Supporting Information for

Effects of Electrolyte Buffer Capacity on Surface Reactant Species and Reaction Rate of CO_2 in Electrochemical CO_2 Reduction

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Table S1. Acid/base rate constants used for the simulation.

Rate constant	Value
k_1	3.71×10^{-2} s^{-1}
k_2	59.44 s^{-1}
k_3	2.23×10^{3} L mol^{-1} s^{-1}
k_4	6.0×10^{9} L mol^{-1} s^{-1}

Table S2. Calculated CO_2 concentration (cCO_2) for 50 μm boundary-layer (BL) thickness or calculated boundary-layer thickness for limiting CO_2 current using the constant OH^- flux model derived from experimental data for J_{lim} and HER FE for different P_{CO2} and applied current densities for (a) KCl and (b) $KHCO_3$ electrolytes.

(a) 0.5 M KCl

P_{CO2} (atm)	HER FE (%)	J_{lim} (nmol cm^{-2} s^{-1})	Current Density (mA cm^{-2})	cCO_2 for BL = 50 μm (mM)	BL for cCO_2 = 0 (μm)
1.34	37.56	10.72	10	30.1	162.4
1.93	67.83	19.79	30	24.2	93.5
2.83	48.64	26.65	30	50.6	119.0
4.04	25.30	33.08	30	88.1	152.7

(b) 0.5 M $KHCO_3$

1.35	87.27	25.19	100	24.9	73.6
1.66	80.01	30.40	100	32.6	76.1
1.92	79.84	38.06	90	44.0	83.4
2.35	71.08	38.15	60	63.2	119.8
2.85	72.86	46.42	90	69.3	92.6

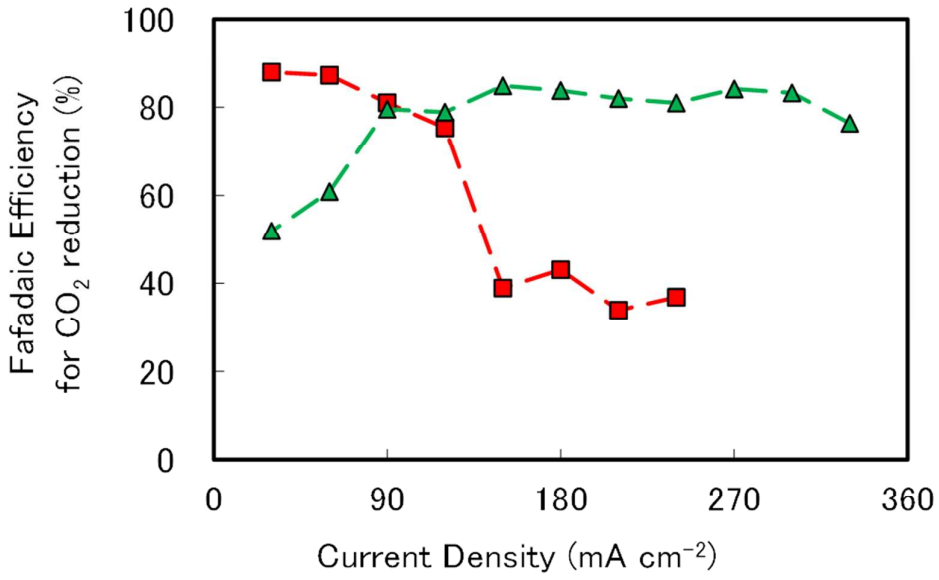

Figure S1. Current density dependence of Faradaic efficiency for CO_2 reduction under 3 atm of CO_2 pressure and stirred (500 rpm) condition. Data are adapted from reference [1].

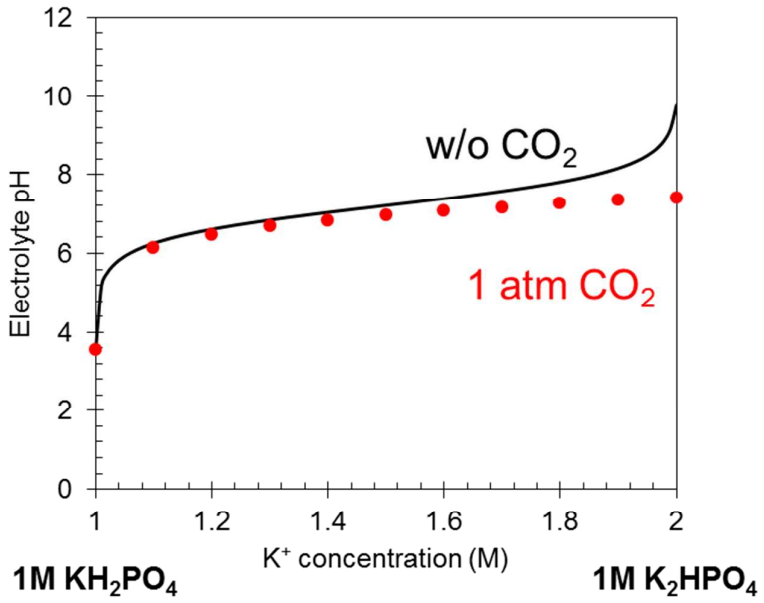

Figure S2. Calculated pH of 1 M phosphate buffer with and without CO_2 as a function of potassium concentration (i.e., K_2HPO_4 and KH_2PO_4 ratio).

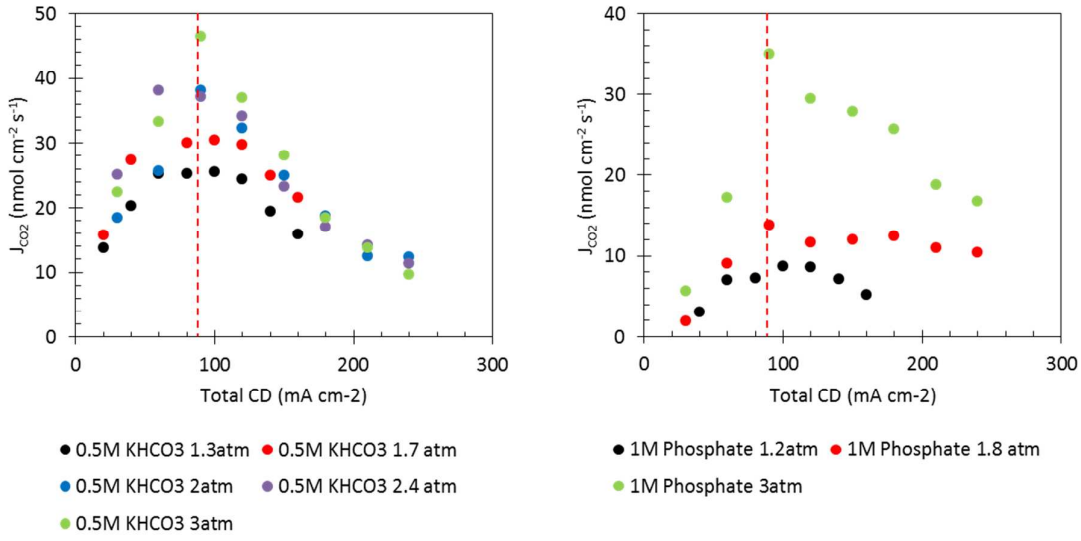

Figure S3. Current density (CD) dependence of CO_2 flux (J_{CO2}) at different CO_2 pressures for (a) $KHCO_3$ (b) K_2HPO_4 + KH_2PO_4

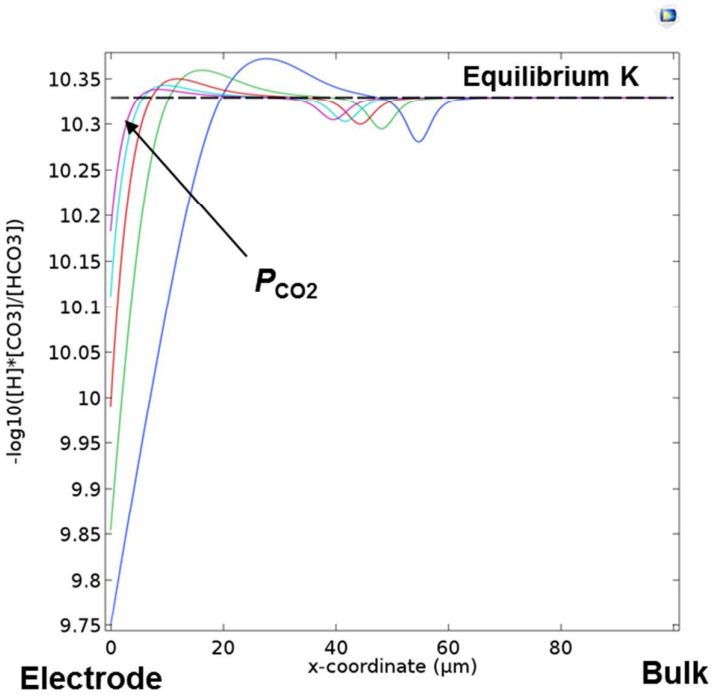

Figure S4. Comparison of calculated equilibrium expression to expected equilibrium coefficient (straight line) for the bicarbonate reaction as a function of boundary-layer position and CO_2 concentration using the 90 mA/cm^2 simulation and 1 M phosphate buffer. Equilibrium is only achieved further away from the electrode. The lines represent different partial pressure of CO_2 and are a proxy for the calculated coefficient using the local concentrations for reaction:

$$HCO_3^- \overset{k_2,k_{-2}}{\longleftrightarrow} H^+ + CO_3^{2-},\ K_2 = 10^{-10.33}\ M$$

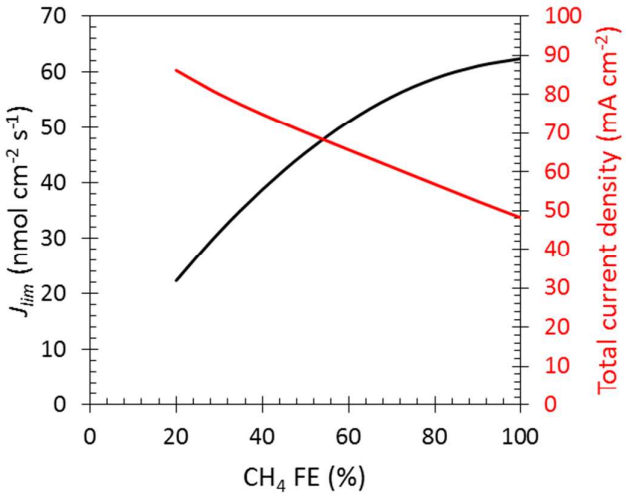

Figure S5. The effect of catalyst selectivity on limiting CO_2 flux assuming only CH_4 and H_2 production for 1 M phosphate buffer electrolyte at P_{CO2} of 1 atm and where the local CO2 concentration is equal to 0. Thus,

$$Total\ current\ density = \frac{8 * F * Jlim}{CH4\ FE}$$

Raw data for figures

Figure 3

P_CO2 (atm)	Fick's	0.5 M KCl	0.5 M KHCO3	1.7M K, 1M B	1.5 M KHCO3
0	0	0	0	0	0
0.5	32.47	8.6608022	27.545	32.279	30.427
1	64.94	16.1255636	47.114	62.41	57.804
1.5	97.41	23.3792818	60.173	85.452	82.606
2	129.88	30.5047417	69.537	102.42	104.72
2.5	162.35	37.5369228	77.354	116.3	124.18
3	194.82	44.4952583	84.536	128.42	141.15
3.5	227.29	51.3927035	91.399	139.41	155.87
4	259.76	58.2383272	98.082	149.6	168.66
4.5	292.23	65.0373115	104.64	159.2	179.81
5	324.7	71.7961341	111.12	168.36	189.67

Figure 4

	Local pH			
P_CO2 (atm)	0.5 M KCl	0.5 M KHCO3	1.7M K, 1M B	1.5 M KHCO3
0.5	11.633	10.257	8.1274	9.6789
1	11.802	10.836	10.292	10.021
1.5	11.904	11.367	10.937	10.266
2	11.979	11.742	11.205	10.473
2.5	12.038	11.93	11.347	10.663
3	12.088	12.037	11.438	10.848
3.5	12.129	12.11	11.502	11.035
4	12.166	12.165	11.552	11.228
4.5	12.199	12.208	11.592	11.432
5	12.228	12.245	11.625	11.635

Figure 6

CH4_FE (%)	Limiting CO2 flux (nmol/(cm^2*s))	Total current density (mA/cm^2)
100	62.41	48.173
90	61.092	52.396
80	58.873	56.804
70	55.552	61.256
60	51.069	65.698
50	45.466	70.189
40	38.807	74.886
30	31.114	80.056
20	22.333	86.191

Figure 7

	CO2 flux (nmol/cm^2/s)		
P (atm)	50 um	100 um	150 um
0	0	0	0
0.5	63.66	1.32	0.00
1	127.34	17.43	0.00
1.5	191.03	47.71	0.04
2	254.72	81.63	0.73
2.5	318.40	115.81	5.25
3	382.11	149.52	17.79
3.5	445.81	182.73	37.18
4	509.52	215.52	60.09
4.5	573.22	248.01	84.32
5	636.94	280.27	108.73

Figure 8

J_lim (nmol cm^-2 s^-1)

P_CO2 (atm)	Fick's	0.5 M KHCO3	1 M KHCO3	1.5 M KHCO3	1 M KH2PO4	1.7M K, 1M B	1M K2HPO4
0.5	32.47	0.006644	15.919	24.831	3.5755	1.3212	2.3694
1	64.94	0.064755	35.202	50.057	15.772	17.432	25.128
1.5	97.41	0.40475	56.031	75.527	34.648	47.706	58.777
2	129.88	1.883	77.928	101.23	57.39	81.634	92.932
2.5	162.35	6.4573	100.62	127.14	82.416	115.81	126.34
3	194.82	16.156	123.98	153.25	108.9	149.52	159.16
3.5	227.29	31.119	147.88	179.54	136.36	182.73	191.6
4	259.76	50.116	172.24	206.01	164.53	215.52	223.8
4.5	292.23	71.843	197	232.62	193.23	248.01	255.83
5	324.7	95.423	222.11	259.39	222.34	280.27	287.74

Surface pH

P_CO2 (atm)	Fick's	0.5 M KHCO3	1 M KHCO3	1.5 M KHCO3	1 M KH2PO4	1.7M K, 1M B	1M K2HPO4
0.5		12.909	11.91	10.658	11.356	11.907	11.954
1		12.848	11.726	10.629	11.401	11.722	11.664
1.5		12.78	11.581	10.611	11.4	11.575	11.445
2		12.702	11.466	10.595	11.388	11.456	11.261
2.5		12.62	11.373	10.581	11.374	11.352	11.11
3		12.54	11.297	10.568	11.36	11.258	10.988
3.5		12.47	11.233	10.556	11.347	11.173	10.89
4		12.409	11.178	10.545	11.334	11.097	10.811
4.5		12.355	11.131	10.534	11.322	11.029	10.746
5		12.306	11.089	10.523	11.311	10.97	10.69

Buffering effects

P_tot (atm)	10^6 s^-1	100 s^-1	1 s^-1	0.01 s^-1
0.5	2.3694	2.3656	1.4058	0.00028264
1	25.128	25.113	20.059	0.058646
1.5	58.777	58.761	52.299	1.6498
2	92.932	92.908	85.859	11.996
2.5	126.34	126.3	118.54	34.253
3	159.16	159.11	150.58	62.485
3.5	191.6	191.54	182.26	92.604
4	223.8	223.73	213.73	122.96
4.5	255.83	255.74	245.08	152.92
5	287.74	287.64	276.35	182.36

References

1. Hashiba, H.; Sato, H. K.; Yotsuhashi, S.; Fujii, K.; Sugiyama, M.; Nakano, Y., A broad parameter range for selective methane production with bicarbonate solution in electrochemical CO_2 reduction. *Sustainable Energy Fuels* **2017,** *1*, 1734-1739.