Supporting information for: Correlating uncertainties of a CO_2 to CO microfluidic electrochemical reactor – A Monte Carlo simulation

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Governing equations

We consider a gas-phase, multi-component flow in all the functional layers of the MFC except for the current collectors (cc) and the electrolyte (elec). For the complete set of governing equations, we consider the conservation of mass, momentum and species in the anode and cathode gas flow fields (ff), gas diffusion layers (gdl) and catalyst layers (cl) and

the conservation of charge in all the functional layers as

$$\nabla \cdot (\rho \mathbf{v}) = S_{\text{mass}}(\text{ff, gdl, cl}), \tag{1}$$

$$\nabla p + \frac{\mu}{\kappa}\mathbf{v} = S_{\text{mom}}(\text{ff, gdl, cl}), \tag{2}$$

$$\nabla \cdot \mathbf{n}_i = S_i, i = \text{CO}_2, \text{CO}, \text{H}_2, \text{H}_2\text{O} \ (\text{ff}^{\text{c}}, \text{gdl}^{\text{c}}, \text{cl}^{\text{c}}), \tag{3}$$

$$\nabla \cdot \mathbf{n}_i = S_i, i = \text{O}_2, \text{H}_2\text{O} \ (\text{ff}^{\text{a}}, \text{gdl}^{\text{a}}, \text{cl}^{\text{a}}), \tag{4}$$

$$\nabla \cdot \mathbf{i}^{(\text{elec})} = S_{\text{pot}}(\text{cl, elec}), \tag{5}$$

$$\nabla \cdot \mathbf{i}^{(s)} = -S_{\text{pot}}(\text{cc, ff, gdl, cl}), \tag{6}$$

where $\mathbf{n}_i$ is the total mass flux given by the Maxwell-Stefan equation as

$$\mathbf{n}_i = -\rho\omega_i \sum_{j=1}^{N} D_{ij}^{\text{eff}} \left[\frac{M_{\text{g}}}{M_j} \left(\nabla\omega_j + \omega_j \frac{\nabla M_{\text{g}}}{M_{\text{g}}} \right) + (x_j - \omega_j)\frac{\nabla p}{p} \right] + \rho\mathbf{v}\omega_i. \tag{7}$$

Here, ω_i and x_j are the mass and molar fractions, D_{ij}^{eff} is the effective multi-component diffusion coefficient, while M_{g} is the molar mass of the gas mixture:

$$M_{\text{g}} = x_{\text{N}_2}M_{\text{N}_2} + x_{\text{CO}_2}M_{\text{CO}_2} + x_{\text{CO}}M_{\text{CO}} + x_{\text{H}_2}M_{\text{H}_2} + x_{\text{H}_2\text{O}}M_{\text{H}_2\text{O}}, \tag{8}$$

at the cathode side and

$$M_{\text{g}} = x_{\text{N}_2}M_{\text{N}_2} + x_{\text{O}_2}M_{\text{O}_2} + x_{\text{H}_2}M_{\text{H}_2} + x_{\text{H}_2\text{O}}M_{\text{H}_2\text{O}}, \tag{9}$$

at the anode side. Additionally, from Ohm's law, the current conservation equations (Eqs.**5** and **6**) can be re-written as

$$\nabla \cdot (-\sigma\nabla\phi_{elec}) = S_{\text{pot}}(\text{cl, elec}), \tag{10}$$

$$\nabla \cdot (-\sigma \nabla \phi_s) = -S_{\text{pot}}(\text{cc, ff, gdl, cl}). \tag{11}$$

In the above equations, 's, elec, a, c' refer to solid, electrolyte, anode and cathode respectively; p is the pressure, $\mathbf{v}$ is the mass-averaged velocity vector, ρ is the density of the gas mixture, μ is the dynamic viscosity, κ is the permeability, $\mathbf{n}_i$ is the mass flux of species i, $\mathbf{i}$ is the current density, ϕ is the electric potential, and S represents the respective source terms which are defined as

$$S_{\text{mass}} = \begin{cases} 0 & \text{(ff, gdl)} \\ Q & \text{(cl)} \end{cases}, \tag{12}$$

$$S_{\text{mom}} = \begin{cases} \nabla \cdot \left[\frac{\mu}{\epsilon} \left(\left(\nabla \mathbf{v} + (\nabla \mathbf{v})^T \right) - \frac{2}{3} (\nabla \cdot \mathbf{v}) \mathbf{I} \right) \right] - \frac{c_{\text{F}} \rho}{\sqrt{\kappa}} \left| \mathbf{v} \right| \mathbf{v} & \text{(g)} \\ 0 & \text{(gdl, cl)} \end{cases}, \tag{13}$$

$$S_i = \begin{cases} 0 & \text{(ff, gdl)} \\ R_i & \text{(cl)} \end{cases}, \tag{14}$$

$$S_{\text{pot}} = \begin{cases} 0 & \text{(ff, gdl, cc, elec)} \\ a_{\text{s}} i_{\text{O}_2} & \text{(cl}^{\text{a}}\text{)} \\ a_{\text{s}} i_{\text{CO}} + a_{\text{s}} i_{\text{H}_2} & \text{(cl}^{\text{c}}\text{)} \end{cases}, \tag{15}$$

where ϵ is the porosity, Q is the mass source term, $\mathbf{I}$ is the identity tensor, R_i is the reaction rate of species i and a_{s} is the specific surface area.

Boundary conditions

Following the Roman numerals in Fig. 1, the boundary/ interface conditions are specified as follows:

Table S1. Boundary/ interface conditions following the Roman numerals in Figure 2.

Position	Boundary conditions
I	$\mathbf{u}\cdot\mathbf{e}_x = U_{\mathrm{g}}^{\mathrm{in,\ c}}, \omega_{\mathrm{CO_2}} = \omega_{\mathrm{CO_2}}^{\mathrm{in}}, \omega_{\mathrm{CO}} = \omega_{\mathrm{H_2}} = \omega_{\mathrm{H_2O}} = 0; U_{\mathrm{g}}^{\mathrm{in,\ c}} = \frac{Q_{\mathrm{g}}^{\mathrm{c}}}{Wh_{\mathrm{ff}}}$.
II	$p = p^{\mathrm{ref}}, \mathbf{n}_i\cdot\mathbf{e}_x = 0$.
III	$\mathbf{u}\cdot\mathbf{e}_x = U_{\mathrm{g}}^{\mathrm{in,\ a}}, \omega_{\mathrm{O_2}} = \omega_{\mathrm{O_2}}^{\mathrm{in}}$; $U_{\mathrm{g}}^{\mathrm{in,\ a}} = \frac{Q_{\mathrm{g}}^{\mathrm{a}}}{Wh_{\mathrm{ff}}}$
IV	$\mathbf{u}\cdot\mathbf{e}_x = 0,\ \mathbf{i}^{(\mathrm{elec,\ s})}\cdot\mathbf{e}_x = 0, \mathbf{n}_i\cdot\mathbf{e}_x = 0$
V	$\phi_{\mathrm{s}} = E_{\mathrm{cell}}$.
VI	$\mathbf{u}\cdot\mathbf{e}_y = 0, \mathbf{n}_i\cdot\mathbf{e}_y = 0$.
VII	$p\vert_{\mathrm{VII}_+} = p\vert_{\mathrm{VII}_-}, \mathbf{u}\cdot\mathbf{e}_y\vert_{\mathrm{VII}_+} = \mathbf{u}\cdot\mathbf{e}_y\vert_{\mathrm{VII}_-}$.
VIII	$\mathbf{i}^{(\mathrm{elec})}\cdot\mathbf{e}_y = 0$.
IX	$\mathbf{u}\cdot\mathbf{e}_y = 0, \omega_{\mathrm{H_2O}} = \frac{p_{\mathrm{sat}}M_{\mathrm{H_2O}}}{pM_{\mathrm{g}}}, \mathbf{n}_i\cdot\mathbf{e}_y = 0$.
X	$\phi_{\mathrm{s}} = 0$.

In the above equations, the vertical walls (IV) are impermeable to all species and are insulated; there is no crossover of CO_2, CO, H_2 and O_2 across the electrolyte. Water is assumed to be in equilibrium with the water vapour in the gas phase and p_{sat} is the vapour pressure of water vapour.

Constitutive relations

All the constitutive relations that are necessary to solve the above equations (Eqs. **1-15**) are provided in Table S2. ϵ_{p} is the percolation threshold porosity (here $\epsilon_{\mathrm{p}} = 0.11$) and α is a fitting parameter for through-plane diffusion (here $\alpha = 0.785$) from the Tomadakis-Sotirchos model[1], v_{i} is the diffusion volume of molecule i, used in correlations by Fuller, Schetter, and Giddings[2] and r_f is the carbon fibre radius (here $r_f = 4.6\ \mu$m)[3].

Table S2. Constitutive relations. Reused from Wu et al.[4].

$R_{\mathrm{CO_2}} =$	$-\frac{a_{\mathrm{CO}} i_{\mathrm{CO}}}{2F} M_{\mathrm{CO_2}}$
$R_{\mathrm{H_2O}} =$	$-\left(\frac{a_{\mathrm{CO}} i_{\mathrm{CO}}}{2F} + \frac{a_{\mathrm{H_2}} i_{\mathrm{H_2}}}{F}\right) M_{\mathrm{H_2O}}$
$R_{\mathrm{CO}} =$	$\frac{a_{\mathrm{CO}} i_{\mathrm{CO}}}{2F} M_{\mathrm{CO}}$
$R_{\mathrm{H_2}} =$	$\frac{a_{\mathrm{H_2}} i_{\mathrm{H_2}}}{2F} M_{\mathrm{H_2}}$
$R_{\mathrm{O_2}}$	$\frac{a_{\mathrm{O_2}} i_{\mathrm{O_2}}}{4F} M_{\mathrm{O_2}}$
$R_{\mathrm{H_2O}} =$	$\frac{a_{\mathrm{O_2}} i_{\mathrm{O_2}}}{2F} M_{\mathrm{H_2O}}$
$Q\vert_{\mathrm{cathode}} =$	$R_{\mathrm{CO_2}} + R_{\mathrm{H_2O}} + R_{\mathrm{CO}} + R_{\mathrm{H_2}}$
$Q\vert_{\mathrm{anode}} =$	$R_{\mathrm{O_2}} + R_{\mathrm{H_2O}}$
$a_{\mathrm{s}} =$	$\frac{1}{\epsilon_{\mathrm{cl}} h_{\mathrm{cl}}}$
$i_{\mathrm{CO}} =$	$i_{\mathrm{CO}}^{\mathrm{ref}} \frac{c_{\mathrm{CO_2}}}{c_{\mathrm{CO_2}}^{\mathrm{ref}}} \exp\left(-\frac{\alpha_{\mathrm{CO}} F}{RT} \eta_{\mathrm{CO}}\right)$
$i_{\mathrm{H_2}} =$	$i_{\mathrm{H_2}}^{\mathrm{ref}} \exp\left(-\frac{\alpha_{\mathrm{H_2}} F}{RT} \eta_{\mathrm{H_2}}\right)$
$i_{\mathrm{O_2}} =$	$i_{\mathrm{O_2}}^{\mathrm{ref}} \exp\left(-\frac{\alpha_{\mathrm{O_2}} F}{RT} \eta_{\mathrm{O_2}}\right)$
$\eta_{\mathrm{CO}} =$	$\phi_s - \phi_l - E_{\mathrm{CO}}$
$\eta_{\mathrm{H_2}} =$	$\phi_s - \phi_l - E_{\mathrm{H_2}}$
$\eta_{\mathrm{O_2}} =$	$\phi_{\mathrm{s}} - \phi_{\mathrm{l}} - E_{\mathrm{O_2}}$
$D_{ij} =$	$\frac{1.01325\times 10^{-2} T^{1.75} \left(\frac{1}{M_i} + \frac{1}{M_j}\right)^{0.5}}{p\left(v_i^{1/3} + v_i^{1/3}\right)}$
$D_{ij}^{\mathrm{eff}} =$	$\epsilon^{1.5} D_{ij}$
$\omega_{\mathrm{N_2}}\vert_{\mathrm{cathode}} =$	$1 - \omega_{\mathrm{CO_2}} - \omega_{\mathrm{CO}} - \omega_{\mathrm{H_2}} - \omega_{\mathrm{H_2O}}$
$\omega_{\mathrm{N_2}}\vert_{\mathrm{anode}} =$	$1 - \omega_{\mathrm{O_2}} - \omega_{\mathrm{H_2O}}$
$\kappa =$	$\frac{\epsilon}{8 \ln^2 \epsilon} \frac{(\epsilon - \epsilon_{\mathrm{p}})^{\alpha+2} r_f^2}{(1-\epsilon_{\mathrm{p}})[(\alpha+1)(\epsilon-\epsilon_{\mathrm{p}})]^2}$

List of other base case parameters

Table S3. List of other base-case parameters that are not varied in the study

Parameter	Value	Units
$c_{\mathrm{CO_2}}^{\mathrm{ref}}$	40.9	mol m^{-3}
c_{F}	0.55	–
E_{CO}	−0.52	V (at pH 7 vs SHE)
$E_{\mathrm{H_2}}$	−0.41	V (at pH 7 vs SHE)
$E_{\mathrm{O_2}}$	0.82	V (at pH 7 vs SHE)
F	96,487	C mol^{-1}
$M_{\mathrm{CO_2}}$	44×10^{-3}	kg mol^{-1}
M_{CO}	28×10^{-3}	kg mol^{-1}
$M_{\mathrm{H_2}}$	2×10^{-3}	kg mol^{-1}
$M_{\mathrm{O_2}}$	32×10^{-3}	kg mol^{-1}
$M_{\mathrm{N_2}}$	28×10^{-3}	kg mol^{-1}
$M_{\mathrm{H_2O}}$	18×10^{-3}	kg mol^{-1}
P^{ref}	1.0	atm (abs)
pH	7.0	–
p_{sat}	3187.7	Pa (abs)
R	8.314	J mol^{-1}
$v_{\mathrm{CO_2}}$	26.9	–
v_{CO}	18.9	–
$v_{\mathrm{H_2}}$	6.12	–
$v_{\mathrm{N_2}}$	17.9	–
$v_{\mathrm{O_2}}$	16.6	–
$v_{\mathrm{H_2O}}$	12.7	–

References

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