Supplementary Information to [Size-modified Poisson-Nernst-Planck approach for modeling a local electrode environment in CO_2 electrolysis]

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1. Bulk Concentrations

Henry's law is assumed to be valid for CO_2 gas and Eq. (1) is used to evaluate the bulk concentration of CO_2 in water.

$$\mathrm{CO_2}_{aq}^{0} = K_H^0 C_{\mathrm{CO_2},g} \tag{1}$$

Henry's constant K_H^0 is temperature dependent and in the presented system the temperature is taken as 298.15 K. The following equation is used to calculate its value[1]:

$$\ln K_H^0 = 93.4517 \times \frac{100}{T} - 60.2409 + 23.3585 \ln \frac{T}{100} \tag{2}$$

CO_2 concentration in an electrolyte will be different than in pure water. The ionic concentration affects the solubility of CO_2. The saturated concentration of CO_2 in the electrolyte ($\mathrm{CO_2}_{aq}$) is then given by:

$$\log\left(\frac{\mathrm{CO_2}_{aq}^{0}}{\mathrm{CO_2}_{aq}}\right) = K_s C_s \tag{3}$$

here C_s is the concentration of electrolyte and for our work it is 0.5 M $KHCO_3$. K_s is the Sechenov's constant given by [2]:

$$K_s = \sum_i (h_{\mathrm{CO_2}} + h_i) n_i \tag{4}$$

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where h_i is the Sechenov parameter for ion i and is given in Table 1. h_{CO_2} is calculated using:

$$h_{CO_2} = h_{CO_2,0} + h_{CO_2,T}(T - 298.15) \tag{5}$$

and n_i is defined as:

$$n_i = \frac{c_i}{C_s} \tag{6}$$

Here c_i represents the ionic concentrations before injecting the CO_2 gas and are calculated from the solution of equilibria of Eqs. (1-3) in the main manuscript. The calculated concentration of saturated CO_2 (CO_{2aq}) is then used to determine the bulk concentration of all other solution species post CO_2 saturation using the same equilibrium equation (Eqs.(1-3) in the main manuscript). This balance is given by (7-11). These equations are solved until a steady state is achieved. The bulk concentration values for all solution species for both 5 and 40 bar pressure are given in Table 3. The bulk rate equations are given by:

$$R_{\mathrm{H^+}} = k_3 - k_{-3}C_{\mathrm{H^+}}C_{\mathrm{OH^-}} \tag{7}$$

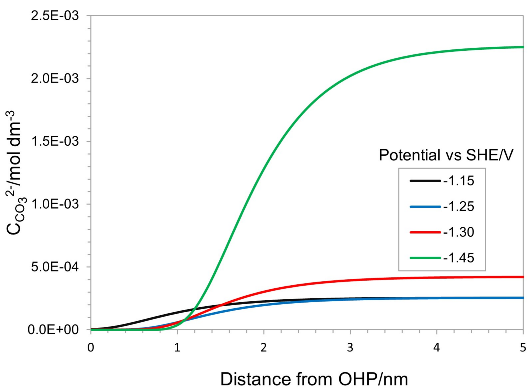
$$R_{\mathrm{CO_2}} = -k_2C_{\mathrm{CO_2}}C_{\mathrm{OH^-}} + k_{-2}C_{\mathrm{HCO_3{}^-}} \tag{8}$$

$$R_{\mathrm{CO_3{}^{2-}}} = k_1C_{\mathrm{HCO_3{}^-}}C_{\mathrm{OH^-}} - k_{-1}C_{\mathrm{CO_3{}^{2-}}} \tag{9}$$

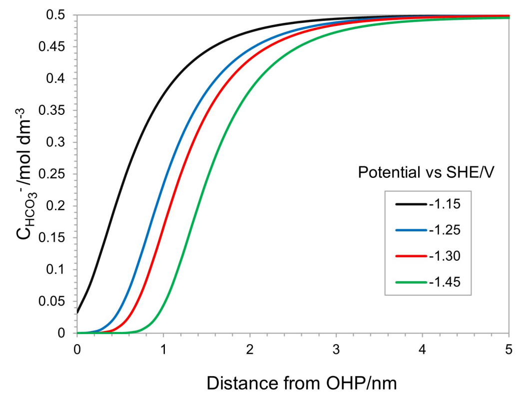
$$R_{\mathrm{HCO_3{}^-}} = -k_1C_{\mathrm{HCO_3{}^-}}C_{\mathrm{OH^-}}k_{-1}C_{\mathrm{CO_3{}^{2-}}} + k_2C_{\mathrm{CO_2}}C_{\mathrm{OH^-}} - k_{-2}C_{\mathrm{HCO_3{}^-}} \tag{10}$$

$$R_{\mathrm{OH^-}} = k_3 - k_{-3}C_{\mathrm{H^+}}C_{\mathrm{OH^-}} - k_2C_{\mathrm{CO_2}}C_{\mathrm{OH^-}} + k_{-2}C_{\mathrm{HCO_3{}^-}} - k_1C_{\mathrm{HCO_3{}^-}}C_{\mathrm{OH^-}} + k_{-1}C_{\mathrm{CO_3{}^{2-}}} \tag{11}$$

2. Supplementary Results



(a)



(b)

Figure 1: Concentration profile of $HCO_3{}^{-}$ and $CO_3{}^{2-}$ near the surface of the electrode at varied applied electrode potentials for a 0.5M $KHCO_3$ solution at 5 bar CO_2 pressure.

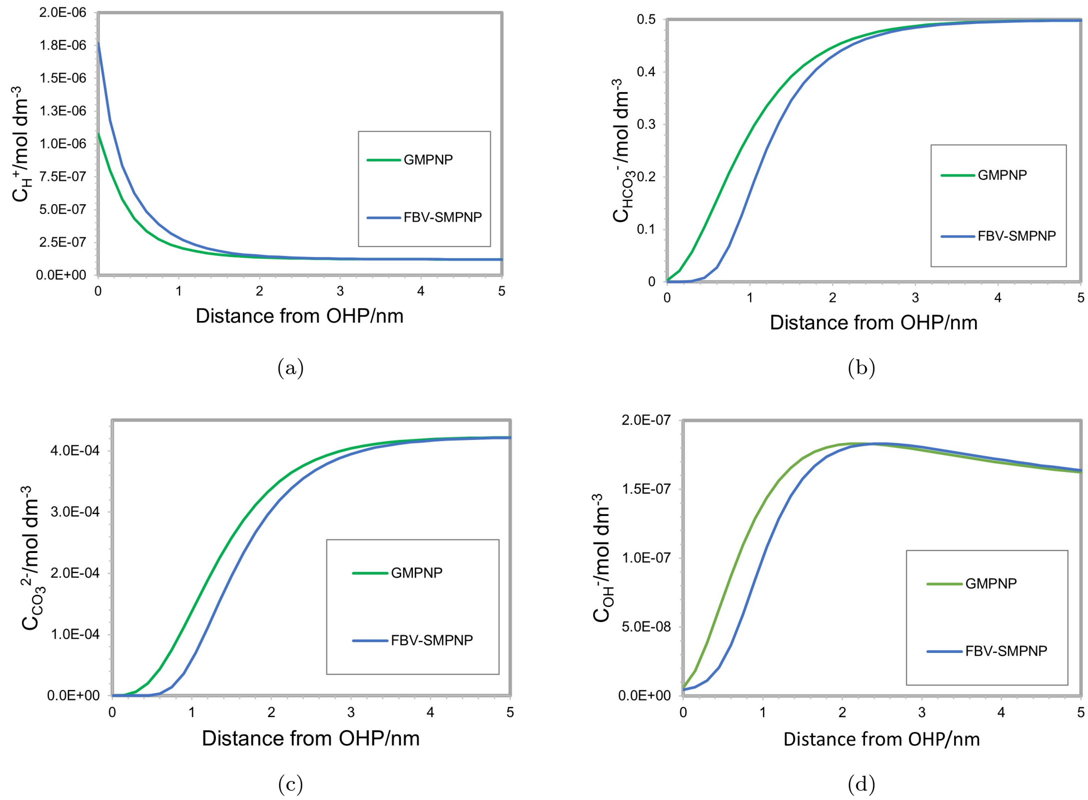


Figure 2: Comparison of concentration profiles of different species using FBV-SMPNP and GMPNP approach for 0.5M $KHCO_3$ solution at -1.3 VS SHE/V in a 5 bar CO_2 electrolyzer.

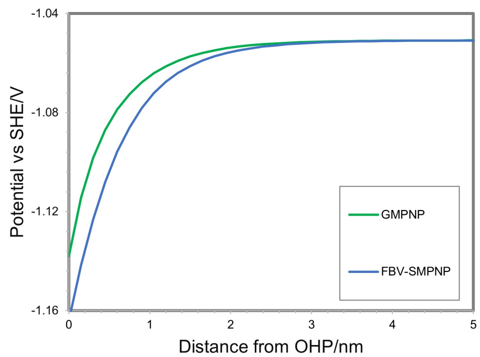


Figure 3: Comparison of electric potential near the electrode surface using FBV-SMPNP and GMPNP approach for a 0.5M $KHCO_3$ solution at applied electrode potential of -1.3 VS SHE/V in a 5 bar CO_2 electrolyzer. The potential profiles become steady after some distance from OHP. This is the point beyond which potential is 0 vs PZC/V (bulk boundary condition).

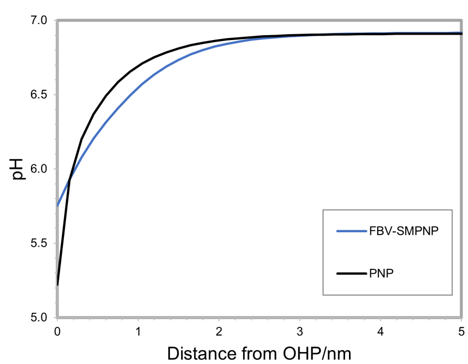


Figure 4: Comparison of pH near the electrode surface using FBV-SMPNP and PNP approach for a 0.5M $KHCO_3$ solution at an applied electrode potential of -1.3 VS SHE/V in a 5 bar CO_2 electrolyzer.

3. Parametric Data

Table 1: Sechenov Parameters ($m^3 kmol^{-1}$). [2]

Species(i)	h_i
${CO_3}^{2-}$	0.1423
OH^-	0.0839
${HCO_3}^-$	0.0967
K^+	0.0922
CO_2,0	-0.0172
CO_2,T	-0.000338

Table 2: Rate Constants.[3, 4]

Constant	Value	Unit
k_1	6.0×10^6	$mol^{-1}m^3s^{-1}$
k_{-1}	1.07×10^6	s^{-1}
k_2	2.23	$mol^{-1}m^3s^{-1}$
k_{-2}	5.23×10^{-5}	s^{-1}
k_3	2.4×10^{-2}	$molm^{-3}s^{-1}$
k_{-3}	2.4×10^6	$mol^{-1}m^3s^{-1}$

Table 3: Bulk Concentrations at 5 and 40 bar CO_2 pressure (mol dm^{-3}).

Species	$C_i(5\,\text{bar})(\text{pH} = 6.9)$	$C_i(40\,\text{bar})(\text{pH} = 6.1)$
${CO_3}^{2-}$	0.23×10^{-3}	0.28×10^{-4}
OH^-	0.82×10^{-7}	0.10×10^{-7}
${HCO_3}^-$	0.49	0.49
K^+	0.50	0.50
H^+	0.12×10^{-6}	0.97×10^{-6}
CO_2	0.17	1.36

Table 4: Diffusivities (m^{2}s^{-1}).[5, 6]

Species	Value
${CO_3}^{2-}$	0.92×10^{-9}
OH^-	5.23×10^{-9}
${HCO_3}^-$	1.18×10^{-9}
K^+	1.95×10^{-9}
CO_2	1.91×10^{-9}
H^+	9.31×10^{-9}

Table 5: Species Sizes (m).[7]

Species	Value
$a_{{CO_3}^{2-}}$	0.788×10^{-9}
a_{OH^-}	0.60×10^{-9}
$a_{{HCO_3}^-}$	0.80×10^{-9}
a_{K^+}	0.66×10^{-9}
a_{CO_2}	0.33×10^{-9}
a_{H^+}	0.56×10^{-9}
a_{H_2O}	0.30×10^{-9}

Table 6: Equilibrium Potential (V vs SHE).[8]

Reaction	Value
$CO_2(aq) + H_2O + 2\,e^- \rightleftharpoons HCOO^- + OH^-$	-0.43
$CO_2(aq) + H_2O + 2\,e^- \rightleftharpoons CO(g) + 2\,OH^-$	-0.53
$2\,H_2O + 2\,e^- \rightleftharpoons H_2(g) + 2\,OH^-$	-0.41

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