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Effects of Electrolyte Buffer Capacity on Surface Reactant Species and Reaction Rate of CO$_2$ in Electrochemical CO$_2$ Reduction

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<Abstract>

In the aqueous electrochemical reduction of CO$_2$, 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 resulting reaction rate of CO$_2$ with varying partial CO$_2$ pressure. Electrolytes investigated include KCl (non-buffered), KHCO$_3$ (buffered by bicarbonate), and phosphate buffered electrolytes. Assuming 100% methane production, the simulation successfully explains the experimental trends of maximum CO$_2$ flux in KCl and KHCO$_3$, and also highlights the difference between KHCO$_3$ and phosphate in terms of pKa as well as the impact of 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 optimize CO$_2$ reduction in aqueous environments.
Electrochemical CO$_2$ reduction (CO$_2$R) is one of the key technologies to realize a sustainable society by converting emitted CO$_2$ to useful chemicals and fuels if combined with surplus energy sources like solar or wind power. For decades, a number of researchers have shown that some transition metals can catalyze CO$_2$ to more reduced products like carbon monoxide (CO), formic acid or formate (HCOOH or HCOO$^-$, respectively), hydrocarbons, alcohols, and other organic materials\textsuperscript{1-4} that can be used for renewable chemicals and fuels.\textsuperscript{5,6}

Although a variety of useful chemicals can be produced from CO$_2$, selectivity control for the desired product is still difficult in CO$_2$R, especially highly reduced products such as hydrocarbons and alcohols.\textsuperscript{3} Moreover, the necessary high surface overpotential and possible competing reactions such as hydrogen-evolution reaction (HER) are problems that prevent practical application of this technology.\textsuperscript{7} One route towards overcoming these problems is to make an efficient catalyst that lowers the overpotential with high selectivity for CO$_2$R.\textsuperscript{8-11} Another way is to manipulate the system parameters to realize the optimum condition for CO$_2$R catalyst, which has been shown to affect significantly the rate and selectivity of CO$_2$R reaction.\textsuperscript{7, 12-17}

Among the parameters that affect the property of CO$_2$R, the electrolyte composition is known to be an important factor. In this research field, potassium bicarbonate (KHCO$_3$) and potassium chloride (KCl) solutions are the most commonly used aqueous electrolytes.\textsuperscript{1, 18-20} While it is evident that the selectivity of CO$_2$R is extremely sensitive to the local conditions and concentrations, properties of the ionic electrolytes in controlling these conditions are often
overlooked. In comparing KHCO₃ and KCl, one of the most important differences is their buffering capacity, where KHCO₃ is a buffered electrolyte while 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. Minimizing the pH difference between surface and the bulk can minimize polarization losses, as well as affect the product distribution. 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. This strongly indicates that the choice of a buffered electrolyte like 0.5 M KHCO₃ is one of the important factors to increase 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, CO₂ concentration, etc, 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, \( J_{lim} \), defined by the authors in a previous report, at various partial CO₂ pressures (\( P_{CO_2} \)) 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 of \( J_{lim} \) vs \( P_{CO_2} \).

<Experimental>
For all of the experiments in this study, a “combinatorial system” is used to perform eight experiments in parallel with changing parameters such as stirring speed, reaction voltage (or current density), $P_{CO_2}$, and temperature. More details about this system are described in our previous report.\textsuperscript{16} We used strip-shaped Cu plates (Nilaco, Japan, 99.99%) with an active surface area of 1 cm$^2$ as the cathode electrode for CO$_2$R. The surface was chemically polished using a mixture of nitric acid 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 Nafion 424 (Aldrich, US). The cathode electrolytes were 0.5 M KCl (Wako, Japan) or 0.5 M KHCO$_3$ or a 1 M phosphate buffer solution (0.7 M K$_2$HPO$_4$; 0.3 M KH$_2$PO$_4$), whereas the anode electrolyte was the same at 3.0 M KHCO$_3$ (Wako, Japan). The phosphate buffer species were chosen to yield a bulk pH of around 7 in the absence of CO$_2$.\textsuperscript{25}

Prior to an experiment, each reactor was first bubbled with Ar and then with CO$_2$, each for 60 min and with a flow rate of 125 sccm (standard cubic centi meter per minute). The reactors were then pressurized with CO$_2$ 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) multi-channel 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 (H$_2$), and FID for CO (with methanizer), CH$_4$, and ethylene (C$_2$H$_4$)). For the analysis of liquid samples, we used a Prominence
(Shimadzu, Japan) high-performance liquid chromatography (HPLC) for HCOO detection and a GC-17A (Shimadzu, Japan) with a TurboMatrix40 (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, \( J_{CO2} \), is given by

\[
J_{CO2} = \frac{n \times i_{PCD}}{z} \sum_p \frac{\dot{i}_p}{\dot{\xi}} = \frac{1}{F} \sum_p \frac{\dot{i}_p}{\dot{\xi}}
\]

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

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 \( \mu \)m 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 CO$_2$, K$^+$, H$,\text{OH}$$^\text{-}$, HCO$_3$$^\text{-}$, CO$_3$$^{2-}$. Additionally, there is Cl$$^\text{-}$$ for KCl electrolyte, and H$_2$PO$_4$$^\text{-}$, HPO$_4$$^{2-}$, and PO$_4$$^{3-}$ for the potassium-phosphate buffer electrolyte.

The flux of each species, $N_i$, is calculated using the Nernst-Planck equation, accounting for migration and diffusion,

$$N_i= -D_i \nabla c_i - z_i \frac{D_i}{RT} F c_i \nabla \phi_l$$ (2)

where $D_i$ and $c_i$, and $z_i$ are the diffusivity, concentration, and charge of species $i$, respectively, and $\phi_l$ is the liquid potential.

Component balances at steady state yield

$$\nabla \cdot N_i = R_i$$ (3)

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

$$-\dot{i}, K_1 = 10^{-6.35}$$
$$+\dot{i} + HCO_3/$$
$$C O_2 + H_2 O k_1, k_{-1} H/i$$
$$2-\dot{i}, K_2 = 10^{-10.33} M$$
$$+\dot{i} + CO_3/$$
$$-\dot{i} k_2, k_{-2} H/i$$
$$HC O_3/$$
$$-\dot{i}, K_3 = K_i / K_w$$
$$-\dot{i} k_3, k_{-3} HC O_3/$$
$$C O_2 + O H/i$$
2. \( K_4 = K_2 / K_w \)  
\(-i \cdot k_4, k_{-4} \cdot H_2O + CO_3^{\text{-}} \)
\(-i \cdot O \cdot H^{\text{+}} \)
\( \text{HCO}_3^{\text{-}} \)

2. \( K_5 = 10^{-7.21} \text{ M}^{-1} \)
\(+i \cdot HP \cdot O_4^{\text{+}} \)
\(-i \cdot k_5, k_{-5} \cdot H^{\text{+}} \)
\( \text{H}_2 \text{PO}_4^{\text{-}} \)

3. \( K_6 = 10^{-12.32} \text{ M}^{-1} \)
\(+i \cdot PO_4^{\text{3-}} \)
\(-i \cdot k_6, k_{-6} \cdot H^{\text{+}} \)
\( \text{HPO}_4^{\text{2-}} \)
\(+i \cdot O \cdot H^{\text{+}}, K_w = 10^{-14} \text{ M}^2 \)  
\( i \cdot \text{H}_2 \text{O} \)  
\( k_{w} \)

where \( k_j \) and \( k_j \) are the forward (left to right) and reverse (right to left) rate constants and \( K_j \) 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.\(^{26} \) We assumed equilibrium for the phosphate buffer reactions and take the rate constants, \( k_5, k_6 \) to be large (\( 10^6 \text{ s}^{-1} \)). The backwards rate constants are then calculated from the relationship

\[
k_{\text{-}j} = \frac{k_j}{K_j}
\]  

Two conditions were investigated: (1) 100% CH\(_4\) conversion, and (2) 90 mA/cm\(^2\) total current density. The boundary conditions are listed in Table 1, where \( i_T \) is the total current density (set to 90 mA/cm\(^2\) based on experimental data, Figure S3), \( k_m \) is the mass-transfer coefficient of species \( i \) at the bulk electrolyte/boundary layer boundary. \( k_m \) is taken to be a
large value, and estimated using \( \frac{D_i}{1 \mu m} \), to allow fast equilibration for each species with its bulk concentration.

The set of differential and algebraic equations are solved simultaneously using the MUMPS solver in COMSOL 5.2a. Instability occurs at high current densities so we solve low current density conditions first and use them as the initial guesses for high current-density conditions.

<Results and Discussions>

While it is known that the use of KHCO\(_3\) results in higher FE as a function of current density compared to KCl (see Figure S1), the mechanism and causality are not definitively determined. There are two possible explanations for this phenomenon: (1) The anion in the electrolyte (Cl\(^-\) vs HCO\(_3^-\)) is affecting the kinetics of the reaction, possibly by interacting with reaction intermediates on the catalyst surface,\(^ {27}\) (2) The buffering capacity of KHCO\(_3\) is affecting species concentration near the electrode surface, in particular changing the pH and the concentration of CO\(_2\) at the electrode surface. To investigate the mass-transport effects of this system, the pressure dependence of the limiting CO\(_2\) flux (the rate of CO\(_2\) consumption where the CO\(_2\) mass-transport is rate-determining-step (CO\(_2\) limited conditions)) for the two electrolytes is compared. At CO\(_2\) limited conditions, the rate of CO\(_2\) consumption should be independent of catalyst kinetics, allowing a direct comparison of mass-transport limitations of systems with different electrolytes.
Since Cu reduces CO$_2$ to multiple products requiring different number 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 CO$_2$ consumption. $J_{\text{lim}}$ describes the rate of CO$_2$ flux to the electrode surface at limiting conditions (i.e. local CO$_2$ concentration becomes zero). At CO$_2$ limited conditions, the rate of CO$_2$ flux to the electrode surface should be equal to the rate of CO$_2$R. Figure 2 shows the pressure dependent $J_{\text{lim}}$ in 0.5 M KHCO$_3$ and 0.5 M KCl electrolyte. As seen from the figure, $J_{\text{lim}}$ in KHCO$_3$ is higher than in KCl at the same $P_{\text{CO2}}$. Moreover, the data points for $J_{\text{lim}}$ in KHCO$_3$ increases nonlinearly with $P_{\text{CO2}}$, whereas in KCl, $J_{\text{lim}}$ increases almost linearly from the zero point, consistent with our previous report. This indicates that the behavior of $J_{\text{lim}}$ in KHCO$_3$ could not be simply explained by the dissolved amount of CO$_2$ increasing with pressure, in which case $J_{\text{lim}}$ should increase proportionally with CO$_2$ concentration in the electrolyte according to Fick’s and Henry’s laws.

To investigate further the origin of such characteristic behavior of $J_{\text{lim}}$ in KHCO$_3$ and KCl electrolyte, a 1-D simulation model was employed assuming 100% CH$_4$ production from CO$_2$. As shown in Figure 1, the model simulates mass transport of each species within the boundary layer between the catalyst surface (point A, local) and bulk electrolyte (point B, bulk). As stated above, different conditions were modeled including the experimentally used conditions: 0.5 M KCl and 0.5 M KHCO$_3$, as well as two additional cases: 1 M phosphate buffer (mixture of 0.3 M KH$_2$PO$_4$ and 0.7 M K$_2$HPO$_4$) and 1.5 M KHCO$_3$, to demonstrate how using an electrolyte with a stronger buffer capacity might improve CO$_2$ transport to the catalyst surface. It should be noted that a direct comparison of the two buffers is complicated by the fact that CO$_2$ will always result in some bicarbonate buffering as shown in Figure S2. Figure 3a shows the simulation result of $P_{\text{CO2}}$
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 CO$_2$ reaction rates (low $P_{\text{CO}_2}$), with the phosphate buffer and 1.5 M KHCO$_3$ system deviating from Fick’s law at a slightly higher $P_{\text{CO}_2}$ compared to 0.5 M KHCO$_3$ and 0.5 M KCl. In contrast, $J_{\text{lim}}$ for KCl increases proportionally with $P_{\text{CO}_2}$ with a slope much smaller than that expected by Fick’s law (i.e., diffusion without reactions). Comparing Figure 2 and Figure 3a, the simulation qualitatively reproduces the nonlinear behavior of $J_{\text{lim}}$ seen in experiments with 0.5 M KHCO$_3$. As shown in Figure 3b and 3c, this behavior is derived from the changes in pH and local CO$_2$ concentration. The CO$_2$ concentration profile deviates from Fick’s law in both electrolytes, with a smaller slope (i.e. smaller CO$_2$ flux) near the electrode surface compared to what is predicted from Fick’s law. This slope determines the rate of CO$_2$ supplied to the electrode, $J_{\text{lim}}$. The deviation from Fick’s law is caused by the consumption of CO$_2$ by OH$^-$ produced during the electron transfer reactions (for each electron consumed one OH$^-$ is produced). As shown in Figure 3c, the bulk pH in 0.5 M KCl and 0.5 M KHCO$_3$ at CO$_2$-saturated condition is ~3.6 and ~7.0, respectively, which agree with experimental observations.$^{16, 28}$ However, as the electrode surface is approached, the pH in both electrolytes rises significantly. Considering acid/base reactions, CO$_2$ is less likely to be present at alkaline conditions (see reactions above),$^{15}$ where OH$^-$ produced through CO$_2$R reacts with CO$_2$ to produce HCO$_3^-$ and CO$_3^{2-}$, which are generally considered not to be reactants for CO$_2$R.$^{24}$ In a buffered system (e.g. KHCO$_3$), the pH within the boundary layer can be somewhat maintained to remain close to bulk pH. In contrast, for the unbuffered KCl system, the pH near the electrode is drastically increased (Figure 3c). These pH effects and impact of 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 under the CO$_2$ mass-transport-limited conditions in Figure 4. This figure clearly illustrates the general linkage between buffering property of the electrolyte and the limiting rate of CO$_2$R. Figure 4 predicts that buffer strength of the electrolyte is one of the design guidelines to achieve high reaction rate in CO$_2$R, where the mass-transport of CO$_2$ is one of the rate-determining factors.$^{14,16}$ Interestingly, while both 1 M phosphate buffer and 1.5 M KHCO$_3$ give a limiting flux greater than 60% maximum flux (Fick’s law prediction), and maintains 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 pKa values for the two buffers. Comparing the pH profiles for 1.5 M KHCO$_3$ 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 pKa values of the buffer chosen can affect the pH, and therefore CO$_2$ supply to the electrode.

From the simulation results shown above, phosphate buffer could be better than KCl and KHCO$_3$ in terms of CO$_2$ mass-transfer due to its stronger buffer capacity and its ability to react with the produced hydroxide without impacting the CO$_2$ 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 $P_{\text{CO}_2}$ in 1 M phosphate buffer solution (0.7 M K$_2$HPO$_4$; 0.3 M KH$_2$PO$_4$) were conducted. Interestingly, the plot of $J_{\text{lim}}$ in phosphate buffer solution shows a downward-convex shape and the value of $J_{\text{lim}}$ in each $P_{\text{CO}_2}$ is less than
that in 0.5 M KHCO₃ as shown in Figure 5. This behavior is different than that predicted, indicating other factors may be occurring including perhaps not 100% conversion to methane and also possibly the existence of unaccounted phenomena such as differences in catalyst selectivity due to phosphate interactions, which has been witnessed on copper previously.²¹

While 100% CH₄ is the most ideal case, it is known that the current catalysts produce various reduction species including H₂, CO, C₂H₄, etc. 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 overall hydroxide generation rate.

To account for the selectivity and better match 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 6(a) shows the comparison of the simulation results between the 100% CO₂R to CH₄ and constant OH⁻ flux models for a boundary layer thickness of 100 μm. As previously discussed, Jₘₚₙ shows a concave dependence on P_CO₂ for the 100% CO₂R model, but a 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) is increasing with the 100% CH₄ model, whereas it is fixed in the 90 mA/cm² one. 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 6(b), the pressure dependence of $J_{\text{lim}}$ is significantly affected by the boundary-layer thickness, where $J_{\text{lim}}$ exhibits a linear shape at the thickness of 50 μm but becomes nonlinear at 100 and 150 μm. This result shows that the thickness of boundary layer is also responsible for the qualitative behavior of pressure dependence of $J_{\text{lim}}$ with 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 similar fashion to 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 7(a) 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 CO₂ concentration and decreasing the impact of hydroxide, thereby enabling a much more Fickian response. In terms of concentrations, low amounts of bicarbonate result in less buffer capacity, which results in lower performance. As shown in the Figure, this effect is sensitive to CO₂ concentration since increased CO₂ results in increased HCO₃⁻ and thus buffering capacity. Such a trend is not as strong with phosphate since due to the additional interactions and pKa differences. Figure 7(a) also demonstrates how the identity of the phosphate buffer impacts $J_{\text{lim}}$. 


From Figure S2, changing the ratio of K$_2$HPO$_4$ and KH$_2$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 CO$_2$ (see Figure S2). Thus, the shaded region in Figure 7(a) indicates how the initial composition and bulk pH of phosphate buffer impact $J_{\text{lim}}$, which have a larger impact at higher concentrations of K$_2$HPO$_4$ (i.e. higher effective bicarbonate concentration under CO$_2$ atmosphere) and eventually resulting in a constant offset as the increased $P_{\text{CO2}}$ 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 $J_{\text{lim}}$. As shown in Figure 7(b), as the kinetics are decreased for the phosphate buffer reaction, $J_{\text{lim}}$ decreases since it is harder for the buffer to mitigate the impact of the constant hydroxide rate, which decreases the CO$_2$ concentration near to the electrode. At very low rates, the phosphate essentially no longer buffers and a response similar to no buffer (e.g., KCl) or low bicarbonate concentration, which could as well 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 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 to determine 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
limiting current or the effective \( \text{CO}_2 \) surface concentration using the model and a total current density. Table S2 shows such results from the experimental data of \( J_{\text{lim}} \) and the measured \( \text{H}_2 \) \( \text{FE} \) 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 \( \mu \text{m} \) or so, but it does vary and so the assumption of 100 \( \mu \text{m} \) boundary layer may not be fully correct. This variation is either due to the simplified model or perhaps the effect of the bubbles of \( \text{H}_2 \) or other gaseous products which is considered to affect the boundary-layer thickness.\(^{29}\) In addition, in agreement with Figure 2, the current density is much higher for KHCO\(_3\) than KCl due to its buffering capacity, although it is interesting to note that the boundary layer is relatively the same between the 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 demonstrate as well that the model is capturing the salient physics.

<Conclusion>

In this paper, we have demonstrated how the electrolyte buffer capacity and identity in terms of pKa affects \( \text{CO}_2 \) transport within the boundary layer and the local \( \text{CO}_2 \) concentration available at the electrode surface for \( \text{CO}_2 \text{R} \). The simple transport model agreed with experimental trends of maximum flux seen for \( \text{CO}_2 \text{R} \) on Cu in different electrolytes, although a deviation from the experiment thought to be kinetic in origin existed when a phosphate buffer was used. Comparing the limiting \( \text{CO}_2 \) flux at different \( P_{\text{CO}_2} \) in KCl and KHCO\(_3\), we observe that both systems deviate from Fick’s law and KHCO\(_3\) gives a higher \( \text{CO}_2 \) flux than KCl electrolyte due to the improved \( \text{CO}_2 \) flux in KHCO\(_3\) caused by the buffering capacity of bicarbonate, leading to a slower increase in local pH and slower homogeneous consumption of \( \text{CO}_2 \) by \( \text{OH}^- \). This is
especially important at high current densities where $\text{OH}^\cdot$ ions are produced in large quantities. The model results showed that the pKa 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 $P_{\text{CO}_2}$ at a constant total current density, and showed that increasing bicarbonate concentration at low pressures ($< \sim 2.5 \text{ atm}$) is more effective in improving CO$_2$ transport when the target product (i.e. CH$_4$) faradaic efficiency remains high; at high pressures ($> \sim 2.5 \text{ atm}$) however, CO$_2$ transport is improved more rapidly with increased $P_{\text{CO}_2}$ when the total current density is held constant. This analysis and approach provides insights for how buffer electrolytes affect the mass-transport of CO$_2$ within the system.

<Supporting Information>

Additional information in the supporting information includes tables for rate constants and additional boundary-layer simulation results, supplemental experimental results, pH calculation of phosphate buffer, the calculation of equilibrium within boundary layer, and the impact of methane faradaic efficiency on total current density using the limiting-current model. The raw data for all figures is also given or referenced. This material is available free of charge via the Internet at http://pubs.acs.org.

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<References>


\[
\text{CO}_2 + \text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{CH}_4 + 8\text{OH}^-
\]

\[N_{OH} = 8N_{CO_2}\]

\[N_{CO_2}\]

**Boundary Layer**

**Bulk**

- $\text{K}^+$, $\text{HCO}_3^-$
- $\text{CO}_3^{2-}$, $\text{CO}_2$, $\text{H}^+$, $\text{OH}^-$
- $\text{CO}_2$ sat.
- 0.5 M $\text{K}^+$
- Species in equilibrium

A

B
Figure 1. Schematic illustration of 1-D simulation model assuming 100% CH₄ faradaic efficiency.
**Figure 2.** CO$_2$ pressure ($P_{CO_2}$) dependence of limiting rate of mass transport of CO$_2$ ($J_{lim}$) in 0.5M KHCO$_3$ (blue triangles) and 0.5M KCl (red squares) solutions (dotted lines are guides for the eye only).
Figure 3. (a) Model results (assuming 100% conversion of CO$_2$ to CH$_4$) of CO$_2$ pressure dependence of $J_{lim}$ in 4 different electrolytes; the dotted line indicates assuming Fick’s law. (b) CO$_2$ concentration and (c) pH within the 100 μm boundary layer at $P_{CO2}$ of 2 atm.
Figure 4. Relationship between normalized \( J_{\text{lim}} \) (to that expected from Fick’s law) and pH change within the boundary layer for 4 different electrolytes.
**Figure 5.** Experimental results of $P_{\text{CO}_2}$ dependence of $J_{\text{lim}}$ in 1 M phosphate buffer (orange circles) compared to 0.5 M KHCO$_3$ (blue triangles).
Figure 6 (a) Comparison of pressure dependence of $J_{\text{lim}}$ between 100% CO$_2$ reduction and constant OH$^-$ flux (corresponding to 90 mA cm$^{-2}$) models with the phosphate buffer solution and 100 μm boundary-layer thickness. (b) The effect of boundary-layer thickness on the pressure dependence of $J_{\text{lim}}$ using the constant OH$^-$ flux model with phosphate buffer solution.
Figure 7. Comparison of pressure dependence of $J_{\text{lim}}$ for (a) 0.5 and 1.5 M KHCO$_3$ and a range of 1 M phosphate from K$_2$HPO$_4$ to KH$_2$PO$_4$ (purple area) and (b) as a function of phosphate buffer kinetic rates (see equation 4) using 1 M K$_2$HPO$_4$. All simulations done assuming 90 mA/cm$^2$ total current density.
Table 1. Boundary conditions for the 1-D models.

<table>
<thead>
<tr>
<th></th>
<th>100% CH₄ model</th>
<th>Constant current density model</th>
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</thead>
<tbody>
<tr>
<td>Electrode boundary</td>
<td>$c_{CO_2}=0$</td>
<td>$c_{CO_2}=0$</td>
</tr>
<tr>
<td></td>
<td>$OH^{-}\dot{i} = -8 N_{CO_2}$</td>
<td>$OH^{-}\dot{i} = -i_l/F$</td>
</tr>
<tr>
<td></td>
<td>$N_{i}$</td>
<td>$N_{i}$</td>
</tr>
<tr>
<td></td>
<td>$N_{i}=0, i \neq CO_2, O H^i$</td>
<td>$N_{i}=0, i \neq CO_2, O H^i$</td>
</tr>
<tr>
<td>Bulk electrolyte bound</td>
<td>$N_{i} = -k_i</td>
<td>c_i - c_i^b</td>
</tr>
<tr>
<td></td>
<td>$\phi_{i}=0$</td>
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</table>

"TOC Graphic"
\[ \text{CO}_2 + \text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{CH}_4 + 8\text{OH}^- \]

\[ N_{\text{CH}_4} = 8N_{\text{CO}_2} \]

Species in equilibrium:
- \( \text{K}^+ \)
- \( \text{HCO}_3^- \)
- \( \text{CO}_3^{2-} \)
- \( \text{CO}_2 \)
- \( \text{H}_2\text{O} \)
- \( \text{OH}^- \)

\[ \text{CO}_2 \text{sat}, \ 0.5 \text{ M K}^+ \]

Graph:
- \( \lambda_{\text{ax}} \) (mol/cm² s)
- \( P_{\text{CO}_2} \) (atm)

- Constant current density model
- 100% \( \text{CH}_4 \) model