Modeling and Simulation of the Spatial and Light-Intensity Dependence of Product Distributions in an Integrated Photoelectrochemical CO₂ Reduction System

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ABSTRACT: A multiphysics model that accounts for the performance of electrocatalysts and triple-junction light absorbers, as well as for the transport properties of the electrolyte and dissolved CO₂, was used to evaluate the spatial and light-intensity dependence of product distributions in an integrated photoelectrochemical CO₂ reduction (CO₂R) cell. Different sets of band gap combinations of triple-junction light absorbers were required to accommodate the optimal total operating current density relative to the optimal partial current density for CO₂R. The simulated product distribution was highly nonuniform along the width of the electrode and depended on the electrode dimensions as well as the illumination intensity. To achieve the same product selectivity as in a potentiostatic, “half-cell” configuration, the electrocatalyst must retain its selectivity over a range of cathode potentials, and this range is dependent on the transport losses and current−voltage relationship of the light absorbers, the geometric parameters of the cell, and the illumination intensity.

A n efficient solar-driven CO₂ reduction system requires effective delivery of CO₂ to the electrode surface, selective reduction of CO₂ by an active electrocatalyst at the cathode, adequate ionic transport between the anolyte and catholyte chambers, and robust and cost-effective methods for separating the products. Electrocatalysts including metals, metal alloys, metal oxides, and semiconductors have been investigated for electrocatalytic CO₂ reduction (CO₂R). For most electrocatalysts operated in contact with aqueous electrolytes, the branching ratio between water reduction (i.e., the hydrogen-evolution reaction, HER) and CO₂R depends on the applied potential. For instance, in a three-electrode potentiostatic configuration, the Faradaic efficiency for the production of formate, HCOO⁻, at the surface of an oxidized Cu foil changes from 5.5% to 32.9% when the potential of the working electrode is changed by ∼20 mV. In contrast to experiments performed using three-electrode potentiostatic configurations, the potential at the cathode of a full photoelectrosynthetic cell depends on the reaction kinetics at the anode surface as well as transport losses associated with solution resistance, electrodialysis, pH gradients, and CO₂ concentration gradients near the surface of the cathode. Modeling and simulation has shown that many test-bed configurations for water-splitting devices produce spatially dependent potential distributions, with variations of >100 mV across the electrode surface even under constant illumination intensity. Moreover, variation in the illumination intensity during operation additionally affects the solar-to-fuel (STF) conversion efficiency for such systems.

Herein, a two-dimensional numerical model has been developed using COMSOL Multiphysics to evaluate the spatial and temporal variation of the product distribution in an integrated photoelectrochemical CO₂ reduction cell driven by triple-junction light absorbers operating at the Shockley–Queisser (S-Q) limit. The current−voltage behaviors and the Faradaic efficiencies of metallic Cu and Ag catalysts, respectively, for CO₂R in 0.10 M bicarbonate solution (pH 6.8) were used to describe the reactions at the cathode. For the metallic Ag catalyst, the following CO₂R reactions were included at the electrode surface:

\[
\begin{align*}
2H^+ + 2e^- & \rightarrow H_2 \\
CO_2 + 2H^+ + 2e^- & \rightarrow HCOOH \\
CO_2 + 2H^+ + 2e^- & \rightarrow CO + H_2O
\end{align*}
\]

For the metallic Cu catalyst, two additional CO₂R reactions were included at the electrode surface:

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Because of the lack of experimental data for OER catalysts at pH 6.8 or in contact with bicarbonate solutions, the current-voltage behavior of a phosphate-containing CoO$_x$, Co-Pi, in 0.10 M K-Pi (aq) solution at pH 7.221 was used to describe the reactions at the anode. No membrane was included in the model, and any transport loss produced by a membrane separator was neglected. The model also assumed robust separation of products by neglecting reactions such as oxidation of the reduced products at the anode, reduction of O$_2$ at the cathode, or recombination of products in the solution.

Figure 1a shows the current-voltage characteristics of three triple-junction light-absorber devices that are operating at the Shockley–Queisser limit, as well as the overall load curve for Ag performing the CO$_2$R reaction and Co-Pi performing the OER in a one-dimensional, face-to-face cell design. The operational current density of the overall reaction, $J_{\text{total}}$, was determined by the crossing point between the load curve (black) and the power curve (green, blue, or red) of the light-absorber device. The optimal $J_{\text{total}}$ of 11.9 mA cm$^{-2}$ was obtained at the maximum power point of the red curve (point A), which corresponded to a band-gap combination of 2.1 eV/1.6 eV/1.2 eV (device 1) and two ideal triple-junction light absorbers (devices 2 and 3) under different illumination intensities.

Figure 1b shows the current-voltage characteristics of three triple-junction light-absorber devices having optimal band-gap combinations of 1.9 eV/1.7 eV/1.5 eV (blue, device 2) and 1.8 eV/1.4 eV/1.0 eV (green, device 3) in a one-dimensional cell configuration. (b) Overall load curve for CO$_2$R and OER and the current-voltage characteristics of two ideal triple-junction light absorbers (devices 2 and 3) that produced the same $J_{\text{CO}_2}$ and $J_{\text{total}}$ at a simulated light intensity of 100 mW cm$^{-2}$ of air mass (AM) 1.5 global illumination.

CO$_2$ + 8H$^+$ + 8e$^-$ → CH$_4$ + 2H$_2$O

2CO$_2$ + 12H$^+$ + 12e$^-$ → C$_2$H$_4$ + 4H$_2$O

Because of the lack of experimental data for OER catalysts at pH 6.8 or in contact with bicarbonate solutions, the current-voltage behavior of a phosphate-containing CoO$_x$, Co-Pi, in 0.10 M K-Pi (aq) solution at pH 7.221 was used to describe the reactions at the anode. No membrane was included in the model, and any transport loss produced by a membrane separator was neglected. The model also assumed robust separation of products by neglecting reactions such as oxidation of the reduced products at the anode, reduction of O$_2$ at the cathode, or recombination of products in the solution.
The two light-absorber structures yielded identical the plateau region of the photodiode curve. In contrast, the load curve and the photodiode characteristic occurred in illumination intensity, because the crossing points between circles, left axis) exhibited a linear dependence on the CO2R catalyst, and on the bottom by a TCO layer and an OER top by a transparent conductive oxide (TCO) layer and a which the triple-junction light absorber (blue) is coated on the light intensity varied from 100 to 20 mW cm\(^{-2}\) e\(^{-}\)

\[ e^{-}\] intensity dependence for devices 2 and 3 of the Faradaic V, larger than that of device 3. Figure 1c shows the light-exhibited a shift in the total operational voltage, from 3.1 to 2.5 range of illumination intensities. The \( J_{\text{CO}2\text{R}} \) for device 3 (green triangles, right axis) remained nearly constant (93% to 95%) over the same spectrum of illumination intensities. The \( J_{\text{CO}2\text{R}} \) of device 2 (blue circles, left axis) exhibited a linear dependence on the illumination intensity, because the crossing points between the load curve and the photodiode characteristic occurred in the plateau region of the photodiode curve. In contrast, \( J_{\text{CO}2\text{R}} \) of device 3 (green circles, left axis) exhibited a weaker dependence on the illumination intensity, because the crossing points occurred at the rising portion of the photodiode curve. Hence, even in a one-dimensional cell architecture as shown in Figure 1, the rate of formation of CO2R products, as well as the ratio of CO2R products to hydrogen, varied as the illumination intensity changed and were dependent on the choice of the light absorbers. The different product branching ratio under varying illumination conditions that result from the diurnal cycle as well as siting of a deployed system will thus have an impact on product mixtures as well as on requirements for product separation and collection processes in solar-driven CO2R devices.

Figure 2a shows a schematic illustration of an integrated, two-dimensional photoelectrosynthetic CO2 reduction cell in which the triple-junction light absorber (blue) is coated on the top by a transparent conductive oxide (TCO) layer and a CO2R catalyst, and on the bottom by a TCO layer and an OER catalyst. The thickness of the TCO layer was set to 10 μm, and the conductivity of the TCO was set to \( 10^5 \text{ S m}^{-1} \). In this cell, a bicarbonate solution that contained 0.1 M NaHCO3(aq) was equilibrated with 1 atm pressure of CO2(g). The concentration of CO2 in the aqueous solution was set to 34 mM, according to Henry’s law. The detailed cell dimensions are summarized in Computational Methods. Figure 2b shows a snapshot of the electrolyte potential profile and the associated current distribution in the PEC cell. The potential profile of the electrolyte was determined by iteratively solving the equations that describe in a two-dimensional simulation domain the current-voltage relationship of the light absorber, transport losses in the electrolyte, and the electrocatalytic performance of the catalysts. Generally, a larger transport loss would result in a larger difference in the electrolyte potentials for the cathode and anode regions, and would result in a smaller kinetic overpotential as well as a smaller operational current density at the electrode surface. As shown in Figure 2b, the operating current densities for the OER and CO2R were concentrated at the edge of the device because of the short ionic path length and the low solution resistive losses at such positions relative to other positions on the device. The CO2R current density at the edge of the electrode was ~4.5 times larger than the CO2R current density at the middle of the electrode. Moreover, when the electrode width was 1.0 cm, the potential at the cathode varied spatially by >400 mV.

Figure 3 shows the distribution of products from water reduction and CO2R, as well as the partial current density for each of the major products, as a function of the normalized distance along the electrode, for the Cu catalyst (Figure 3a) and for the Ag catalyst (Figure 3b) in an integrated PEC CO2 reduction cell under 100 mW cm\(^{-2}\) of simulated AM 1.5 G illumination. The normalized distance along the electrode was a unitless parameter that was defined as the distance from one end of the electrode normalized to the width of the electrode. Because a series of band-gap combinations would yield the same \( J_{\text{CO}2\text{R}} \) the band-gap combinations that produced the optimum \( J_{\text{total}} \) were used for the Cu catalyst (2.1 eV/1.6 eV/1.1 eV) and the Ag catalyst (2.1 eV/1.6 eV/1.2 eV) to permit evaluation of the resulting spatial distribution of the reduction products under such conditions. The mathematical forms of the transport losses modeled for the two-dimensional PEC cell are described in Computational Methods and include the resistive loss and electrodialysis of the electrolyte, as well as the
concentration overpotentials associated with pH gradients and CO₂ concentration gradients at the electrode surface. Moderate agitation and convection of the electrolyte was assumed by taking the thickness of the hydrodynamic boundary layer to be 100 μm. Consequently, under 100 mW cm⁻² illumination, the voltage losses due to pH gradients, CO₂ concentration gradients, and electrodialysis of the electrolyte were <100 mV for the largest electrode width. The resistive loss in the bicarbonate solution comprised the largest component of the transport loss in the system. Because no membrane was included and moderate convection (boundary layer thickness = 100 μm) was introduced in the model, small voltage losses due to the pH gradients and electrodialysis were obtained in the calculation relative to the losses that are present and have been evaluated quantitatively for near-neutral pH systems for water-splitting reactions.²²,²³

For the Cu catalyst, H₂ was the dominant (nearly 100 mol % of the total) product near the edge of the electrode because of the small solution transport losses, high overpotential for the CO₂R, and high Faradaic efficiency for hydrogen evolution at such potentials. In contrast, at the midpoint of the electrode, ~52% of the current led to H₂(g). Similar variations of the product distributions were observed when Ag was the CO₂R electrocatalyst. Thus, the spatial variation of the product distributions as shown in Figure 3, and the resulting overall product branching ratio in full electrochemical devices, could be very different from the Faradaic efficiency for production of various products determined by three-electrode measurements under well-controlled potentials with equipotential electrode surfaces. Numerical modeling of photoreactors that have realistic dimensions, under realistic operating conditions, therefore is needed to obtain a firm prediction of the performance of the whole cell by using the intrinsic materials properties of the system in conjunction with the transport properties of the reactant, product, and reaction media.

Figure 4a shows the integrated current densities over the electrode width for H₂ (black), CO (blue), and formate (red), as a function of the width of the electrode, in a cell with Ag as the CO₂R catalyst. As the electrode width increased from 1.0 mm to 1.0 cm, the integrated partial current density for H₂ (black) decreased from 8 mA cm⁻² to 1.4 mA cm⁻², and the integrated partial current density for CO (blue) increased slightly, from 3.5 mA cm⁻² to 4.4 mA cm⁻². The reduction in transport losses as the electrode width decreased resulted in the change in the integrated current densities as well as in the spatial variation of the product distribution.

Figure 4b shows the dependence of the potential at the surface of the cathode on the width of the electrode, under 100 mW cm⁻² of simulated AM 1.5 G illumination. The surface potential at any particular location on the cathode was determined by the overall transport losses (solution resistive loss, electrodialysis of electrolyte, and voltage losses associated with pH gradients and CO₂ concentration gradients), the current–voltage characteristics of the light absorbers, the
behavior of the OER catalyst, and the lateral conduction properties of the TCO layers. The spatial variation in the potential of the cathode produced a variable product distribution along the width of the electrode. Panels c and d of Figure 4 show the partial current density as a function of the normalized distance along the electrode when the electrode width was set to 1.0 mm and 5.0 mm, respectively. Under constant illumination (100 mW cm$^{-2}$), the cathode surface potential varied by >400 mV when the electrode width was 1.0 cm, but the cathode surface potential varied by <50 mV when the electrode width was decreased to 1.0 mm. The greater variation in surface potential for the larger electrode resulted in a greater variation in the product distribution along the surface of the larger electrode than the smaller electrode; thus, the two electrodes would yield different product distributions: the 1 mm electrode yields 65% H$_2$, 28% CO, and 7% formate, while the 5 mm electrode yields 43% H$_2$, 51% CO, and 6% formate. To achieve the same level of selectivity as in a potentiostatically controlled, “half-cell” configuration, nearly constant Faradaic efficiencies for the products are required across the operating voltage windows (indicated by the gradient bars in Figure 4b). As the electrode dimension increased, the voltage window of required constant Faradaic efficiency also increased. Note that the selectivity of the CO$_2$R catalyst in this study was defined as maintaining the ratios of Faradaic efficiencies among all of the various reduced products in the system. Depending on the end-use of the reduced products, a mixture of carbon-containing products, including products in liquid or gaseous phases or both, could be valuable. The model described herein can be used to design the cell geometry to produce the desired product branching ratios in a realistic PEC cell under various illumination conditions.

Figure 5a shows the integrated current densities over the electrode width for H$_2$ (black), CO (blue), and formate (red) as a function of the illumination intensity, with Ag as the CO$_2$R catalyst. The integrated partial current density for all of the products increased as the illumination intensity increased. However, the partial current density did not scale linearly with the illumination intensity. The product distribution also varied because of the nonmonotonic product distribution produced by the Ag catalyst as a function of potential. Figure 5b shows the cathode surface potential and its variation as a function of the illumination intensity, when the electrode width was set to 1.0 cm. Furthermore, panels c and d of Figure 5 show the detailed partial current density of H$_2$ (black), CO (blue), and formate (red) as a function of the normalized distance along the electrode under 20 and 60 mW cm$^{-2}$ of simulated AM 1.5 G illumination. For an integrated PEC cell having this specific design, with an electrode width of 1.0 cm under varying illumination intensities, achieving the same product selectivity as in a potentiostatically controlled three-electrode, “half-cell” configuration would require a constant CO$_2$R Faradaic efficiency for potentials in the range between 0.98 and 1.50 V versus the reversible hydrogen electrode (RHE).
In summary, integrated photoelectrosynthetic CO₂R cells will require a different triple-junction light absorber to optimize \(J_{\text{CO}_2}\) than the light-absorber structure that optimizes \(J_{\text{total}}\). The partial current densities for each of the reduction products will depend on the electrode dimensions and on the illumination intensity. The surface potential variation in a realistic cell under varying light intensities, relative to a potentiostatically controlled, “half-cell” configuration, would require catalysts with a substantial voltage window within which the Faradaic control, intensity. The surface potential variation in a realistic cell under illumination conditions.

**COMPUTATIONAL METHODS**

The coupled equations under the corresponding boundary conditions for the one-dimensional and two-dimensional cell architectures were solved using a commercial finite-element program, COMSOL Multiphysics. In the one-dimensional cell architecture, the cathode and anode were arranged face-to-face and were separated by 4 mm. In the two-dimensional cell architecture (Figure 2a), the ratio between the width of the photoelectrodes and the width of the entire unit cell was set to 0.9. The electrolyte height above the cathode surface and below the anode surface was set to 5 mm. A hydrodynamic boundary layer with a thickness of 100 \(\mu\)m was used to account for moderate convection near the photoelectrode. To account for the convective forces in the cell, effective diffusion coefficients for solution species were used beyond the hydrodynamic boundary layer in the bulk solution.

The current−voltage behavior of the triple-junction light-absorber device was obtained from the Shockley−Queisser model and was subsequently fitted using the ideal diode relationship:

\[
J = J_{ph} - J_0 \exp \left( \frac{q(V + JR_{sh})}{kT} \right) - 1
\]

The transport of electrons and holes within the TCO layer was described using Ohm’s Law:

\[
\dot{i} = -\sigma \nabla \phi_i
\]

where \(i\) represents the current density; \(\sigma\) is the electrical conductivity of the TCO layer, and \(\nabla \phi_i\) is the electric potential gradient within the TCO layer.

The current density versus potential characteristics and the Faradaic efficiency of the metallic Cu and Ag catalysts for CO₂R were based on experimental data\(^{20}\) and were fitted into piecewise functions, in which the subfunctions were described by the Butler−Volmer relation:

\[
J_{\text{OER/CO}_2\text{R}} = J_{0,\text{OER/CO}_2\text{R}} \left( \exp \left( \frac{\alpha_{\text{OER/CO}_2\text{R}}Fq\eta}{RT} \right) - 1 \right) - \exp \left( -\frac{\alpha_{\text{OER/CO}_2\text{R}}Fq\eta}{RT} \right)
\]

where \(J_{0,\text{OER/CO}_2\text{R}}\) is the exchange-current density for the OER or CO₂R reaction, respectively and \(\alpha_{\text{OER/CO}_2\text{R}}\) and \(\alpha_{\text{OER/CO}_2\text{R}}\) are the anodic and cathodic transfer coefficients, respectively, for the OER or the CO₂R reaction. The overpotential, \(\eta\), is defined as

\[
\eta = \phi_i - \phi_0
\]

where \(\phi_i\) and \(\phi_0\) are the corresponding electric and electrolyte potential at the electrode−electrolyte interface and \(\phi_0\) is the equilibrium potential. The solution transport that includes diffusion, migration, convection, and bulk reactions of water or buffer dissociation was given by the Nernst−Planck equation. Ionic species, including protons, hydroxide, bicarbonate, carbonate, and potassium ions, as well as neutral species including water, dissolved CO₂, and carbonic acid, were included in the model. The net flux of species in the electrolyte can be written as the sum of fluxes due to migration, diffusion, and convection

\[
N_i = -D_i \nabla c_j - z_i \mu_i F \nabla \phi_i + v_i c_i
\]

where \(\phi_i\) is the electric potential, \(v\) the velocity, \(c_i\) the concentration, \(D_i\) the diffusion coefficient, \(z_i\) the charge number, \(\mu_i\) the mobility of ions, and \(N_i\) the molar flux of the \(i\)th species. The convection term in the simulation was approximated by a hydrodynamic boundary layer with a thickness of 100 \(\mu\)m.

The transport loss, \(\Delta \phi_{\text{transport}}\) in the system includes the solution losses, \(\Delta \phi_{\text{solution}}\), the voltage losses associated with pH gradients, \(\Delta \phi_{\text{pHgradient}}\) and CO₂ concentration gradients at the electrode surface, \(\Delta \phi_{\text{CO}_{2}\text{gradient}}\). The transport loss was given by

\[
\Delta \phi_{\text{transport}} = \Delta \phi_{\text{solution}} + \Delta \phi_{\text{pHgradient}} + \Delta \phi_{\text{CO}_{2}\text{gradient}}
\]

The solution loss, \(\Delta \phi_{\text{solution}}\) was given by

\[
\Delta \phi_{\text{solution}} = \int \frac{1}{K} \text{d}x + \sum \int \frac{P_z D_i \nabla c_i}{K} \text{d}x
\]

where the first term represents the ohmic resistive loss and the second term represents the electrodialysis loss; \(\phi\) is the electric potential, \(K\) the conductivity of the electrolyte, \(J\) the current density, \(x\) the distance along the axis of the one-dimensional model, \(F\) Faraday’s constant, \(z\) the charge number, \(D_i\) the diffusion coefficient, \(c_i\) the molar concentration of the \(i\)th species, \(R\) the gas constant, and \(T\) the absolute temperature.

The Nernstian potential losses associated with the pH gradients, \(\Delta \phi_{\text{pHgradient}}\) and CO₂ concentration gradients, \(\Delta \phi_{\text{CO}_{2}\text{gradient}}\), at the surface of the electrodes can be expressed as

\[
\Delta \phi_{\text{pHgradient}} = 2.303 \frac{RT}{F} (\text{pH cathode} - \text{pH anode})
\]

\[
\Delta \phi_{\text{CO}_{2}\text{gradient}} = \frac{59 (mV)}{n} \log \left( \frac{P_{\text{CO}_{2}\text{cathode}}}{P_{\text{CO}_{2}\text{bulk}}} \right)
\]

\(n\) is the number of electrons transferred in the CO₂ reduction process; for example, \(n = 2\) for CO₂ to formate and \(n = 8\) for CO₂ to methane. \(P_{\text{CO}_{2}\text{cathode}}\) and \(P_{\text{CO}_{2}\text{bulk}}\) are the partial pressures of CO₂ at the cathode surface and in the bulk solution, respectively.

The chemical reactions included in the bicarbonate solution in this study were

\[
\text{CO}_2 + \text{H}_2\text{O} \xrightarrow{k_1} \text{H}^+ + \text{HCO}_3^-
\]
CO₂ + OH⁻ \stackrel{k_{1+}}{\rightleftharpoons} HCO₃⁻ (10)

HCO₃⁻ \stackrel{k_{1-}}{\rightleftharpoons} H⁺ + CO₃²⁻ (11)

HCO₃⁻ + OH⁻ \stackrel{k_{1+}}{\rightleftharpoons} H₂O + CO₃²⁻ (12)

H₂O \rightleftharpoons H⁺ + OH⁻ (13)

where \( k_{1+}, k_{1-}, k_{2+}, k_{2-}, k_{3+}, \) and \( k_{3-} \) are the forward rate constants and \( k_{4+}, k_{4-}, k_{5+}, \) and \( k_{5-} \) are the reverse rate constants, respectively, for each reaction. Table 1 summarizes the rate constants and diffusion coefficients of solution species in the simulation.²⁴⁻²⁶

Table 1. Rate Constants and Diffusion Coefficients of Solution Species in the Simulation²⁴⁻²⁶

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Diffusion Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ + H₂O ( \rightleftharpoons ) H⁺ + HCO₃⁻</td>
<td>( k_{1+} = 0.037 \text{ s}^{-1} )</td>
<td>( D_{H⁺} = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} )</td>
</tr>
<tr>
<td>CO₂ + OH⁻ ( \rightleftharpoons ) H⁺ + CO₃²⁻</td>
<td>( k_{1+} = 7.83 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1} )</td>
<td>( D_{OH⁻} = 9.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} )</td>
</tr>
<tr>
<td>HCO₃⁻ ( \rightleftharpoons ) H⁺ + CO₃²⁻</td>
<td>( k_{1-} = 2.23 \times 10^{4} \text{ M}^{-1} \text{ s}^{-1} )</td>
<td>( D_{H⁺} = 1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} )</td>
</tr>
<tr>
<td>HCO₃⁻ + OH⁻ ( \rightleftharpoons ) H₂O + CO₃²⁻</td>
<td>( k_{1+} = 4.85 \times 10^{-5} \text{ s}^{-1} )</td>
<td>( D_{CO₃²⁻} = 0.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} )</td>
</tr>
<tr>
<td>H₂O ( \rightleftharpoons ) H⁺ + OH⁻</td>
<td>( k_{1-} = 2.5 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1} )</td>
<td>( D_{CO₂} = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} )</td>
</tr>
</tbody>
</table>

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


(22) Jin, J.; Walczak, K.; Singh, M. R.; Karp, C.; Lewis, N. S.; Xiang, C. An experimental and modeling/simulation-based evaluation of the efficiency and operational performance characteristics of an integrated,


