Supporting Information

Mass Transfer Effects in CO₂ Reduction on Cu Nanowire Electrocatalysts

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1. Characterization of the Reduced Cu nanowires



Figure S1. X-ray diffraction patterns of the oxidized Cu mesh (in air at 600 °C, 8h) and the Cu nanowires derived from the reduction of CuO nanowires (ECR, HR-150 and HR-300).

2. Estimation of Surface Roughness Factors

The double-layer capacitance was used to estimate the surface roughness factors of the Cu nanowires [1]. By plotting the width of the double layer against the scan rate, the non-Faradaic capacitance of the electrode is determined as the slope (Figure S2). The derived capacitance of the Cu nanowires was then compared to the value reported for polycrystalline Cu (Cu-poly), with the ratio giving the surface roughness factor (Table S1) [2]. The current densities per geometric area of the electrode (J_{tot} and J_{CO2}) were divided by the surface roughness factor to obtain the specific activities (j_{tot} and j_{CO2}), namely current densities per ECSA of Cu.

Table S1. Roughness factors from capacitance measurements of catalysts used in this study.

Sample	Capacitance (mF/cm ²)	Surface Roughness Factor
HR-300	0.676	23
HR-150	4.22	145
ECR	10.47	356



Figure S2. Capacitance measurements for the HR-300 Cu NWs. (a) Cyclic voltammetry scans in a non-faradaic region at different scan rates. (b) Plot of double-layer width against the scan rate, where the slope gives the non-Faradaic capacitance of the electrode.

3. Essentials of the Transport Model

We applied a recently developed transport model to calculate the CO_2 concentration on the surface of the Cu nanowires [3]. Considering the acid-base equilibria (equations 1-5) of CO_2 hydrolysis reactions:

$$CO_2(aq) + H_2O \Leftrightarrow H_2CO_3$$
, with $K_1 = 2.63 \times 10^{-3}$ (1)

$$H_2CO_3 \Leftrightarrow HCO_3^- + H^+, \quad K_2 = 2.5 \times 10^{-4}$$
 (2)

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+, \quad K_3 = 4.69 \times 10^{-11}$$
 (3)

$$CO_2(aq) + 0H^- \Leftrightarrow HCO_3^-, K_4 = 4.44 \times 10^7 1/M$$
 (4)

$$HCO_3^- + OH^- \Leftrightarrow CO_3^{2-} + H_2O, K_5 = 4.66 \times 10^3 \ 1/M$$
 (5)

and the electrochemical reduction reactions occurring on the nanowire surface (equations 6-13):

$$H_2 0 + 2e^- \longrightarrow H_2 + 20H^- \tag{6}$$

$$CO_2(aq) + H_2O + 2e^- \to CO + 2OH^-$$
 (7)

$$CO_2(aq) + H_2O + 2e^- \longrightarrow HCOO^- + OH^-$$
(8)

$$CO_2(aq) + 6H_2O + 8e^- \rightarrow CH_4 + 8OH^-$$
 (9)

$$2CO_2(aq) + 9H_2O + 12e^- \to C_2H_5OH + 12OH^-$$
(10)

$$2CO_2(aq) + 8H_2O + 12e^- \to C_2H_4 + 12OH^-$$
(11)

$$2CO_2(aq) + 10H_2O + 14e^- \to C_2H_6 + 14OH^-$$
(12)

$$3CO_2(aq) + 13H_2O + 18e^- \to C_3H_7OH + 18OH^-$$
(13)

we constructed a series of partial differential equations (equations 14-17):

$$\frac{\partial [CO_2(aq)]}{\partial t} = D_{CO_2} \frac{\partial^2 [CO_2(aq)]}{\partial x^2} - [CO_2(aq)][OH^-]k_{4f} + [HCO_3^-]k_{4r}$$
(14)
$$- r_{COR}(x)$$

$$\frac{\partial [HCO_3^-]}{\partial t} = D_{HCO_3^-} \frac{\partial^2 [HCO_3^-(aq)]}{\partial x^2} + [CO_2(aq)][OH^-]k_{4f} - [HCO_3^-]k_{4r} - [HCO_3^-][OH^-]k_{5f} + [CO_3^{2-}]k_{5r}$$
(15)

$$\frac{\partial [CO_3^-]}{\partial t} = D_{CO_3^-} \frac{\partial^2 [CO_3^-(aq)]}{\partial x^2} + [HCO_3^-][OH^-]k_{5f} - [CO_3^{2-}]k_{5r}$$
(16)

$$\frac{\partial [OH^{-}]}{\partial t} = D_{OH^{-}} \frac{\partial^{2} [OH^{-}]}{\partial x^{2}} - [CO_{2}(aq)][OH^{-}]k_{4f} + [HCO_{3}^{-}]k_{4r} - [HCO_{3}^{-}][OH^{-}]k_{5f} + [CO_{3}^{2-}]k_{5r} + r_{OH^{-}}COR + r_{OH^{-}}HER$$
(17)

where *t* is time, x is position within the boundary layer, *D* is the effective diffusion coefficient for a given species and *k*'s are the rate constants referring to reactions (4) and (5) ("*f*" and "*r*" state the forward and reverse, respectively). We assume the boundary layer of the model is equivalent to the thickness of the nanowires since the dense nanowires will prevent convective motion of electrolyte. In these equations, the consumption (r_{COR} for CO₂ reduction) and generation (r_{OH} -^{*COR*} and r_{OH} -^{*HER*}, for the production of hydroxide from the CO₂ reduction and hydrogen evolution, respectively) terms are added to account for the electrochemical reactions along the Cu nanowires (equations 6-13). For simplicity we assume the availability of water molecules in the coordination sphere does not affect the equilibrium constants (K1 – K5) (equations 1-5) on the surface of the Cu nanowires due to the change in the hydrolysis of carbonate anions from that of the bulk electrolyte.[4,5] To solve the PDE the following a series of boundary and initial conditions were applied. First, the boundary at the bulk electrolyte interface (i.e. when x=0) is set to equal the equilibrium constants which are readily accessible from literature [3,6]:

$$[CO_2(aq)]_{x=0, \ t\ge 0} = [CO_2(aq)]_{eq}$$
(18)

$$[HCO_3^-]_{x=0, \ t\ge 0} = [HCO_3^-]_{eq} \tag{19}$$

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$$[CO_3^{2-}]_{x=0, \ t\ge 0} = [CO_3^{2-}]_{eq}$$
⁽²⁰⁾

$$[OH^{-}]_{x=0, \ t\geq 0} = [OH^{-}]_{eq} \tag{21}$$

At t=0, no electrochemical reactions have taken place therefore the initial concentrations in the boundary layer are equal to the equilibrium concentration values:

$$[CO_2(aq)]_{x \ge 0, t=0} = [CO_2(aq)]_{eq}$$
(22)

$$[HCO_3^-]_{x \ge 0, t=0} = [HCO_3^-]_{eq}$$
(23)

$$[CO_3^{2-}]_{x \ge 0, t=0} = [CO_3^{2-}]_{eq}$$
⁽²⁴⁾

$$[OH^{-}]_{x \ge 0, t=0} = [OH^{-}]_{eq}$$
⁽²⁵⁾

Finally, we set the base of the nanowires ($x = \delta$) to be a reflective impermeable wall:

$$D_A \frac{\partial [A]}{\partial x}_{x=\delta, t>0} = 0$$
(26)

where *A* represents CO_2 , HCO_3^- , CO_3^{2-} or OH^- . By assuming a first-order dependence of the reaction rate we can write:

$$r_{COR}(x) = k_{COR}[CO_2]_x \tag{27}$$

where the rate constant, k_{COR} , is related to the total CO₂ consumption rate on the electrode by:

$$r_{COR}^{total} = \int_{0}^{\delta} r_{CO_2}(x) dx = \int_{0}^{\delta} k_{COR} [CO_2]_x dx$$
(28)

The total CO_2 consumption rate can be derived from the experimentally measured CO_2 reduction activity, including the total current density (*j*) and the Faradaic efficiency (FE) for each product, via:

$$r_{COR}^{total} = \left(\frac{j}{F}\right) \sum_{i} \frac{FE_i \cdot n_i}{z_i}$$
(29)

where n_i and z_i represent the stoichiometric coefficients (e.g., $n_i = 1$ for CO and $n_i = 2$ for ethanol) and electron transfer number (e.g., $z_i = 2$ for CO and $z_i = 12$ for ethanol) for a given product of CO₂ reduction (equations 6-13). Similarly, the generation of hydroxide is also distributed within the boundary layer. From (equations 6-13), the hydroxide formation is a result of both CO₂ reduction (COR) and HER:

$$r_{OH^{-}}^{total} = r_{OH^{-}}^{COR, total} + r_{OH^{-}}^{HER, total}$$
(30)

which are further related to the experimentally measured catalytic activities by:

$$r_{OH^{-}}^{COR, \ total} = \left(\frac{j}{F}\right) \sum_{i} \frac{FE_i \cdot m_i}{z_i}$$
(31)

$$r_{OH}^{-HER, \ total} = \left(\frac{j}{F}\right) \frac{FE_{H_2} \cdot m_{H_2}}{Z_{H_2}}$$
 (32)

Here m_i and z_i are the stoichiometric coefficient of hydroxide and electron transfer number, respectively, for a given reaction. The distribution of hydroxide formation from CO₂ reduction along the Cu nanowires should be consistent with that for CO₂ consumption (equation 27), namely also proportional to the local CO₂ concentration:

$$r_{OH^{-}}^{COR}(x) = k_{OH^{-}}^{COR} [CO_2]_x$$
(33)

where the rate constant is given by:

$$r_{OH^{-}}^{COR, \ total} = \int_{0}^{\delta} r_{OH^{-}}^{COR}(x) dx = \int_{0}^{\delta} k_{OH^{-}}^{COR} [CO_2]_x dx$$
(34)

By comparing equation (34) with equation (28), we can see that k_{OH} -^{*COR*} and k_{COR} are linearly correlated to each other, with the ratio determined by the stoichiometric coefficients and electron transfer numbers as indicated by equations. (29, 31). In the case of a planar electrode with a smooth surface, these consumption and generations terms will be moved into the boundary conditions (namely all the reactions only take place at x = δ), after which the transport becomes solely a diffusion problem as solved by Gupta *et. al* [6].

Considering the abundance of water in the electrolyte, we assume hydroxide formation from the HER can be treated as zero order, namely independent on the concentrations of CO₂ and (bi)carbonate. The local pH may have an effect on the HER activity, but the variation may not be significant and is not considered in the present model.[7,8] We acknowledge the sluggish kinetics of CO₂ reduction could be mainly limited by the hydrogenation of intermediate CO_{ad} species[9,10] or CO-CO coupling[11,12], and CO_{ad} would impede the HER activity on the Cu surface[13]. Although the exact coverage of CO_{ad} at a given position in the boundary layer ($0 < x < \delta$) is unknown, it likely decreases as *x* increases, following the drop of CO₂ concentration due to the reduction reactions and increase of local pH. For simplicity, we assume the rate of hydroxide formation from HER increases linearly with the depth in the boundary layer:

$$r_{OH^{-}}^{HER}(x) = qx \tag{35}$$

where the coefficient q is given by the experimentally measured HER activity from equation (32):

$$r_{OH^{-}}^{HER, \ total} = \int_{0}^{\delta} r_{OH^{-}}^{HER}(x) dx = \int_{0}^{\delta} qx dx$$
(36)

We then solve the PDEs (equations 14-17)) using Matlab R2016b by applying the initial conditions (equations 18-21, 26), boundary conditions (equations 22-25) and rate conditions (equations 27, 33, 35). We performed iterative analysis to calculate the rate constant k_{COR} , with the experimental inputs of the electrode current (*j*) and Faradaic efficiencies (FE_i and FE_{H_2}) at any given potential.

4. Calculation of CO₂ Conversion Rate

The CO₂ conversion rates were calculated on the basis of experimentally measured current densities and FEs using

$$CO_{2,cons} = \left(\frac{j}{F}\right) \sum_{i=1}^{n} n_i \frac{FE\%_i}{z_i},\tag{37}$$

where $CO_{2, cons}$ stands for the rate of CO_2 consumption (mols s⁻¹ cm⁻²), *j* the current density (A/cm², either geometric or specific), *F* faraday's constant, n_i the stoichiometric coefficient of CO_2 in the reaction equation toward the given product *i* (e.g., $n_i = 1$ for CO and 2 for ethanol), *FE%_i* the faradaic efficiency of species *i* and *z_i* the moles electrons transferred per mole of species *i*.

5. Calculation of the Maximal CO₂ Flux

The maximum CO_2 flux was calculated using tabulated values for the bulk diffusivity and solubility of CO_2 in 0.1 M KHCO₃, see equation (38).

$$CO_{2,flux} = -D_{b,H_2O} \left(\frac{\mu_{H_2O}}{\mu_{KHCO_3}}\right) \left(\frac{1000[CO_2]_{KHCO_3} - 0}{0 - \delta}\right)$$
(38)

The maximum CO₂ flux, CO_{2,flux} (mol m⁻¹ s⁻¹) is found by multiplying the solubility of CO₂ in 0.1 M KHCO₃, [CO₂]_{KHCO3} (mols/L) by the diffusivity through KHCO₃. The diffusivity through KHCO₃ is found by multiplying the bulk diffusion coefficient in infinitely diluted H₂O, D_{b,H2O} (m²/s), by the viscosity change $\left(\frac{\mu_{H_2O}}{\mu_{KHCO_3}}\right)$. The viscosity of water and 0.1 M KHCO₃ at 25 °C are 0.890 mPa*s and 1.015 mPa*s, respectively [14,15].

4. References

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