Supporting Information of “Deciphering electrochemical interactions in metal-polymer catalysts for CO\textsubscript{2} reduction”

Xingyu Wang\textsuperscript{1}, Sanjubala Sahoo\textsuperscript{2,3}, Jose Gascon\textsuperscript{4}, Mikhail Bragin\textsuperscript{5}, Fangyuan Liu\textsuperscript{2}, Julia Olchowski\textsuperscript{1}, Samuel Rothfarb\textsuperscript{1}, Yuankai Huang\textsuperscript{1}, Wenjun Xiang\textsuperscript{1}, Pu-Xian Gao\textsuperscript{2,3}, S. Pamir Alpay\textsuperscript{2,3}, Baikun Li\textsuperscript{*}

\textsuperscript{1}Department of Civil and Environmental Engineering, University of Connecticut, Storrs, Connecticut 06269-3037, USA
\textsuperscript{2}Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269-3136, USA
\textsuperscript{3}Department of Materials Science and Engineering, University of Connecticut, Storrs, Connecticut 06269-3136, USA
\textsuperscript{4}Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269-3037, USA
\textsuperscript{5}Department of Electrical and Computer Engineering, University of Connecticut, Storrs, Connecticut 06269-3037, USA
Theory S1. Theory of Multiscale Model

S1.1 Transport and distribution model (system level).

The system level implements the transport of molecules in the catholyte and the cathode surface. To well correspond with our experimental evaluation, the catholyte is set to be 0.1M of $\text{KHCO}_3$ solution in the multiscale model development, and all the molecular distribution and pH (6.8 with saturated CO$_2$) are assumed to be even and homogenous in the bulk phase under the mixing effect due to the continuous sparging of CO$_2$, meaning that the only diffusion resistance comes from the heterogenous cathode-bulk boundary layer ($10 \, \mu \text{m}$). As the concentration of catholyte is considered dilute, Poisson-Nernst-Plank (PNP) equation achieved by coupling Nernst-Planck equation (Eq.1) and Poisson equation (Eq.2) together, is used for the profiling of bulk solution mass conservations$^1$:

\[
\frac{\partial c_i}{\partial t} = \nabla \cdot D_i \left( \nabla c_i + \frac{z_i c_i \nabla \phi}{k_B T} \right) \quad \text{(Eq.1)}
\]

\[-\nabla (\varepsilon_w \varepsilon_0 \nabla \phi) - \lambda \sum_i z_i c_i = Q \quad \text{(Eq.2)}\]

In which $c_i$ and $z_i$ are the concentration and charge of molecules in the solution. Here we consider the existence of $\text{CO}_2$, $\text{H}^+$, $\text{OH}^-$, $\text{K}^+$/Na$^+$, $\text{HCO}_3^-$, and $\text{CO}_3^{2-}$ in the electrolyte. The boundary conditions for $c_i$ and $z_i$ in Nernst-Planck equation and Poisson Equation have been defined in Table S7. $D_i$ represents diffusion coefficients of molecules, which can be found in Table S8. $k_B$ and $T$ are Boltzmann constant and temperature ($20 \, ^\circ\text{C}$ or 293K), respectively. $\phi$ is the electrostatic potential. $\varepsilon_w$ and $\varepsilon_0$ represent the dielectric permittivity water and vacuum. $Q$ is the permanent charge density, which is calculated through Eq.3$^2$:

\[
Q(x) = \sum_i z_i \delta(x - x_i) \quad \text{(Eq.3)}
\]
Where x represents the position/distance from the cathode surface and the $\delta$ is the $\delta$-function for discrete charge calculation. The existence of homogenous buffer reaction (CO$_2$ hydration and acid-base equilibrium) due to the coexistence of CO$_2$, H$^+$, OH$^-$, HCO$_3^-$, and CO$_3^{2-}$ associated pH with the concentration of CO$_2$, where the correlation has been summarized below (in the form of H$^+$ association/dessociation):

\begin{align*}
CO_2 + H_2O &\leftrightarrow H_2CO_3 \\
H_2CO_3 &\leftrightarrow H^+ + HCO_3^- \\
HCO_3^- &\leftrightarrow H^+ + CO_3^{2-} \\
H_2O &\leftrightarrow H^+ + OH^- \\
\end{align*}

For the solution close to the cathode surface, as there is no obvious concentration divergence beyond 5nm from the cathode surface, we determine that the Helmholtz layer of the continuum model mainly exists in this region (Figure 1). The aggregation effect of cations leads to a different transport phenomenon compared to the diluted bulk solution. Because the PNP equation might fail within the CO$_2$RR onset range in our study (absolute value: $\sim 0.4V - 1.5V$ vs RHE), which is above the thermal potential (\(\frac{k_B T}{e} = 25 mV\)), Stefan-Maxwell equation is applied (Eq.4) in the hydraulic boundary near the cathode surface:\

\[ \nabla \ln a_i = \sum_i \frac{c_i (J_j - J_i)}{cD_{ij}(c_j - c_i)} \]  

(Eq.4)

Where $a_i$ and $J_i$ is the activity and flux of molecules. $c$ is the total molar concentration. $D_{ij}$ is Stefan-Maxwell diffusion coefficient, which is calculated through Darken equation (Eq.5)\(^5\):

\[ D_{ij} = c_i D_j + c_j D_i \]  

(Eq.5)

In the Helmholtz layer area, CO$_2$ tends to be absorbed onto the cathode surface, where the adsorption energy can be described through thermodynamic model (Eq.6)\(^6\):
\[ \Delta G_{\text{CO}_2} = -RT \ln \left( \frac{K_L}{\gamma} \right) \]  

(Eq.6)

where \( K_L, \gamma \) are Langmuir equilibrium constant and activity coefficient.

**S1.2 Electrochemistry model (molecular level).**

The molecular level of electrochemistry describes the reduction kinetics and losses contributed by the mass transport and charge transfer. As the kinetics of the cathode is described through microkinetic models, for the anode surface, only oxygen evolution reaction (OER) is expected to happen, which can be described by Tafel kinetics (Eq.7):

\[ j_a = j_{0a} \cdot e^{\frac{2\alpha_{\text{ER}} \eta}{RT}} \]  

(Eq.7)

Where the \( j_0 \) and \( \alpha \) was set to be \( 4.684 \times 10^{-9} \text{mA/cm}^2 \) and 0.5 respectively.\(^8\)

The cathodic kinetics is determined through microkinetic model. The reaction rates of elementary steps in the Mechanism I and Mechanism II are calculated through the power-law of rate equation separately (Theory S2), where the rate constant is determined through transition state theory (Eq.8):

\[ k_i = \frac{k_B T}{h} \cdot e^{\left( \frac{\Delta G}{k_B T} \right)} \]  

(Eq.8)

In which \( k_i \) is the rate constant and \( h \) is the Planck number. \( \Delta G \) represents the activation free energy for the \( i^{th} \) reaction, which is calculated through the quantum chemistry model (the atomistic level) using VASP. \( c_i \) here represents the concentration in the Helmholtz layer near the cathode surface, which is different from bulk concentration and is determined in the transport and distribution model (the system level). In the microkinetic model, the power rate law associated with transition state theory shifts from quasi-monomolecular surface adsorption kinetics for Eley-Rideal (ER)
mechanism (Eq.9) towards bimolecular surface adsorption kinetics for Langmuir-Hinshelwood (LH) mechanism (Eq.10):

\[ r = k_1 c^*_{CO_2} \theta^* \cdot H^+ \]  
(Eq. 9)

\[ r = k_2 \theta^*_{CO_2} \theta^* \cdot H^+ \]  
(Eq. 10)

where \( k \) is the rate constant calculated from transition state theory, \( \theta^*_{CO_2} \) and \( \theta^* \cdot H^+ \) represents the adsorbed \( CO_2 \) and \( H^+ \) on the cathode surface, and \( c^*_{CO_2} \) is the \( H^+ \) concentration in Helmholtz layer.

The major difference of ER (Eq.9) and LH (Eq.10) is reflected on the \( CO_2 \) representation from unabsorbed form (\( c^*_{CO_2} \)) to absorbed form (\( \theta^*_{CO_2} \)), as well as the change of kinetic constant \( k \).

The effect of \( Cu-Cation-CO_2 \) triple binder electron bridge is considered by introducing a cation coverage factor \( \theta^*_{cation} \) to explicate the change of reaction rate. \( \theta^*_{cation} \) is set to be consistent with the cation-Cu ratio in VASP calculation.

With the cathodic current density acquired experimentally, the incorporation of experimental current density into the molecular level delivers quantitative coefficients of thermodynamic charge transfer during \( CO_2 \)RR. Therefore, we can deduce the charge transfer coefficient on cathode as Eq.11:

\[ \alpha_c = -\frac{RT}{zF\eta} \log \left( \frac{j_e}{j_a} \right) \]  
(Eq.11)

Where \( j_e \) is the cathodic exchange current density and can be acquired using the microkinetic model (Eq.12):

\[ j_e = Fk_1(c^{1-\beta}_{ox} c^\beta_{re}) \]  
(Eq.12)

Where \( c_{ox} \) and \( c_{re} \) represents the redox pair in each elementary step described in Theory S2. \( \beta \) is the symmetry factor, which can be assumed with free energy barrier (\( \Delta G^* \)) and the reaction free energy (\( \Delta G \)) from Vienna ab initio Simulation Package (VASP) (Eq.13):
\[ \beta = \frac{\Delta G^*}{\Delta G} \]  
(Eq.13)

At the heterogenous interface of cathode and catholyte, impedances always exist due to the mass/charge transfer. Moreover, the separation of charges caused by the alternation of the ion distribution in the Helmholtz layer also contributes to the impedance. The charge distribution on the cathode surface on the electrode side represents the charge contributed by the applied potential (Eq.14):

\[ \rho_{surf} = \frac{\epsilon_0 \epsilon_0 \phi}{xS} \]  
(Eq.14)

The xS represents the distance of the inner Helmholtz layer. The cumulation of ions on the solution side near cathode surface boosts ionic charge density (Eq.15):

\[ \rho_{ion} = \sum_i n_i z_i e_0 \cdot e^{\frac{iF \phi}{RT}} \]  
(Eq.15)

\( n_i \) is the molar quantity of the molecule and \( e_0 \) is the elementary charge \((1.602 \times 10^{-19} \text{ C})\). The separation of charge results in a barrier for the mass and charge transport, which is quantified through mass transport loss (Eq.16) and ohmic resistance (Eq.17), respectively:

\[ \eta_{mass} = \frac{RT}{zF} \cdot \ln \frac{j_L}{j_L - j} \]  
(Eq.16)

\[ R_{electrode} + R_{electrolyte} = \frac{\phi}{j} \]  
(Eq.17)

\( j_L \) is the maximum current density where all the CO\(_2\) molecules are consumed. Here we assume this number to be 10 mA/cm\(^2\) from the average value of current density tests. The pristine Cu electrode resistance \( R_{electrode} \) is determined through the EIS test to be 10.4 \( \Omega/cm^2 \).

At the initiation stage of the reaction, the partial voltage to overcome the activation energy of the reduction reaction can be quantified through the activation loss (Eq.18):
\[ \eta_{\text{act}} = \frac{RT}{\alpha_c F} \ln \frac{j}{j_e} \]  
(Eq.18)

Moreover, the continuous consumption of CO\(_2\) and H\(^+\) contributes to a reversible drop of cathodic potential, which can be quantified as Nernstian loss (Eq.19)\(^{16}\):

\[ \eta_{\text{Nernstian}} = \frac{RT}{F} \ln \left( \frac{c_{H^+ - \text{bulk}}}{c_{H^+ - \text{cathode}}} \right) + \frac{RT}{zF} \ln \left( \frac{c_{CO_2 - \text{bulk}}}{c_{CO_2 - \text{cathode}}} \right) \]  
(Eq.19)

The correlations of the major equations above were ascribed in **Figure S25**.

**S1.3 Quantum chemistry (the atomistic level).**

The simulation of the atomistic level is delivered through the density functional theory (DFT) using Vienna ab initio Simulation Package (VASP). First-principles based studies are performed within generalized gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerhof (PBE) for the exchange and correlation functional\(^{17}\). As a catalyst system, the Cu surface is considered to investigate the CO\(_2\) reduction mechanism. The (111) surface of Cu is considered due to its high stability compared to other Cu surfaces\(^{18}\). The surface is constructed from the bulk FCC crystal structure with equilibrium lattice parameters \(a = 3.64\ \text{Å}\) which is in good agreement with experimental values (3.61 Å). The surface consists of (3×4) supercells of bulk FCC Cu lattice.

Periodic boundary conditions are applied along the surface plane with a simulation box (13.37 × 10.29 × 22.31) Å\(^3\) where a 16 Å vacuum is kept along the z-direction. The top two layers of the Cu(111) surface are allowed to relax while the rest atoms are fixed to constrain to bulk bond lengths.

The adsorption energy (E\(_{\text{ads}}\)) of the molecules on Cu(111) is calculated as

\[ E_{\text{ads}} (\text{eV}) = E[\text{molecule@Cu(111)}] - E[\text{Cu(111)}] - E(\text{molecule}) \]  
(Eq.20)
where, the first, second, and third terms on the right hand side represent the total energies of molecule@Cu(111) complex, the Cu(111) support, and the various single molecules, respectively. The reaction pathway for the CO$_2$ reduction mechanisms is studied using the constrained energy minimization method, where a series of images are created between the reactant and the product to investigate the reaction pathway.

The effect of PTFE is demonstrated where a monomer (TFE) of PTFE is introduced in the vicinity of the co-adsorbed reactant (CO$_2$) and reaction intermediates such as COOH, HCOO, CH$_2$O, CHO and CH$_4$. The adsorption energy of the respective molecules with PTFE is defined as;

\[ E_{\text{ads}}(eV) = E\{\text{molecule@Cu(111)}@\text{TFE}\} - E\{\text{Cu(111)}@\text{TFE}\} - E\{\text{molecule}\} \]  

where, the first, second and the third terms indicate the total energies of the Cu+TFE+molecule complex, polymer-Cu complex and the molecules (e.g., CO$_2$, COOH, HCOO, CH$_2$O, CHO and CH$_4$), respectively.

One of the key quantities that drives the reaction kinetics is the energy barrier (EB) which is defined as the total energy difference between the transition state geometry and the reactant.

\[ EB = E_{\text{TS}} - E_{\text{Reactant}} \]  

where the $E_{\text{TS}}$ and $E_{\text{Reactant}}$ are the total energies of the transition state structure and the reactant, respectively.

The orbital-projected spin-polarized density of states (DOS) is calculated using Gaussian smearing with a broadening parameter value 0.05 eV. A cut-off energy of 300 eV is used for clean Cu(111) while for the adsorbed the adsorbed systems, a value of 400 eV is used. Using different energy cut-off energy values for the plane wave expansion of wave function does not change the DOS significantly. The Fermi level remains the same. A same k-mesh (3×3×1) and same exchange-
correlation functionals (GGA-PBE) for the geometry optimization are used for the DOS calculations.

All computations are carried out using the Vienna *ab initio* Simulation Package (VASP) with the plane wave basis set\(^\text{19}\). The projector-augmented wave method is used for the electron-core interactions\(^\text{20}\). The energy cut-off for the plane waves is taken as 400 eV. The Brillouin zone integrations are done with (3×3×1) k-points mesh. The total energy convergence criteria for geometry optimization are fixed to \(10^{-6}\) eV. The partial charge analysis on each atomic species is done by using the Bader charge method\(^\text{21}\).

For the free energy change profiles of proton-electron coupled reduction process, as well as the activation energy used in transition state theory, the computational hydrogen electrode (CHE) is implemented in this study (Eq.23)\(^\text{22}\):

\[
\Delta G = E(\text{Product}) - E(\text{Reactant}) - \left[ \frac{1}{2}E(H_2) - eU - 0.059 \times pH \right] \tag{Eq.23}
\]

Where \(\mu\) represents free energy of reactants/intermediates/products. All those energies have been calculated from VASP as described above. The pH is selected to be 6.8, which is consistent with our experimental setups.

**S1.4 Adjustment of model parameter with existence of polytetrafluoroethylene (PTFE).**

The adjustment of surface affinity and polarity is executed by modifying the Cu catalyst with polytetrafluoroethylene (PTFE) that renders binding property of the electrode and carries spatial affinity towards non-charged CO\(_2\)\(^\text{23,24}\). Consistently, in the multi-scale model settings, PTFE with exceptionally low dipole moment possesses a relative permittivity (\(\varepsilon\)) of 2.1 due to the low electric polarizability of fluorine compared to water of 80. Given the paltry wettability of PTFE in the water phase, here we assume there is only one layer of water molecules in the inner Helmholtz Layer and the polarity and surface capacitance of the PTFE-Cu cathode is around 40 times lower.
than the pristine Cu cathode. In addition, the SEM imaging and EDAX composition analysis indicate that the surface coverage of Cu alters with different ratios of PTFE additives. With a thin layer of the PTFE-Cu mixture catalyst (<10 µm, Figure 2b) casted directly on the surface of carbon cathode, the diffusion of species is only considered in one dimension (Figure 1b). At such a short distance, the difference between the diffusions across PTFE and Cu is trivial, and thus we ignore the possible path in the PTFE structure and assume that PTFE-Cu cathode has the same surface, and the diffusion coefficients (Table S8) are shared for the species diffusion in both Cu and PTFE.
Theory S2. Elementary steps of CO₂RR according to numbers of electron transfer.

Cathode (CO₂RR-CO Generation):

*CO₂ + *H⁺ + e⁻ ↔ **COOH  
(1st electron transfer, R1)

**COOH + e⁻ ↔ *CO + **OH⁻ (aq)  
(2nd electron transfer, R2)

Cathode (CO₂RR-CH4 Generation Mechanism I):

Note: first step from CO₂ to CO was same as above

*CO + *H⁺ + 3 * + 2 e⁻ ↔ ****C + **OH⁻ (aq)  
(1st & 2nd electron transfer, M1R1)

****C + *H⁺ + e⁻ ↔ ****CH + 2 *  
(3rd electron transfer, M1R2)

****CH + *H⁺ + e⁻ ↔ ****CH₂ + 2 *  
(4th electron transfer, M1R3)

****CH₂ + *H⁺ + e⁻ ↔ *CH₃ + 2 *  
(5th electron transfer, M1R4)

*CH₃ + *H⁺ + e⁻ ↔ CH₄(g) + 2 *  
(6th electron transfer, M1R5)

Cathode (CO₂RR-CH4 Generation Mechanism II):

Note: first step from CO₂ to CO was same as above

*CO + *H⁺ + e⁻ ↔ **HCO  
(1st electron transfer, M2R1)

**HCO + *H⁺ + e⁻ ↔ ***H₂CO  
(2nd electron transfer, M2R2)

***H₂CO + *H⁺ + e⁻ ↔ ***H₃CO  
(3rd electron transfer, M2R3)

***H₃CO + *H⁺ + e⁻ ↔ H₄C⋅**O + 2 *  
(4th electron transfer, M2R4)

H₄C⋅**O + *H⁺ + 2 e⁻ ↔ H₄C⋅**OH + 2 *  
(5th electron transfer, M2R5)
Figure S1. Comparison of the multiscale model in this study with other methods\textsuperscript{3,25–31}.

Compared to previously reported multiscale studies, our method outperforms conventional models that are based solely on molecular structures and enabled discovery of the deterministic role of the surface reaction processes. Our molecular level functions as a bridge connecting the continuum model (system level) and quantum/atomistic model (atomistic level) using an electrochemical spectrum model. Verifying the multiscale model through experiments further improves the integrity of our study.
Figure S2. (a) Cathodic potential drop outside the Helmholtz layer; (b) Cathodic K\(^+\) concentration outside the Helmholtz layer; (c) Cathodic H\(^+\) concentration outside the Helmholtz layer; and (d) Cathodic CO\(_2\) concentration outside the Helmholtz layer.
Figure S3. (a) Variation of $K^+$ concentration with potential on the Cu cathodes at different PTFE ratios from 0% to 20%; (b) Variation of $H^+$ concentration with potential on the Cu cathodes at different PTFE ratios from 0% to 20%.
Figure S4. Variation of Nernstian loss contributed by H⁺ with potential on the Cu cathodes at different PTFE ratios from 0% to 20%.
Figure S5. Binding energy of reagents, intermediates, and products in the reaction of CO$_2$RR and HER.
Figure S6. Bonding energy and bonding distances of major CO$_2$RR reactants, intermediates, and products. Units of EB is eV in these figures. The EB values of the mentioned species are in agreement with previously reported studies$^{32}$. 

---

$^{32}$
Figure S7. Barrier energy of CO$_2$ activation. This diagram shows the configuration of transition states of activated CO$_2$ after the first proton-electron pair. It demonstrates the stable configuration of the CO$_2$-Cu(111) characterized by the parallel adsorption of CO$_2$ onto the Cu surface. The adsorption energy is found to be -0.31 eV indicating the physisorption nature of the CO$_2$ onto the Cu surface in the beginning.
Figure S8. Barrier energy of CO generation. This diagram shows the process of dissociation of the HO-CO bond.
Figure S9. During CO protonation, the Density of state (DOS) results of (a) free CO, (b) \(^{\text{*}}\text{CO} + \text{H} \) as reactants, (c) transition state of \(^{\text{*}}\text{CO} + \text{H} \), and (d) final product of \(^{\text{*}}\text{HCO} \).
Figure S10. Configurations of reactants, transition states and products in Mechanism I. M1R1 represents “Mechanism I, reaction step 1”, with the same for all others.
Figure S11. Configurations of reactants, transition states and products in Mechanism II. M2R1 represents “Mechanism II, reaction step 1”, with the same for all others.
**Figure S12.** Reaction pathways for the CO$_2$RR indicating the barrier energies of CO protonation for CH$_4$ formation under Mechanism I. The color codes represent the reaction series happening towards the CH$_4$ formation.
Figure S13. Reaction pathways for the CO$_2$RR indicating the barrier energies of CO protonation for CH$_4$ formation under Mechanism 2. The color codes represent the chain of reactions happening towards the CH$_4$ formation.
Figure S14. Complete energy profile comparison of CO$_2$RR towards CH$_4$ generation through Mechanisms I and II.
Figure S15. Ohmic resistance of the pristine Cu cathode and PTFE-Cu cathode at different PTFE ratios from 0% to 20%.

Increment: 50.78%
Figure S16. Current density of overall system including HER and CO$_2$RR, and the Faradaic efficiency (FE) of HER and CO$_2$RR, separately.
Figure S17. Difference of Faradaic efficiency (FE) and current density of the CO$_2$RR system with 0.1 M KHCO$_3$ (green line) and 0.1M NaHCO$_3$ (blue line).
Figure S18. Side view and top view diagrams of electron cloud of K$^+$-CO$_2$ and Na$^+$-CO$_2$. 
• Nearly parallel orientation of CO$_2$ on K-Cu(111) is highly preferred.
• CO$_2$ is located near potassium atom.
• Irregular stretching of C-O bond distances compared to that of the free CO$_2$ (dCO=1.16 Å).
• Presence of potassium ion enhances the BE of CO$_2$.

Figure S19. Configurations of K$^+$ on the Cu catalyst and its stabilization effect with absorbed CO$_2$ molecules.
Figure S20. Configurations of Na$^+$ on the Cu catalyst and its stabilization effect with absorbed CO$_2$ molecules.
Figure S21. Simplified equivalent circuit of the CO$_2$RR system and the electrochemical impedance spectroscopy (EIS) experimental results of the pristine Cu and PTFE-Cu cathodes at different PTFE ratios from 0% to 20%.
Figure S22. (a) EIS experimental results of H⁺ diffusion across proton exchange membrane (PEM) towards the pristine Cu and PTFE-Cu cathodes with the PTFE ratios from 5% to 20% under -0.5V; (b) EIS experimental results of H⁺ diffusion across PEM towards the pristine Cu and PTFE-Cu cathodes with the PTFE ratios from 5% to 20% under -1V.
Figure S23. (a) The Faradaic efficiency (FE) of Sn catalyst with the PTFE ratios of 0%, 5%, 10%, 15%, and 20%; and (b) Faradaic efficiency (FE) of Ag catalyst with the PTFE ratios of 0%, 5%, 10%, 15%, and 20% under the external potential of -2.1V vs Ag/AgCl.
Figure S24. Variation of $H^+$, $K^+$, $CO_2$, and electrical potential in the Helmholtz layer and bulk solution under pH from 6 to 14. (a) Cathodic $H^+$ concentration in Helmholtz layer and bulk solution; (b) Cathodic $K^+$ concentration in Helmholtz layer and bulk solution; (c) Cathodic $CO_2$ concentration in Helmholtz layer and bulk solution; (d) Cathodic potential drop in Helmholtz layer and bulk solution.
Figure S25: Diagram of the system setup for the CO$_2$RR experiments.
Figure S26. Governing equations at each layer of the multiscale model. The dash line box categorizes the equations according to the three levels of the multiscale model as is discussed in the main context. The vertical lines in different colors define the spatial location that each equation is applied in the CO$_2$RR system.
<table>
<thead>
<tr>
<th>80%Cu 20% PTFE</th>
<th>85%Cu 15% PTFE</th>
<th>90%Cu 10% PTFE</th>
<th>95%Cu 5% PTFE</th>
<th>100%Cu 0% PTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="SEM Image" /></td>
<td><img src="image2" alt="SEM Image" /></td>
<td><img src="image3" alt="SEM Image" /></td>
<td><img src="image4" alt="SEM Image" /></td>
<td><img src="image5" alt="SEM Image" /></td>
</tr>
</tbody>
</table>

**Figure S27.** The corresponding SEM images of EDAX mappings in Figure 2b.
Table S1. Percentage of Cu and PTFE in the cathodes for experiment, as well as the original SEM and EDAX mapping for each Cu-PTFE ratio

<table>
<thead>
<tr>
<th></th>
<th>Theoretical 80%Cu</th>
<th>Theoretical 85%Cu</th>
<th>Theoretical 90%Cu</th>
<th>Theoretical 95%Cu</th>
<th>Theoretical 100%Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>81.86%</td>
<td>84.76%</td>
<td>89.55%</td>
<td>91.89%</td>
<td>100%</td>
</tr>
<tr>
<td>PTFE</td>
<td>18.14%</td>
<td>15.24%</td>
<td>10.45%</td>
<td>8.11%</td>
<td>0%</td>
</tr>
</tbody>
</table>
Table S2. Barrier energy and free energies of CO generation.

<table>
<thead>
<tr>
<th></th>
<th>Barrier Energy (eV)</th>
<th>Free Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>1.89</td>
<td>0.52</td>
</tr>
<tr>
<td>R2</td>
<td>0.87</td>
<td>0.44</td>
</tr>
</tbody>
</table>
Table S3. Barrier energies and free energies of CH$_4$ generation in Mechanism I.

<table>
<thead>
<tr>
<th></th>
<th>Barrier Energy (eV)</th>
<th>Free Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1R1</td>
<td>1.14</td>
<td>0.4</td>
</tr>
<tr>
<td>M1R2</td>
<td>0.75</td>
<td>-1.24</td>
</tr>
<tr>
<td>M1R3</td>
<td>0.5</td>
<td>-0.12</td>
</tr>
<tr>
<td>M1R4</td>
<td>0.83</td>
<td>-0.23</td>
</tr>
<tr>
<td>M1R5</td>
<td>0.73</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Table S4. Barrier energies and free energies of CH$_4$ generation in Mechanism II.

<table>
<thead>
<tr>
<th></th>
<th>Barrier Energy (eV)</th>
<th>Free Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1S1</td>
<td>0.68</td>
<td>1.2</td>
</tr>
<tr>
<td>M2S2</td>
<td>1.42</td>
<td>0.17</td>
</tr>
<tr>
<td>M2S3</td>
<td>0.44</td>
<td>0.35</td>
</tr>
<tr>
<td>M2S4</td>
<td>0.28</td>
<td>-3.33</td>
</tr>
<tr>
<td>M2S5</td>
<td>0.77</td>
<td>0.64</td>
</tr>
</tbody>
</table>
### Table S5. Bond length and distance of molecules between molecule and Cu atom (Unit: Å).

<table>
<thead>
<tr>
<th></th>
<th>(d_{C-O})</th>
<th>(d_{C-H})</th>
<th>(d_{\perp Cu})</th>
<th>(d_{O-H})</th>
<th>(d_{C-C})</th>
<th>(d_{H-H})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOO</td>
<td>1.27</td>
<td>1.11</td>
<td>1.99</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>CH(_3)O</td>
<td>1.44</td>
<td>1.10</td>
<td>1.37</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>COOH</td>
<td>1.30</td>
<td>/</td>
<td>2.00</td>
<td>0.98</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>CHO</td>
<td>1.25</td>
<td>1.12</td>
<td>1.90</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>CO</td>
<td>1.17</td>
<td>/</td>
<td>1.57</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>C(_2)H(_5)OH</td>
<td>1.45</td>
<td>1.10</td>
<td>2.27</td>
<td>0.97</td>
<td>1.52</td>
<td>/</td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td>/</td>
<td>1.08</td>
<td>2.04</td>
<td>/</td>
<td>1.27</td>
<td>/</td>
</tr>
<tr>
<td>CH(_2)O</td>
<td>1.22</td>
<td>1.11</td>
<td>2.37</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>/</td>
<td>1.09</td>
<td>3.24</td>
<td>/</td>
<td>1.33</td>
<td>/</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>/</td>
<td>1.09</td>
<td>3.12</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>1.18</td>
<td>/</td>
<td>3.51</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>H</td>
<td>/</td>
<td>/</td>
<td>0.98 (Note)</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>H(_2)</td>
<td>/</td>
<td>/</td>
<td>3.46</td>
<td>/</td>
<td>/</td>
<td>0.75</td>
</tr>
</tbody>
</table>

**Note:** The chemisorption bond length of Cu-H is 1.74 Å.
Table S6. T-tests of Faradaic efficiency (FE) results obtained for CH\textsubscript{4} and CO.

a. CH\textsubscript{4} FE t-statistics table:

<table>
<thead>
<tr>
<th></th>
<th>0%</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0</td>
<td>-0.113</td>
<td>-0.409</td>
<td>-0.073</td>
<td>-0.143</td>
</tr>
<tr>
<td>5%</td>
<td>-0.113</td>
<td>0</td>
<td>-0.294</td>
<td>0.04</td>
<td>-0.025</td>
</tr>
<tr>
<td>10%</td>
<td>-0.409</td>
<td>-0.294</td>
<td>0</td>
<td>0.333</td>
<td>0.28</td>
</tr>
<tr>
<td>15%</td>
<td>-0.073</td>
<td>0.04</td>
<td>0.333</td>
<td>0</td>
<td>-0.066</td>
</tr>
<tr>
<td>20%</td>
<td>-0.143</td>
<td>-0.025</td>
<td>0.28</td>
<td>-0.066</td>
<td>0</td>
</tr>
</tbody>
</table>

b. CO FE t-statistics table:

<table>
<thead>
<tr>
<th></th>
<th>0%</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0</td>
<td>-0.704</td>
<td>0.097</td>
<td>0.276</td>
<td>1.246</td>
</tr>
<tr>
<td>5%</td>
<td>-0.704</td>
<td>0</td>
<td>0.666</td>
<td>0.776</td>
<td>1.541</td>
</tr>
<tr>
<td>10%</td>
<td>0.097</td>
<td>0.666</td>
<td>0</td>
<td>0.158</td>
<td>0.934</td>
</tr>
<tr>
<td>15%</td>
<td>0.276</td>
<td>0.776</td>
<td>0.158</td>
<td>0</td>
<td>0.711</td>
</tr>
<tr>
<td>20%</td>
<td>1.246</td>
<td>1.541</td>
<td>0.934</td>
<td>0.711</td>
<td>0</td>
</tr>
</tbody>
</table>
Table S7. Boundary condition of Nernst-Planck equation and Poisson equation.

<table>
<thead>
<tr>
<th></th>
<th>(c_{0, \text{init}}) (Variable) (mol/m(^3))</th>
<th>(c_{\infty, \text{Bulk}}) (Constant) (mol/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CO_2)</td>
<td>0</td>
<td>(1.55 \times 10^{-5})</td>
</tr>
<tr>
<td>(H^+)</td>
<td>1.1138</td>
<td>1.1138</td>
</tr>
<tr>
<td>(OH^-)</td>
<td>0.74659</td>
<td>0.74659</td>
</tr>
<tr>
<td>(K^+)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(HCO_3^-)</td>
<td>59.943</td>
<td>59.943</td>
</tr>
<tr>
<td>(CO_3^{2-})</td>
<td>1.7584</td>
<td>1.7584</td>
</tr>
</tbody>
</table>
Table S8. Diffusion coefficients of molecules$^{33}$.

<table>
<thead>
<tr>
<th></th>
<th>Diffusion Coefficient $(10^{-9} \text{ m}^2/\text{s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2$</td>
<td>1.6</td>
</tr>
<tr>
<td>$H^+$</td>
<td>9.31</td>
</tr>
<tr>
<td>$OH^-$</td>
<td>5.27</td>
</tr>
<tr>
<td>$K^+$</td>
<td>1.96</td>
</tr>
<tr>
<td>$Na^+$</td>
<td>1.33</td>
</tr>
<tr>
<td>$HCO_3^-$</td>
<td>1.18</td>
</tr>
<tr>
<td>$CO_3^{2-}$</td>
<td>0.955</td>
</tr>
</tbody>
</table>
Reference:


