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

*Hiroshi Hashiba,¹ Lien-Chun Weng,^{2,3} Yikai Chen,⁴ Hiroki K. Sato,¹ Satoshi Yotsuhashi,¹
Chengxiang Xiang,⁴ Adam Z. Weber^{*2}*

¹ Advanced Research Division, Panasonic Corporation, Sōraku-gun, Kyoto 619-0237, Japan

² Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley,
CA 94720, USA

³ Department of Chemical and Biomolecular Engineering, University of California, Berkeley,
CA 94720, USA

⁴ Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, CA,
91125, USA

E-mail address: azweber@lbl.gov

<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 resulting reaction rate of CO₂ with varying partial CO₂ pressure. Electrolytes investigated include KCl (non-buffered), KHCO₃ (buffered by bicarbonate), and phosphate buffered electrolytes. Assuming 100% methane production, the simulation successfully explains the experimental trends of 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 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 CO₂ reduction in aqueous environments.

<Introduction>

Electrochemical CO₂ reduction (CO₂R) is one of the key technologies to realize a sustainable society by converting emitted CO₂ 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 CO₂ to more reduced products like carbon monoxide (CO), formic acid or formate (HCOOH or HCOO⁻, respectively), hydrocarbons, alcohols, and other organic materials¹⁻⁴ 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 highly reduced products such as hydrocarbons and alcohols.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.⁷ One route towards 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 condition for CO₂R catalyst, which has been shown to affect significantly the rate and selectivity of CO₂R reaction.^{7,}

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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, 18-20} 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

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3 overlooked.²¹⁻²³ In comparing KHCO_3 and KCl , one of the most important differences is their
4 buffering capacity, where KHCO_3 is a buffered electrolyte while KCl is not. The buffered
5 electrolyte could compensate for the hydroxide ions (OH^-) produced by CO_2R and HER, and
6 maintain the electrode surface pH close to the bulk value during the electrolysis.²⁴ Minimizing
7 the pH difference between surface and the bulk can minimize polarization losses,¹⁵ as well as
8 affect the product distribution.⁷ The authors have recently found that the methane (CH_4)
9 production rate from CO_2R is significantly increased by simply using 0.5 M KHCO_3 instead of
10 0.5 M KCl with a polycrystalline copper (Cu) catalyst.¹⁷ This strongly indicates that the choice
11 of a buffered electrolyte like 0.5 M KHCO_3 is one of the important factors to increase the
12 reaction rate of CO_2R , although the origins of such an enhancement remain unknown. To obtain
13 a comprehensive understanding of how the choice of electrolyte affects the activity and
14 selectivity of CO_2R , a detailed analysis of the electrolyte speciation and concentrations,
15 including the pH, CO_2 concentration, *etc*, near the electrode surface is required.
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34 In this study, the effects of buffered electrolytes were investigated using both
35 experimental and simulation approaches. The limiting reaction rates of CO_2 , J_{lim} , defined by the
36 authors in a previous report,¹⁶ at various partial CO_2 pressures (P_{CO_2}) and electrolyte
37 compositions were obtained both experimentally and from a one-dimensional (1-D) model. The
38 model enables one to examine concentrations and effects at and near the electrode surface and is
39 used to explain the experimental trends of J_{lim} vs P_{CO_2} .
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52 <Experimental>

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3 For all of the experiments in this study, a “combinatorial system” is used to perform eight
4 experiments in parallel with changing parameters such as stirring speed, reaction voltage (or
5 current density), P_{CO_2} , and temperature. More details about this system are described in our
6 previous report.¹⁶ We used strip-shaped Cu plates (Nilaco, Japan, 99.99%) with an active surface
7 area of 1 cm² as the cathode electrode for CO₂R. The surface was chemically polished using a
8 mixture of nitric acid and phosphoric acid (S-710, Sasaki Chemical, Japan). Platinum wire (BAS,
9 Japan) was used as the anode electrode and saturated Ag/AgCl (Corr instruments, US) was used
10 as the reference electrode. Each cell was divided into cathode and anode compartments with
11 Nafion 424 (Aldrich, US). The cathode electrolytes were 0.5 M KCl (Wako, Japan) or 0.5 M
12 KHCO₃ or a 1 M phosphate buffer solution (0.7 M K₂HPO₄: 0.3 M KH₂PO₄), whereas the anode
13 electrolyte was the same at 3.0 M KHCO₃ (Wako, Japan). The phosphate buffer species were
14 chosen to yield a bulk pH of around 7 in the absence of CO₂.²⁵

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32 Prior to an experiment, each reactor was first bubbled with Ar and then with CO₂, each
33 for 60 min and with a flow rate of 125 sccm (standard cubic centi meter per minute). The
34 reactors were then pressurized with CO₂ to the experimental values. Electrochemical
35 measurements were performed to ascertain the current density while also controlling the stirring
36 speed inside the reactor. Galvanostatic measurements with BT2000 (Arbin, US) multi-channel
37 potentiostats were performed up to 100 C, with a different current density set in each reactor
38 used to obtain the current density dependence of the product distribution for each single
39 experimental condition. All experiments were done at 25°C. After the measurements, gas
40 samples were transferred to a 7890A (Agilent, CA, USA) gas chromatograph (GC), which
41 quantitatively analyzed the reaction products (TCD for hydrogen (H₂), and FID for CO (with
42 methanizer), CH₄, and ethylene (C₂H₄)) For the analysis of liquid samples, we used a
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3 Prominence (Shimadzu, Japan) high-performance liquid chromatography (HPLC) for HCOO^-
4 detection and a GC-17A (Shimadzu, Japan) with a TurboMatrix40 (PerkinElmer, MA, USA)
5 headspace system (HS-GC) for the detection of aldehydes and alcohols. The Faradaic efficiency
6 (FE) is determined by dividing the charge ascribed to each product by the total charge passed.
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8 The reaction rate of CO_2 , J_{CO_2} , is given by
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$$J_{\text{CO}_2} = \sum_p J_p = \frac{1}{F} \sum_p \left(\frac{n \times i_{\text{PCD}}}{z} \right)_p \quad (1)$$

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19 where z and n represent the numbers of electrons and reactants necessary for the reaction,
20 respectively, and F represent Faraday's constant. The subscript p denotes a reaction product from
21 CO_2 , and i_{PCD} is the partial current density of each product (the product of the total current
22 density and FE). J_{lim} is determined as the maximum value of J_{CO_2} as plotted against current
23 density.
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34 <Simulation>

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38 A one-dimensional, isothermal, steady-state model simulates the hydrodynamic boundary
39 layer region near the electrode (see Figure 1). The boundary layer thickness was set to be 100
40 μm for the base case, and varied to examine boundary-layer thickness effects. There is no
41 convection within the hydrodynamic boundary layer, and the double-layer region, where
42 electroneutrality does not hold, is neglected as it is very thin in these electrolytes. The species in
43 the system are: dissolved CO_2 , K^+ , H^+ , OH^- , HCO_3^- , CO_3^{2-} . Additionally, there is Cl^- for KCl
44 electrolyte, and H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} for the potassium-phosphate buffer electrolyte.
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The flux of each species, N_i , is calculated using the Nernst-Planck equation, accounting for migration and diffusion,

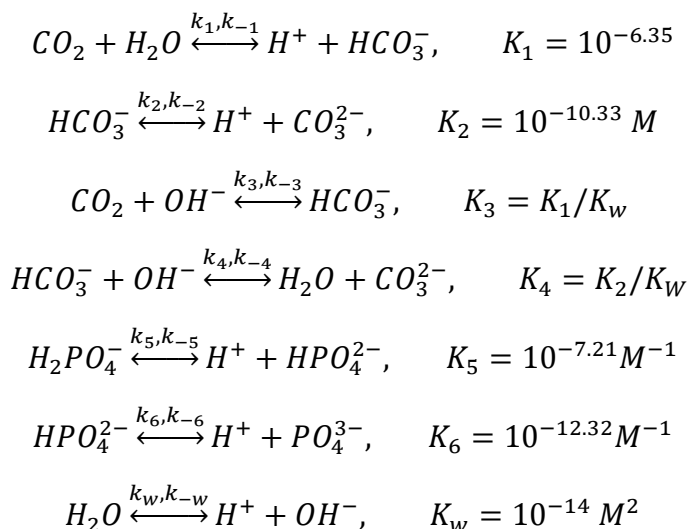
$$N_i = -D_i \nabla c_i - z_i \frac{D_i}{RT} F c_i \nabla \phi_l \quad (2)$$

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

Component balances at steady state yield

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

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



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

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3 the phosphate buffer reactions and take the rate constants, k_5, k_6 to be large (10^6 s^{-1}). The
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5 backwards rate constants are then calculated from the relationship
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$$k_{-i} = \frac{k_i}{K_i} \quad (4)$$

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12 Two conditions were investigated: (1) 100% CH_4 conversion, and (2) 90 mA/cm^2 total
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14 current density. The boundary conditions are listed in Table 1, where i_T is the total current
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16 density (set to 90 mA/cm^2 based on experimental data, Figure S3), k_{m_i} is the mass-transfer
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18 coefficient of species i at the bulk electrolyte/boundary layer boundary. k_{m_i} is taken to be a
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20 large value, and estimated using $\frac{D_i}{1 \mu\text{m}}$, to allow fast equilibration for each species with its bulk
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22 concentration.
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28 The set of differential and algebraic equations are solved simultaneously using the
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30 MUMPS solver in COMSOL 5.2a. Instability occurs at high current densities so we solve low
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32 current density conditions first and use them as the initial guesses for high current-density
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34 conditions.
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41 <Results and Discussions>

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44 While it is known that the use of KHCO_3 results in higher FE as a function of current
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46 density compared to KCl (see Figure S1), the mechanism and causality are not definitively
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48 determined. There are two possible explanations for this phenomenon: (1) The anion in the
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50 electrolyte (Cl^- vs HCO_3^-) is affecting the kinetics of the reaction, possibly by interacting with
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52 reaction intermediates on the catalyst surface,²⁷ (2) The buffering capacity of KHCO_3 is affecting
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3 species concentration near the electrode surface, in particular changing the pH and the
4 concentration of CO₂ at the electrode surface. To investigate the mass-transport effects of this
5 system, the pressure dependence of the limiting CO₂ flux (the rate of CO₂ consumption where
6 the CO₂ mass-transport is rate-determining-step (CO₂ limited conditions)) for the two
7 electrolytes is compared. At CO₂ limited conditions, the rate of CO₂ consumption should be
8 independent of catalyst kinetics, allowing a direct comparison of mass-transport limitations of
9 systems with different electrolytes.
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20 Since Cu reduces CO₂ to multiple products requiring different number of electrons, we
21 cannot directly compare the limiting current density (LCD) between cases. Instead of LCD, we
22 use our previously-defined “limiting rate of mass transport” (J_{lim}) to characterize the maximum
23 rate of CO₂ consumption.¹⁶ J_{lim} describes the rate of CO₂ flux to the electrode surface at limiting
24 conditions (i.e. local CO₂ concentration becomes zero). At CO₂ limited conditions, the rate of
25 CO₂ flux to the electrode surface should be equal to the rate of CO₂R. Figure 2 shows the
26 pressure dependent J_{lim} in 0.5 M KHCO₃ and 0.5 M KCl electrolyte. As seen from the figure, J_{lim}
27 in KHCO₃ is higher than in KCl at the same P_{CO_2} . Moreover, the data points for J_{lim} in KHCO₃
28 increases nonlinearly with P_{CO_2} , whereas in KCl, J_{lim} increases almost linearly from the zero
29 point, consistent with our previous report.¹⁶ This indicates that the behavior of J_{lim} in KHCO₃
30 could not be simply explained by the dissolved amount of CO₂ increasing with pressure, in
31 which case J_{lim} should increase proportionally with CO₂ concentration in the electrolyte
32 according to Fick’s and Henry’s laws.
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50 To investigate further the origin of such characteristic behavior of J_{lim} in KHCO₃ and KCl
51 electrolyte, a 1-D simulation model was employed assuming 100% CH₄ production from CO₂.
52 As shown in Figure 1, the model simulates mass transport of each species within the boundary
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3 layer between the catalyst surface (point A, local) and bulk electrolyte (point B, bulk). As stated
4 above, different conditions were modeled including the experimentally used conditions: 0.5 M
5 KCl and 0.5 M KHCO_3 , as well as two additional cases: 1 M phosphate buffer (mixture of 0.3 M
6 KH_2PO_4 and 0.7 M K_2HPO_4) and 1.5 M KHCO_3 , to demonstrate how using an electrolyte with a
7 stronger buffer capacity might improve CO_2 transport to the catalyst surface. It should be noted
8 that a direct comparison of the two buffers is complicated by the fact that CO_2 will always result
9 in some bicarbonate buffering as shown in Figure S2. Figure 3a shows the simulation result of
10 P_{CO_2} dependence of J_{lim} . Comparing the different electrolytes, one can see that for both the
11 bicarbonate and phosphate buffers, J_{lim} initially follows Fick's law at low CO_2 reaction rates (low
12 P_{CO_2}), with the phosphate buffer and 1.5 M KHCO_3 system deviating from Fick's law at a
13 slightly higher P_{CO_2} compared to 0.5 M KHCO_3 and 0.5 M KCl. In contrast, J_{lim} for KCl
14 increases proportionally with P_{CO_2} with a slope much smaller than that expected by Fick's law
15 (i.e., diffusion without reactions). Comparing Figure 2 and Figure 3a, the simulation qualitatively
16 reproduces the nonlinear behavior of J_{lim} seen in experiments with 0.5 M KHCO_3 . As shown in
17 Figure 3b and 3c, this behavior is derived from the changes in pH and local CO_2 concentration.
18 The CO_2 concentration profile deviates from Fick's law in both electrolytes, with a smaller slope
19 (i.e. smaller CO_2 flux) near the electrode surface compared to what is predicted from Fick's law.
20 This slope determines the rate of CO_2 supplied to the electrode, J_{lim} . The deviation from Fick's
21 law is caused by the consumption of CO_2 by OH^- produced during the electron transfer reactions
22 (for each electron consumed one OH^- is produced). As shown in Figure 3c, the bulk pH in 0.5 M
23 KCl and 0.5 M KHCO_3 at CO_2 -saturated condition is ~ 3.6 and ~ 7.0 , respectively, which agree
24 with experimental observations.^{16, 28} However, as the electrode surface is approached, the pH in
25 both electrolytes rises significantly. Considering acid/base reactions, CO_2 is less likely to be
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3 present at alkaline conditions (see reactions above),¹⁵ where OH^- produced through CO_2R reacts
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5 with CO_2 to produce HCO_3^- and CO_3^{2-} , which are generally considered not to be reactants for
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7 CO_2R .²⁴ In a buffered system (e.g. KHCO_3), the pH within the boundary layer can be somewhat
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9 maintained to remain close to bulk pH. In contrast, for the unbuffered KCl system, the pH near
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11 the electrode is drastically increased (Figure 3c). These pH effects and impact of buffering
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13 capacity can be used to explain the other curves in Figure 3a. Using a stronger buffer, either
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15 higher concentration bicarbonate buffer or phosphate buffer, J_{lim} further increases and
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17 approaches Fick's law, due to the lower pH attained at the surface of the electrode (see Figure
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19 3c).
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25 To explore these effects in more detail, J_{lim} is normalized by the value estimated under
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27 Fick's law and plotted as a function of the pH difference from bulk electrolyte to electrode
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29 surface under the CO_2 mass-transport-limited conditions in Figure 4. This figure clearly
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31 illustrates the general linkage between buffering property of the electrolyte and the limiting rate
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33 of CO_2R . Figure 4 predicts that buffer strength of the electrolyte is one of the design guidelines
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35 to achieve high reaction rate in CO_2R , where the mass-transport of CO_2 is one of the rate-
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37 determining factors.^{14, 16} Interestingly, while both 1 M phosphate buffer and 1.5 M KHCO_3 give
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39 a limiting flux greater than 60% maximum flux (Fick's law prediction), and maintains the
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41 surface pH to be within 4 units of the bulk pH, they do not follow the same trend. The reason for
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43 this is the difference in pKa values for the two buffers. Comparing the pH profiles for 1.5 M
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45 KHCO_3 and 1 M phosphate buffer (Figure 3c), we can see that bicarbonate buffer maintains the
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47 pH near 10, while phosphate buffer electrolyte has two distinct regions of stable pH: one near pH
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49 7.5 and the other near pH 11. These results indicate that both the buffering capacity, and the pKa
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51 values of the buffer chosen can affect the pH, and therefore CO_2 supply to the electrode.
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3 From the simulation results shown above, phosphate buffer could be better than KCl and
4 KHCO₃ in terms of CO₂ mass-transfer due to its stronger buffer capacity and its ability to react
5 with the produced hydroxide without impacting the CO₂ from the bicarbonate equilibrium
6 directly (i.e., it in essence helps to decouple these phenomena). To see the effect of phosphate
7 buffer experimentally, a series of experiments with varying P_{CO_2} in 1 M phosphate buffer
8 solution (0.7 M K₂HPO₄: 0.3 M KH₂PO₄) were conducted. Interestingly, the plot of J_{lim} in
9 phosphate buffer solution shows a downward-convex shape and the value of J_{lim} in each P_{CO_2} is
10 less than that in 0.5 M KHCO₃ as shown in Figure 5. This behavior is different than that
11 predicted, indicating other factors may be occurring including perhaps not 100% conversion to
12 methane and also possibly the existence of unaccounted phenomena such as differences in
13 catalyst selectivity due to phosphate interactions, which has been witnessed on copper
14 previously.²¹

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31 While 100% CH₄ is the most ideal case, it is known that the current catalysts produce
32 various reduction species including H₂, CO, C₂H₄, etc. Except for HCOO⁻, all of the other
33 electron transfer products produce one OH⁻ per e⁻ consumed, which impacts the local pH at the
34 electrode surface. For example, Figure S5 shows how the limiting CO₂ flux increases with CH₄
35 FE assuming that the catalyst produces only CH₄ and H₂ for the 1 M phosphate buffer case at 1
36 atm CO₂ assuming that the local CO₂ concentration at the electrode is 0. The total current density
37 decreases as CH₄ FE increases since it switches from a two-electron process for HER to an eight-
38 electron process for CH₄ production. The lower total current density produces less OH⁻, which
39 explains the increase in limiting CO₂ flux, and highlights the importance of overall hydroxide
40 generation rate.

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3 To account for the selectivity and better match experimental conditions, we considered a
4 model where the total current density was fixed without specifying the product distribution (i.e.,
5 the OH^- flux is linearly proportional to the total current density). For the total current density, 90
6 mA/cm^2 was chosen as it represented the total current density at which maximum CO_2 flux was
7 achieved during experiments (see Figure S3). Figure 6(a) shows the comparison of the
8 simulation results between the 100% CO_2R to CH_4 and constant OH^- flux models for a
9 boundary layer thickness of 100 μm . As previously discussed, J_{lim} shows a concave dependence
10 on P_{CO_2} for the 100% CO_2R model, but a downward-convex behavior with pressure for the
11 constant OH^- flux model. The difference is due to the way in which the pH changes with current
12 density in that the current (and thus OH^- production) is increasing with the 100% CH_4 model,
13 whereas it is fixed in the 90 mA/cm^2 one. These results highlight the importance of how the
14 model can be used to perhaps diagnose what is occurring near the surface in terms of pH and FE.
15 The crossover point between the models is associated with the case of 90 mA/cm^2 being the
16 limiting current density for 100% CO_2R to CH_4 . Moreover, as shown in Figure 6(b), the pressure
17 dependence of J_{lim} is significantly affected by the boundary-layer thickness, where J_{lim} exhibits a
18 linear shape at the thickness of 50 μm but becomes nonlinear at 100 and 150 μm . This result
19 shows that the thickness of boundary layer is also responsible for the qualitative behavior of
20 pressure dependence of J_{lim} with constant OH^- flux model.
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47 To explore the impact of buffer capacity in more detail using this model, different buffers
48 and buffer concentrations associated with bulk pH (see Figure S2) are made in a similar fashion
49 to the simulations above. This provides a good comparison since the total hydroxide generation
50 flux is constant at the total current density and thus the differences in J_{lim} can also be correlated
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3 to different FEs. As Figure 7(a) shows, the normalized J_{lim} by Fick's law (similar to Figure 4) as
4 a function of P_{CO_2} for various buffer concentrations and identities demonstrates different shapes.
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6 Obviously, the increase in buffer concentration plays an important role in controlling the local
7 CO_2 concentration and decreasing the impact of hydroxide, thereby enabling a much more
8 Fickian response. In terms of concentrations, low amounts of bicarbonate result in less buffer
9 capacity, which results in lower performance. As shown in the Figure, this effect is sensitive to
10 CO_2 concentration since increased CO_2 results in increased HCO_3^- and thus buffering capacity.
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12 Such a trend is not as strong with phosphate since due to the additional interactions and pKa
13 differences. Figure 7(a) also demonstrates how the identity of the phosphate buffer impacts J_{lim} .
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15 From Figure S2, changing the ratio of K_2HPO_4 and KH_2PO_4 with the same amount of phosphate
16 results in different bulk pH values due to the buffer, which is also impacted by the effective
17 bicarbonate concentration and its buffering by dissolved CO_2 (see Figure S2). Thus, the shaded
18 region in Figure 7(a) indicates how the initial composition and bulk pH of phosphate buffer
19 impact J_{lim} , which have a larger impact at higher concentrations of K_2HPO_4 (i.e. higher effective
20 bicarbonate concentration under CO_2 atmosphere) and eventually resulting in a constant offset as
21 the increased P_{CO_2} results in more bicarbonate buffering. Finally, there is a question about how
22 the kinetics of the buffer reactions (see Table S1 and equations above) impact the value of J_{lim} .
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24 As shown in Figure 7(b), as the kinetics are decreased for the phosphate buffer reaction, J_{lim}
25 decreases since it is harder for the buffer to mitigate the impact of the constant hydroxide rate,
26 which decreases the CO_2 concentration near to the electrode. At very low rates, the phosphate
27 essentially no longer buffers and a response similar to no buffer (e.g., KCl) or low bicarbonate
28 concentration, which could as well explain some of the differences between experiment and the
29 model. It is important to note that even at the higher rates that are taken from general literature,
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3 equilibrium between CO₂ and bicarbonate is not achieved next to the electrode surface (see
4 Figure S4), and in fact varies significantly. These findings highlight that the assumption of
5 equilibrium for the acid/base reactions is incorrect and that there is a need to measure the buffer
6 kinetics in solutions of interest.
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13 As noted above, the boundary-layer thickness is an important factor to determine the
14 behavior of CO₂ mass transport and local CO₂ concentration at the electrode surface. It is
15 expected that one can alter the boundary-layer thickness due to convection as well as just due to
16 hydrogen or other gaseous-product formation. To explore this aspect further in terms of
17 analyzing the experimental data, one can calculate the effective boundary-layer thickness for
18 limiting current or the effective CO₂ surface concentration using the model and a total current
19 density. Table S2 shows such results from the experimental data of J_{lim} and the measured H₂ FE
20 in 0.5 M KCl and KHCO₃ solutions. From the calculations, it is clear that the boundary-layer
21 thickness is on the order of 100 μm or so, but it does vary and so the assumption of 100 μm
22 boundary layer may not be fully correct. This variation is either due to the simplified model or
23 perhaps the effect of the bubbles of H₂ or other gaseous products which is considered to affect
24 the boundary-layer thickness.²⁹ In addition, in agreement with Figure 2, the current density is
25 much higher for KHCO₃ than KCl due to its buffering capacity, although it is interesting to note
26 that the boundary layer is relatively the same between the cases with it being somewhat thinner
27 for KHCO₃ due to the higher current densities and thus higher HER rates. The similarity in
28 boundary-layer thicknesses demonstrate as well that the model is capturing the salient physics.
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54 **<Conclusion>**
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3 In this paper, we have demonstrated how the electrolyte buffer capacity and identity in
4 terms of pKa affects CO₂ transport within the boundary layer and the local CO₂ concentration
5 available at the electrode surface for CO₂R. The simple transport model agreed with
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7 experimental trends of maximum flux seen for CO₂R on Cu in different electrolytes, although a
8 deviation from the experiment thought to be kinetic in origin existed when a phosphate buffer
9 was used. Comparing the limiting CO₂ flux at different P_{CO_2} in KCl and KHCO₃, we observe that
10 both systems deviate from Fick's law and KHCO₃ gives a higher CO₂ flux than KCl electrolyte
11 due to the improved CO₂ flux in KHCO₃ caused by the buffering capacity of bicarbonate, leading
12 to a slower increase in local pH and slower homogeneous consumption of CO₂ by OH⁻. This is
13 especially important at high current densities where OH⁻ ions are produced in large quantities.
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15 The model results showed that the pKa value significantly affects the shape of the pH profile
16 within the boundary layer, which can also be impacted by overall buffer concentrations and
17 kinetics, where equilibrium is not achieved next to the electrode surface. Finally, we considered
18 the case where we increased the P_{CO_2} at a constant total current density, and showed that
19 increasing bicarbonate concentration at low pressures (< ~ 2.5 atm) is more effective in
20 improving CO₂ transport when the target product (i.e. CH₄) faradaic efficiency remains high; at
21 high pressures (> ~ 2.5 atm) however, CO₂ transport is improved more rapidly with increased
22 P_{CO_2} when the total current density is held constant. This analysis and approach provides insights
23 for how buffer electrolytes affect the mass-transport of CO₂ within the system.
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51 <Supporting Information >
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3 Additional information in the supporting information includes tables for rate constants and
4 additional boundary-layer simulation results, supplemental experimental results, pH calculation
5 of phosphate buffer, the calculation of equilibrium within boundary layer, and the impact of
6 methane faradaic efficiency on total current density using the limiting-current model. The raw
7 data for all figures is also given or referenced. This material is available free of charge via the
8 Internet at <http://pubs.acs.org>.
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21 <Acknowledgement>

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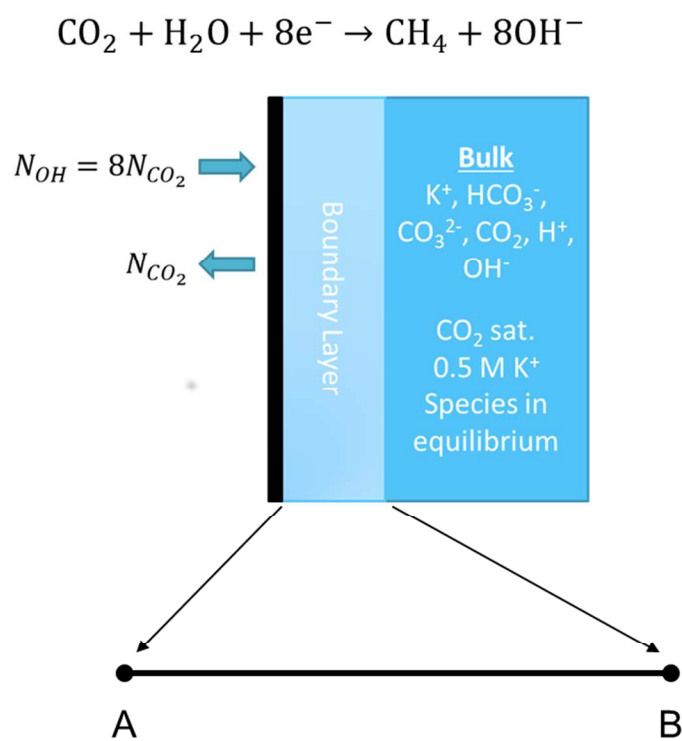


Figure 1. Schematic illustration of 1-D simulation model assuming 100% CH₄ faradaic efficiency

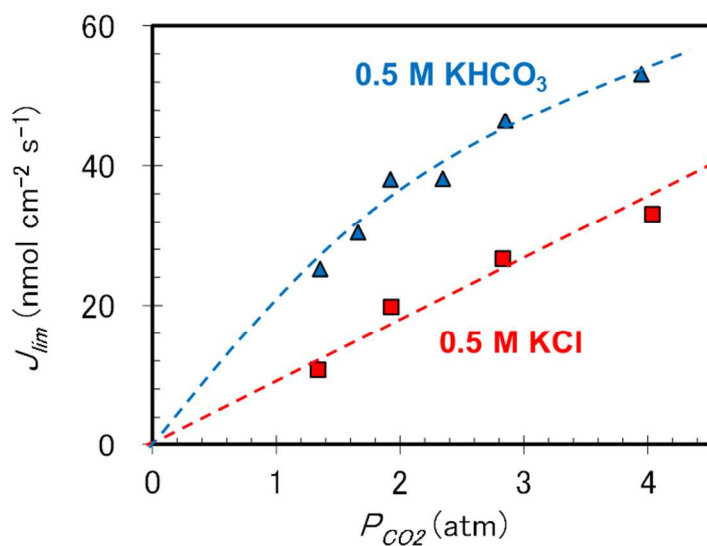


Figure 2. CO₂ pressure (P_{CO_2}) dependence of limiting rate of mass transport of CO₂ (J_{lim}) in 0.5M KHCO₃ (blue triangles) and 0.5M KCl (red squares) solutions (dotted lines are guides for the eye only).

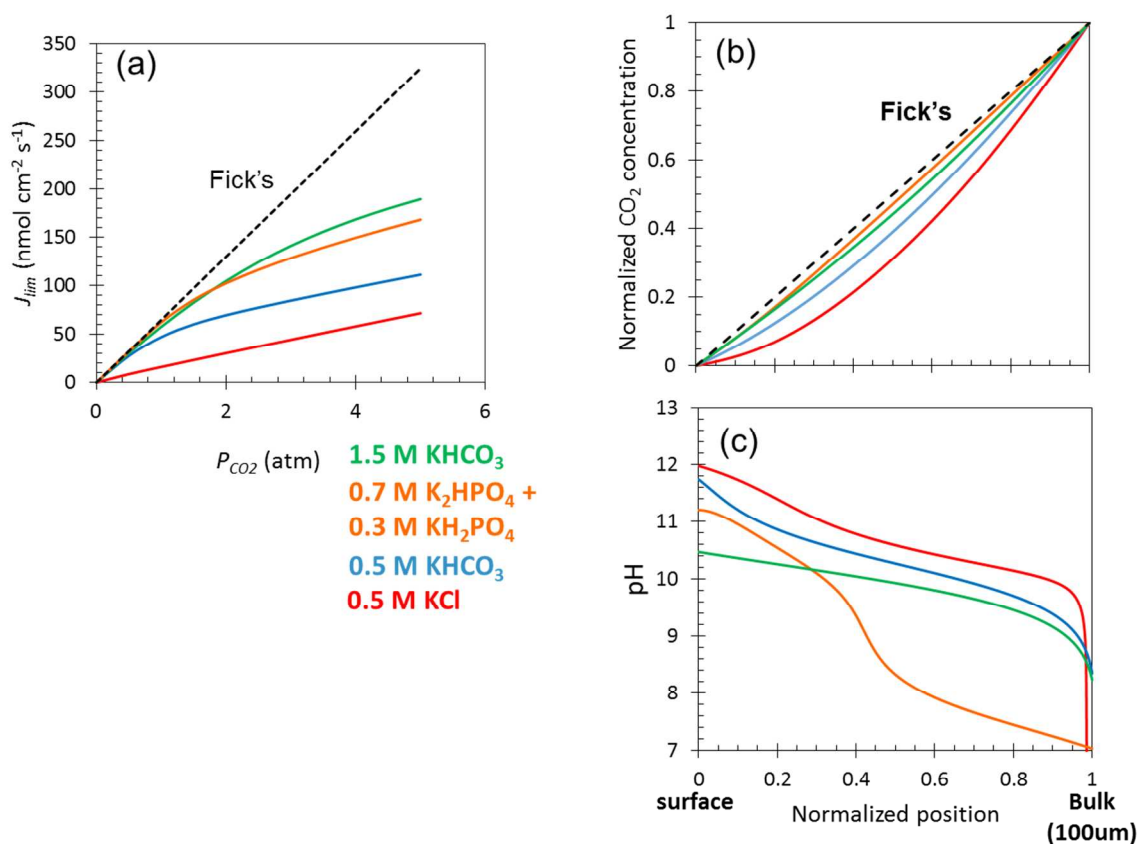


Figure 3. (a) Model results (assuming 100% conversion of CO_2 to CH_4) of CO_2 pressure dependence of J_{lim} in 4 different electrolytes; the dotted line indicates assuming Fick's law. (b) CO_2 concentration and (c) pH within the 100 μm boundary layer at P_{CO_2} of 2 atm.

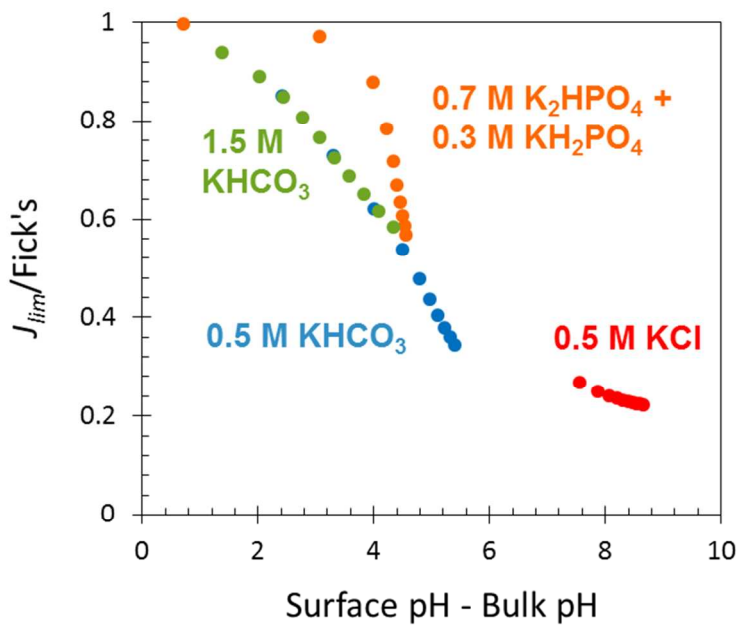


Figure 4. Relationship between normalized J_{lim} (to that expected from Fick's law) and pH change within the boundary layer for 4 different electrolytes.

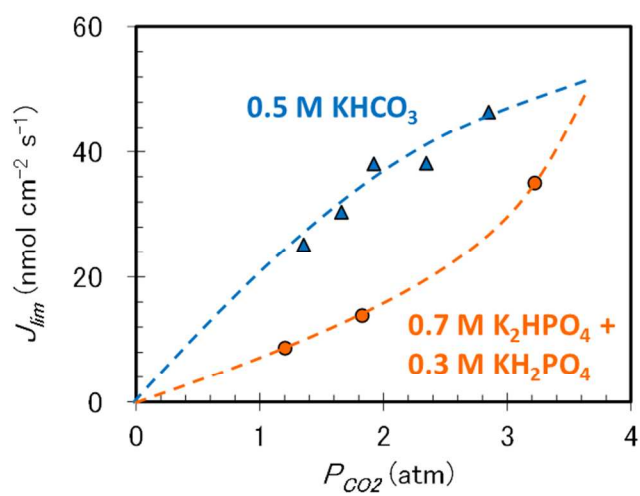


Figure 5. Experimental results of P_{CO_2} dependence of J_{lim} in 1 M phosphate buffer (orange circles) compared to 0.5 M KHCO₃ (blue triangles).

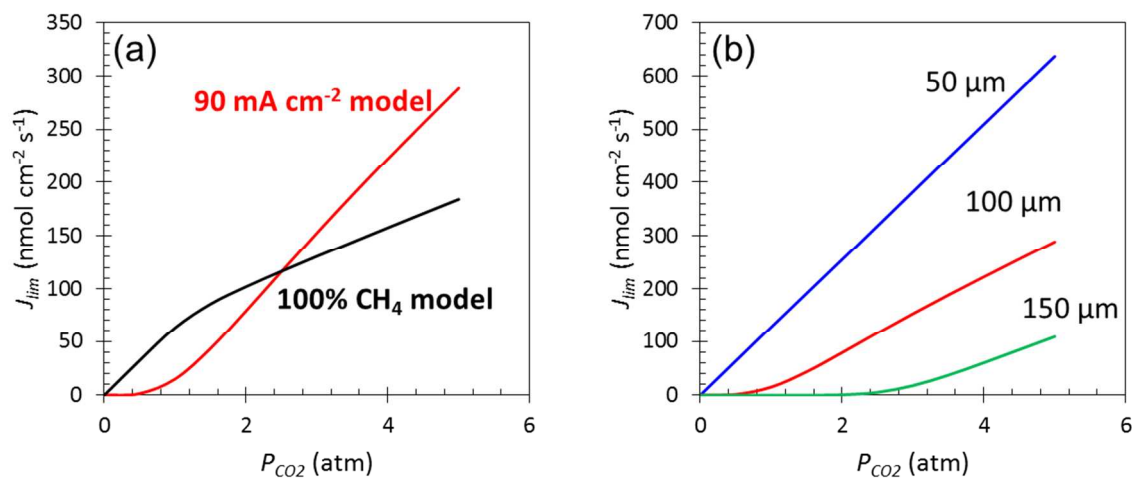


Figure 6 (a) Comparison of pressure dependence of J_{lim} between 100% CO₂ reduction and constant OH⁻ flux (corresponding to 90 mA cm⁻²) models with the phosphate buffer solution and 100 μm boundary-layer thickness. (b) The effect of boundary-layer thickness on the pressure dependence of J_{lim} using the constant OH⁻ flux model with phosphate buffer solution.

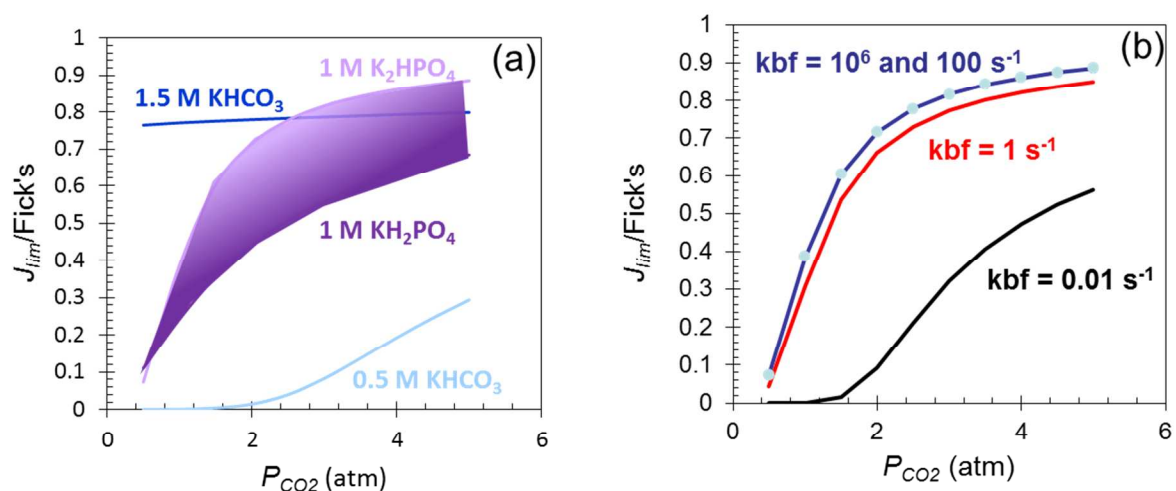


Figure 7. Comparison of pressure dependence of J_{lim} for (a) 0.5 and 1.5 M $KHCO_3$ and a range of 1 M phosphate from K_2HPO_4 to KH_2PO_4 (purple area) and (b) as a function of phosphate buffer kinetic rates (see equation 4) using 1 M K_2HPO_4 . All simulations done assuming 90 mA/cm^2 total current density.

Table 1. Boundary conditions for the 1-D models.

	100% CH₄ model	Constant current density model
	$c_{CO_2} = 0$	$c_{CO_2} = 0$
Electrode boundary	$N_{OH^-} = -8N_{CO_2}$	$N_{OH^-} = -i_T/F$
	$N_i = 0, i \neq CO_2, OH^-$	$N_i = 0, i \neq CO_2, OH^-$

Bulk electrolyte boundary	$N_i = -k_i(c_i - c_i^b)$	
	$\phi_l = 0$	

TOC Graphic

