1. INTRODUCTION

Carbon dioxide electrolysis has the potential to help decarbonize chemical and fuel production by (re)using CO2 as a sustainable alternative to fossil feedstocks and circumventing emissions-intensive production steps such as cracking and reforming. High-temperature solid oxide CO2 electrolyzers that convert CO2 into CO and O2 are already commercially available.1 Intense R&D efforts in academia and industry have led to substantial advances in low-temperature CO2 electrolysis.2–4 The major appeal of low-temperature electrolysis is the ability to produce valuable multien carbon (C2+) products, including ethylene, ethanol, and propanol, by using Cu electroreduction catalysts.5 However, the development of these systems has been plagued by the fundamental problem of CO2 reacting with hydroxide (OH−) generated at the cathode surface to form carbonate (CO32−), which leads to parasitic carbon and energy losses.6 Progress has been achieved in overcoming the carbon loss by using cell configurations that transport protons to CO32− to release CO2, but these systems exacerbate the energy losses.7,8

An alternative to direct CO2 electrolysis to C2+ products (CO2R) is to perform a two-step process comprising an initial CO2-to-CO conversion and subsequent CO-to-C2+ electrolysis (COR). The CO2-to-CO conversion could be performed by using solid oxide electrolysis or water electrolysis combined with reverse water gas shift catalysis. CO electrolysis can be performed using Cu-based cathode materials to produce the same C2+ products as direct CO2 electrolysis because CO is the intermediate on the pathways to these products during CO2 reduction.9 In comparison to CO2 carbonation, the analogous reaction of CO with OH− to form formate (HCOO−) is very slow, which enables the use of alkaline electrolytes in CO electrolysis to achieve substantially lower cell voltages with minimal nonfaradaic parasitic losses.10 Although this two-step strategy nominally has more process complexity, it can in principle provide higher overall energy conversion efficiency and carbon yield for the CO2 to C2+ conversion.11–13

The engineering challenges of COR differ from CO2R because of differences in the gas solubilities, reaction rates, product distributions, and tolerance to Electrolyte composition.14 As with CO2R,11–13,15 COR must be evaluated by a comprehensive assessment of multiple figures of merit: current density, cell potential, Faradaic efficiency (FE), single pass CO
conversion, and durability. We focus here on the COR gas diffusion electrode (GDE) because it is the component of CO electrolysis cells with the greatest need for improvement. Modeling is critical to understand and improve COR GDEs because multiple interrelated chemical and physical phenomena determine their performance, mechanistic understanding of their behavior under operating conditions is lacking,\(^1\) and in situ measurements of GDE properties are difficult.\(^1\) A number of recent works\(^2\)–\(^11\) have modeled different aspects of CO2R at gas diffusion cathodes. These models have used continuum equations for momentum and mass transport and variations of the current-overpotential equation and Poisson Nernst–Planck equations to assess the effects of GDE design and operating conditions. By contrast, to our knowledge, COR GDEs have not previously been studied in a comprehensive model framework.

We model a COR GDE with a catalyst layer (CL) composed of wetted catalyst particles and a hydrophobic gas transporting medium (GTM) adjacent to a carbon fiber based gas diffusion layer. Using GDEs with this design in which the catalyst particles were Cu nanoparticles and the GTM was composed of PTFE nanoparticles, we recently demonstrated steady-state CO electrolysis at 200 mAh/cm² with a cell voltage of 2.13 V, 76% FE for CO reduction products, and 73.5% single-pass conversion.\(^12\) Using a GDE catalyst layer composed of Cu nanoparticles and a covalent organic framework (COF) as a GTM, Ozden et al. recently reported steady-state CO electrolysis at 240 mAh/cm² with a cell voltage of 2.4 V, 80% FE, and 91% single-pass conversion.\(^13\) Another study reported an optimal ethylene FE of 40% at 1 A/cm² and a cell voltage of 2.9 V for CO electrolysis using a catalyst layer prepared from CuO nanosheets and PTFE.\(^14\) A current density of \(\sim 1.8\) A/cm² with a COR FE of 71% was recently reported for a catalyst layer composed of oxide-derived Cu nanoparticles and MgAl layered double hydroxides, although a cell potential was not provided.\(^15\)

In our model, fully coupled gas and ion transport and multiple competing electrokinetic reactions are solved in two dimensions that account for an interdigitated flow field design. We also combine a co-optimization of figures of merit with an investigation along orthogonal operating parameter axes. This approach allows for a more complete exploration of the parameter space than previous CO2R models, which have focused here on the catalyst layer when passed through the cell, where the remainder of the CO flows from the inlet to outlet without reacting. Conversion is calculated using the difference of the gas flux, \(N_i\), between inlet and outlet.

\[
\text{conversion} = \frac{N_{\text{CO, inlet}} - N_{\text{CO, outlet}}}{N_{\text{CO, inlet}}} \tag{2}
\]

The full cell voltage (eq 3) can be written as the sum of the anode and cathode overpotentials \(\eta_{\text{anode}}\) and \(\eta_{\text{cathode}}\) and the thermodynamic potential for COR \(U_{\text{thermo}}\) and the Ohmic voltage drop \(\Phi_{\text{R}}\). The cell potential is a key determinant of electrolyzer energy consumption and by extension total energy consumption for the process.

\[
V_{\text{cell}} = \eta_{\text{cathode}} + U_{\text{thermo}} + \Phi_{\text{R}} + \eta_{\text{anode}} \tag{3}
\]

For this model, the system is run galvanostatically, with a defined current density and a measured overpotential. High current densities reduce cell manufacturing costs because a smaller active area is required for the same throughput. Low overpotential is necessary to reduce operating electricity costs, which have a dramatic impact on the technoeconomic models.\(^11\) Although it is not considered in this model because of the difficulties in modeling long-term performance, cell stability is another critical performance metric. Using the performance metrics output by the model, we also estimate the total energy efficiency for the CO reduction process, which includes both the energy required to power the electrolyzer and the energy required to separate the resulting gaseous product streams. For this simplified analysis, we note that distillation of 1% ethanol in water is about an order of magnitude more energy intensive than pressure swing adsorption or cryogenic distillation of the product gases.\(^16\) Therefore, we do not include the liquid separation in our calculations and assume that ethylene is the only valorized product. Briefly, we choose an arbitrary ethylene production rate basis, calculate the total current required for the electrolyzer, and multiply by the full cell voltage to obtain the total electrolyzer power. Using the Faradaic efficiency and CO conversion, we determine the flow rate of each gaseous species, add the flow rates together, and multiply by the energy required per total volume of gas to obtain the separation unit power requirement. Lastly, we add the two power terms together and divide by the basis to convert to the energy requirement for the system (MJ/kg ethylene), as shown in SI, Section S8.

The model encompasses a COR GDE in contact with an ion transporting layer, which could be either a liquid electrolyte or an ion exchange membrane. The model treats both configurations equivalently with the implicit assumption that the wetting behavior of the catalyst layer remains the same. Most recent CO₂ and CO electrolysis cells have used Cu catalyst layers a few microns thick

2. EXPERIMENTAL SECTION

The figures of merit considered here are Faradaic efficiency (FE), cell potential, single pass CO conversion, and current density. For FE, we consider \(H_2\) and the combined FE for all COR products, which are referred to as \(\text{CO}_2\) products. Since we are modeling the entire catalyst layer, we write FE in terms of a volumetric current density \(i_k^{\text{iso}}\) for the \(k\)th reduction reaction.

\[
\text{FE}_k = \frac{i_k^{\text{iso}}}{\sum_i i_i^{\text{iso}}} \tag{1}
\]

The single-pass CO conversion is the percentage of CO that reacts in the catalyst layer when passed through the cell, where the remainder of the CO flows from the inlet to outlet without reacting. Conversion is calculated using the difference of the gas flux, \(N_i\), between inlet and outlet.

\[
\text{concentration} = \frac{N_{\text{CO, inlet}} - N_{\text{CO, outlet}}}{N_{\text{CO, inlet}}} \tag{2}
\]
composed of Cu catalyst particles held together by ionomeric binder. We have recently reported catalyst layers (CLs) that are tens of microns thick and enable the use of higher Cu catalyst loadings. These thicker layers incorporate Teflon nanoparticles to create hydrophobic gas channels that provide effective CO transport throughout the entire CL (see Figure 1b). At high current densities, electrochemical reactions at the catalyst surface deplete the concentration of dissolved CO gas in the electrolyte region surrounding the catalyst particles. This region must be 10 μm or less in order to quickly regain equilibrium with the gas pore concentration of CO (SI, Section S4). Thus, CLs must balance hydrophobicity (increasing gas transport) with hydrophilicity (allowing electrolyte wetting) to maximize the performance and avoid flooding or drying out. In addition, catalyst particles must be distributed such that they remain in electrical contact with the cathode since Teflon is an insulating material. We note, however, that the model described herein is not limited to these “thick” layers, and minor modifications would make it applicable to a variety of catalyst layer formulations.

Computationally resolving the processes in each pore is prohibitively expensive at the cell scale because pore sizes are in nanometers and CL dimensions are tens of microns. We considered control volumes incorporating both GTM and catalyst, as shown in Figure 1c, which are much larger than the microscopic geometry shown in Figure 1d. For each control volume, we employed conservation laws (eqs 12 and 20) to consider advection, diffusion, electromigration, and reactions in a way that homogenizes the effects of the underlying microstructure. Therefore, we use averaged properties like porosity and tortuosity for the catalyst layer and gas diffusion layer regions. Given our goal of identifying optimal cell-level regimes of operation, our results below suggest that the fidelity of our model is sufficient to quantitatively predict experimental trends.

We also assume the model domain remains at a constant temperature and the concentration of KOH does not change since hydroxide ions are the charge transport carriers for the cell. While water transport can impact performance, it is difficult to characterize and quantify experimentally. We therefore did not add an arbitrary saturation parameter to capture water transport effects, as it would not improve the model beyond its effect as an adjustable parameter.

Although some previous studies have pointed toward triple phase boundaries as being the key reaction sites for CO₂ reduction, our model invokes transport in the absence of triple phase boundaries because high reaction rates are possible through dissolution of CO in bulk electrolyte alone. Electrocatalysis at triple phase boundaries would require exotic geometries with a very small fraction of sites performing catalysis at very high specific current densities. The model schematic, shown in Figure 2, depicts a 2D cross-section of the GDL/CL structure in contact with interdigitated flow fields. The interdigitated design distributes reactant gas across a series of inlet channels relatively homogeneously, unlike a serpentine flow field. In addition, the reactant gas is forced over the flow field ribs, which increases the permeation into the gas diffusion and catalyst layers. Flow through this porous medium is laminar, not turbulent,
because gas velocity is slow and momentum transport due to collision with pore walls smooths out fluctuations in velocity. Accordingly, the equations below are derived in the laminar regime.\(^{40}\)

This 2D model permits calculation of the outlet product distribution and flow rate, given an inlet reactant flow. We average along the third dimension, down the length of the channel, because the critical processes of flow into and out of the domain and electrochemical reactions happen in the other two dimensions. Other work shows variations of partial pressure of reactants and products in this dimension,\(^{39}\) which merits further investigations to optimize flow field geometries.

Because interdigitated flow fields typically have a large number of channels, periodic boundary conditions that mimic an infinite array of channels can successfully capture flows in the \(x\) direction. Our model simulates one periodically repeating pattern of channels and ribs such that species can flow in either direction from an inlet channel. At the electrolyte interface, the low solubility of reactant and product gases and the lack of tracking liquid products naturally lead to enforcing a no-flux condition for all species. The inlet channel requires a specified flux and reactant gas composition, and flow field ribs do not allow gases to pass through.

\[ N_{\text{inlet}} = N_{\text{CO,inlet}} \text{ and } N_{\text{electrolyte}} = N_{\text{rib}} = 0 \text{ and } p_{\text{outlet}} = p \quad (4) \]

The outlet channel has a defined pressure \(p\) (set experimentally by a back pressure regulator) and outflow conditions on the species composition. Using outflow conditions rather than imposing fluxes or compositions is necessary to allow for the product distribution to develop unhindered. The conditions are applied by upwinding the mole fractions of each species, i.e., setting the mole fraction at the cell face equal to that of the interior cell center. Critically, this treatment allows for the determination of the reactant conversion.

The two competing electrochemical reactions at the cathode are CO reduction (eqs 5–9) and water reduction (eq 10), commonly termed hydrogen evolution. CO reduction generally produces a variety of liquid and gaseous products, but we choose to focus exclusively on ethylene as the gaseous product and grouped liquid products together to simplify the analysis. The liquid products are all soluble in the electrolyte solution and are assumed to be produced in small enough quantities so as to not change properties like conductivity or gas solubility.

\[ 2\text{CO}(aq) + 6\text{H}_2\text{O}(l) + 8e^- \rightarrow \text{C}_2\text{H}_4(g) + 8\text{OH}^-(aq) \quad (5) \]
\[ 3\text{CO}(aq) + 7\text{H}_2\text{O}(l) + 8e^- \rightarrow \text{C}_2\text{H}_5\text{OH}(l) + 8\text{OH}^-(aq) \quad (6) \]
\[ 3\text{CO}(aq) + 10\text{H}_2\text{O}(l) + 12e^- \rightarrow \text{C}_3\text{H}_8\text{OH}(l) + 12\text{OH}^-(aq) \quad (7) \]
\[ 2\text{CO}(aq) + 3\text{H}_2\text{O}(l) + 4e^- \rightarrow \text{CH}_3\text{COOH}(aq) + 3\text{OH}^-(aq) \quad (8) \]
\[ 3\text{CO}(aq) + 8\text{H}_2\text{O}(l) + 10e^- \rightarrow \text{CH}_2=\text{CHCH}_2\text{OH}(l) + 10\text{OH}^-(aq) \quad (9) \]
\[ 2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) \quad (10) \]

At the anode, the charge is balanced through the oxygen evolution reaction, although our analysis is restricted to the cathode.

\[ 4\text{OH}^-(aq) \rightarrow \text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \quad (11) \]

Electrochemical reactions transform electronic current into ionic current and vice versa, but the total current must be conserved.

\[ \nabla i_i = -\nabla i_j = -\sum_k i_k^{\text{V}} \quad (12) \]

where \(i_i\) is the current density in the solid phase, \(i_j\) is the current density in the liquid phase (due to the flux of ions). For the cathodic electrochemical equations shown above, there is a 1:1 correspondence between the electrons consumed and the ions generated. The current-overpotential equation\(^ {41}\) can be written generally for any reaction \(k\) for cases where the overpotential is significantly larger than the thermal voltage such that the backward reaction is negligible.

\[ i_k^{\text{V}} = i_k^{\text{V}} \left( \frac{c_j^{\text{eq}}}{c_j^{\text{eq}}} \right) \exp \left( \frac{\alpha F}{RT} \eta \right) \quad \text{where} \quad i_k^{\text{V}} = k_c^{\text{V}} \exp \left( \frac{E_i^{\text{V}}}{RT} \right) \quad (13) \]

where \(c_j^{\text{eq}}\) is the concentration of the reactant species in the electrolyte at the reaction site, \(\alpha\) is the transfer coefficient, and \(\eta\) is the overpotential. This equation simplifies to give a Tafel slope when mass transport effects (contained in the concentration term) are negligible and the temperature is constant. Since experimentally measured Tafel slopes for the CO reduction products are similar to each other and consistent with a rate-limiting step of a one-electron transfer to CO, the rate law is first order in CO for those reactions.\(^ {43}\)

Given the assumption of homogeneously distributed electrolyte solution, the hydrogen evolution reaction is zeroth order in \(\text{H}_2\text{O}\) concentration. Experimental Tafel plots provide the exchange current density (for the geometric electrode area) and transfer coefficient for each product species (Tafel data taken in the “high” overpotential regime but before mass transport limitations occur, as shown in Figure S5).

The definition of overpotential for this model, from ref 42, is “the potential of the electrode (relative to the solution) minus the value at equilibrium or open-circuit.”

\[ \eta_{\text{avg}} = V - U_{\text{avg}} \quad \text{where} \quad V = \Phi_i - \Phi_e \text{ and } U_{\text{avg}} \]
\[ = \frac{U^0_{\text{avg}} + \frac{RT}{nF} \ln \left( \frac{k_{C2}}{k_{C2}} \right)}{U^0_{\text{avg}} - \frac{2.303RT}{F} \text{pH}} \quad \text{and} \quad U^0_{\text{avg}} \]
\[ = \sum_k FE_k U^0_k \quad (14) \]

At any point in the catalyst layer, \(V\) is the difference in the electrostatic potential between the solid phase and the (liquid phase) region just outside the double layer. The Nernst equation determines \(U\), the value at equilibrium. Given experimental values referenced to NHE, the calculation of the overpotential should account for both the pH difference between the electrolyte and the reference electrode as well as the standard electrode potential, as shown in eq 14. Note that since the reactants are neutral species, the departures from electroneutrality in the double layer do not significantly alter the reactant concentration, so the Frumkin correction can safely be ignored. Writing Ohm’s Law for the electrolyte permeating the catalyst layer results in a voltage penalty due to the transport of electrogenerated ions in the layer.

\[ i_i = -\sigma^{\text{eff}} \nabla \Phi_i \quad (15) \]

where \(\sigma^{\text{eff}}\) is the effective conductivity and \(\Phi_i\) is the potential of the liquid phase. For the sake of completeness, the Poisson–Nernst–Planck (PNP) equations with an appropriate double layer modification rigorously describe ion transport in electrolyte solutions. However, their use would dramatically complicate the model with little overall impact on the results since none of the reactant species are ions governed by the equations. The only impact would be a slightly improved calculation of the variation in the overpotential across the catalyst layer.

Conveniently, we can combine Ohm’s Law with this definition of the overpotential to write a single equation that is more computationally tractable. The gradient of potential in the liquid phase defined by Ohm’s Law is equal to the gradient of overpotential throughout the catalyst layer. This is because the only spatially varying term in the definition of the overpotential is \(\Phi_i\). Since the solid phase of the electrode has extremely high conductivity,\(^ {33}\) we assume \(\Phi_i\) is constant. In addition, \(U^{\text{ref}}\) is roughly constant, and we assume that the concentration variation across the catalyst layer has a negligible effect on the pH, so the concentration term in the Nernst equation is also constant. With \(V \Phi_i = -V \eta\), eqs 12, 13, and 15 can be combined (using the definition of the Laplacian as the divergence of a gradient of a function) to write
Since both exchange currents and transfer coefficients experimentally differ among the three reactions, the ratio of current going to each reaction changes with the overpotential.

To balance momentum in a multicomponent gas phase mixture transported through porous media, we combine three forms of transport: Maxwell–Stefan diffusion, Knudsen diffusion, and viscous flux.\textsuperscript{44} In general, momentum transfer occurs when molecules of one species collide with their own species or other species. The result is that for Maxwell–Stefan diffusion, the flow of any species is dependent on the properties and quantities of every other species. When pore diameters are comparable to mean free path lengths, Knudsen diffusion occurs because momentum transfer to the wall via molecules directly hitting the wall accounts for a significant portion of the total momentum transfer. For the base case, the Knudsen number is 0.033, which is between 0.01 and 10, the range of significant Knudsen behavior (SI, Section S4). Effects of porosity and tortuosity of the media are captured in the effective Maxwell-Stefan and Knudsen diffusion coefficients. In addition to diffusive fluxes, a pressure driven viscous flux completes the momentum balance. In these regimes, inertial and turbulent terms are not included.\textsuperscript{40} The ideal gas law used in this derivation is a reasonable approximation for these pressure and temperature regimes. A thorough treatment of the dusty gas model by two classic textbooks\textsuperscript{40,44} gives a solid theoretical underpinning for this set of momentum transport equations. Gravity and magnetic fields do not play a significant role in transport of gaseous or ionic species.\textsuperscript{45}

\begin{equation}
\dot{V}_p \eta = - \frac{1}{\sigma_{\text{eff}}^i} \left[ \left( \dot{\sigma}_{\text{eff}}^i \right) + \left( \alpha_{\text{eff}}^i \right) \right] \left( \frac{\partial c_i}{\partial x} \right) \exp \left( \frac{-RT}{\alpha_{\text{eff}}^i} (\eta - \epsilon_c^i) \right) - \frac{RT}{\alpha_{\text{eff}}^i} (\eta - \epsilon_c^i) \\
+ \dot{\sigma}_{\text{eff}}^i \left( \frac{\partial c_i}{\partial x} \right) \exp \left( \frac{-RT}{\epsilon_c^i} (\eta - \epsilon_c^i) \right) - \frac{RT}{\epsilon_c^i} (\eta - \epsilon_c^i) \\
+ \dot{\sigma}_{\text{eff}}^i \left( \frac{\partial c_i}{\partial x} \right) \exp \left( \frac{-RT}{\epsilon_c^i} (\eta - \epsilon_c^i) \right) - \frac{RT}{\epsilon_c^i} (\eta - \epsilon_c^i)
\end{equation}

(16)

For all species, where $p_i$ is the partial pressure of species $i$, $N_i$ is the diffusive component of the flux, $D_{ij}^{\text{diff}}$ is the effective Maxwell–Stefan diffusion coefficient, and $D_{ij}^{\text{K}}$ is the effective Knudsen diffusion coefficient.

The total viscous contribution to the flux is given by

\begin{equation}
\dot{V}_p = \sum_{j \neq i} \frac{RT}{D_{ij}^{\text{K}}} (y_i N_j^D - y_j N_i^D) - \frac{RT}{D_{ij}^{\text{diff}}} N_i^D
\end{equation}

(17)

Figure 3. Results for the base case geometric and kinetic parameters and operating conditions. (A, B) Pressure difference in Pa within the model domain for CO and gaseous products, respectively, referenced to the lowest pressure region of the domain (see SI, Section S4 for details). Gaseous products are pushed away from the inlet by the incoming flux of CO. Partial pressures are 0.5 bar CO, 0.24 bar ethylene, and 0.26 bar hydrogen. (C) Distribution of overpotential within the domain, inset shows the same data along a 1D slice. (D) Distribution of Faradaic efficiency within the domain, inset shows the same data along a 1D slice.

\[ V^2 \eta = - \frac{1}{\sigma_{\text{eff}}^i} \left[ \left( \dot{\sigma}_{\text{eff}}^i \right) + \left( \alpha_{\text{eff}}^i \right) \right] \left( \frac{\partial c_i}{\partial x} \right) \exp \left( \frac{-RT}{\alpha_{\text{eff}}^i} (\eta - \epsilon_c^i) \right) - \frac{RT}{\alpha_{\text{eff}}^i} (\eta - \epsilon_c^i) \\
+ \dot{\sigma}_{\text{eff}}^i \left( \frac{\partial c_i}{\partial x} \right) \exp \left( \frac{-RT}{\epsilon_c^i} (\eta - \epsilon_c^i) \right) - \frac{RT}{\epsilon_c^i} (\eta - \epsilon_c^i) \\
+ \dot{\sigma}_{\text{eff}}^i \left( \frac{\partial c_i}{\partial x} \right) \exp \left( \frac{-RT}{\epsilon_c^i} (\eta - \epsilon_c^i) \right) - \frac{RT}{\epsilon_c^i} (\eta - \epsilon_c^i)
\]
also known as Darcy’s law, where \( \mu \) is the viscosity, and \( K^{eff} \) is the effective permeability coefficient or Darcy’s constant. The total flux of each species, then, is given by

\[
N_i = yN^r + N^D
\]  

(19)

In addition to transport in the gas phase, the reactant CO must dissolve into the wetting layer and be transported to the catalyst surface. Calculations (SI Section S4) show that catalyst particles must be within about 10 \( \mu m \) of the gas transporting medium in order for the concentration of CO in the electrolyte to quickly regain equilibrium. This transport resistance is not significant for our catalyst layer domain geometries, so we accordingly assume it is negligible. This calculation validates the use of Teflon in thicker catalyst layers to keep the Cu domain size to micron scale. Careful deposition to create consistently sized catalyst layer domains that maintain electrical conductivity with the cathode is thus an important experimental consideration.

Naturally, a material balance must be written for all species. The partial pressure of each species is governed by the transport fluxes and electrochemical reactions at the point of interest. In the gas diffusion layer, the reaction term is discarded.

\[
\frac{1}{RT} \frac{dp_i}{dt} = -V \cdot N_i + R_i
\]

(20)

where \( \epsilon \) is porosity, \( p \) is the interstitial partial pressure, \( N_i \) is the molar flux density, and \( R_i \) is a generalized reaction rate term. The rate of creation or destruction of a species is given by eq 21, where \( \xi_i \) is determined by the particular electrochemical reaction in eq 13 above.

\[
R_i = -\sum \xi_i \frac{V}{n_F} \frac{\partial x_i}{\partial x}
\]

(21)

It is defined as follows, where \( \xi_i \) is the stoichiometric coefficient in the reaction, \( \xi_i \) is the volumetric current density, and \( n_F \) is the number of electrons transferred.

The model was custom programmed with Anaconda Python 3 using the SciPy and NumPy packages for the model itself, the pandas package for data transfer, and the Matplotlib package for plotting. The 2D model was fully coupled at each time step and run until a steady state was achieved. The computational domain was discretized with a staggered mesh where scalar variables were stored in the cell centers, and the derivatives of scalar variables were stored on the cell edges. We used a second order finite difference scheme in space for all terms and a first order Explicit Euler scheme in time for the reaction terms. The transport equations were treated with a custom-built time implicit scheme to overcome the stiffness limitations due to the extremely small diffusion time scale. In doing so, since the boundaries are periodic in the \( x \)-direction, eq 16 and (separately) eqs 18 and 20 were solved using Fourier Transform schemes that greatly improved computational efficiency. The details of this scheme are further described in SI. An integral constraint on eq 16 set the minimum value of the overpotential such that the total current on the electrolyte boundary matched the applied current.

Both grid refinement and time refinement studies over an order of magnitude have been performed (Figures S3 and S4, respectively) and show that the base case parameters result in appropriately small errors. These parameters are 1.5 million timesteps for 75 s of time simulated by the model and a 16 \( \times \) 32 \( (x \times y) \) grid. The simulations take roughly 24 h on Stanford’s Sherlock 3.0 cluster using a single node with a 32-core AMD EPYC 7502 processor allotted 100GB of RAM. Cases with more extreme parameter values can take up to 2 days since they can require finer time steps and longer simulation times.

3. RESULTS AND DISCUSSION

In order to provide a more stringent test of its ability to capture the underlying physics, the model was not tuned with any adjustable parameters. We used experimental values for parameters like the exchange current density but did not tune the model by changing any parameters once it was built. Given the validation results presented below, we expect our model captures the important underlying physics of the cathode and can deliver actionable results based on accurate figures of merit. In particular, the CO conversion is calculated and analyzed as a relevant performance metric. Material properties, geometric parameters, and kinetic parameters (Tables S1 and S2) were all intentionally matched with the experiments performed in ref 32, but not tuned while running the model.

We show the detailed results of the model in Figure 3 in order to confirm that the model is functioning properly. These results will also surface new intuitions about dynamics in the catalyst layer that are both difficult to obtain experimentally and informative for further optimization. Flow fields and pressure variations in both reactant (CO) and product gases are shown in Figure 3a and b, respectively. The gas flux vector fields show that CO enters from the inlet channel and travels up to the catalyst layer to react, forming products, and then both products and reactants flow out of the outlet channel. At steady state, pressure variations in these two dimensions within the GDL and CL are quite small, as shown by the scale of the figures in Pa rather than in bar. The partial pressure of each species is almost constant throughout the domain because the viscous fluxes are large compared with the domain size (SI Section S4). Viscous fluxes trace the path from the inlet to outlet taken by much of the inlet gas. In addition, reactive fluxes consume CO and generate \( \text{H}_2 \) and \( \text{C}_2\text{H}_4 \) in the catalyst layer. Diffusive fluxes bring products from the catalyst layer to the middle of the domain, smoothing out variations in pressure, and can, to some extent, counteract the inlet flux.

The overpotential (Figure 3c) varies across the height of the catalyst layer by approximately 15 mV in the base case and is constant across the width of the flow field, since ions do not flow in that direction. The gradient across the catalyst layer occurs because hydroxide ions that are electrogenerated throughout the layer are transported from the layer by an electric field to the bulk electrolyte, creating an Ohmic resistance loss. The overpotential is correspondingly largest (most negative) at the interface with the electrolyte where there is the maximum ion current. In the model, no ions can enter the gas diffusion layer so the slope of the overpotential at that point is zero. The slope on the electrolyte side is set by the total current density, which determines the rate of hydroxide ions produced. Variations on the order of 10 mV are relatively small, but small changes can significantly alter current densities because the current is exponentially dependent on the overpotential. The virtually uniform partial pressure of gases means the gradient is created exclusively by ion transport, not reactant availability.

In Figure 3d, the FE toward multicarbon products varies slightly with position in the CL, which is a direct result of the corresponding range of overpotential values across that layer. Ideally, all of the CO would flow into the catalyst layer and react, but some fraction always flows back out of the catalyst layer to the outlet without reacting. At the base case current density (Table S1), a significant fraction of the CO reacts to form products, which reduces the partial pressure of CO in the catalyst layer to approximately 0.5 bar (Figure 3a, see caption). This partial pressure appears in the concentration prefactor of the current-overpotential equation, where it significantly impacts the Faradaic efficiency. Therefore, a clear trade-off is presented between a high conversion of CO (resulting in a low
partial CO pressure) and high Faradaic efficiency (requiring a high partial CO pressure).

We posit that future work could productively implement a 1D model that captures the main features of the existing 2D model. Since Figure 3a,b shows that the partial pressure of gases is almost uniform throughout the domain, the gas phase can be characterized as well-mixed. This 1D model must still resolve the variation in overpotential through the catalyst layer and have appropriate boundary conditions for the gas flow. To that end, we define a control volume of the catalyst layer (since

Figure 4. (A, B) Validation of model by experimental results taken in a similar cathode configuration. (A) Dependence of figures of merit on pressure showing reasonable agreement for all figures. (B) Dependence of figures of merit on inlet flow rate showing reasonable agreement for all figures. (C–F) Sensitivity analyses for relevant operating and catalyst layer conditions. (C–E) Dependence of figures of merit on current density, temperature, and catalyst loading (represented by the electrochemically active surface area (ECSA) of the catalyst layer), respectively. (F) Pathways toward optimization of cell performance through minimizing the total energy required for given operating and catalyst layer conditions. Sample calculations for total energy requirements can be found in SI, Section S8.
the gas diffusion layer only impacts partial pressure distributions) with an identical treatment of the electrochemical reactions. Instead of solving the Maxwell–Stefan diffusion equation and Darcy’s Law, we simply apply a constraint on the total pressure for the system (defined by the outlet set pressure) using the well-mixed gas assumption. This leads to a straightforward calculation of the outlet gas flow, which dramatically simplifies the model.

\[ N_{\text{outlet}} = \sum_i N_i + N_{\text{inlet}} \quad \text{and} \quad N_{\text{inlet}} = \gamma_i N_{\text{outlet}} \quad (22) \]

We note that the naive boundary condition on gas flow from the 1D geometry of the catalyst layer would lead to a no-flux condition at the electrolyte layer, as is present in the 2D model. However, that would not allow the inlet and outlet partial pressures to be defined independently, which would make solving for the CO conversion impossible. The best direction for a 1D domain that solves for conversion follows the streamlines of gas flow, as illustrated in Figure 2a.

To confirm the theory that a 1D model could reproduce the main findings, we wrote a version with the same parameters as the 2D model using the boundary condition and simplifications above and 1D equations (SI, Section S9). This 1D model consistently reproduces the figures of merit from the 2D model (within a few percent) for a reasonable range of operating conditions. For the base case shown in Figure 3, the 1D model calculates an overall Faradaic efficiency, which is 2% different, single pass CO conversion, which is 10% different, and overpotential, which is 1% different. For cases that are not gas transport limited, the 1D model matches the 2D results even more closely, since the partial pressures of gases in 2D are more uniform. We believe that future work could find this model form useful when interrogating physics other than gas transport resistances.

Validating models is a necessary precondition to assessing their wider applicability, especially for configurations or data sets that are difficult to experimentally build or acquire. As Figure 4 shows, the model fits Faradaic efficiency, CO conversion, and overpotential trends for a wide range of outlet pressures and inlet flow rates. The slight overprediction of the Faradaic efficiency at higher pressures may be due to heterogeneity in the channel length dimension, which is not modeled in our 2D setup. Generally, increasing the pressure should decrease the overpotential as more reactant is provided to the catalyst surface. However, as Faradaic efficiency increases, the averaged value of \( U^0 \) increases which counterbalances that effect to some extent. At high flow rates, the experimental flow field may be distributing gas unevenly which could account for underpredictions of overpotential.

Notably, this model uses kinetic data from experimentally collected Tafel measurements but does not use any adjustable parameters to further fit the model to these experiments. In particular, the close fit of the CO conversion has not been shown in other models, and it is a strong confirmation of our model’s ability to capture the meaningful physics of the system. Simply validating the JV curve can be done with just a zero-dimensional set of equations (summing the transport resistances) and therefore does not confirm a model’s multidimensional claims.

An actionable result from this study is exhibited in Figure 4a, which shows that increasing the outlet set pressure improves performance across all figures of merit, and therefore, future experimental works are not expected to achieve their best performance if they do not operate at elevated pressure. This improvement stems from an increase in the reactant concentration at the reaction surface, which is a function of the partial pressure and Henry’s Law, shown below.

\[ c_{\text{CO,dissolved}} = K_{\text{H,CO}} \rho_{\text{CO}} \]

where

\[ K_{\text{H,CO}} = \frac{d(\ln(K_i))}{d(1/T)} \left( \frac{1}{T - 298} \right) \]

In particular, this is relevant for CO reduction since the solubility of CO in electrolyte at room temperature and pressure is only about 1 mM. The reaction concentration prefactor term in eq 13 controls the fraction of the total current density going toward \( C_2 \) products and thus directly impacts the Faradaic efficiency. In addition, increasing the kinetic rate will also decrease the overpotential for a given current density. Lastly, improving the FE while keeping other parameters the same will lead to higher reactant consumption, and thus an improvement in CO conversion, since the flow rate is set on a molar basis. At high pressures, the velocity of gas coming into the channel slows down to compensate.

Increasing the flow rate at a given current density (Figure 4b) increases the partial pressure of CO in the catalyst layer by flowing in reactant gas faster than it can react. This leads to an increase in FE and decrease in overpotential (see above), but at the cost of significantly decreased CO conversion. This trade-off means that an optimal current density/flow rate ratio can be calculated. For our system, 125 mA:1 sccm provides optimal performance, minimizing the total energy required for the process for a wide range of current densities and flow rates. This design criterion has been interrogated but not explicitly established before and should be considered as a general rule, although the values may differ for different product selectivity distributions. As expected, Figure 4e shows that increasing the current density has the opposite effect of increasing flow rate, thus, the trade-off.

As we increase the current density, the total reactant consumption and product generation increase accordingly, driven by an increase in the overpotential. Figure 4e shows that the CO conversion increases to almost 100% at 600 mA/cm\(^2\) because the cell is consuming almost all of the CO flowing into the domain. The total Faradaic efficiency declines at high current densities because of the low reactant gas concentration in the CL.

Increasing the temperature, shown in Figure 4d, improves reaction kinetics which decreases the overpotential but unexpectedly reduces FE, and thus CO conversion. Given the structure of the Faradaic exponential term (eq 13) with temperature as the denominator, increasing the temperature should require increasing the overpotential to maintain the same reaction rate. However, the exchange current density is governed by Arrhenius kinetics as well (Table S1), which operate in the opposite direction. Here, since the argument of the exponential is negative, increasing the temperature will increase the reaction rate at a given overpotential. Since we are in the Marcus normal region, we see that the increased driving force due to the Arrhenius equation outweighs the force due to the Faradaic exponential term.

However, this effect is counterbalanced by the temperature dependence of Henry’s Law (eq 23), which shows dramatic decreases in solubility with increasing temperature. This causes the concentration of CO in the wetting layer to drop, lowering FE and CO conversion accordingly. Taking these two results...
Anode, as well. This combined decrease in cell voltage may
throughout the cell and the decrease of overpotential at the
temperature should include its effect on ionic conductivity
together explains our model output. A full analysis of changing
pressure and 4 sccm/cm² (otherwise, base case operating conditions).

Figure 5. Further optimization for performance at high current densities. (A) Dependence of figures of merit on current density at 8 bar applied
pressure and 4 sccm/cm² (otherwise, base case operating conditions). (B) Dependence of figures of merit on current density at 10 bar applied
pressure, 8 sccm/cm², 15 °C, and 400% of base case ECSA (otherwise, base case operating conditions).

was always well hydrated. Further research, both experimental
and theoretical, to better understand the wetting behavior for a
wide variety of experimental designs is greatly needed.

We took the optimization a step further by changing
multiple operating conditions and kinetic parameters simulta-
neously to target high performance at current densities greater
than 500 mA/cm². As Figure 5a shows, we can achieve
remarkably high conversion and FE simultaneously at high
current densities. Of course, this means operating at a higher
overpotential, which increases the power supplied to the
electrolyzer (since P = IV), but it greatly reduces the
electrolyzer area needed per volume of product. For this set
of conditions, 1 A/cm² seems about optimal, as going any
higher would not provide significant improvements in CO
conversion and would come at the cost of higher overpotential
and lower FE. Pushing the optimization even further in Figure
5b indicates that 2 A/cm² with high conversion and ethylene
production may be possible with the concomitant increase in
ECSA. We note that other challenges such as maintaining an
appropriate catalyst wetting and evenly distributing gas
through the flow field may arise at these high current densities,
but they are not considered in this model.

4. CONCLUSIONS

Ensuring the catalyst layer is well homogenized keeps
consistent wetting properties and avoids islands of the
nonreactive catalyst. Although our model did not address the
possibility of heterogeneity in this way, any significant
heterogeneity was expected to have detrimental impacts on
performance by decreasing the ECSA. For operating
conditions, increasing pressure to about 8 bar, as long as
Henry’s Law is valid, is the most critical improvement to
current experimental designs. Perhaps unsurprisingly, the base
case parameters that were reached after extensive experimen-
tation are already reasonably close to the optimum catalyst
loading and current density/flow rate ratio. Knowing the ratio,
however, in combination with high pressure and good flow
gas distribution allows for higher current densities without
sacrificing other performance metrics.
Summary of equations, tables defining variables and parameters used in the model, mathematical estimates of modeling assumptions, performance studies of a variety of additional model parameters, further explanations of electrochemistry modeling details, and calculation of energy efficiency and kinetic constants (PDF)

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Notes
The authors declare no competing financial interest.

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