Effects of Electrolyte Buffer Capacity on Surface Reactant Species and the Reaction Rate of CO₂ in Electrochemical CO₂ Reduction

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ABSTRACT: In the aqueous electrochemical reduction of CO₂, the choice of electrolyte is responsible for the catalytic activity and selectivity, although there remains a need for more in-depth understanding of electrolyte effects and mechanisms. In this study, using both experimental and simulation approaches, we report how the buffer capacity of the electrolytes affects the kinetics and equilibrium of surface reactant species and the resulting reaction rate of CO₂ with varying partial CO₂ pressure. Electrolytes investigated include KCl (nonbuffered), KHCO₃ (buffered by bicarbonate), and phosphate-buffered electrolytes. Assuming 100% methane production, the simulation successfully explains the experimental trends in maximum CO₂ flux in KCl and KHCO₃ and also highlights the difference between KHCO₃ and phosphate in terms of pKa as well as the impact of the buffer capacity. To examine the electrolyte impact on selectivity, the model is run with a constant total current density. Using this model, several factors are elucidated, including the importance of local pH, which is not in acid/base equilibrium, the impact of buffer identity and kinetics, and the mass-transport boundary-layer thickness. The gained understanding can help to optimize CO₂ reduction in aqueous environments.

INTRODUCTION

Electrochemical CO₂ reduction (CO₂R) is one of the key technologies in realizing a sustainable society by converting emitted CO₂ to useful chemicals and fuels if combined with surplus energy sources such as solar and wind power. For decades, a number of researchers have shown that some transition metals can catalyze CO₂ to more reduced products such as carbon monoxide (CO), formic acid or formate (HCOOH or HCOO⁻, respectively), hydrocarbons, alcohols, and other organic materials¹⁶ that can be used for renewable chemicals and fuels.⁵,⁶

Although a variety of useful chemicals can be produced from CO₂, selectivity control for the desired product is still difficult in CO₂R, especially for highly reduced products such as hydrocarbons and alcohols.⁵ Moreover, the necessary high surface overpotential and possible competing reactions such as the hydrogen-evolution reaction (HER) are problems that prevent the practical application of this technology.⁷ One route toward overcoming these problems is to make an efficient catalyst that lowers the overpotential with high selectivity for CO₂R.⁸−¹¹ Another way is to manipulate the system parameters to realize the optimum conditions for the CO₂R catalyst, which has been shown to affect the rate and selectivity of the CO₂R reaction significantly.⁷¹²−¹⁷

Among the parameters that affect the property of CO₂R, the electrolyte composition is known to be an important factor. In this research field, potassium bicarbonate (KHCO₃) and potassium chloride (KCl) solutions are the most commonly used aqueous electrolytes.¹,¹²−¹⁷ While it is evident that the selectivity of CO₂R is extremely sensitive to the local conditions and concentrations, properties of the ionic electrolytes in controlling these conditions are often overlooked.²³−¹⁸ In comparing KHCO₃ and KCl, one of the most important differences is their buffering capacity, where KHCO₃ is a buffered electrolyte but KCl is not. The buffered electrolyte could compensate for the hydroxide ions (OH⁻) produced by CO₂R and HER and maintain the electrode surface pH close to the bulk value during the electrolysis.²³−²⁴ Minimizing the pH difference between the surface and the bulk can minimize polarization losses¹⁵ as well as affect the product distribution.²⁵ The authors have recently found that the methane (CH₄) production rate from CO₂R is significantly increased by simply using 0.5 M KHCO₃ instead of 0.5 M KCl with a polycrystalline copper (Cu) catalyst.¹⁷ This strongly indicates...
that the choice of a buffered electrolyte such as 0.5 M KHCO₃ is one of the important factors in increasing the reaction rate of CO₂R, although the origins of such an enhancement remain unknown. To obtain a comprehensive understanding of how the choice of electrolyte affects the activity and selectivity of CO₂R, a detailed analysis of the electrolyte speciation and concentrations, including the pH and CO₂ concentration near the electrode surface, is required.

In this study, the effects of buffered electrolytes were investigated using both experimental and simulation approaches. The limiting reaction rates of CO₂, \( J_{\text{lim}} \), defined by the authors in a previous report, were determined at various partial CO₂ pressures (\( P_{\text{CO}_2} \)) and electrolyte compositions were obtained both experimentally and from a one-dimensional (1-D) model. The model enables one to examine concentrations and effects at and near the electrode surface and is used to explain the experimental trends in \( J_{\text{lim}} \) vs \( P_{\text{CO}_2} \).

**EXPERIMENTAL SECTION**

For all of the experiments in this study, a “combinatorial system” is used to perform eight experiments in parallel with changing parameters such as the stirring speed, reaction voltage (or current density), \( P_{\text{CO}_2} \), and temperature. More details about this system are described in our previous report. We used strip-shaped Cu plates (Nilaco, Japan, 99.99%) with an active surface area of 1 cm² as the cathode electrode for CO₂R. The surface was chemically polished using a mixture of nitric acid (3720, Aldrich, US) and phosphoric acid (S-710, Sasaki Chemical, Japan). Platinum wire (BAS, Japan) was used as the anode electrode, and saturated Ag/AgCl (Corr instruments, US) was used as the reference electrode. Each cell was divided into cathode and anode compartments with Naflon 424 (Aldrich, US). The cathode electrolytes were 0.5 M KCl (Wako, Japan) or 0.5 M KHCO₃ or a 1 M phosphate buffer solution (0.7 M K₂HPO₄/0.3 M KH₂PO₄), whereas the anode electrolyte was the same at 3.0 M KHCO₃ (Wako, Japan). The phosphate buffer species were chosen to yield a bulk pH of around 7 in the absence of CO₂.

Prior to an experiment, each reactor was first bubbled with Ar and then with CO₂, each for 60 min at a flow rate of 125 sccm (standard cubic centimeters per minute). The reactors were then pressurized with CO₂ to the experimental values. Electrochemical measurements were performed to ascertain the current density while also controlling the stirring speed inside the reactor. Galvanostatic measurements with BT2000 (Arbin, US) multichannel potentiostats were performed up to 100 °C, with a different current density set in each reactor used to obtain the current density dependence of the product distribution for each single experimental condition. All experiments were done at 25 °C. After the measurements, gas samples were transferred to a 7890A (Agilent, CA, USA) gas chromatograph (GC), which quantitatively analyzed the reaction products (TCD for hydrogen (H₂) and FID for CO (with methanizer), CH₄, and ethylene (C₂H₄)). For the analysis of liquid samples, we used a Prominence (Shimadzu, Japan) high-performance liquid chromatograph (HPLC) for HCOO⁻ detection and a GC-17A (Shimadzu, Japan) with a TurboMatrix (PerkinElmer, MA, USA) headspace system (HS-GC) for the detection of aldehydes and alcohols. The Faradaic efficiency (FE) is determined by dividing the charge ascribed to each product by the total charge passed. The reaction rate of CO₂, \( J_{\text{CO}_2} \), is given by

\[
J_{\text{CO}_2} = \frac{1}{F} \sum_{p} \left( \sum_{i} \frac{n_i J_{\text{CD}}}{z_i} \right)
\]

where \( z \) and \( n \) represent the numbers of electrons and reactants necessary for the reaction, respectively, and \( F \) represent Faraday’s constant. Subscript \( p \) denotes a reaction product from CO₂, and \( i_{\text{CD}} \) is the partial current density of each product (the product of the total current density and FE). \( J_{\text{lim}} \) is determined as the maximum value of \( J_{\text{CO}_2} \) as plotted against current density.

**Simulation.** A one-dimensional, isothermal, steady-state model simulates the hydrodynamic boundary layer region near the electrode (see Figure 1). The boundary layer thickness was set to be 100 μm for the base case and varied to examine boundary-layer thickness effects. There is no convection within the hydrodynamic boundary layer, and the double-layer region, where electroneutrality does not hold, is neglected as it is very thin in these electrolytes. The species in the system are dissolved CO₂, K⁺, H⁺, OH⁻, HCO₃⁻, CO₃²⁻, and CO₂. Additionally, there is Cl⁻ for KCl electrolyte and H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻ for the potassium-phosphate buffer electrolyte.

The flux of each species, \( N_j \), is calculated using the Nernst–Planck equation, accounting for migration and diffusion,

\[
N_j = -D_j \nabla c_j - z_j \frac{D_j}{RT} F c_i \nabla \phi_i
\]

where \( D_j \), \( c_j \), and \( z_j \) are the diffusivity, concentration, and charge of species \( i \), respectively, and \( \phi_i \) is the liquid potential.

Component balances at steady state yield

\[
\nabla N_i = R_i
\]

where \( R_i \) is the source term for species \( i \). Within the electrolyte, the bicarbonate acid/base, phosphate acid/base (for phosphate
buffer cases, and water-dissociation reactions contribute to the source term according to

$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-, \quad K_i = 10^{-6.35}$$

$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}, \quad K_2 = 10^{-10.33}\text{M}$$

$$\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^-, \quad K_3 = K_i/K_w$$

$$\text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{CO}_3^{2-}, \quad K_4 = K_2/K_w$$

$$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}, \quad K_5 = 10^{-7.21}\text{M}^{-1}$$

$$\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}, \quad K_6 = 10^{-12.32}\text{M}^{-1}$$

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- , \quad K_w = 10^{-14}\text{M}$$

where $k_i$ and $k_j$ are the forward (left to right) and reverse (right to left) rate constants and $K_i$ is the equilibrium coefficient for reaction $j$. The forward rate constants for the bicarbonate acid/base and water dissociation reactions are listed in Table S1. The mechanism and causality are not definitively determined. There are two possible explanations for this phenomenon: (1) The anion in the electrolyte ($\text{Cl}^-$ vs $\text{HCO}_3^-$) is affecting the kinetics of the reaction, possibly by interacting with reaction intermediates on the catalyst surface. (2) The buffering capacity of $\text{KHCO}_3$ is affecting the species concentration near the electrode surface, in particular, changing the pH and the concentration of $\text{CO}_2$ at the electrode surface. To investigate the mass-transport effects of this system, the pressure dependence of the limiting $\text{CO}_2$ flux (the rate of $\text{CO}_2$ consumption where the $\text{CO}_2$ mass transport is the rate-determining step ($\text{CO}_2$ limited conditions)) for the two electrolytes is compared. Under $\text{CO}_2$ limited conditions, the rate of $\text{CO}_2$ consumption should be independent of catalyst kinetics, allowing a direct comparison of mass-transport limitations of systems with different electrolytes.

Since $\text{Cu}$ reduces $\text{CO}_2$ to multiple products requiring different numbers of electrons, we cannot directly compare the limiting current density (LCD) between cases. Instead of LCD, we use our previously defined limiting rate of mass transport ($J_{\text{lim}}$) to characterize the maximum rate of $\text{CO}_2$ consumption. $J_{\text{lim}}$ describes the rate of $\text{CO}_2$ flux to the electrode surface under limiting conditions (i.e., the local $\text{CO}_2$ concentration becomes zero). Under $\text{CO}_2$ limited conditions, the rate of $\text{CO}_2$ flux to the electrode surface should be equal to the rate of $\text{CO}_2R$.

Table 1. Boundary Conditions for the 1-D Models

<table>
<thead>
<tr>
<th>Condition</th>
<th>100% CH$_4$ model</th>
<th>Constant current density model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode boundary</td>
<td>$c_{\text{CO}_2} = 0$</td>
<td>$c_{\text{CO}_2} = 0$</td>
</tr>
<tr>
<td></td>
<td>$N_{\text{OH}^-} = -8N_{\text{CO}_2}$</td>
<td>$N_{\text{OH}^-} = -i_T/F$</td>
</tr>
<tr>
<td></td>
<td>$N_i = 0, i \neq \text{CO}_2, \text{OH}^-$</td>
<td>$N_i = 0, i \neq \text{CO}_2, \text{OH}^-$</td>
</tr>
<tr>
<td>Bulk electrolyte boundary</td>
<td>$N_i = -k_i(c_i - c_i^0)$</td>
<td>$\phi = 0$</td>
</tr>
</tbody>
</table>

In Figure 1, the model simulates the mass transport of each species within the boundary layer between the catalyst surface (point A, local) and the bulk electrolyte (point B, bulk). As stated above, different conditions were modeled, including the experimentally

![Figure 2](image-url)
used conditions (0.5 M KCl and 0.5 M KHCO₃) as well as two additional cases (1 M phosphate buffer (mixture of 0.3 M KH₂PO₄ and 0.7 M K₂HPO₄) and 1.5 M KHCO₃) to demonstrate how using an electrolyte with a stronger buffer capacity might improve CO₂ transport to the catalyst surface. It should be noted that a direct comparison of the two buffers is complicated by the fact that CO₂ will always result in some bicarbonate buffering as shown in Figure S2. Figure 3a shows the simulation result of the \( P_{\text{CO₂}} \) dependence of \( J_{\text{lim}} \). Comparing the different electrolytes, one can see that for both the bicarbonate and phosphate buffers \( J_{\text{lim}} \) initially follows Fick’s law at low CO₂ reaction rates (low \( P_{\text{CO₂}} \)), with the phosphate buffer and 1.5 M KHCO₃ system deviating from Fick’s law at a slightly higher \( P_{\text{CO₂}} \) compared to 0.5 M KHCO₃ and 0.5 M KCl. In contrast, \( J_{\text{lim}} \) for KCl increases proportionally with \( P_{\text{CO₂}} \) with a slope much smaller than that expected by Fick’s law (i.e., diffusion without reactions). Comparing Figures 2 and 3a, the simulation qualitatively reproduces the nonlinear behavior of \( J_{\text{lim}} \) seen in experiments with 0.5 M KHCO₃. As shown in Figure 3b,c, this behavior is derived from the changes in pH and local CO₂ concentration. The CO₂ concentration profile deviates from Fick’s law in both electrolytes, with a smaller slope (i.e., smaller CO₂ flux) near the electrode surface compared to what is predicted from Fick’s law. This slope determines the rate of CO₂ supplied to the electrode, \( J_{\text{lim}} \). The deviation from Fick’s law is caused by the consumption of CO₂ by OH⁻ produced during the electron-transfer reactions (for each electron consumed, one OH⁻ is produced). As shown in Figure 3c, the bulk pH values in 0.5 M KCl and 0.5 M KHCO₃ under CO₂ saturation are \( \sim 3.6 \) and \( \sim 7.0 \), respectively, which agree with experimental observations.¹⁶,²⁸ However, as the electrode surface is approached, the pH in both electrolytes increases significantly. Considering acid/base reactions, CO₂ is less likely to be present under alkaline conditions (see reactions above),¹⁵ where OH⁻ produced through CO₂R reacts with CO₂ to produce HCO₃⁻ and CO₃²⁻, which are generally considered not to be reactants for CO₂R.²⁴ In a buffered system (e.g., KHCO₃), the pH within the boundary layer can be somewhat maintained to remain close to the bulk pH. In contrast, for the unbuffered KCl system, the pH near the electrode is drastically increased (Figure 3c). These pH effects and the impact of the buffering capacity can be used to explain the other curves in Figure 3a. Using a stronger buffer, either higher-concentration bicarbonate buffer or phosphate buffer, \( J_{\text{lim}} \) further increases and approaches Fick’s law due to the lower pH attained at the surface of the electrode (see Figure 3c).

To explore these effects in more detail, \( J_{\text{lim}} \) is normalized by the value estimated under Fick’s law and plotted as a function of the pH difference from bulk electrolyte to electrode surface.

Figure 3. (a) Model results (assuming 100% conversion of CO₂ to CH₄) of CO₂ pressure dependence of \( J_{\text{lim}} \) in four different electrolytes; the dotted line indicates the assumption of Fick’s law. (b) CO₂ concentration and (c) pH within the 100 μm boundary layer at \( P_{\text{CO₂}} \) of 2 atm.
under the CO₂ mass-transport-limited conditions in Figure 4. This figure clearly illustrates the general linkage between the buffering property of the electrolyte and the limiting rate of CO₂R. Figure 4 predicts that the buffer strength of the electrolyte is one of the design guidelines to achieving a high reaction rate in CO₂R, where the mass transport of CO₂ is one of the rate-determining factors. Interestingly, while both 1 M phosphate buffer and 1.5 M KHCO₃ give a limiting flux greater than 60% maximum flux (Fick’s law prediction) and maintain the surface pH to be within 4 units of the bulk pH, they do not follow the same trend. The reason for this is the difference in pH profiles for 1.5 M KHCO₃ and 1 M phosphate buffer (Figure 3c), we can see that bicarbonate buffer maintains the pH near 10, while phosphate buffer electrolyte has two distinct regions of stable pH: one near pH 7.5 and the other near pH 11. These results indicate that both the buffering capacity and the pH values of the buffer chosen can affect the pH and therefore the CO₂ supply to the electrode.

From the simulation results shown above, phosphate buffer could be better than KCl and KHCO₃ in terms of CO₂ mass transfer due to its stronger buffer capacity and its ability to react with the produced hydroxide without impacting the CO₂ from the bicarbonate equilibrium directly (i.e., it in essence helps to decouple these phenomena). To see the effect of phosphate buffer experimentally, a series of experiments with varying P_CO₂ in 1 M phosphate buffer solution shows a downward-convex shape and the value of J_lim in each P_CO₂ is less than that in 0.5 M KHCO₃ as shown in Figure 5. This behavior is different than that predicted, indicating that other factors may be occurring, including perhaps not 100% conversion to methane and also possibly the existence of unaccounted for phenomena such as differences in catalyst selectivity due to phosphate interactions, which has been witnessed on copper previously.

While 100% CH₄ is the most ideal case, it is known that the current catalysts produce various reduction species including H₂, CO, and C₂H₂. Except for HCOO⁻, all of the other electron-transfer products produce one OH⁻ per e⁻ consumed, which impacts the local pH at the electrode surface. For example, Figure S5 shows how the limiting CO₂ flux increases with CH₄ FE assuming that the catalyst produces only CH₄ and H₂ for the 1 M phosphate buffer case at 1 atm CO₂ assuming that the local CO₂ concentration at the electrode is 0. The total current density decreases as CH₄ FE increases since it switches from a two-electron process for HER to an eight-electron process for CH₄ production. The lower total current density produces less OH⁻, which explains the increase in limiting CO₂ flux and highlights the importance of the overall hydroxide generation rate.

To account for the selectivity and better match the experimental conditions, we considered a model where the total current density was fixed without specifying the product distribution (i.e., the OH⁻ flux is linearly proportional to the total current density). For the total current density, 90 mA/cm² was chosen as it represented the total current density at which maximum CO₂ flux was achieved during experiments (see Figure S3). Figure 6a shows the comparison of the simulation results between the 100% CO₂R model and constant OH⁻ flux models for a boundary layer thickness of 100 μm. As previously discussed, J_lim shows a concave dependence on P_CO₂ for the 100% CO₂R model but downward-convex behavior with pressure for the constant OH⁻ flux model. The difference is due to the way in which the pH changes with current density in that the current and thus OH⁻ production are increasing with the 100% CH₄ model, whereas it is fixed in the 90 mA/cm² case. These results highlight the importance of how the model can be used to perhaps diagnose what is occurring near the surface in terms of pH and FE. The crossover point between the models is associated with the case of 90 mA/cm² being the limiting current density for 100% CO₂R to CH₄. Moreover, as shown in Figure 6b, the pressure dependence of J_lim is significantly affected by the boundary-layer thickness, where J_lim exhibits a linear shape at a thickness of 50 μm but becomes nonlinear at 100 and 150 μm. This result shows that the thickness of the boundary layer is also responsible for the qualitative behavior of the pressure dependence of J_lim with a constant OH⁻ flux model.
To explore the impact of buffer capacity in more detail using this model, different buffers and buffer concentrations associated with bulk pH (see Figure S2) are made in a fashion similar to that of the simulations above. This provides a good comparison since the total hydroxide generation flux is constant at the total current density and thus the differences in $J_{\text{lim}}$ can also be correlated to different FEs. As Figure 7a shows, the normalized $J_{\text{lim}}$ by Fick’s law (similar to Figure 4) as a function of $P_{\text{CO}_2}$ for various buffer concentrations and identities demonstrates different shapes. Obviously, the increase in buffer concentration plays an important role in controlling the local $\text{CO}_2$ concentration and decreasing the impact of hydroxide, thereby enabling a much more Fickian response. In terms of concentrations, small amounts of bicarbonate result in less buffer capacity, which results in lower performance. As shown in the figure, this effect is sensitive to the $\text{CO}_2$ concentration since increased $\text{CO}_2$ results in increased $\text{HCO}_3^-$ and thus increased buffering capacity. Such a trend is not as strong with phosphate because of the additional interactions and $pK_a$ differences. Figure 7a also demonstrates how the identity of the phosphate buffer impacts $J_{\text{lim}}$. From Figure S2, changing the ratio of $\text{K}_2\text{HPO}_4$ and $\text{KH}_2\text{PO}_4$ with the same amount of phosphate results in different bulk pH values due to the buffer, which is also impacted by the effective bicarbonate concentration and its buffering by dissolved $\text{CO}_2$ (see Figure S2). Thus, the shaded region in Figure 7a indicates how the initial composition and bulk pH of phosphate buffer impact $J_{\text{lim}}$, which have a larger impact at higher concentrations of $\text{K}_2\text{HPO}_4$ (i.e., higher effective bicarbonate concentration under a $\text{CO}_2$ atmosphere), eventually resulting in a constant offset as the
increased $P_{CO_2}$ results in more bicarbonate buffering. Finally, there is a question about how the kinetics of the buffer reactions (see Table S1 and equations above) impact the value of $J_{lim}$. As shown in Figure 7b, as the kinetics are decreased for the phosphate buffer reaction, $J_{lim}$ decreases since it is harder for the buffer to mitigate the impact of the constant hydroxide rate, which decreases the CO$_2$ concentration close to the electrode. At very low rates, the phosphate essentially no longer buffers and the response is similar to no buffer (e.g., KCl) or low bicarbonate concentration, which could also explain some of the differences between experiment and the model. It is important to note that even at the higher rates that are taken from the general literature, equilibrium between CO$_2$ and bicarbonate is not achieved next to the electrode surface (see Figure S4) and in fact varies significantly. These findings highlight that the assumption of equilibrium for the acid/base reactions is incorrect and that there is a need to measure the buffer kinetics in solutions of interest.

As noted above, the boundary-layer thickness is an important factor in determining the behavior of CO$_2$ mass transport and local CO$_2$ concentration at the electrode surface. It is expected that one can alter the boundary-layer thickness due to convection as well as just due to hydrogen or other gaseous-product formation. To explore this aspect further in terms of analyzing the experimental data, one can calculate the effective boundary-layer thickness for the limiting current or the effective CO$_2$ surface concentration using the model and the total current density. Table S2 shows such results from the experimental data of $J_{lim}$ and the measured H$_2$ FE in 0.5 M KCl and KHCO$_3$ solutions. From the calculations, it is clear that the boundary-layer thickness is on the order of 100 $\mu$m or so but does vary, so the assumption of a 100 $\mu$m boundary layer may not be fully correct. This variation is due to either the simplified model or perhaps the effect of the bubbles of H$_2$ or other gaseous products, which is considered to affect the boundary-layer thickness. In addition, in agreement with Figure 2, the current density is much higher for KHCO$_3$ than for KCl because of its buffering capacity, although it is interesting that the boundary layer is relatively the same between cases, with it being somewhat thinner for KHCO$_3$ due to the higher current densities and thus higher HER rates. The similarity in boundary-layer thicknesses also demonstrates that the model is capturing the salient physics.

**CONCLUSIONS**

In this article, we have demonstrated how the electrolyte buffer capacity and identity in terms of $pK_a$ affect CO$_2$ transport within the boundary layer and the local CO$_2$ concentration available at the electrode surface for CO$_2$R$_e$. The simple transport model agreed with experimental trends in maximum flux seen for CO$_2$R$_e$ on Cu in different electrolytes, although a deviation from the experiment thought to be kinetic in origin existed when a phosphate buffer was used. By comparing the limiting CO$_2$ flux at different $P_{CO_2}$ values in KCl and KHCO$_3$, we observe that both systems deviate from Fick's law and KHCO$_3$ gives a higher CO$_2$ flux than does the KCl electrolyte due to the improved CO$_2$ flux in KHCO$_3$ caused by the buffering capacity of bicarbonate, leading to a slower increase in local pH and slower homogeneous consumption of CO$_2$ by OH$^-$. This is especially important at high current densities where OH$^-$ ions are produced in large quantities. The model results showed that the $pK_a$ value significantly affects the shape of the pH profile within the boundary layer, which can also be impacted by overall buffer concentrations and kinetics, where equilibrium is not achieved next to the electrode surface. Finally, we considered the case where we increased the $P_{CO_2}$ at a constant total current density and showed that increasing bicarbonate concentration at low pressures (<~2.5 atm) is more effective at improving CO$_2$ transport when the target product (i.e., CH$_4$) faradaic efficiency remains high; at high pressures (>~2.5 atm), however, CO$_2$ transport is improved more rapidly with increased $P_{CO_2}$ when the total current density is held constant. This analysis and approach provide insights for how buffer electrolytes affect the mass transport of CO$_2$ within the system.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b11316.

Rate constants and additional boundary-layer simulation results, supplemental experimental results, pH calculation of phosphate buffer, calculation of the equilibrium within the boundary layer, and the impact of methane faradaic efficiency on the total current density using the limiting-current model. The raw data for all figures is also given or referenced. (PDF)

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**Notes**

The authors declare no competing financial interest.

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