers C₂ product generation and anodic reactions essential to resolve crossover dynamics and overall efficiency. The model assumes a constant concentration of dissolved CO₂ at the GDE:catalyst interface (modeled via fixed concentration of CO₂ at x = 0). For the anolyte on the right-hand side, we employ a diffusion boundary-layer thickness of 100 μm (calculated in Note S3) to the right of the porous anode and fix the right-most boundary concentration at the equilibrium bulk concentration. The GDE is covered with a wetted, porous Cu-catalyst layer, which is stabilized by carbon nanoparticles and graphite. The membrane separates the cathode and anode, and the anolyte is distributed within both the porous anode and the anode flow field. The species modeled include dissolved CO₂, CO₃²⁻, HCO₃⁻, OH⁻, H⁺, K⁺, and H₂O.

The numerical model of species transport with coupled-charge transfer reactions was developed in a one-dimensional COMSOL model (COMSOL Multiphysics,
version 5.4, Stockholm, Sweden). The model incorporates polarization losses (ohmic, diffusive, and Nernstian), CO₂ solubility (pressure, temperature, and Sechenov effects; provided in Note S1 and Table S1), species transport (diffusive, reactive, and electromigrative), current density, and charge-transfer reactions at the cathode and anode toward CO₂RR, HER, and OER. The simulated charge-transfer reactions were fit to experimentally observed rates and validated against multiple experimental conditions (Figure S5). Feature conductivities and porosities were taken from empirical values.

Species transport and pH distribution through the cell
Efficient utilization of CO₂ is essential for the practical application of CO₂ electrocatalysis; however, a significant amount of CO₂ is lost because of HCO⁻/CO₃²⁻ generation and can result in local salt precipitation at the cathode. Figure 2 illustrates the pH and species distribution through the MEA for varying current densities. As the current density is increased, the production of OH⁻ at the cathode also increases (Figure 2A) (Equations 7–10). As a result, the local pH at the cathode rises with the current density, which increases the conversion of CO₂ to CO₃²⁻ and HCO⁻ (Equations S6–S10). For example, for CO₂R to CO, one molecule of CO₂ reduces to one molecule of CO, forming two OH⁻ molecules (Equation 8). One of those OH⁻ molecules can react with an incoming CO₂, forming HCO⁻, which will then react subsequently with the other OH⁻ molecules to form...
CO$_3^{2-}$. This CO$_3^{2-}$ (Figure 2B) then migrates through the cell, and—under the low-pH conditions at the anode—will convert back to CO$_2$ and leave the cell through the anolyte. The pH within the anode region at high current density is less than the expected pH of 4.8 because of the diminished buffering capacity of dilute bicarbonate, coupled with the rapid accumulation of protons near the catalyst (similar to the accumulation of hydroxide at the cathode). Additionally, CO$_2$ bubbles will form if the CO$_2$ concentration surpasses the local solubility limit, so we set the solubility limit as the upper CO$_2$ concentration bound in the model, leading to variability in dissolved organic carbon (Figure S6). Dissolved CO$_2$ (Figure 2C) and HCO$_3^-$ (Figure 2D) are also present in lower concentrations within the membrane in equilibrium with the CO$_3^{2-}$. Therefore, for CO$_2$ to CO, the theoretical CO$_2$ utilization is 50% (i.e., for every two CO$_2$ molecules that enter the MEA, only one is reduced, and the other will leave through the anode) if CO$_3^{2-}$ is the charge carrier. For CO$_2$ to C$_2$H$_4$ and EtOH, this utilization decreases further because two CO$_2$ molecules are reduced, whereas six molecules form CO$_3^{2-}$, yielding a maximum utilization of 25%. Utilization is further decreased if HCO$_3^-$ migrates through the membrane rather than CO$_3^{2-}$; as in the low-current cases (<150 mA/cm$^2$) of the CO$_3^{2-}$ subpanel, Figure 2D. Considering the CO$_2$ to CO example, the theoretical utilization rate is reduced from 50% to 33% if HCO$_3^-$ is the charge carrier. Thus, HCO$_3^-$/CO$_3^{2-}$ formation and transport through the membrane must be reduced to achieve high CO$_2$ utilization. Moreover, shifting charge-carrying duties from CO$_3^{2-}$ to OH$^-$ (which occurs at high current density [>900 mA/cm$^2$]; Figure S1D) will improve the energy efficiency of the system because of the greater mobility of the smaller ion. Carbonate formation also causes salt formation and the electromigrative and diffusive transport of K$^+$ toward the cathode, as well as local K$^+$ accumulation (Figure 2F; as high as 6 M near the cathode at 1 A cm$^{-2}$), coupled with CO$_3^{2-}$ generation and lower hydration (Figure 2E), results in undesired K$_2$CO$_3$ salt precipitation at the cathode, especially at elevated current densities.

**Ion flux in the membrane**

The relative concentration of anionic species in the membrane, as well as the total flux (Figure 3), highlights the dominance of the ion flux via the carbonate transport for the base case of 150 mA cm$^{-2}$. The total flux is composed of diffusive and electromigrative flux, as given in Equation 5. For that case, CO$_3^{2-}$ and HCO$_3^-$ ions remain more abundant than OH$^-$ through the membrane, although the flux of HCO$_3^-$ is almost exclusively negative (toward the cathode). This negative flux results from the intense concentration gradient (shown in Figure 2D) and exceeds the electromigrative flux toward the anode. Increasing current density will result in increased OH$^-$ transport (shown in Figure S1) through the cell, as well as sharper concentration gradients at the AEM:anode junction. For example, H$^+$ accumulation (Equation 6) and lower buffering capacity at high current density allow the dissolved CO$_2$ to penetrate deeper into the AEM. Moreover, carbonate remains the primary charge carrier under baseline conditions, so CO$_2$ crossover remains a challenge.

**Mitigating carbonate transport**

We interrogated the full MEA system to discover routes to reduce carbonate crossover and associated CO$_2$ loss. We modeled the effect of varying the applied potential, the CO$_2$ partial pressure, the ion-exchange membrane thickness, and the membrane charge. To condense the transport findings in Figure 3, we employed a carbonate crossover metric based on the anionic species flux defined as follows:

$$\eta_{\text{anion}} = \frac{\int J_{\text{HCO}_3^-} \, dx + \int J_{\text{CO}_3^{2-}} \, dx}{\int J_{\text{OH}^-} \, dx},$$

(Equation 1)
where $J_i$ is the spatially varying total flux of the given ion $i$. Therefore, conditions at which $\eta_{\text{anion}}$ are low are favorable for preventing CO$_2$ loss from carbonate crossover. Figure 4 shows the $\eta_{\text{anion}}$ partial-dependence analysis when varying the given system parameters. Partial dependence illustrates the relationships between the target feature (e.g., $\eta_{\text{anion}}$) and the independent variables after marginalizing over the other features, yielding a low-dimensional graph. The dependencies in Figure 4 were resolved with machine learning applied to discrete simulation outcomes—a 60-fold intensification of computational effort (e.g., a coarse set of five variables calculated at five conditions would require $5^5$ points and four computer-years with simulations alone or 50 points and 25 days when accelerated with the machine-learning approach). Further discussion regarding machine-learning modeling is included in the Experimental procedures section.

Decreasing the CO$_2$ partial pressure (Figure 4A) of the supply decreases the CO$_2$ concentration at the cathode, thereby decreasing the carbonate formation and the subsequent transport through the membrane (while increasing the relative OH$^-$ transport; Figure S2C). Therefore, decreasing the partial pressure is one route to mitigate CO$_2$ loss through carbonate formation. The CO$_2$ partial pressure will also decrease from inlet to outlet as the CO$_2$ is consumed and replaced with product gas, suggesting that carbonate formation will vary significantly in reactors that achieve high CO$_2$ utilization.

Further, when AEMs (i.e., membranes with a positive charge) are used, increasing the magnitude of the applied potential and, thus, increasing the current density,
decreases the relative flux of carbonate to OH\(^{-}\) (see the dark island in the upper right of Figure 4B). However, decreasing the potential will decrease the \(n\) for neutral and negatively charged membranes (i.e., non-selective ionic membranes/spacers and CEMs, respectively) (see the bottom-left corner of Figure 4B).

The AEM properties strongly influence ion transport of MEA electrolyzers. Decreasing the membrane thickness increases the \(OH^{-}\) transport and leads to negative total carbonate species flux in certain regions (Figure S2A). Thus, a thinner AEM mitigates \(CO_{2}\) crossover more effectively (Figure 4A). The membrane charge has a surprising effect on the carbonate flux; higher-magnitude membrane charge yields lower \(n\) because of greater overall ion uptake in the membrane, whereas a more-neutral membrane charge yields decreased \(OH^{-}\) membrane uptake and flux (Figure 4B). The AEM configuration (with a typical charge of 1 M) allows for significant anion uptake, which ultimately results in high carbonate formation and flux. However, for the CEM (charge < 0 M), the carbonate flux is strongly mitigated at a less-negative potential (Figure 4B). The CEM enables greater \(K^{+}\) and \(H^{+}\) transport, which lowers the \(n\) because of a large negative \(HCO_{3}^{-}\) concentration gradient coupled with a large \(pH\) (and \(OH^{-}\)) gradient from the cathode to the anode (Figure S3). The CEM configuration, which may decrease the overall carbonate flux, is likely to result in salt precipitation as \(K^{+}\) and \(CO_{3}^{2-}\) accumulate at the cathode.

**CO\(_{2}\) utilization**

To investigate the utilization of reacted \(CO_{2}\) (i.e., \(CO_{2}\) that either goes to product or is lost to carbonate), we employed a \(CO_{2}\) utilization-efficiency metric (Figure 5), which is the ratio of the \(CO_{2}\) reduction rate in the cathode layer to the sum of the \(CO_{2}\) reduction rate and the \(HCO_{3}^{-}\) and \(CO_{3}^{2-}\) fluxes through the cell as follows:

\[
\eta_{CO_{2}} = \frac{R_{CO_{2}R}}{R_{CO_{2}R} + J_{HCO_{3}^{-}} + J_{CO_{3}^{2-}}} \tag{Equation 2}
\]

where \(R_{CO_{2}R}\) is the rate of \(CO_{2}\) reduction at the cathode, and \(J\) is the flux of \(HCO_{3}^{-}\) and \(CO_{3}^{2-}\). The reacted \(CO_{2}\) via electroreduction can be as low as 24%, which agrees well with experimental findings that show ~30% of reacted \(CO_{2}\) goes toward product formation.
formation for CO$_2$R on Cu$^{34}$ (or ~50% for CO$_2$R on Ag$^{53}$). Nevertheless, system parameters can be tuned to mitigate this low utilization. Similar to $\eta_{\text{anion}}$, when the membrane thickness decreases, $\eta_{\text{CO}_2}$ increases sharply (Figure 5A). At 10 $\mu$m thickness, the utilization metric, $\eta_{\text{CO}_2}$, exceeds unity because of the negative (toward the cathode) aggregate carbonate flux. This represents a 2-fold increase in utilization relative to the base-case conditions. The decreased reaction length enables H$^+$, with greater mobility than either HCO$_3^-$ or CO$_3^{2-}$, to travel quickly from the anode and neutralize the carbonate species. Additionally, the HCO$_3^-$ diffusion gradient (and total flux; Figure S2A) toward the cathode allows for total carbonate flux toward the cathode, which enables greater utilization. Decreasing the CO$_2$ partial pressure also enables greater CO$_2$ utilization (Figure S2C) by mitigating carbonate formation and favoring OH$^-$ flux over carbonate flux (Figure 5B). Recent experimental CO$_2$R investigations have also shown little change to electrochemical performance at lower partial pressures of the reactant feedstock, indicating that there is a viable operating zone between the full reactant concentration and the onset of HER.$^{53-55}$

Nernstian overpotential

We investigated the effect of varying system parameters on the energy efficiency as represented by the Nernstian overpotential (Figure 6), defined as follows:

$$\eta_N = \frac{RT}{F} \log \frac{c_{\text{OH}}^+}{c_{\text{OH}}^-},$$

(Equation 3)

where superscripts C and A denote the cathode and anode, respectively.$^{36}$ Reduced membrane thicknesses (Figure 6A) decrease the Nernstian overpotential and also increase the CO$_2$ utilization because of the lower carbonate crossover and lower pH differential between the cathode and the anode (Figure 2A). Although ultra-thin, robust membranes may be difficult to implement experimentally, the potential gains in the overall system energy efficiency motivate further efforts in this regard. Furthermore, reducing the supply of partial pressure decreases the cathode to anode pH gradient—in particular because of the much higher anode pH—which decreases the Nernstian losses (Figure 6B). The low-carbonate crossover attained at low partial pressure increases the electrical efficiency because of the increased OH$^-$ mobility as compared with HCO$_3^-$ or CO$_3^{2-}$. Furthermore, the open-circuit voltage (OCV) under CO$_2$ and N$_2$ were experimentally measured at ~0.401 V and ~0.428 V, respectively, indicating negligible CO$_2$ crossover occurs when the cell is not polarized. Overall, thin membranes and low pressure can realize both reduced Nernstian potential and reduced CO$_2$ loss from crossover.

Figure 5. Partial dependence of reacted CO$_2$ utilization

(A and B) Partial dependence of CO$_2$ utilization (x100%) relative to membrane thickness and membrane charge (A) and CO$_2$ partial pressure and membrane porosity (B).
Depending on the reaction conditions, CO₂R can generate a range of products (CO, C₂H₄, EtOH, acetate, and n-propanol). Ethylene and ethanol have especially high market value¹,² and can exhibit high selectivity on Cu catalysts in MEAs.²⁵ We investigated parameters that yield high energy efficiency in the production of EtOH and C₂H₄ selectivity (Figure 7). An AEM (with a positive membrane charge) under moderately negative potential (Figure 7A) and high CO₂ partial pressure (Figure 7B) is key to efficient C₂ product evolution, offering 21% energy efficiency (single points in Figure 7), relative to <10% for lower current density and membrane-charge configurations. However, juxtaposing those optimal conditions with those of Figures 4 and 5 indicate that trade-offs must be made to achieve high efficiency and low carbonate crossover. Common across all metrics is the high potential magnitude and the high membrane charge. Low partial pressure has adverse effects on C₂EE, but improves CO₂ utilization. Nevertheless, decreasing membrane thickness has a more-significant effect on decreasing carbonate transport, and, therefore, moderately low partial pressure and thin membranes can achieve a promising compromise across all metrics.

Product crossover
Increasing energy efficiency must be achieved in tandem with increasing the collection efficiency for the desired product. In the production of EtOH, reducing crossover from the cathode to the anolyte is essential. Although some EtOH produced at the cathode will enter the cathode gas stream, much of the liquid product will pass through the membrane and enter the anolyte, which necessitates the separation of liquid products from the anolyte. If ethanol can enter the gas stream, a simple condenser can separate the gas-phase EtOH from the other gases, CO₂, CO, and C₂H₄.²⁵ Therefore, mitigating EtOH crossover to the anolyte would greatly improve the overall system efficiency.

Machine learning analysis of MEA EtOH crossover data from Gabardo et al.²⁵ yields motivating trends (Figure 8). We highlight the most useful features to predict the cathode:anode ethanol ratio (Figure 8A) after training a gradient-boosted regression model. We show the ordered, normalized values (all importances sum to unity), meaning that current density is the most significant, followed by temperature. Variation in catalyst thickness was found to have very little effect on crossover. The partial dependence plots (Figures 8B and 8C) can be seen as a visualization of the expected target value, given the variation in specific input features. As the current density
increases, the EtOH faradaic efficiency and the overall production increase dramatically (Figure 8B). The inherent vaporization volatility allows for greater EtOH evaporation at the cathode. Furthermore, temperature has a significant role (Figure 8B) because increasing the temperature also increases the evaporation and transport through the GDE. Lastly, decreased CO2 partial pressure and flow rate have less of an effect (Figure 8C) but still increase the EtOH ratio.

Consequently, with knowledge of the effect of various experimental parameters on the EtOH cathode:anode ratio, the trained gradient-boosted regression model predicts the potential optimal conditions for the highest EtOH ratio (Table 1). By probing unknown regions that were not visited experimentally, machine learning enables predictions based on novel combinations of features.

As previously observed experimentally, high current density and temperature are crucial to mitigate EtOH crossover to the anode. Furthermore, decreasing partial pressure increases cathode pH, which increases EtOH selectivity, as well as EtOH recovery from the cathode stream. Temperature and partial pressure also strongly affect both CO2 solubility and EtOH evaporation rate. By tuning the CO2 availability and EtOH evaporation, both the EtOH ratio and the selectivity can be improved. Lastly, performing similar analysis for C2H4 selectivity (Figure S4) enables tuning of the parameters toward high C2H4 selectivity (Table S5). Similar to EtOH crossover, current density remains the most important factor because high reaction rates are required for C2 products. CO2 flow rate and partial pressure also have significant roles because decreasing either will increase the cathode pH, which promotes C2H4 production.

In this work, we modeled CO2R to multi-carbon products in an MEA electrolyzer to elucidate conditions that reduce CO2 and liquid-product crossover to increase CO2 utilization and energy efficiency. The high cathode pH in the current CO2R electrolyzers leads to the production of CO32- and HCO3-, which leads to salt precipitation and diminished reacted CO2 utilization (efficiency calculated via Equation 2) in the form of carbonate crossover through the membrane. However, by decreasing CO2 partial pressure and increasing current density and maintaining a sufficient

![Figure 7. Partial dependence of multi-carbon energy efficiency](image-url)
concentration of CO$_2$ at the catalyst layer, we show that carbonate formation can be mitigated substantially. Further, increases in CO$_2$ utilization and reduction in Nernstian losses can be achieved with decreased membrane thickness. We determined that product crossover in multi-carbon ethanol-producing cells is most sensitive to current density. These results improve our understanding of MEAs and motivate targeted experimental investigation, especially regarding membrane structure, which will ultimately enable stable, high-rate, and selective CO$_2$R.

**EXPERIMENTAL PROCEDURES**

**Resource availability**

**Lead contact**
Further information and requests for resources should be directed to and will be fulfilled by the lead contact Prof. David Sinton (sinton@mie.utoronto.ca).

**Materials availability**
This study did not generate new, unique materials.

**Data and code availability**
All data reported in this paper will be shared by the lead contact upon reasonable request. Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

**Geometry**
At the left-hand side boundary (the cathode catalyst/GDE interface), no flux is specified for all species, except CO$_2$ (for which the concentration is specified).

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**Figure 8. EtOH crossover**

(A–C) Feature importance when predicting the ethanol cathode/anode ratio (A) and the partial dependence of the EtOH cathode/anode ratio (B) relative to temperature and current density and partial dependence of EtOH cathode/anode ratio relative to CO$_2$ flow rate and CO$_2$ partial pressure (C).
Equilibrium values are specified at the right-side boundary at the edge of the anolyte diffusion-boundary layer. The cathode potential is applied at the left boundary, and the ground is applied at the anode right boundary.

Species transport
Species transport in the various layers, including electrochemistry in porous electrodes near polymer interfaces, is based on fundamentals presented by Newman and Thomas-Alyea\textsuperscript{56} and others.\textsuperscript{57,58} This transport is characterized by the Poisson-Nernst-Planck set of equations coupled with electroreduction and acid-base equilibrium reactions:

\[ \frac{\partial c_i}{\partial t} + \frac{\partial J_i}{\partial x} = R_i, \]  
\text{(Equation 4)}

where \( J_i \) is the molar flux, given by the following:

\[ J_i = -D_i \frac{\partial c_i}{\partial x} - z_i D_i \frac{c}{RT} \frac{\partial \phi}{\partial x}, \]  
\text{(Equation 5)}

where \( D_i \) and \( z_i \) are the diffusion coefficient and the charge of the different species, respectively, specified in Table S2.\textsuperscript{59} CO\(_2\) solubility and acid-base equilibria equations are provided in Notes S1 and S2.

Charge transfer reactions
Species reactions, \( R_i \), are determined by the carbonate equilibria equations,\textsuperscript{14,60} as well as by the experimentally fit values for the charge-transfer reactions for CO, H\(_2\), C\(_2\)H\(_4\), and EtOH evolution (Equations 7–10, respectively, which occur in the cathode domain) and the OER (anodic domain; Equation 6):

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \]  
\text{(Equation 6)}

\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \]  
\text{(Equation 7)}

\[ \text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{CO} + 2\text{OH}^- \]  
\text{(Equation 8)}

\[ 2\text{CO}_2 + 8\text{H}_2\text{O} + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 12\text{OH}^- \]  
\text{(Equation 9)}

\[ 2\text{CO}_2 + 9\text{H}_2\text{O} + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 12\text{OH}^- \]  
\text{(Equation 10)}

via the Tafel equation:

\[ i = \left( \frac{c_{\text{CO}_2}}{c_{\text{CO}_2,\text{ref}}} \right)^d i_0 \exp \frac{\alpha F \eta}{RT}, \]  
\text{(Equation 11)}

where \( c_{\text{CO}_2} \) is the local CO\(_2\) concentration, \( c_{\text{CO}_2,\text{ref}} \) is the CO\(_2\) solubility saturation concentration (equations in the Supplemental information), \( d \) is the stoichiometric coefficient for CO\(_2\) in the respective reaction, \( i_0 \) is the exchange current density, \( \alpha \) is the transfer coefficient, and \( \eta \) is the cathodic overpotential \((\eta = \phi_s - \phi_l - E_0)\), where \( \phi_s \) is the electrode potential, \( \phi_l \) is the electrolyte potential, and \( E_0 \) is the equilibrium potential.

Table 1. Predicting optimal conditions for the highest cathode:anode ethanol ratio

| Current density (mA cm\(^{-2}\)) | Partial pressure (atm) | T (°C) | CO\(_2\) flow rate (SCCM) | EtOH cathode:anode |
|----------------------------------|------------------------|--------|--------------------------|-------------------|
| 359                             | 0.64                   | 58     | 76                       | 2.19              |
| 347                             | 0.46                   | 58     | 22                       | 2.18              |
| 374                             | 0.10                   | 51     | 74                       | 2.16              |
| 372                             | 0.50                   | 50     | 45                       | 2.16              |
| 400                             | 0.70                   | 55     | 21                       | 2.14              |

Equilibrium values are specified at the right-side boundary at the edge of the anolyte diffusion-boundary layer. The cathode potential is applied at the left boundary, and the ground is applied at the anode right boundary.
potential of the reaction at pH 7); for which, values are provided in Table S3. Furthermore, we employed pH-independent Tafel equations (as this has been observed in alkaline conditions) and encapsulate the multi-step nature of the reactions in the transfer coefficient.

The electrolyte and electrode potential and current are given by Ohm’s Law:

\[ i_l = -\sigma_l \frac{\partial \phi_l}{\partial x}, \frac{\partial i_l}{\partial x} = 0, \]

(Equation 12)

\[ i_s = -\sigma_s \frac{\partial \phi_s}{\partial x}, \frac{\partial i_s}{\partial x} = 0, \]

(Equation 13)

where \( \sigma_l \) and \( \sigma_s \) are the electrolyte and electrode conductivity, respectively, given in Table S4.

**Poisson equation and AEM charge density**

The species electromigration is determined by \( V = \phi_l + \Psi \), where \( \Psi \) is given by the Poisson equation, which also maintains electroneutrality and induces the space charge for the ion-exchange membrane:

\[ \varepsilon_0 \varepsilon_r \frac{\partial^2 \Psi}{\partial x^2} = \sum F z_i c_i + \rho_{AEM}, \]

(Equation 14)

where \( \varepsilon_0 \) and \( \varepsilon_r = 80 \) are the vacuum and relative permittivity, respectively, and \( \rho_{AEM} \) is specified in the membrane and is zero elsewhere.

**Porous-domain effective diffusion**

Porous domains with a Bruggeman model effective diffusivity,

\[ D_{eff} = \varepsilon^3 D_0, \]

(Equation 15)

were employed for all layers, except the electrolyte diffusion-boundary layer. The porosity is 0.6 in the Cu catalyst and carbon layers, 0.1 in the AEM (with a further reduction in diffusion coefficients for the cations by 90%), and 0.9 in the anode.

Base model values: unless otherwise specified, the model parameter values are as follows in Experimental input.

**Experimental input**

The parameters in Tables S3 and S4 are system specific and were fit to match the partial current-density values of the experimental data from the ethylene- and ethanol-producing MEA system of Gabardo et al. The MEA simulation domain was based on characteristic dimensions and properties from that experimental system, allowing a direct comparison. The primary independent variables in those experiments were the applied potential, the cathode catalyst layer thickness, the CO\(_2\) partial pressure, the temperature, and the inlet gas flow rate. The measured values of current density, product faradaic efficiency, and CO\(_2\) utilization were inputs to the model here. Model validation and comparisons with other MEA experimental results are provided in Figure S5.

**Gradient-boosted regression model**

Electrocatalytic CO\(_2\) conversion is an inherently multi-parameter process, with the coupled influence of potential, partial pressure, and membrane properties, among others, all influencing key outcomes of faradaic efficiency, energy efficiency, and CO\(_2\) utilization. Machine learning enables efficient exploration of the complex parameter space, and limits the number of computational parameter combinations required (listed...
in Table 2). To predict the individual target-dependent variables (i.e., carbonate crossover, CO₂ utilization, Nernstian overpotential, EtOH cathode to anode crossover, and C₂H₄ selectivity), we employed XGBoost (version 0.90), a gradient-boosted tree-ensemble method in the scikit-learn application programming interface (API; version 0.21.3). The primary advantage of XGBoost is that over-fitting of the data is mitigated by effective regularization. To predict simulation targets (e.g., carbonate crossover), we trained individual regression models on relevant input parameters, such as applied potential, membrane thickness, CO₂ partial pressure, membrane porosity, and membrane charge. The model takes in those five features and outputs a continuous scalar field, i.e., the target. Model parameters, such as the number of estimators, depth, and learning rate, are tuned via a randomized search with 5-fold cross-validation until a minimum mean-squared error between the predicted and actual target values is obtained. For the EtOH crossover and C₂H₄ selectivity cases, the model was, instead, trained on experimental data from Gabardo et al. In all cases, the R² score after training via 5-fold cross-validation was greater than 0.9.

Feature importance (based on gain) was then calculated on the entire dataset with the optimal model coefficients for each individual target, and the three or four most important features were used in the final analysis to improve predictions and to highlight partial dependence. The feature importance shows the utility of a given feature in predicting the target. For example, given equal feature importance for all features means that variation in different features would produce a similar variation in the target value. Furthermore, removing features of low importance will yield more-efficient, leaner machine learning models, whereas removing important features will yield ineffective models.

Training a machine learning model to predict the target allows the data to be greatly condensed and expressed via partial dependence. This approach shows the relationship between one or two variables and the target, marginalizing over the other features. The result is a low-dimensional graph that elucidates feature-target relationships, rather than necessitating interpretation of multiple scatterplots or a high-dimensional space. For the given partial-dependence plots, we segmented the target into seven equal bins and show contour labels for the interior values (excluding the minimum and maximum).

**SUPPLEMENTAL INFORMATION**

Supplemental information can be found online at [https://doi.org/10.1016/j.xcrp.2021.100522](https://doi.org/10.1016/j.xcrp.2021.100522).

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| Parameter                        | Base value [varied limits] (unit) |
|----------------------------------|-----------------------------------|
| Applied potential                | −4.2 [−3.8, −5.2] (V)             |
| Cathode catalyst layer thickness | 150 (nm)                          |
| Ion-exchange membrane thickness  | 100 [10, 200] (µm)                |
| CO₂ partial pressure             | 1 [0.1, 1] (atm)                  |
| Temperature                      | 20 (°C)                           |
| Membrane porosity (electrolyte volume fraction) | 0.1 [0.1, 0.6] |
| Membrane space charge            | 1 [−2, 1] (M)                     |
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AUTHOR CONTRIBUTIONS

Conceptualization, methodology, formal analysis, C.M.; investigation, C.M. and C.P.O.; writing – original draft, C.M., C.M.G, C.P.O, J.P.E., and D.S.; writing – reviewing & editing, C.M., C.M.G., C.P.O., J.P.E., J.W., Y.X., E.H.S., and D.S.; supervision and funding acquisition, E.H.S. and D.S.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental information

Reducing the crossover of carbonate and liquid products during carbon dioxide electroreduction

Christopher McCallum, Christine M. Gabardo, Colin P. O'Brien, Jonathan P. Edwards, Joshua Wicks, Yi Xu, Edward H. Sargent, and David Sinton
Figure S1. Relative anion concentration and species flux in AEM
Anion ratio and pH (see Figure 3A), and anion flux (Figure 3B) through AEM for increasing current density at base conditions.
Anion ratio and pH (see Figure 3A) and anion flux (Figure 3B) through membrane when tuning system parameters (holding other parameters at base conditions): (A) decrease membrane thickness to 10 \( \mu \text{m} \), (B) increase membrane thickness to 200 \( \mu \text{m} \), (C) decrease CO\(_2\) partial pressure to 0.1 atm, and (D) employ neutral membrane instead of AEM.
Figure S3. Species concentration distribution from the cathode to the anolyte for varying membrane charge

High pH at the cathode drives CO$_3^{2-}$ formation, as well as high K$^+$ concentration, which may result in salt precipitation for CEMs. See Figure 2.
Figure S4. Feature importance when predicting ethylene selectivity.
Feature importance when predicting ethylene selectivity for varying system parameters. Current density is the strongest predictor of selectivity since high ethylene production occurs at high current density.
Figure S5. Model validation relative to 3 experimental datasets (A-D) show faradaic efficiency of CO, H2, EtOH, C2H4, respectively versus current density for the proposed model and 3 experimental MEA datasets 1-3.
Dissolved inorganic carbon (DIC). The dip within the anode arises from the CO$_2$ leaving solution.
SUPPLEMENTAL NOTES

Note S1: CO₂ solubility
The quantity of dissolved CO₂ in solution is determined by the temperature, pressure, and solution salinity. Assuming CO₂ acts as an ideal gas, the dissolved amount is given by Henry’s Law: 4,5

\[ [CO_2]_{aq,0} = K_0 [CO_2]_g; \]  
\[ \ln K_0 = 93.4517 \left( \frac{100}{T} \right) - 60.2409 + 23.3585 \ln \left( \frac{T}{100} \right), \] 

where \( T \) is the temperature of the solution in °K. The solubility is further diminished due to high concentration of ions in solutions according to the Sechenov Equation: 6,7

\[ \log \left( \frac{[CO_2]_{aq}}{[CO_2]_{aq,0}} \right) = K_s C_s, \]  
where \( K_s = \sum (h_{ion} + h_G) \)  
\[ h_G = h_{G,0} + h_f (T - 298.15), \]

| Ion       | \( h_{ion} \) |
|-----------|---------------|
| K⁺        | 0.0922        |
| HCO₃⁻     | 0.0967        |
| CO₃²⁻     | 0.1423        |

Table S1. Sechenov constants

Note S2: Carbonate Equilibria
CO₂, CO₃²⁻, HCO₃⁻, OH⁻, H⁺, and H₂O are all in equilibrium in solution as given by: 8–11

\[ CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \]  
(K₁)  
\[ HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \]  
(K₂)  
\[ CO_2 + OH^- \leftrightarrow HCO_3^- \]  
(K₃)  
\[ HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \]  
(K₄)  
\[ H_2O \leftrightarrow H^+ + OH^- \]  
(K₅)

where the rate constants are a function of temperature and salinity.

Note S3: Diffusion Layer Thickness
The diffusion boundary layer thickness, 12
\[ \delta \approx \left( \frac{D}{v} \right)^{\frac{1}{3}} \left( \frac{\nu x}{D} \right)^{\frac{1}{2}} \]  

(S11)

is 100 \( \mu m \) based on a flow rate of 10 mL/min, channel dimensions of 0.76 mm, and downstream distance, \( x \), of 2 cm, and \( v \) of 1e-6 m\(^2\)s\(^{-1}\).

Table S2. Infinite dilution diffusion constants and charge

| Ion     | \( h_{ion} \) | Charge |
|---------|---------------|--------|
| CO\(_2\) | 1.91          | 0      |
| CO\(_3^{2-}\) | 0.923      | -2     |
| HCO\(_3^-\) | 1.185      | -1     |
| H\(^+\)  | 9.31         | +1     |
| OH\(^-\)  | 5.273        | -1     |
| K\(^+\)  | 1.96         | +1     |

Table S3. Fitted Tafel constants

| Reaction | \( i_0 \) (A/m\(^2\)) | \( \alpha \) | \( E_0 \) (V) \(^{13}\) |
|----------|------------------------|-------------|-------------------|
| COER     | 9.7e7                  | 0.08        | -0.51             |
| C\(_2\)H\(_4\)ER | 1.1e6       | 0.1         | -0.33             |
| HER      | 5.3e6                  | 0.08        | -0.41             |
| EtOHER   | 5.4e5                  | 0.07        | -0.32             |
| OER      | 1e-1                   | 0.6         | 0.82              |

Table S4. System conductivities

| Domain   | \( \sigma \) (S/m) |
|----------|--------------------|
| Cu catalyst | 0.8e5             |
| Carbon    | 1.0e6              |
| AEM       | 8.0                |
| Anode     | 1.4e7              |
| Electrolyte | 4.56              |

Table S5. Predicting optimal conditions for greatest ethylene selectivity

| Current Density (mA cm\(^2\)) | Partial pressure (atm) | T (°C) | CO\(_2\) flow rate (sccm) | FE C\(_2\)H\(_4\) | EtOH cathode:anode |
|-------------------------------|------------------------|--------|--------------------------|-----------------|--------------------|
| 364                           | 0.83                   | 22     | 11                       | 0.49            | 0.40               |
| 351                           | 0.19                   | 40     | 17                       | 0.48            | 1.50               |
| 339                           | 0.56                   | 28     | 29                       | 0.48            | 0.45               |
| 324                           | 0.82                   | 38     | 29                       | 0.48            | 1.34               |
| 377                           | 0.29                   | 26     | 43                       | 0.45            | 0.48               |

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