Supporting Information

Interplay of Homogeneous Reactions, Mass Transport and Kinetics in Determining Selectivity of the Reduction of CO₂ on Gold Electrodes

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| Index                                                                 | Page |
|----------------------------------------------------------------------|------|
| 1. Experimental section                                              | S3   |
| 2. Electrochemical surface area determination                        | S7   |
|   Figure S1. CVs used for electrochemical surface area determination | S7   |
|   Table S1. Calculated roughness from surface area measurements      | S7   |
| 3. Figure S2. Custom electrochemical cell                            | S8   |
| 4. Evaluation of electrode deactivation and poisoning                 | S9   |
|   Figure S3. CO and H₂ partial current density                       | S9   |
|   Figure S4. Chronoamperometric traces                               | S9   |
| 5. Electrolysis in additional buffer                                 | S10  |
|   Figure S5. CO and H₂ faradaic efficiency and partial current density| S10  |
| 6. Calculation of concentrations in bicarbonate solutions             | S11  |
| 7. Determination of the diffusion layer thickness                     | S12  |
|   Figure S6. Plateau current density for proton reduction on gold    | S12  |
| 8. H₂ geometrical and electrochemical surface area current densities  | S13  |
|   Figure S7. H₂ partial current densities on gold                    | S13  |
| 9. Modeling of kinetic interference of a chemical step                | S14  |
|   Scheme S1. Simplified CO₂ reduction mechanism with kinetic interference | S14  |
|   Figure S8. Koutecký-Levich simulations with kinetic interference   | S15  |
| 10. Simulations                                                       | S16  |
|   Table S2. List of species in solution used in simulations           | S16  |
|   HER limited by H₂CO₃ or H₃O⁺ replenishment                         | S16  |
|   CDR for leaf and wire electrodes with Volmer linear law            | S17  |
|   CDR for leaf and wire electrodes with adjusted rate constant       | S18  |
|   Surface pH for leaf and wire electrodes                             | S18  |
|   Figure S9. Correlation of simulated rate constant with pH          | S19  |
|   CDR and HER for the film electrode                                 | S19  |
|   Figure S10. H₂ and CO current densities and FE(CO)                 | S20  |
| 11. Simplified modeling of CO₂ depletion in a catalyst layer          | S21  |
| References                                                            | S24  |
1. Experimental section

Materials and chemicals. All chemicals and solutions were used without further processing unless otherwise stated. Silicon wafers (4'' <100> 0.001-0.005 ohm/cm² n-type) were purchased from Nova Electronic Materials. 0.93 ± 0.03 µm diameter polystyrene nanospheres in a 10% aqueous suspension was purchased from Thermo Fisher Scientific. Gold plating solution, Orotemp 24 Rack (potassium aurocyanide 1.0%, pH 5.8 ± 0.5) and Techni Gold 25 ES RTU (sodium sulfite 4.0%, sodium gold sulfite 1.6%, pH 7-7.5) were purchased from Technic. Triton X-100, hydrochloric acid (99.999% trace metals basis), sodium bicarbonate (≥99.7% puriss, ACS reagent), sodium perchlorate (≥99.99% trace metals basis), and a gas mixture of hydrogen, oxygen, carbon monoxide, and carbon dioxide of 0.05% w/w each were purchased from Sigma Aldrich. Potassium chloride was purchased from Strem Chemicals. Spectroscopic pure graphite rods were purchased from SPI Supplies. Buffered Oxide Etch 7:1 (BOE) and plain glass microscope slides (75 × 25 × 1 mm³) were purchased from VWR. Argon (research grade) and carbon dioxide (pure clean grade) were purchased from Airgas.

Instrumentation. Wet oxidation was completed with a Tystar Tytan 4600 wet/dry oxide furnace. Scanning Electron Microscope (SEM) images were acquired using Zeiss Ultra55 SEM. Oxygen reactive ion etching (RIE) was performed with an Anatech Barrel SCE-106 Plasma system. Deep reactive ion etching (DRIE) for the fabrication of high aspect ratio structures was accomplished with an Omega LPX SPTS Rapier DRIE system. Electron beam evaporation was performed with a Denton Explorer 14 Electron Beam Evaporator. Electrochemical deposition of gold, surface area measurement voltammograms, and steady-state electrochemical measurements employed a CHI Instruments 760D potentiostat. Gaseous products were detected using an SRI Instruments multiple gas analyzer #3 gas chromatograph.

Gold nanowire array fabrication. Nanowire arrays were fabricated in a top-down method via nanosphere lithography. Briefly, a layer of 0.93 ± 0.03 µm diameter polystyrene nanospheres was spin-coated on a silicon wafer at 500 rpm for 10 s, 1000 rpm for 120 s, and 1400 rpm for 30 s. The diameter of the nanospheres was decreased using oxygen plasma RIE at 100 W and 40 sccm oxygen flow rate for 120 s. The wafer was then etched in a DRIE (SPTS Rapier) to yield an array of nanowires. Wire thinning was completed by growing a wet oxide layer of target thickness 60 nm around the nanopillars at 1000 °C and subsequent etching of the oxide in BOE at room temperature. The resulting nanowire arrays had characteristic dimensions of: 10 µm height, 350 nm diameter, and 580 nm interwire spacing.

A conventional three-electrode electrochemical cell positioned in a Teflon cell was used for the electrodeposition of gold with a Pt mesh counter electrode, an Ag/AgCl reference electrode, and the Si wire array as the working electrode. The Teflon cell exposed a 3.9 cm² area of the silicon wire arrays for electrodeposition. A diamond tip pen was used to scratch the corner of the silicon to facilitate better electrical contact. Prior to electrodeposition, Si wire arrays were submerged in BOE in order to etch any native oxide that forms on the surface of silicon. Gold was electrodeposited on the pillar array by applying a potential of –900 mV vs Ag/AgCl (CHI instruments, 3 M
KCl) in the Orotemp 24 Rack solution and limiting the charge passed to 2 coulombs. The electrochemical cell and electrodes were thoroughly washed in nanopure water following deposition.\textsuperscript{2}

**Gold film evaporation.** Glass slides were coated with a 10 nm titanium adhesion layer followed by a 200 nm gold layer by electron beam evaporation. Gold was evaporated at a rate of 2 Å/s and titanium was evaporated at a rate of 1 Å/s. Slides were used as is as a substrate for leaf deposition as well as for CDR.

**Gold leaf electrodeposition.** A conventional three-electrode electrochemical cell positioned in a Teflon cell was used for the electrodeposition of gold with a Pt mesh counter electrode, an Ag/AgCl reference electrode, and a gold coated glass slide as the working electrode. The Teflon cell exposed a 3.9 cm\(^2\) area of the gold coated glass slide for electrodeposition. Gold leaves were electrodeposited on the film by applying a potential of \(-800\) mV vs Ag/AgCl (CHI instruments, 3 M KCl) in the Techni Gold 25 ES RTU solution and limiting the charge passed to 1.2 coulombs. The electrochemical cell and electrodes were thoroughly washed in nanopure water following deposition.

**CO\(_2\) reduction steady-state measurements.** Unless otherwise stated, all electrolyte was 0.1 M NaHCO\(_3\) with 0.5 M NaClO\(_4\) supporting electrolyte. The electrolyte was prepared with nanopure water and was further purified by capacitive deionization with graphite rods at 2.2 V for 16 h. All potentials were measured against Ag/AgCl (3 M KCl, Leak-Free, Warner Instruments) and converted to the Standard Hydrogen Electrode (SHE) scale according to,

\[
E_{\text{SHE}} = E_{\text{Ag/AgCl}} + 0.1976
\]

where \(E_{\text{SHE}}\) is the converted potential vs. SHE, and \(E_{\text{Ag/AgCl}}\) is the experimentally measured potential vs Ag/AgCl reference electrode.

All steady state measurements were performed in a custom designed, polyether ether ketone (PEEK) plastic, two-compartment, gas-tight electrochemical cell (Figure S2) separated by an anion exchange membrane (AMV-N, SELEMION, AGC Engineering). The custom designed cell allows for large area electrodes to be used and exposes only a 1.53 cm\(^2\) geometric area to solution. The resistance of the cell was 20.5 ± 1.5 ohms depending on electrode and was compensated during electrolysis. Between electrolyses, the cell was thoroughly rinsed and kept in nanopure water. The cathodic compartment contained 25 mL of solution and approximately 10 mL of headspace. Prior to steady state measurements, the solution was sparged and headspace degassed with CO\(_2\) for 1 h. During steady-state measurements the solution in the cathodic compartment was stirred at 650 rpm and was continuously sparged with CO\(_2\) at a flow rate of 15 sccm. For measurements exhibiting total currents lower than 1 mA, the flow rate was decreased to 7.5 sccm. Gas flowing from the headspace of the cathodic cell flows directly into a GC, which was programmed to run at the end of every 10 min potentiostatic measurement. The GC was equipped with a MolSieve 5A and 2m silica gel column with Argon as the carrier gas. H\(_2\) and CO were detected by a thermal conductivity
detector and a methanizer-flame ionization detector set, respectively. The H2 and CO faradaic efficiencies and partial current densities were calculated as follows,

\[ j_{CO} = \frac{PA}{\alpha} \times FR \times \frac{nFp_0}{RT} \times (A)^{-1} \]

\[ j_{H2} = \frac{PA}{\beta} \times FR \times \frac{nFp_0}{RT} \times (A)^{-1} \]

where PA is the peak area as measured by the GC for the appropriate gas, \( \alpha \) and \( \beta \) are calibration factors for CO and H2, respectively, determined from GC signals corresponding to a known concentration of gas in a mixture to determine the concentration of product as measured by the GC. FR is the flow rate = 15 sccm, A is the electrode area = 1.53 cm\(^2\); \( p_0 \) is the pressure in the electrochemical cell = 14.77 psi, and \( T = 293 \) K. Faradaic efficiencies do not sum to 100% due to headspace equilibration time and instrument detection limits at low current density; in these cases faradaic efficiencies were normalized such that the FE(CO) and FE(H2) summed to 100\%.

The data presented in Figures 2A-2D, and subsequently reproduced in other figures, is the average value obtained from three separate measurements each using new electrodes with data collection over the entire potential range occurring on a single electrode.

**Electrochemical surface area measurement.** The electrochemical surface area of the gold electrodes was measured using the charge associated with the removal of a chemisorbed oxygen monolayer and underpotential deposition of copper. The film electrode was assumed to have roughness 1 (i.e. total electrochemically active surface area equal to projected surface area) and the roughness factors of the leaf and wire electrodes were calculated relative to the film electrode. The two surface area measurement methods agreed within 7% for each electrode. The average roughness factors were taken for simulation and data analysis.

Oxide dissolution: Electrodes were submerged in a 0.05 M H\(_2\)SO\(_4\) solution that was degassed with N\(_2\). Platinum mesh and Ag/AgCl electrodes were used as the counter and reference electrodes, respectively. CVs from 0.2 V vs. SHE to 1.7 V vs. SHE with a scan rate of 50 mV/s were acquired until the traces converged. The reduction wave at ca 1.0 V vs. SHE was integrated.

Copper underpotential deposition: Electrodes were submerged in a 0.5 M H\(_2\)SO\(_4\) with 0.1 M CuSO\(_4\) solution that was degassed with N\(_2\). A platinum mesh and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. CVs from 0.283 V to 0.683 V vs. SHE with a scan rate of 50 mV/s were acquired until the traces converged. The broad anodic wave at 0.6 V vs. SHE was integrated.

**Evaluation of electrode deactivation and poisoning.** Potential electrode poisoning was investigated by conducting steady state measurements to evaluate current hysteresis and with anodic CO stripping between potential steps on the leaf electrode.

Current hysteresis: Steady-state measurements were conducted as described above from \(-0.8\) V to \(-1.5\) V vs. SHE with decreasing applied potential. Immediately, the reverse sweep was conducted from \(-1.5\) V to \(-0.8\) V vs. SHE.
**CO stripping**. Steady-state measurements were conducted as described above from –0.8 V to –1.5 V vs with decreasing applied potential. Immediately prior to each measurement, an anodic sweep from –0.4 V to 0.4 V vs. SHE with a scan rate of 50 mV/s was applied to anodically oxidize CO from the surface of the electrode.\(^5\)

**Electrolysis in additional buffer.** Steady-state measurements were conducted as described above from –0.8 V to –1.5 V vs. SHE. However, 0.5 M NaClO\(_4\) supporting electrolyte was replaced with 0.49 M Na\(_2\)HPO\(_4\) + 0.01 M NaH\(_2\)PO\(_4\). The buffer composition was chosen to have a similar bulk pH of the buffer system containing only 0.1 M NaHCO\(_3\).

**Determination of the diffusion layer thickness.** The diffusion layer thickness of the custom designed cell under reaction conditions was determined by measuring the current associated with the hydrogen evolution reaction (HER) with a platinum film. A 100 nm thick platinum film was evaporated on glass microscope slides with a 10 nm titanium adhesion layer. Under the same conditions as bulk electrolysis (1.53 cm\(^2\) active electrode area, 25 mL solution, 15 sccm gas flow, 650 rpm stirring), the plateau current associated with HER was measured in a pH 2.92 HCl solution with 0.5 M KCl.

**Safety Statement.** No unexpected or unusually high safety hazards were encountered.
2. Electroactive surface area

Figure S1. A Cyclic voltammograms corresponding to the dissolution of surface gold oxide layers on the gold film (black), leaf (blue), and wire (red) electrodes. The peak arising at 1.2 V vs. SHE was integrated to determine the charge associated with surface oxide dissolution. B Cyclic voltammograms corresponding to the underpotential deposition of copper on the gold film (black), leaf (blue), and wire (red) electrodes. The peak arising at 0.6 V vs. SHE was integrated to determine the charge associated with copper underpotential deposition.

Table S1. Calculated roughness from surface area measurements

| Electrode | Oxide dissolution charge (C) | Cu UPD charge (C) | $R_f$ by oxide dissolution | $R_f$ by Cu UPD | Average $R_f$ |
|-----------|-----------------------------|-------------------|--------------------------|-----------------|---------------|
| Film      | $2.36 \times 10^{-3}$       | $6.94 \times 10^{-4}$ | 1 $^a$                  | 1 $^a$          | 1             |
| Leaf      | $9.94 \times 10^{-3}$       | $3.14 \times 10^{-3}$ | 4.21                     | 4.52            | 4.37          |
| Wire      | $3.68 \times 10^{-2}$       | $1.06 \times 10^{-2}$ | 15.59                    | 15.28           | 15.44         |

$^a$Roughness assumed to be 1
3. Custom designed electrochemical cell

Figure S2. Custom designed airtight electrochemical cell machined from PEEK plastic. The cell facilitates the use of large electrodes and obviates the need for cutting electrodes and creating of reliable electrical contacts as sufficiently large electrodes can be contacted by the potentiostat leads directly. The cell exposes a circular 1.53 cm² portion of the electrode to the electrolyte. A membrane is used to separate the cathodic and anodic chambers of the electrochemical cell.
4. Evaluation of electrode deactivation and poisoning

**Figure S3.** Partial current densities for CO (green) and H₂ (blue) production obtained by electrolysis on the leaf electrode in a solution of 0.1 M of NaHCO₃ and 0.5 M of NaClO₄ under a CO₂ atmosphere with A increasing (●) and decreasing (○) overpotential and B anodic CO stripping linear voltammetry sweeps of the same electrode immediately prior to electrolysis steps.

**Figure S4.** Representative chronoamperometric traces obtained by electrolysis on the leaf electrode in a solution of 0.1 M of NaHCO₃ and 0.5 M of NaClO₄ under a CO₂ atmosphere with increasing overpotential (Figure S3A, ●). The current is the total overall current observed.
5. Electrolysis in additional buffer

**Figure S5.** A Faradaic efficiency and B partial current density for CO (green) and H₂ (blue) production on a leaf electrode in a solution containing 0.1 M NaHCO₃, 0.49 M Na₂HPO₄ and 0.01 M NaH₂PO₄. Increased proton donor concentration results in elevated HER faradaic efficiency and partial current density.
6. Concentrations of bicarbonate for solutions of NaHCO₃ under CO₂ atmosphere

We note $C^0$ is the concentration of NaHCO₃ introduced in solution and $C^\infty$ is the concentration of the supporting electrolyte NaClO₄.

The requirement for mass conservation is,

$[\text{Na}^+] = C^0 + C^\infty$; $[\text{ClO}_4^-] = C^\infty$

The requirement for electroneutrality is,

$[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] + [\text{ClO}_4^-] = [\text{Na}^+] + [\text{H}^+]$

Equilibrium conditions are,

$[\text{CO}_2] = K_{\text{Henry}} = 0.038 \text{ M}$

$K_{a1} = \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} [\text{H}^+] = 10^{−3.6}; K_{a2} = \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} [\text{H}^+] = 10^{−10.32}; K_c = [\text{H}^+][\text{OH}^-] = 10^{−14}$

$= 10^{−10.32}; K_c = [\text{H}^+][\text{OH}^-] = 10^{−14}$

and

$K_{\text{hyd}} = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2]} = 1.7 \times 10^{−3}$

From above $[\text{H}_2\text{CO}_3] = 1.7 \times 10^{−3} \cdot [\text{CO}_2] = 6.5 \times 10^{−5} \text{ M}$

leading to,

$\frac{K_{a1}}{[\text{H}^+]} [\text{H}_2\text{CO}_3] + 2 \frac{K_{a1}}{[\text{H}^+] [\text{H}^+]} [\text{H}_2\text{CO}_3] + \frac{K_c}{[\text{H}^+]} = C^0 + [\text{H}^+]$

Simplification leads to,

$C^0 + [\text{H}^+] + [\text{OH}^-] - \frac{K_c}{[\text{H}^+]} \approx C^0$

hence,

$[\text{H}^+] = \frac{K_{a1}[\text{H}_2\text{CO}_3] + \sqrt{(K_{a1}[\text{H}_2\text{CO}_3])^2 + 8K_{a1}K_{a12}[\text{H}_2\text{CO}_3]C^0}}{2C^0}$

$[\text{CO}_2] = K_{\text{Henry}} = 0.038 \text{ M}$

$[\text{HCO}_3^-] = \frac{K_{a1}K_{\text{hyd}}K_{\text{Henry}}}{[\text{H}^+]}$
7. Determination of the diffusion layer thickness

Reduction of protons on Pt electrode is a fast electrochemical process leading to a plateau current ($i_{p,\infty}$) at large overpotential with,

$$\frac{i_{p,\infty}}{S} = \frac{F D_{H^+} [H^+]_\infty}{\delta} = 0.55 \text{ mA/cm}^2$$

Taking $D_{H^+} = 9.3 \times 10^{-5} \text{ cm}^2/\text{s}$, $F = 96500 \text{ C/mol}$, and the plateau current from Figure S6, shown below, we obtain $\delta = 190 \text{ µm}$.

**Figure S6.** Proton reduction on a flat $S = 1.53 \text{ cm}^2$ Pt electrode in a 1 mM HCl solution (pH = 2.92) with 0.5 M KCl supporting electrolyte and under the same hydrodynamics conditions as electrocatalysis experiments on gold electrodes for CDR (i.e. same electrolysis cell, 1.53 cm$^2$ active electrode area, 20 mL solution, 10 sccm gas flow, 650 rpm stirring).
8. H₂ geometrical and electrochemical surface area current densities

**Figure S7.** H₂ partial current densities on gold film (black), leaf (blue) and wire (red) electrodes normalized with \( A \) electrochemical surface area and \( B \) geometrical surface area. At low overpotential, HER partial current density is proportional to the electrochemical surface area of the electrode.
9. Modeling of kinetic interference of a chemical step

We consider a film (roughness factor = $R_f$, geometrical surface area = $S_{geom}$). The film is conductive and, at the interface of the film material, CO$_2$ can be reduced producing that a current $i_{CO}$ is flowing through the electrode. We consider the following simplified mechanism:

$$\text{AS} + \text{CO}_2 + e^- \rightleftharpoons (\text{CO}_2^-)_{ads}$$

$$\text{(CO}_2^-)_{ads} \rightleftharpoons \text{l}$$

$$\text{l} + e^- \rightarrow \text{CO}_{ads}$$

$$\text{CO}_{ads} \rightarrow \text{fast}^a \rightarrow \text{CO} + \text{AS}$$

**Scheme S1.** Simplified mechanism for CO$_2$ reduction considering potential kinetic interference due to a chemical step following the initial electron transfer, where AS represents a free active site for reaction and I is an intermediate. $^a$ fast due to the reduction being much easier than the first electron transfer. $^b$ fast due to zeroth order dependence of CO production on CO.$^5$

According to the proposed mechanism:

$$i_{CO} = 2FS_{geom}R_f(k_f \Gamma_{AS}[\text{CO}_2]_{x=0} - k_b(\Gamma^0 - \Gamma_{AS}))$$

where $\Gamma_{AS}$ is the concentration of free active sites and $\Gamma^0$ is the total concentration of active sites, whereby remaining active sites may be involved in reaction with intermediates CO$_2$$_{ads}$, I, and CO$_{ads}$. Rewriting the equation leads to:

$$i_{CO} = 2FS_{geom}R_fk_f\Gamma^0[\text{CO}_2]_{x=0} \{1 - (1 + \frac{k_b}{k_f[\text{CO}_2]_{x=0}})(1 - \frac{\Gamma_{AS}}{\Gamma^0})\}$$

Simplification with $\frac{k_b}{k_f} = \exp\left(\frac{F}{RT} (E - E_1^0)\right)$, where $E_1^0$ is the standard potential of the first inner-sphere electron transfer, leads to:

$$i_{CO} = 2FS_{geom}R_fk_f\Gamma^0[\text{CO}_2]_{x=0} \{1 - (1 + \frac{\exp\left(\frac{F}{RT} (E - E_1^0)\right)}{[\text{CO}_2]_{x=0}})(1 - \frac{\Gamma_{AS}}{\Gamma^0})\}$$

Due to steady state conditions, $\frac{d(\Gamma^0 - \Gamma_{AS})}{dt} = \frac{i_{CO}}{2FS_{geom}} - k(\Gamma^0 - \Gamma_{AS}) = 0$, where $k$ is the rate constant of the chemical step following the initial electron transfer. Thus,

$$i_{CO} = \frac{1}{\frac{1}{2FS_{geom}R_fk_f\Gamma^0[\text{CO}_2]_{x=0}} + \frac{1}{2FS_{geom}\Gamma^0k}(1 + \frac{\exp\left(\frac{F}{RT} (E - E_1^0)\right)}{[\text{CO}_2]_{x=0}})}$$
At low overpotential, a Butler-Volmer behavior is observed experimentally. Therefore \( i_{\text{CO}} \approx 2FS_{\text{geom}}Rt_k f\Gamma^0 [\text{CO}_2]_{x=0} \) with \( k f\Gamma^0 = k_{f,\text{CO}_2}^{\text{ap}} \) (corresponding to eq 4 in the text) following the Butler-Volmer rate law. Hence, 

\[
\frac{\exp \frac{F}{RT} (E - E^0)}{[\text{CO}_2]_{x=0}} \ll 1 \quad \text{as long as } [\text{CO}_2] \text{ at the electrode is not too small, i.e. } E < -1.3 \text{ V due to the onset of mass transport limitations and homogeneous consumption of } \text{CO}_2 \text{ at } E > -1.3 \text{ V. Therefore,}
\]

\[
i_{\text{CO}} = \frac{1}{2FS_{\text{geom}}Rt_k f\Gamma^0 [\text{CO}_2]_{x=0} + 2FS_{\text{geom}}\Gamma^0 k}
\]  

(S1)

Eq S1, with \( 2FS_{\text{geom}}Rt_k f\Gamma^0 [\text{CO}_2]_{x=0} \) derived from the Butler-Volmer rate law and \( [\text{CO}_2]_{x=0} \) corrected for mass transport and homogeneous reactions models the influence of kinetic interference of a chemical step (step 2; \( \text{CO}_2^- \rightarrow \text{I} \)) on \( i_{\text{CO}} \) by adjusting \( 2FS_{\text{geom}}\Gamma^0 k \). As seen in Figures 8a and 8b, \( i_{\text{CO}} \) cannot be accounted for by interference of a chemical step following the initial electron transfer. Thus, \( k \) is large and therefore, \( \frac{i_{\text{CO}}}{2FS_{\text{geom}}} = k (\Gamma^0 - \Gamma_{\text{AS}}) \) resulting from the steady-state measurement conditions leads to \( (\Gamma^0 - \Gamma_{\text{AS}}) \rightarrow 0 \), i.e. \( \Gamma_{\text{AS}} \approx \Gamma^0 \). In other words, sluggish chemical steps following the initial transfer does not influence the reaction kinetics.

**Figure S8.** Partial current densities normalized by geometric surface area for CO considering kinetic interference of a chemical step on the A leaf and B wire electrode. Squares (black) show experimental data; dashed lines (black) show Koutecký-Levich simulations with concentrations of species modified owing to homogeneous reactions and mass transport; full lines show deviations from the Koutecký-Levich simulations considering kinetic interference of a chemical step according to equation (S1) with: \( 2F\Gamma^0 k = 2 \) (green), 6 (light green), 25 (turquoise), 50 (blue) mA/cm².
10. Simulations

Simulations have been performed using DigiElch program. Steady state currents and concentrations are obtained by performing 100s chronoamperometry simulation with an initial potential 0.3 V vs. SHE jumping to the desired applied potential $E$ at $t = 0$. Electrode geometry is planar with a surface area 1 cm$^2$. Finite 1D diffusion is considered with a $\delta = 190$ µm layer thickness and concentrations at their initial values for all species at the far right end of the cell. For all simulations, $T = 293$ K.

Partial current densities for H$_2$ and CO are obtained from,

$$ j_{H_2} = 2 \frac{FD_{H_2}[H_2]_{x=0}}{\delta} \quad \text{and} \quad j_{CO} = 2 \frac{FD_{CO}[CO]_{x=0}}{\delta} $$

where $[H_2]_{x=0}$ and $[CO]_{x=0}$ are the concentrations of H$_2$ and CO, respectively, at the electrode surface at $t = 100$ s.

**Table S2.** relevant species in solution used in simulations

| Species      | Diffusion coefficient (cm$^2$ s$^{-1}$) | Initial concentration (M) b |
|--------------|----------------------------------------|------------------------------|
| H$_2$O       | 0.1 $^a$                               | 1                            |
| CO$_2$       | $1.9 \times 10^{-5}$                   | 0.038                        |
| HCO$_3^-$    | $1.2 \times 10^{-5}$                   | 0.1                          |
| H$_3$O$_2^+$ | $9.3 \times 10^{-5}$                   | -                            |
| OH$^-$       | $5.3 \times 10^{-5}$                   | -                            |
| H$_2$CO$_3$  | $10^{-5}$                              | -                            |
| CO$_3^{2-}$  | $0.9 \times 10^{-5}$                   | -                            |
| H$_2$        | $10^{-5}$                              | -                            |
| CO           | $10^{-5}$                              | -                            |

$^a$ value large enough to prevent any change of H$_2$O concentration in the reaction layer. $^b$ The actual concentrations are calculated by the program taking into account homogeneous chemical reactions listed in Table 1 of the text and leading to values given in Table 2 of the text.

Electrochemical reactions for CO (CDR) and H$_2$ (HER) production at the electrode surface ($x = 0$) are detailed below for each specific simulation.

a. Simulations of HER limited by H$_2$CO$_3$ or H$_3$O$^+$ replenishment

Simulations of H$_2$ production current density in conditions where HER is limited by H$_2$CO$_3$ replenishment are obtained considering the following electrochemical reactions:

| Reaction                  | $E^0$ (V vs. SHE) | $k_s$  | $\alpha$ |
|---------------------------|-------------------|--------|----------|
| H$_2$CO$_3$ + e$^-$ ⇌ I + HCO$_3^-$ | 0                 | 1 $^a$ | 0.5      |
| I + H$_2$CO$_3$ + e$^-$ ⇌ H$_2$ + HCO$_3^-$ | 1 $^b$            | $10^4$ $^c$ | 0.5      |

$^a$ large enough for the current density to be potential independent. $^b$ positive enough for the intermediate I to be reduced very easily and not accumulate. $^c$ large enough for the intermediate I to be reduced very fast and not accumulate.
The simulated current density in the range of potential –0.7 to –0.9 V is constant and equal to 0.989 mA/cm². This value is higher than the experimentally observed current densities for all three electrodes in this range of potential indicating that H₂CO₃ can be a competent HER substrate in this range of potential.

Simulations of H₂ production current density in conditions where HER is limited by H₃O⁺ replenishment are obtained considering the following electrochemical reactions:

| Reaction | \( E^0 \) (V vs. SHE) | \( k_s \) | \( \alpha \) |
|----------|-----------------|--------|--------|
| \( \text{H}_3\text{O}^+ + e^- \rightleftharpoons \text{I} + \text{H}_2\text{O} \) | 0     | 1 \(^a\) | 0.5    |
| \( \text{I} + \text{H}_3\text{O}^+ + e^- \rightleftharpoons \text{H}_2 + \text{H}_2\text{O} \) | 1 \(^b\) | \( 10^4 \)^{c} | 0.5    |

\(^a\) large enough for the current density to be potential independent. \(^b\) positive enough for the intermediate I to be reduced very easily and not accumulate. \(^c\) large enough for the intermediate I to be reduced very fast and not accumulate.

The simulated current density in the range of potential –0.7 to –0.9 V is constant and equal to 0.0584 mA/cm². This value is smaller than the experimentally observed value for the leaf and wire electrodes in the –0.7 to –0.9 V range, indicating that H₃O⁺ cannot be a competent HER substrate in this range of potential.

Experimental data:

| \( E \) (V vs. SHE) | \( j_{\text{H}_2} \) (mA/cm²\text{geom}) Film electrode | \( j_{\text{H}_2} \) (mA/cm²\text{geom}) Leaf Electrode | \( j_{\text{H}_2} \) (mA/cm²\text{geom}) Wire Electrode |
|-----------------|-------------------|-------------------|-------------------|
| –0.7            | 0.0247            | 0.1381            | 0.3060            |
| –0.8            | 0.0418            | 0.1440            | 0.4206            |
| –0.9            | 0.0894            | 0.1011            | 0.3840            |

b. Simulations of CDR for leaf and wire electrodes with Volmer linear law

(i) Simulations of CO production current density in conditions where CDR is limited a linear Volmer law and with HCO₃⁻ as proton donor are obtained considering the following electrochemical reactions:

| Reaction | \( E^0 \) (V vs. SHE) | \( k_s \) | \( \alpha \) |
|----------|-----------------|--------|--------|
| \( \text{CO}_2 + e^- \rightleftharpoons \text{I} \) | 0     | \( R_t \times 8.2 \times 10^{-14} \)^{a} | 0.5    |
| \( \text{I} + \text{HCO}_3^- + e^- \rightleftharpoons \text{IH} + \text{CO}_3^{2-} \) | 1 \(^b\) | \( 10^4 \)^{c} | 0.5    |

\(^a\) \( R_t = 4.37 \) for the leaf electrode and 15.44 for the wire electrode. \(^b\) positive enough for the intermediate I to be reduced very easily and not accumulate. \(^c\) large enough for the intermediate I to be reduced very fast and not accumulate.

An addition homogeneous reaction is added to take into account a second proton transfer to release CO,

\[ \text{IH} + \text{HCO}_3^- \rightleftharpoons \text{CO} + \text{CO}_3^{2-} \quad K = 10^{20}, \quad k_f = 10^{10} \]

where \( k_f \) large enough for the intermediate IH to react at the electrode surface not accumulate.
(ii) Simulations of CO production current density in conditions where CDR is limited a linear Volmer law and with H$_2$O as proton donor are obtained considering the following electrochemical reactions:

| Reaction | $E^0$ (V vs. SHE) | $k_s$ | $\alpha$ |
|----------|-------------------|-------|----------|
| CO$_2$ + H$_2$O + e$^-$ $\rightleftharpoons$ I + OH$^-$ | 0 | $R_f \times 8.2 \times 10^{-14}$ | 0.5 |
| I + H$_2$O + e$^-$ $\rightleftharpoons$ CO + OH$^-$ | 1$^b$ | $10^4$ | 0.5 |

*$R_f = 4.37$ for the leaf electrode and 15.44 for the wire electrode. $^b$ positive enough for the intermediate I to be reduced very easily and not accumulate. $^c$ large enough for the intermediate I to be reduced very fast and not accumulate

Simulations with (i) or (ii) lead to the same current densities (shown in Figures 4C and 4D). Note that in the case of the wire electrode, d was adjusted to 175 $\mu$m to better match the current density at high overpotential.

c. Simulations of CDR for leaf and wire electrodes with adjusted rate constant

Simulations of CO production current density in conditions where CDR is described by an adjusted rate and with H$_2$O as proton donor are obtained considering the following electrochemical reactions:

| Reaction | $E^0$ (V vs. SHE) | $k_s$ | $\alpha$ |
|----------|-------------------|-------|----------|
| CO$_2$ + H$_2$O + e$^-$ $\rightleftharpoons$ I + OH$^-$ | 0 | $R_f \times 8.2 \times 10^{-14}$ | 0.5 |
| I + H$_2$O + e$^-$ $\rightleftharpoons$ CO + OH$^-$ | 1$^b$ | $10^4$ | 0.5 |

*$R_f = 4.37$ for the leaf electrode and 15.44 for the wire electrode. $^b$ positive enough for the intermediate I to be reduced very easily and not accumulate. $^c$ large enough for the intermediate I to be reduced very fast and not accumulate

$k_{CO_2}^{ap}(E)$ is adjusted at each potential for the simulated CO current density to match the experimental value. Results are shown in Figure 5 with,

$$k_{f,CO_2}^{ap}(E) = k_{CO_2}^{ap}(E) \cdot \exp\left(-\frac{0.5FE}{RT}\right)$$

d. Simulated surface pH for leaf and wire electrodes

Simulations are performed considering only CDR for both leaf and wire electrodes and a potential adjusted rate constant for CDR.

| Reaction | $E^0$ (V vs. SHE) | $k_s$ | $\alpha$ |
|----------|-------------------|-------|----------|
| CO$_2$ + H$_2$O + e$^-$ $\rightleftharpoons$ I + OH$^-$ | 0 | $R_f \times k_{CO_2}^{ap}(E)$ | 0.5 |
| I + H$_2$O + e$^-$ $\rightleftharpoons$ CO + OH$^-$ | 1$^b$ | $10^4$ | 0.5 |

*$R_f = 4.37$ for the leaf electrode and 15.44 for the wire electrode. $^b$ positive enough for the intermediate I to be reduced very easily and not accumulate. $^c$ large enough for the intermediate I to be reduced very fast and not accumulate
$k_{CO_2}^{ap}(E)$ is adjusted at each potential for the simulated CO current density to match the experimental value. Surface pH values are obtained at each potential taking $[H_3O^+]_x=0$ from the simulated concentration profiles. Figure S9 shows the results of the simulation.

![Graph showing correlation between adjusted intrinsic rate constant $k_{CO_2}^{ap}(E)$ and the simulated surface pH for leaf (blue) and wire (red) electrodes.]

**Figure S9.** Correlation between adjusted intrinsic rate constant $k_{CO_2}^{ap}(E)$ and the simulated surface pH for leaf (blue) and wire (red) electrodes.

e. **Simulated of CDR and HER for the film electrode**

Simulations are performed considering the potential adjusted rate constant for CDR as determined on leaf and wire electrodes.

| Reaction | $E^0$ (V vs. SHE) | $k_s$ | $\alpha$ |
|----------|------------------|-------|--------|
| CO$_2$ + H$_2$O + e$^-$ $\rightleftharpoons$ I + OH$^-$ | 0 | $k_{CO_2}^{ap}(E)$ | 0.5 |
| I + H$_2$O + e$^-$ $\rightleftharpoons$ CO + OH$^-$ | 1$^a$ | $10^4$ | 0.5 |

$a$ positive enough for the intermediate I to be reduced very easily and not accumulate. $b$ large enough for the intermediate I to be reduced very fast and not accumulate.

HER is simulated considering the following electrochemical reactions:

| Reaction | $E^0$ (V vs. SHE) | $k_s$ | $\alpha$ |
|----------|------------------|-------|--------|
| HCO$_3^-$ + e$^-$ $\rightleftharpoons$ I$^-$ + CO$_3^{2-}$ | 0 | $k_{CO_2}^{ap}(E)$ | 0.5 |
| I$^-$ + HCO$_3^-$ + e$^-$ $\rightleftharpoons$ H$_2$ + CO$_3^{2-}$ | 1$^a$ | $10^4$ | 0.5 |

$a$ positive enough for the intermediate I to be reduced very easily and not accumulate. $b$ large enough for the intermediate I to be reduced very fast and not accumulate.
Figure S10. A Experimental (full lines) and simulated (dashed lines) H₂ (red) and CO (blue) current densities on a film electrode. B Experimental (black) and simulated (red) FE(CO) on a film electrode.
11. Simplified modeling of CO₂ depletion in a catalyst layer

We consider a porous film (thickness = \( d_f \) geometrical surface area = \( S \)). The film is conductive (i.e. equivalent to a porous electrode) and, at the interface of the film material and the pores, CO₂ can be reduced producing that a current \( i_{co} \) is flowing through the electrode. The electrochemical reaction produces CO and hydroxide ions which can readily react with CO₂.

At steady-state, the simplified diffusion-reaction equations for CO₂ and hydroxide in the film are:

\[
D_{CO_2} \frac{d^2[CO_2]}{dx^2} - k_{OH^-}[CO_2][OH^-] - \frac{1}{2F} \frac{dj_{co}}{dx} = 0
\]

\[
D_{OH^-} \frac{d^2[OH^-]}{dx^2} - k_{OH^-}[CO_2][OH^-] + \frac{1}{F} \frac{dj_{co}}{dx} = 0
\]

with

\[
k_{OH^-} = 2.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}, \quad D_{CO_2} = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}
\]

\[
dj_{co} = \frac{di_{co}}{S} = 2FR_fk_{f,CO_2}^{ap}(E)[CO_2] \frac{dx}{df}
\]

Hence,

\[
D_{CO_2} \frac{d^2[CO_2]}{dx^2} - k_{OH^-}[CO_2][OH^-] - \frac{R_fk_{f,CO_2}^{ap}(E)}{df}[CO_2] = 0
\]

\[
D_{OH^-} \frac{d^2[OH^-]}{dx^2} - k_{OH^-}[CO_2][OH^-] + \frac{2R_fk_{f,CO_2}^{ap}(E)}{df}[CO_2] = 0
\]

We assume a steady-state for hydroxide ions, i.e.

\[
k_{OH^-}[CO_2][OH^-] \approx 2 \frac{R_fk_{f,CO_2}^{ap}(E)}{df}[CO_2]
\]

Therefore,

\[
D_{CO_2} \frac{d^2[CO_2]}{dx^2} - 3 \frac{R_fk_{f,CO_2}^{ap}(E)}{df}[CO_2] = 0
\]

With the boundary conditions:

\[
[CO_2]_{x=0} = [CO_2]_{sat} \text{ (with } [CO_2]_{sat} = 0.38 \text{ M) and } \left( \frac{d[CO_2]}{dx} \right)_{x=d_f} = 0
\]

Resolution:
\[ [\text{CO}_2] = A \exp \left( -\frac{x}{\mu} \right) + B \left( \frac{x}{\mu} \right) \]

with
\[
\mu = \sqrt[3]{\frac{D_{\text{CO}_2}}{3 R_f k_{f,\text{CO}_2}^a(E)}}
\]

with boundary conditions:

\[ A + B = [\text{CO}_2]_{\text{sat}} \]

\[
\left( \frac{d[\text{CO}_2]}{dx} \right)_{x=d_f} = \frac{1}{\mu} \left[ -A \exp \left( -\frac{d_f}{\mu} \right) + B \exp \left( \frac{d_f}{\mu} \right) \right] = 0
\]

Thus,

\[
[\text{CO}_2] = [\text{CO}_2]_{\text{sat}} \frac{\exp \left( \frac{d_f-x}{\mu} \right) + \exp \left( \frac{x-d_f}{\mu} \right)}{\exp \left( -\frac{d_f}{\mu} \right) + \exp \left( \frac{d_f}{\mu} \right)}
\]

Introducing,

\[ \lambda = \frac{d_f}{\mu}; \alpha = \frac{[\text{CO}_2]}{[\text{CO}_2]_{\text{sat}}}; \gamma = \frac{x}{d_f} \]

leads to,

\[ \alpha = \frac{\exp(\lambda(1-\gamma)) + \exp(\lambda(\gamma-1))}{\exp(-\lambda) + \exp(\lambda)} \]

\[ j_{\text{CO}} = 2FR_f k_{f,\text{CO}_2}^a(E) \int_0^{d_f} [\text{CO}_2] \frac{dx}{d_f} = 2Fk_{f,\text{CO}_2}^a(E)[\text{CO}_2]_{\text{sat}} \frac{R_f \times \tanh \lambda}{\lambda} \]

i.e.

\[ j_{\text{CO}} = 2F[\text{CO}_2]_{\text{sat}} \sqrt{R_f k_{f,\text{CO}_2}^a(E) \times \frac{D_{\text{CO}_2}}{3d_f}} \tanh \left( \sqrt{\frac{3R_f k_{f,\text{CO}_2}^a(E) d_f}{D_{\text{CO}_2}}} \right) \]

To get full use of the catalyst layer, the following condition is required: \( d_f \ll \mu \)

so that:

\[ j_{\text{CO}} = 2Fk_{f,\text{CO}_2}^a(E)[\text{CO}_2]_{\text{sat}}R_f \]

The condition \( d_f \ll \mu \) leads to, taking \( D_{\text{CO}_2} = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \), \( R_f = 20 \), \( k_{f,\text{CO}_2}^a(E) = 10^{-3} \text{ cm s}^{-1} \):
\[ d_f \ll \frac{D_{\text{CO}_2}}{3R_f k_{f,\text{CO}_2}^a(E)} \approx 3.15 \, \mu m \]
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