

Supporting information

Simulating electric field and current density in nanostructured electrocatalysts

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Supplementary note 1

EDL effects on the E-field magnitude and distribution

Generally, EDL is a structure formed at the electrolyte-electrode interface due to the simultaneous aggregation or depletion of electrons within the electrode and counter-ionic species in the vicinity of the electrode surface under an externally applied potential. Here, we introduce the structure of the EDL described by commonly used Gouy-Chapman-Stern (GCS) model,¹ which has the predicted properties of the EDL similar to that observed experimentally. For a negatively charged electrode, the electrons on the electrode surface attract the solvated cations in the electrolyte moving towards the electrode to neutralize the electrons and maintain the electroneutrality. In the GCS model, a layer of solvated cations adhered to the electrode surface is referred to as Stern layer. Due to a comparatively larger size of the solvated cation compared to the electron size, the cations in the Stern layer are not able to fully neutralize the electrons on the electrode surface. As a result, more cations are continually attracted to the vicinity of the Stern layer via the Coulomb force. These cations are loosely attracted by the electrode and are not in direct contact with it, comprising a so-called diffuse layer. Typically, the identity and the concentration of the cations in the electrolyte determine the structure of the EDL. For instance, the thickness of Stern layer varies from 0.3 nm to 1 nm, depending on the type of the solvated cation. Furthermore, the extension of the diffuse layer into the electrolyte solution depends on the shielding ability of the cation against the electrode potential. The latter is determined by the ionic strength of the cation, which is a function of the valence charge and concentration of the cation. The width of the diffuse layer can be evaluated theoretically using the Debye length theory,² or experimentally by the ambient pressure X-ray photoelectron spectroscopy³. Considering the electrolytes with the concentrations of 0.1 M to 5M are commonly used in CO₂RR electrolysis⁴ to have a good ion conductivity, the diffuse layer can only extend into the electrolyte solution by 1 nm to 2 nm, suggesting the potential in the electrolyte drops to zero beyond this range. Due to the fast drop of the electrode potential within a very short distance, high E-field are generated at the electrode-electrolyte interface. Waegle and co-works performed the vibrational Stark spectroscopy to investigate the interfacial E-field and found that it is roughly in the range of 10⁸ V/m to 10⁹ V/m (0.01 V/Å to 0.1 V/Å) at applied potentials of -1.0 V to 0 V vs Ag/AgCl.⁵

Supplementary note 2

Details of the electrochemical simulation domain and the nanostar electrode

Briefly, the electrolytic cell is a 5000 nm × 5000 nm square with a 50 nm-thick substrate placed at the bottom as shown in Figure S5. A nanostar electrode is placed at the middle of the substrate. The shape of the nano-star electrode is generated from the function: $R_{\text{star}}(r, \theta; R_0, r_0) = r_0 + (R_0 - r_0) \cos^2 \frac{5\theta}{2}$, with two parameters, R_0 and r_0 , being 100 nm and 50 nm, respectively.

The distance of the star center above the substrate surface is 83.66 nm, which is slightly smaller than the geometric height of the star center. As a result, the contacts of the nano-star with the substrate surface are two segments of *ca.* 3.6 nm rather than two points. The Stern layer is a uniform layer that is 0.33 nm above the electrode surface, as is indicated by the blue border in Figure S5b. The material for the nano-electrode and substrate is chosen gold. The electrolyte is 0.5M KHCO₃ aqueous solution saturated with CO₂ (38 mM). The temperature of the system is 293.15 K and the electrolyte is unstirred.

Supplementary note 3

Derivation of PB, PNP, MPB and GMPNP models

Derivation of the Poisson-Boltzmann (PB) equation

In the Poisson-Boltzmann model, the distribution of ionic species, $\rho(\mathbf{r})$, at equilibrium follows the Boltzmann distribution:

$$\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r}) = \sum_i z_i F C_i^* e^{-\left(\frac{z_i F \phi(\mathbf{r})}{RT}\right)} \quad (S1)$$

Here z_i and C_i^* are the charge and the bulk concentration of the i^{th} ion species, $\phi(\mathbf{r})$ is the electric potential within the electrolyte, T is the temperature of the system, F is the Faraday constant, and R is the ideal gas constant. Note that z_i is positive for cations and negative for anions. The second ingredient of the model is the Poisson's equation:

$$\nabla \cdot (\epsilon_0 \epsilon_r \nabla \phi(\mathbf{r})) = -\rho(\mathbf{r}) \quad (S2)$$

In eqn S2, ϵ_0 and ϵ_r are the vacuum permittivity and the relative permittivity of the media (in aqueous solutions, ϵ_r is the relative permittivity for water). Substitute eqn S1 into eqn S2, one obtains the Poisson-Boltzmann (PB) equation:

$$\nabla \cdot (\epsilon_0 \epsilon_r \nabla \phi(\mathbf{r})) = - \sum_i z_i F C_i^* e^{-\left(\frac{z_i F \phi(\mathbf{r})}{RT}\right)} \quad (S3a)$$

For symmetrical binary electrolyte ($z_+ = -z_- = z$, $C_{cation}^* = C_{anion}^* = C^*$), the PB equation can be further simplified to a hyperbolic form:

$$\nabla \cdot (\epsilon_0 \epsilon_r \nabla \phi(\mathbf{r})) = 2zFC^* \sinh\left(\frac{zF}{RT} \phi(\mathbf{r})\right) \quad (S3b)$$

Derivation of the Poisson-Nernst-Planck (PNP) equation (without magnetic force)

The principle of the PNP model is mass conservation. For any point in electrolyte within a time period, the concentration change of a species equals the difference between the species flow inside the point and that flow outside. In the context of electrolysis, only the diffusion and the electric migration are usually considered, resulting in the following differential equation:

$$\frac{\partial C_i(\mathbf{r})}{\partial t} = -\nabla \cdot \mathbf{J}_i(\mathbf{r}) = -\nabla \cdot \left(-D_i \nabla C_i(\mathbf{r}) - \frac{D_i z_i F C_i(\mathbf{r})}{RT} \nabla \phi(\mathbf{r}) \right) \quad (S4)$$

In eqn S4, J_i , C_i , and D_i are the flux, the concentration, and the diffusion coefficient of the i^{th} species, while the definition of other variables follows those in the derivation of PB equation. In this work, we are interested in an equilibrium state, in which the concentration of ionic species does not change with respect to time. This gives the PNP equation:

$$\frac{\partial C_i(\mathbf{r})}{\partial t} = \nabla \cdot \left(D_i \nabla C_i(\mathbf{r}) + \frac{D_i z_i F C_i(\mathbf{r})}{RT} \nabla \phi(\mathbf{r}) \right) = 0 \quad (S4a)$$

The Lattice Gas Approximation^{6,7}

In both the PB and the PNP model, the ions are treated as point charge and thus can aggregate to form unphysically high ion concentration at high electrode voltage. To correct this, the size of the ions is introduced to the PB and the PNP model via the lattice gas approximation. In this approximation, the electrolyte is divided into small cubic cells of size a . Each cell is assumed to have only three possible contents: a cation, an anion, or solvent. To better validate this assumption, the parameter a is chosen close to the diameter of the ionic species. Given the logic of the lattice gas approximation, it is worth noting that despite the parameter a being usually referred to as the 'diameter of the ionic species', it is actually associated with

the fineness of the three-state cell, and is chosen according to the size of the ions. In additionally, methods derived using the lattice gas approximation only applies to the electrolyte systems whose cations and anions are of similar size.

Using the lattice gas approximation, the internal energy, U , and the entropy, S , of an electrolyte system can be written as follows:

$$U = \int d\mathbf{r} \left(-\frac{\varepsilon}{2} |\nabla\psi|^2 + z_+ e C_+ \psi + z_- e C_- \psi - \mu_+ C_+ - \mu_- C_- \right) \quad (S5)$$

In eqn S5, the definition of z , C , and ψ follows those in the previous derivation. The chemical potential is denoted in μ . e is the elementary charge. The ε parameter is the product of ε_0 and ε_r for a given medium. The '+' and the '-' subscript denotes the property of cationic and anionic species, respectively.

The first term in eqn S5 is the electric self-energy, while the following two terms arise from charge separation of ionic species under external electric potential. The last two are the chemical potential of ionic species.

The entropy of the system can be obtained from the Gibbs entropy:

$$-S = k_B \sum_{i=(+, -, w)} p_i \ln(p_i) \quad (S6)$$

In eqn S6, k_B is the Boltzmann's constant, and p_i is the probability of the system in the i^{th} state. According to the lattice gas approximation, a cell has three states. The probability of the cell being occupied by a cation, an anion, and water is denoted p_+ , p_- , and p_w . Obviously, p_+ and p_- can be calculated from the concentration of the ionic species, and p_w can be calculated from the fact that the three probabilities sum up to unity.

$$p_+ = C_+ a^3 \quad (S7a)$$

$$p_- = C_- a^3 \quad (S7b)$$

$$p_w = 1 - p_+ - p_- \quad (S7c)$$

The Gibbs entropy of the electrolyte system is:

$$\begin{aligned} S &= -k_B \sum_{cell} (p_+ \ln p_+ + p_- \ln p_- + p_w \ln p_w) \\ &= -\frac{k_B}{a^3} \int d\mathbf{r} [C_+ a^3 \ln(C_+ a^3) + C_- a^3 \ln(C_- a^3) \\ &\quad + (1 - C_+ a^3 - C_- a^3) \ln(1 - C_+ a^3 - C_- a^3)] \end{aligned} \quad (S8)$$

The Helmholtz free energy of the system is

$$F = U - TS \quad (S9)$$

For an equilibrium state, F should be minimized with respect to the change of the electric potential and the ion concentrations, thus

$$\frac{\partial F}{\partial \psi} = 0, \frac{\partial F}{\partial C_+} = 0, \frac{\partial F}{\partial C_-} = 0 \quad (S10)$$

The lattice gas approximation consists two assumptions: one is that each cube only has three possible contents: a cation, an anion, or pure water; the other is that the content of different cubes is independent of each other. To simultaneously validate the two assumptions to the maximum extent, the value of a is usually taken the diameter of the ionic species, and thus the parameter a is usually referred to as the effective solvent diameter. The probability of a cube holding a cation or an anion depends on the local concentration of the ionic species and

the probability of water is calculated using the sum of the three probabilities being unity (eqn S7a-c).

It should be emphasized that although the parameter a is named the effective solvent diameter, it is a space partition parameter whose optimal value happen to be the diameter of the ions. Thus, the practice of incorporating different a values from the actual size of (bare or solvated) cations and anions should be discarded. In addition, if the size of the cation differs too much from that of anion, the two assumptions of the lattice gas approximation can no longer hold simultaneously as the first assumption requires an a value less than the smaller ion diameter and the second one requires an a value more than the larger ion diameter. Thus, one should ensure that the cation and the anion are of similar size before applying lattice gas approximation related methods. If both ionic species are of spherical shape and have the smaller and the larger radius of r_{min} and r_{max} respectively, we propose the condition $r_{min}/r_{max} > 0.74$ as the criterium of two ions being of similar size (see SI for derivation).

Derivation of Modified Poisson-Boltzmann (MPB) Equation⁶

In the following derivation, we evaluate the three equations in eqn S10 to establish the MPB equation. For the simplicity of the mathematical derivation, we consider symmetric binary electrolyte of charge z ($z_+ = -z_- = z$), and bulk concentration C^* .

1) Evaluating $\partial F/\partial\psi=0$

Since C_+ , C_- , and ψ are three independent variables, S does not have dependence on ψ , thus $\partial S/\partial\psi=0$. At low electric potential, $\partial\epsilon/\partial\psi=0$, too. Thus, the Helmholtz free energy becomes:

$$\frac{\partial F}{\partial\psi} = \frac{\partial U}{\partial\psi} = \int d\mathbf{r} \left[\left(-\frac{1}{2} |\nabla\psi|^2 \frac{\partial\epsilon}{\partial\psi} - 2\epsilon\nabla^2\psi \right) + zeC_+ - zeC_- \right] = 0 \quad (\text{S10a})$$

Assume low electric potential such that $\partial\epsilon/\partial\psi=0$, we get the Poisson's Equation:

$$\epsilon\nabla^2\psi = -ze[C_+ - C_-] \quad (\text{S10b})$$

2) Evaluating $\partial F/\partial C_+=0$ and $\partial F/\partial C_-=0$:

$$\begin{aligned} \frac{\partial F}{\partial C_+} &= \frac{\partial U}{\partial C_+} - T \frac{\partial S}{\partial C_+} = \int d\mathbf{r} \left(ze\psi - \mu_+ - C_+ \frac{\partial\mu_+}{\partial C_+} + k_B T \ln \frac{C_+ a^3}{1 - C_+ a^3 - C_- a^3} \right) \\ &= 0 \end{aligned} \quad (\text{S10c})$$

Similarly:

$$\begin{aligned} \frac{\partial F}{\partial C_-} &= \frac{\partial U}{\partial C_-} - T \frac{\partial S}{\partial C_-} = \int d\mathbf{r} \left(-ze\psi - \mu_- - C_- \frac{\partial\mu_-}{\partial C_-} + k_B T \ln \frac{C_- a^3}{1 - C_+ a^3 - C_- a^3} \right) \\ &= 0 \end{aligned} \quad (\text{S10d})$$

Furthermore, we assume μ_+ and μ_- are constants, which is $\partial\mu_{\pm}/\partial C_{\pm} = 0$. When there is no external electric potential ($\psi = 0$), the equilibrium state of the electrolyte can be described as $C_+ = C_- = C^*$. Meanwhile, the derivative of F with respect to C_+ and C_- are both 0. Substituting the condition into eqn S10c and S10d, one get:

$$\left. \frac{\partial F}{\partial C_+} \right|_{C_+=C^*} = -\mu_+ + k_B T \ln \frac{C^* a^3}{1 - 2C^* a^3} = 0 \quad (\text{S10e})$$

$$\left. \frac{\partial F}{\partial C_-} \right|_{C_-=C^*} = -\mu_- + k_B T \ln \frac{C^* a^3}{1 - 2C^* a^3} = 0 \quad (\text{S10f})$$

Solve eqn S10e and eqn S10f, one gets

$$\mu_+ = \mu_- = k_B T \ln \frac{C^* a^3}{1 - 2C^* a^3} \quad (\text{S10g})$$

Substitute eqn S10g back to eqn S10c, one gets

$$ze\psi - k_B T \ln \frac{C^* a^3}{1 - 2C^* a^3} + k_B T \ln \frac{C_+ a^3}{1 - C_+ a^3 - C_- a^3} = 0 \quad (\text{S10h})$$

Rearrange eqn S10h, one can eventually get

$$\begin{aligned} \frac{ze\psi}{k_B T} &= \ln \left(\frac{C^* a^3}{1 - 2C^* a^3} \frac{1 - C_+ a^3 - C_- a^3}{C_+ a^3} \right) \\ e^{-\frac{ze\psi}{k_B T}} &= \frac{C_+}{C^*} \frac{1 - 2C^* a^3}{1 - C_+ a^3 - C_- a^3} \\ C_+ &= C^* e^{\frac{ze\psi}{k_B T}} \frac{1 - C_+ a^3 - C_- a^3}{1 - 2C^* a^3} \end{aligned} \quad (\text{S10i})$$

Similarly, one can obtain

$$C_- = C^* e^{\frac{ze\psi}{k_B T}} \frac{1 - C_+ a^3 - C_- a^3}{1 - 2C^* a^3} \quad (\text{S10j})$$

In principle, by aligning eqn S10i and S10j, one can solve for C_+ and C_- . The solution is:

$$C_+ = \frac{C^* e^{\frac{ze\psi}{k_B T}}}{1 - 2C^* a^3 + C^* a^3 e^{\frac{ze\psi}{k_B T}} + C^* a^3 e^{\frac{ze\psi}{k_B T}}} \quad (\text{S10k})$$

$$C_- = \frac{C^* e^{\frac{ze\psi}{k_B T}}}{1 - 2C^* a^3 + C^* a^3 e^{\frac{ze\psi}{k_B T}} + C^* a^3 e^{\frac{ze\psi}{k_B T}}} \quad (\text{S10l})$$

Substitute eqn S10k and S10l into eqn S10b, we get the formula of the MPB model for symmetrical binary electrolyte of charge z and concentration C^* .

$$\begin{aligned} \varepsilon \nabla^2 \psi &= -ze[C_+ - C_-] \\ &= -ze \left[\frac{C^* e^{\frac{ze\psi}{k_B T}} - C^* e^{\frac{ze\psi}{k_B T}}}{1 - 2C^* a^3 + C^* a^3 e^{\frac{ze\psi}{k_B T}} + C^* a^3 e^{\frac{ze\psi}{k_B T}}} \right] \\ &= 2zeC^* \left[\frac{\sinh\left(\frac{ze\psi}{k_B T}\right)}{1 - 2C^* a^3 + 2C^* a^3 \cosh\left(\frac{ze\psi}{k_B T}\right)} \right] \end{aligned} \quad (\text{S10m})$$

Derivation of the Generalized Modified Poisson Nernst Planck (GMPNP) equation⁷

We start from the chemical potential established in eqn X10c and eqn X10d with the assumption that the chemical potential are constants ($\partial\mu_{\pm}/\partial C_{\pm} = 0$). The expression for chemical potential is then:

$$\mu_{\pm} = \frac{\partial F}{\partial C_{\pm}} = \pm ze\psi + k_B T \ln \left(\frac{C_{\pm} a^3}{1 - C_{+} a^3 - C_{-} a^3} \right) \quad (\text{S11})$$

The GMPNP model relies the following postulate for near equilibrium mass transport:

$$\frac{\partial C_{\pm}}{\partial t} = \nabla \cdot J_{\pm} = \nabla \cdot (b_{\pm} C_{\pm} \nabla \mu_{\pm}) = 0 \quad (\text{S12})$$

In eqn S12, J_{\pm} and b_{\pm} is the flux and the mobility of the ionic species. Substituting eqn S11 into eqn S12:

$$\begin{aligned} J_{\pm} &= b_{\pm} C_{\pm} \nabla \left(\pm ze\psi + k_B T \ln \left(\frac{C_{\pm} a^3}{1 - C_{+} a^3 - C_{-} a^3} \right) \right) \\ &= b_{\pm} C_{\pm} \left(\nabla(\pm ze\psi) + k_B T \nabla \left(\ln \left(\frac{C_{\pm} a^3}{1 - C_{+} a^3 - C_{-} a^3} \right) \right) \right) \\ &= \frac{\pm ze D_{\pm} C_{\pm} \nabla \psi}{k_B T} + D_{\pm} C_{\pm} \nabla \ln \left(\frac{C_{\pm} a^3}{1 - C_{+} a^3 - C_{-} a^3} \right) \\ &= \frac{\pm ze D_{\pm} C_{\pm} \nabla \psi}{k_B T} + D_{\pm} C_{\pm} \left(\frac{\nabla C_{\pm}}{C_{\pm}} + \frac{a^3 (\nabla C_{+} + \nabla C_{-})}{(1 - C_{+} a^3 - C_{-} a^3)} \right) \\ &= \frac{\pm ze D_{\pm} C_{\pm} \nabla \psi}{k_B T} + D_{\pm} \nabla C_{\pm} + D_{\pm} C_{\pm} \left(\frac{a^3 (\nabla C_{+} + \nabla C_{-})}{(1 - C_{+} a^3 - C_{-} a^3)} \right) \end{aligned} \quad (\text{S12a})$$

In eqn S12a, $D_{\pm} = k_B T b_{\pm}$ is the diffusion coefficient of the ionic species. For an equilibrium state, the total flux of the ionic species should be 0, which gives

$$\frac{\pm ze D_{\pm} C_{\pm} \nabla \psi}{k_B T} + D_{\pm} \nabla C_{\pm} + D_{\pm} C_{\pm} \left(\frac{a^3 (\nabla C_{+} + \nabla C_{-})}{(1 - C_{+} a^3 - C_{-} a^3)} \right) = 0 \quad (\text{S12b})$$

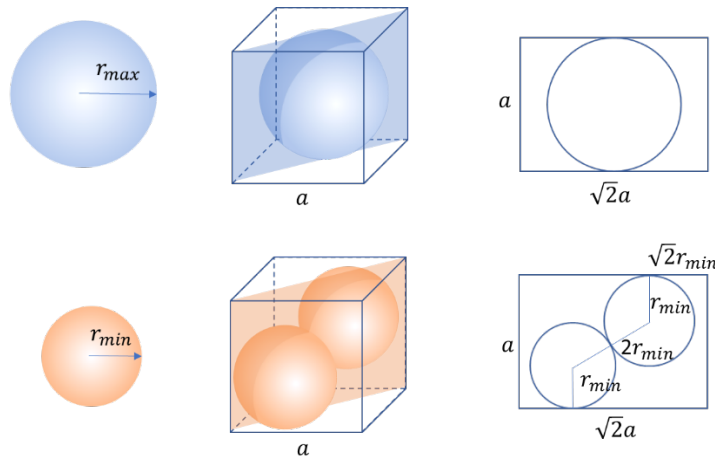
Note that the Poisson equation is still valid

$$\varepsilon \nabla^2 \psi = -[z_{+} e C_{+} - z_{-} e C_{-}] \quad (\text{S13})$$

The GMPNP model is then established by solving the equation set composed of eqn S12b and S13.

Derivation of the recommend threshold for size similarity.

As is shown in the diagram below, we consider an extreme condition in which the box that can perfectly encapsulate one larger ion can also perfectly enclose two smaller ions.



The geometric relation between r_{min} , r_{max} , and a satisfies the following:

For r_{max} , we have $r_{max} = a/2$ (top right)

For r_{min} , we have $(a - 2r_{min})^2 + (\sqrt{2}a - 2\sqrt{2}r_{min})^2 = 4r_{min}^2$. (bottom right)

Solve it, we find $r_{min} = (2 - 2\sqrt{6}/3)a$

The ratio, $r_{min}/r_{max} = (4 - 4\sqrt{6}/3) \approx 0.74$

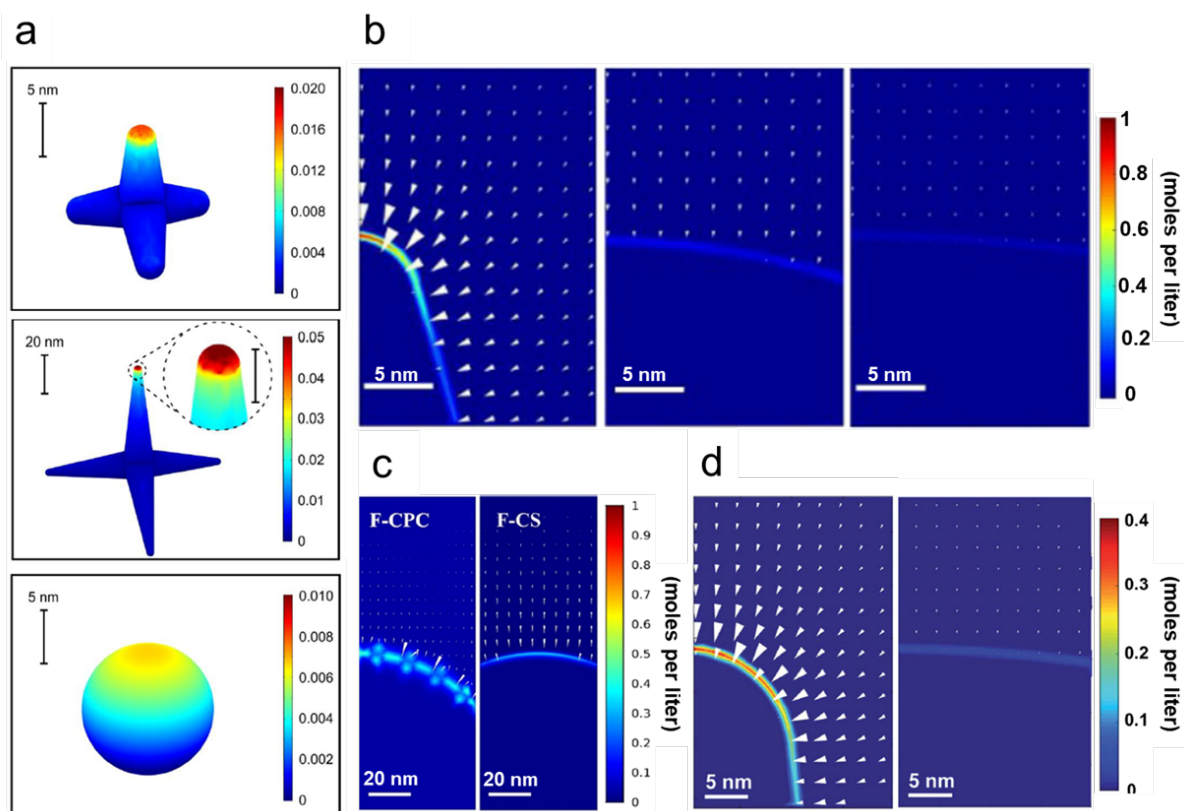


Figure S1. Computed distribution of electron density on the surface of various nanostructured electrodes. (a) CuPd electrodes including 7-nm CuPd tetrapods, 50-nm CuPd tetrapod, and CuPd nanoparticle.⁸ (b) Au electrodes including Au needles, Au rods and Au particle.⁹ (c) Fluorine doped carbon electrodes including fluorine-doped cage-like porous carbon (F-CPC) and fluorine-doped carbon sphere (F-CS).¹⁰ (d) Cu@Sn electrodes including Cu@Sn nanocone and bulk Sn.¹¹

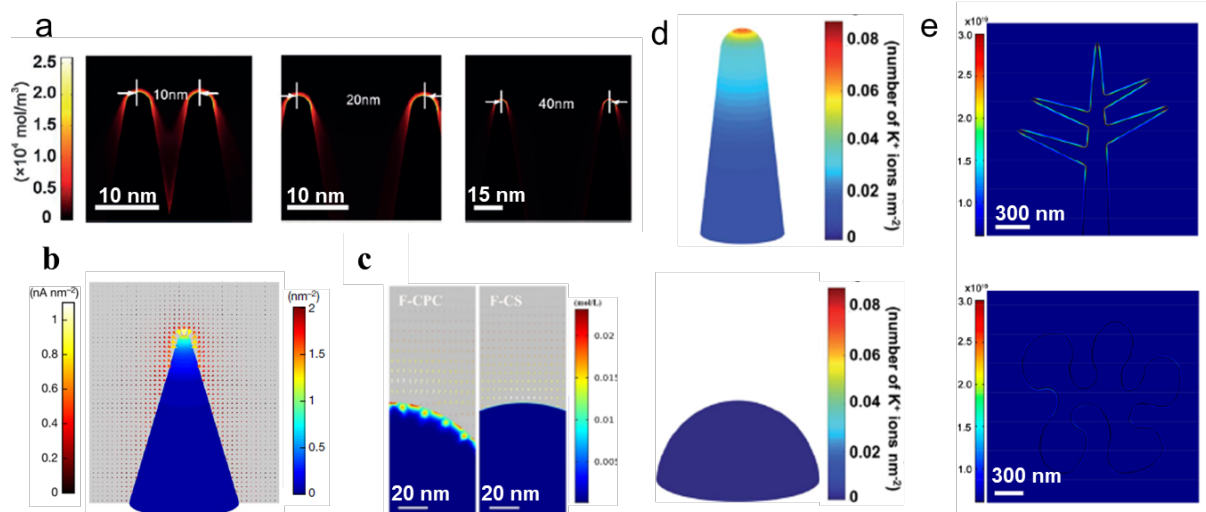


Figure S2. Computed distribution of K⁺ density distribution on the surface of various nanostructured electrodes. (a) CdS needles with different gaps.¹² (b) Au needle.⁹ (c) Fluorine doped carbon electrodes including fluorine-doped cage-like porous carbon (F-CPC) and fluorine-doped carbon sphere (F-CS).¹⁰ (d) Cu@Sn electrodes including Cu@Sn nanocone and bulk Sn.¹¹ (e) Cu dendrites (Cu-D) and Cu particles (Cu-P).¹³

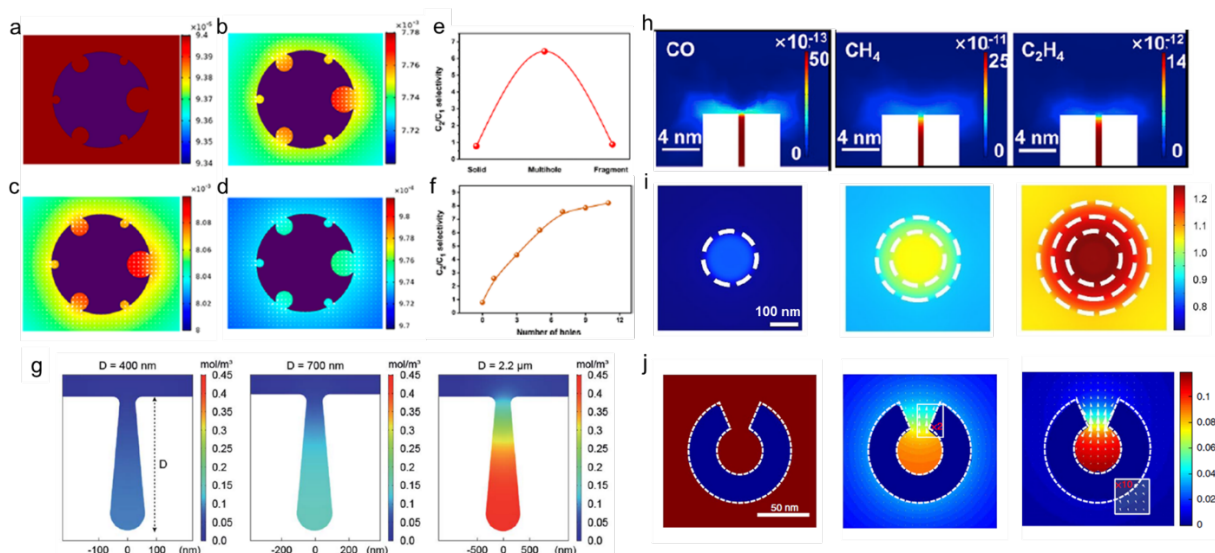


Figure S3. Computed concentration of species on various nanostructured electrodes. (a-f) Species of CO_2 , C_1 , C_2 , and C_3 around multi-hollow Cu_2O electrode: the concentration distribution of (a) CO_2 , (b) C_1 , (c) C_2 , (d) C_3 , and the species C_2/C_1 ratio as a function of (e) different catalysts and (f) number of holes, Colour scale, in mol/L.¹⁴ (g) hydroxide ion (OH^-) around c-wrinkle cavities with different D parameters ranging 400nm to 2.2 μm .¹⁵ (h) Species of CO , CH_4 and C_2H_4 around copper-porphyrin frameworks, Colour scale, in mol/ m^3 .¹⁶ (i) Species C_2/C_1 concentration ratio over single 1-shell, 2-shell and 3-shell hollow multi-shell structured copper.¹⁷ (j) CO , C_2 and C_3 concentrations on the Cu nanocavity electrode, colour scale, in mmol/L.¹⁸

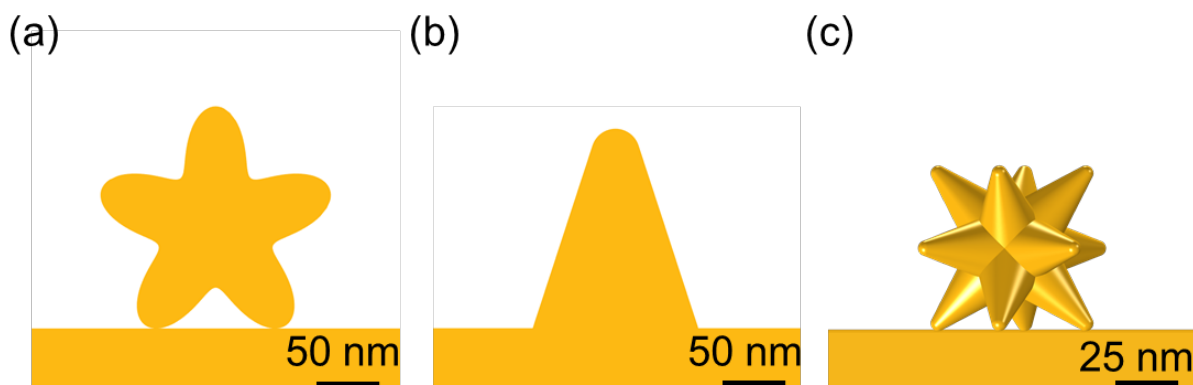


Figure S4. The electrode geometries used in this work: (a) 2D nanostar, (b) 2D nanocone, and (c) 3D branched nanoparticle.

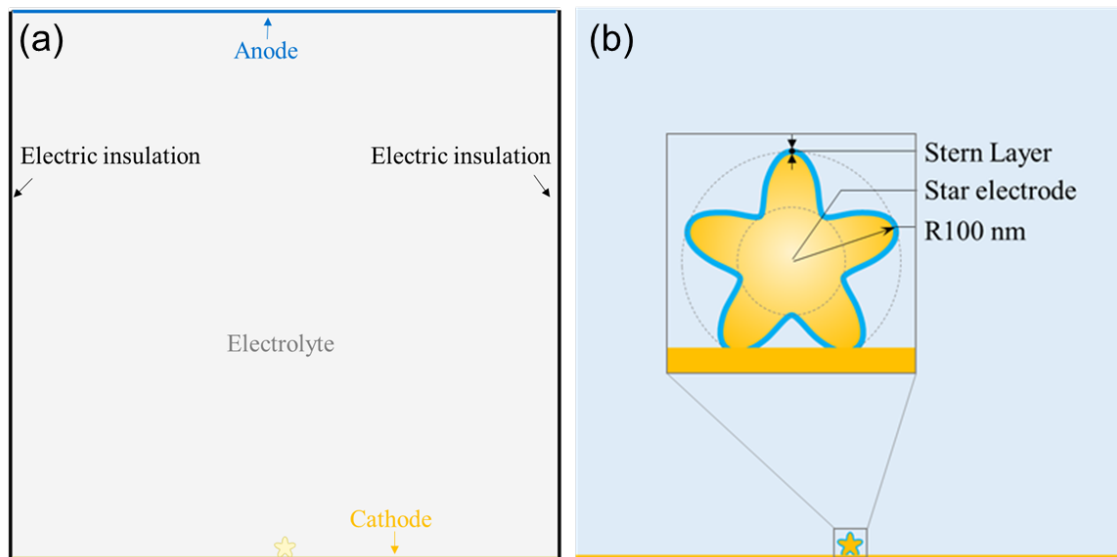


Figure S5. a) FEM simulation domain setup and b) the dimension of the star electrode.

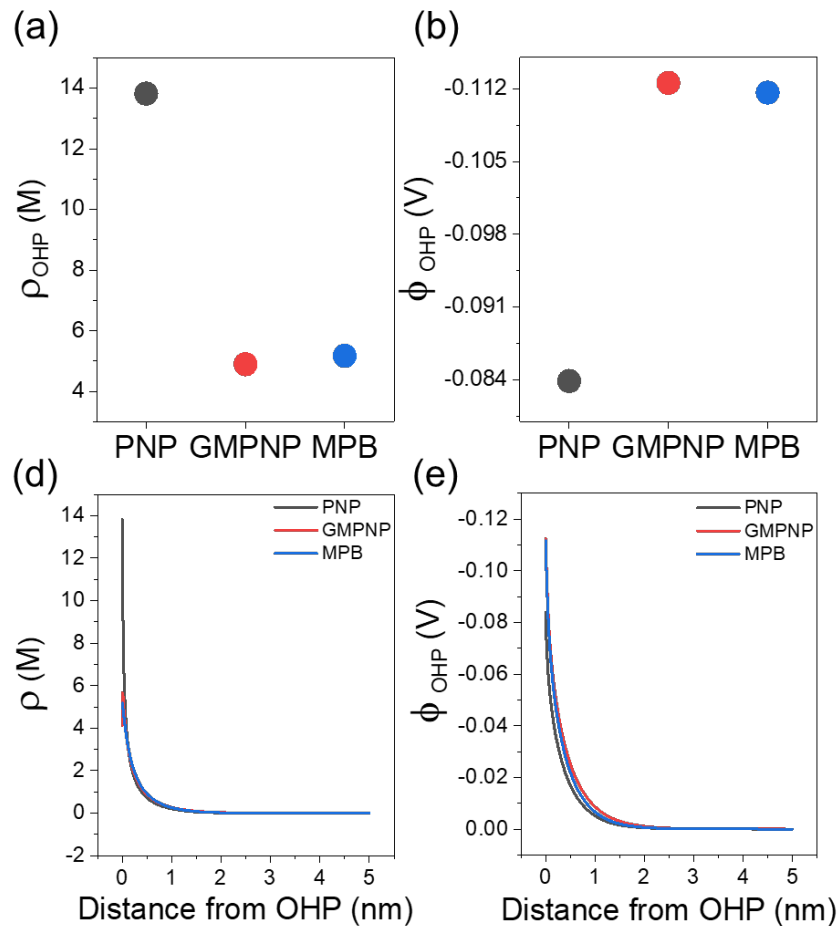


Figure S6. Comparison between results obtained from Poisson-Nernst-Planck (PNP) model, a generalized modified PNP (GMPNP) model and modified Poisson-Boltzmann model for (a,d) space charge density (ρ), (b,e) potential (ϕ) Subscript OHP means the measurement at OHP. Considering the difficulty in solving GMPNP numerically, all results are obtained using a planar model with applied potential of -0.4 V vs PZC and the electrolyte of 0.5 M KHCO_3 .

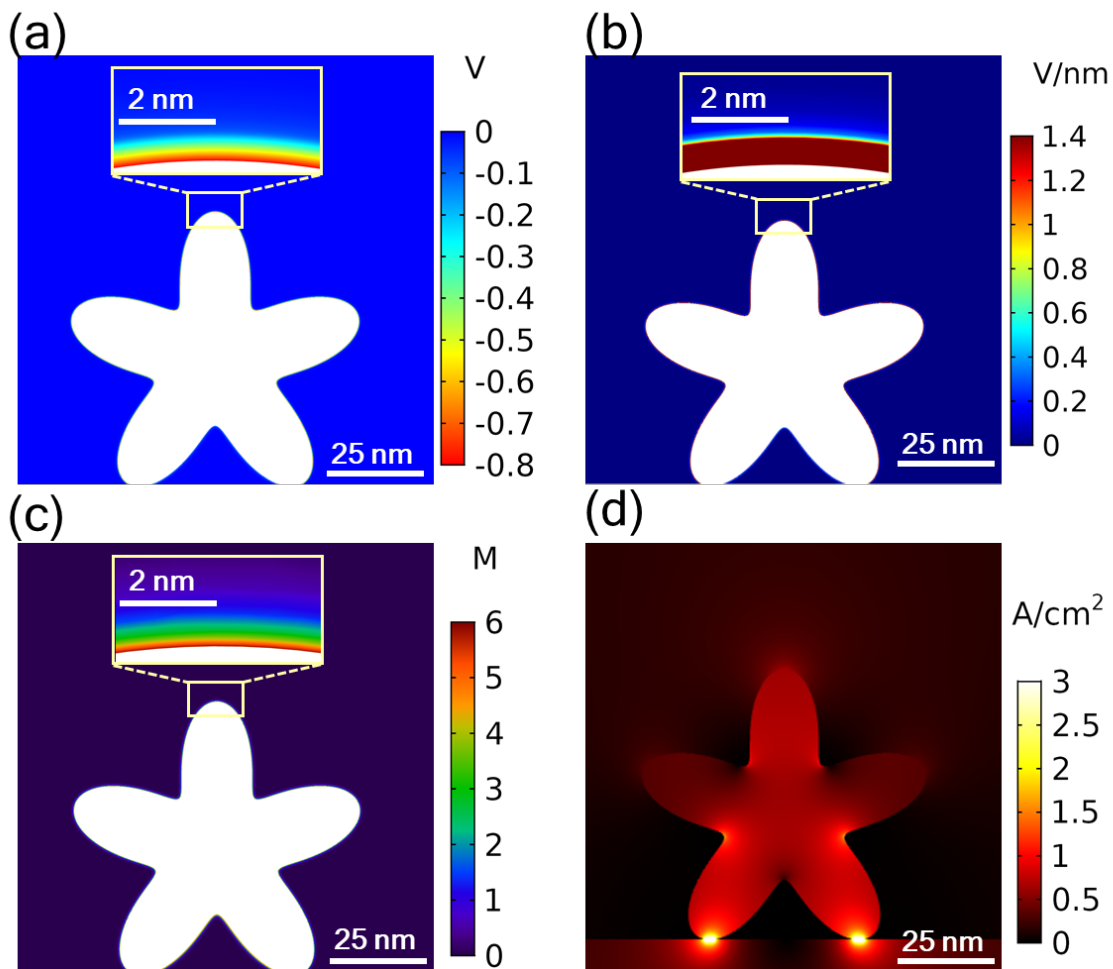


Figure S7. Simulations performed for 2D nanostar nanoparticle. (a) The potential (ϕ), (b) electric field (E-field) (c) K^+ concentration and (d) current density in metal (J_{metal}) and adjacent electrolyte ($J_{electrolyte}$). The results in (a), (b) and (c) are obtained from MPB & Booth model with the electrolyte of 500 mM $KHCO_3$ and potential of -0.8V vs PZC, the reaction current density ($J_{electrolyte}$) in (d) is calculated using J_{Sec+M} .

Procedures for simulating E-field and current densities in nanoelectrodes

Links to the tutorial videos:

1) FEM simulations of nanoscale electrocatalysts: E-field distribution

<https://youtu.be/wBlkXgplpwg>

2) FEM simulations of nanoscale electrocatalysts: electrode current density

https://youtu.be/adH_eoU0GP8

3) FEM simulations of nanoscale electrocatalysts: reaction current density distribution

<https://youtu.be/a8Su3rCyhIU>

Detailed procedure of E-field simulation in COMSOL and the corresponding parameters

Step 1: Units Setup

1. Length unit: nm

2. Angular unit: radians

Step 2: Parameter definitions

1. Parameters for constructing the nanostar electrode

Name	Expression	Description
r0	30[nm]	inner radius of star
R0	70[nm]	outer radius of star
h_sub	50[nm]	height of substrate
w_sub	5000[nm]	width of substrate
theta1	$-(72)/360 \cdot 2 \cdot \pi$	An angle for modelling the nanostar
y_b_s	$(r0 + (R0 - r0) \cdot (\cos(\theta1 \cdot 5) + 1) / 2) \cdot \sin(\theta1) + (R0 - r0) \cdot \cos(72/360 \cdot 2 \cdot \pi)$	y coordinate of nanostar bottom
sy_offset	-3.2[nm]	The cut off part of the nanostar
d_edl	0.33[nm]	thickness of the electric double layer
h_dom	5000[nm]	height of simulation domain
w_dom	5000[nm]	width of simulation domain

2. Parameters for setting up the physical interfaces

Name	Expression	Description
v_c	-0.8[V]	cathode potential vs PZC
v_a	0[V]	anode potential
c_bulk	500[mM]	electrolyte bulk concentration
T	293.15[K]	temperature
e	1.602176634E-19[C]	electron charge
beta	1.41e-8[m/V]	a constant in Booth model
Kb	1.381E-23 [m ² *kg*K ⁻¹ *s ⁻²]	Boltzmann constant
n	1.33	the refractive index of the electrolyte
rp	78	relative permittivity
NA	6.022E23[mol ⁻¹]	Avogadro's number

The parameters required in the simulation should be defined in advance for convenience. These pre-defined parameters can then be used in subsequent simulations, avoiding entering these values and equations repeatedly.

Step3: Geometry modelling

Three different options of geometry modelling in COMSOL

1. Use built-in geometry primitives
2. Use mathematical expression
3. Use 'Import' function

The model can be constructed in a 3D modeling software (e.g., 3D Max and Solidworks) saved as a .mphbin or .stl file, which then can be imported into COMSOL.

1. Nanostar electrode modelling (mathematical expression)

Parameter Name: theta

Range: min: 0 max: 2π

x expressions: $(r_0 + (R_0 - r_0) * (\cos(\theta * 5) + 1) / 2) * \cos(\theta)$

y expressions: $(r_0 + (R_0 - r_0) * (\cos(\theta * 5) + 1) / 2) * \sin(\theta)$

Rotation angle: $18/360 * 2\pi$

2. Electric double layer modelling (mathematical expression)

Parameter name: theta

Range: min: 0 max: 2π

x expression:

$((r_0 + (R_0 - r_0) * (\cos(\theta * 5) + 1) / 2) + \sqrt{1 + (5 * (R_0 - r_0) * \sin(5 * \theta) / (2 * (r_0 + (R_0 - r_0) * (\cos(\theta * 5) + 1) / 2)))^2} * d_{edl}) * \cos(\theta)$

y expression:

$((r_0 + (R_0 - r_0) * (\cos(\theta * 5) + 1) / 2) + \sqrt{1 + (5 * (R_0 - r_0) * \sin(5 * \theta) / (2 * (r_0 + (R_0 - r_0) * (\cos(\theta * 5) + 1) / 2)))^2} * d_{edl}) * \sin(\theta)$

Rotation angle: $18/360 * 2\pi$

3. Substrate modelling (geometry primitivities)

Width: w_{sub}

Height: h_{sub}

Position: x: 0

Position: y: $y_{b_s} - h_{sub} / 2 + sy_offset$

The substrate is introduced in the model and integrated with the nanostar geometry to represent substrate-supported nanoparticles used as an electrode.

4. Electrolyte domain modelling (geometry primitivities)

Width: w_{dom}

Height: h_{dom}

Position x: $-w_{\text{dom}}/2$ y: $y_{\text{b}_s} + sy_{\text{offset}}$

5. Add 'Union' function

Union" function is used to integrate the substrate and the nanostar, thereby making a continuous geometric model.

Step4: Material Setup

Add materials from built-in material bank in COMSOL

Water(liquid)

Gold(solid)

Step5: Defining domains and boundary conditions for the model

1. cathode surface boundary
2. anode surface boundary
3. OHP surface boundary
4. electrolyte domain
5. electrolyte_OHP domain
6. sub_nanostar_OHP domain
7. OHP domain

In this step, the boundaries and domains used in the simulation are defined in advance for the purpose of convenience.

Step 6: 'Electrostatic' interface setup

1. diffuse layer

electric potential anode: v_a

surface charge density OHP: ρ_{surf}

space charge density: $-d_{\text{sc}}$

2. Stern layer

electric potential cathode: v_c

electric potential ohp: V

Step 7: 'Variable' definition in Component

Name	Expression	Description
deltaphi	$v_c - V$	potential difference
V	$2 \cdot (0.66[\text{nm}])^3 \cdot N_A \cdot c_{\text{bulk}}$	the packing parameter
rho_surf	$\epsilon_{\text{surf}} \cdot \text{const} \cdot \text{deltaphi} / d_{\text{edl}}$	surface charge density on OHP
d_sc	$(2 \cdot e \cdot N_A \cdot c_{\text{bulk}} \cdot \sinh(e \cdot V / k_B / T)) / (1 + 2 \cdot v \cdot (\sinh(e \cdot V / k_B / T / 2))^2)$	space charge density

Step 8: 'Mesh' setup

Size 1 Max: 0.33 [nm] Min: 0.01 [nm]

Free Triangular

There two options of the mesh for 2D simulation in COMSOL: 'Free triangular' and 'Mapped'. Here, Free triangular mesh is applied as an example.

Step 9: 'Study' setup

Study type: Stationary

A stationary analysis solver for stationary displacement or a steady-state condition.

Run the study

Hit 'Compute'

Depending on how detailed the model is, the run time can vary from min to hours.

Step 10: Plotting 'Results'

Plotting electric field:

Variable name: es.normE

The variable name can be found in 'Component 1' > 'Electrostatic_diffuse_layer' > 'Electric'

Detailed procedure of reaction current density simulation in COMSOL and the corresponding parameters

Step1: Units setup

Length unit: nm

Angular unit: radians

Step2: Parameter definitions

Name	Expression	Description
v_c	-0.3[V]	cathode potential vs RHE
v_a	0[V]	anode potential vs RHE
c_bulk	500[mM]	electrolyte bulk concentration
c_bulk_CO2	38[mol/m ³]	CO2 bulk concentration
T	293.15[K]	temperature
D_HCO3	1.185e-9[m ² *s ⁻¹]	Diffusion coefficient of HCO3
D_K	1.957e-9[m ² *s ⁻¹]	Diffusion coefficient of K
D_CO2	1.91e-9[m ² *s ⁻¹]	Diffusion coefficient of CO2
Ve_eq_c	-0.11 [V]	Equilibrium potential of CO2 to CO

The parameters required in the simulation should be defined in advance for convenience. These pre-defined parameters can then be used in subsequent simulations, avoiding entering these values and equations repeatedly.

Step3: Geometry modelling

Import the pre-built geometry file using 'import' function;

The model was constructed in electric field simulation in COMSOL saved as a .mphbin file, which can be imported into COMSOL for reaction current density simulation by using 'import' function.

Step4: Material Setup

Add materials from built-in material bank in COMSOL

Water(liquid)

Gold(solid)

Step5: Defining domains and boundary conditions for the model

1. cathode surface boundary
2. anode surface boundary
3. nanostar surface boundary

In this step, the boundaries and domains used in the simulation are defined in advance for the purpose of convenience.

Step 6: 'Tertiary Current Distribution, Nernst-Plank (tcd)' interface setup

COMSOL provides various types of reaction current density simulation in Electrochemistry module:

1. Primary Current Distribution
2. Secondary Current Distribution
3. Tertiary Current Distribution
4. The modelling approach based on combining Secondary Current Distribution with the mass transport effect can be achieved by combining the Secondary Current Distribution interface with Transport of Diluted Species (tds).

Here, Tertiary Current Distribution is performed as an example.

1. Dependent variables

Number of variables: 3

Concentration: HCO_3 , K, CO_2

2. Electrolyte

Diffusion coefficient: D_{HCO_3} D_{K} D_{CO_2}

Charge number: Z_{HCO_3} : -1 Z_K : 1 Z_{CO_2} : 0

3. Initial values:

K: c_{bulk} CO_2 : $c_{\text{bulk_CO}_2}$

4. Concentration:

CO , K: c_{bulk} CO , CO_2 : $c_{\text{bulk_CO}_2}$ Boundary: anode_surface

5. Electrode reaction on cathode surface

Number of participating electrons: 2

Stoichiometric coefficients:

V_k : 0

V_{CO_2} : -1

Equilibrium potential: $V_{\text{eq_c}}$

6. Electrode kinetics

COMSOL provides various types of Kinetics expression type:

- Concentration dependent kinetics
- Butler-Volmer
- Linearized Butler-Volmer
- Tafel equation

Here, Concentration dependent kinetics is applied as an example.

Kinetic expression type: Concentration dependent kinetics

Exchange current density: $1\text{e}2[\text{A}/\text{m}^2]$

Anodic transfer coefficient: 0.5

Cathodic transfer coefficient: 0.5

Reduced species expression: 1

Oxidized species expression: $\text{CO}_2/c_{\text{bulk_CO}_2}$

7. Anode surface

Electrolyte potential: v_a

Step 7: 'Mesh' setup

Size 1 Max: 10 [nm] Min: 1 [nm]

Free Triangular

There are two options of the mesh for 2D simulation in COMSOL: 'Free triangular' and 'Mapped'. Here, Free triangular mesh is applied as an example

Boundary layer

Number of Boundary layer: 8

Boundary layer stretching factor: 1.2

Boundary layer is required to mesh the electrode surface properly considering the importance of the surface reaction to this simulation.

Step 8: 'Study' setup

Study type: Stationary

A stationary analysis solves for stationary displacements or a steady-state condition;

Run the study

Hit 'Compute';

Depending on how detailed the model is, the run time can vary from min to hours;

Step 9: Plotting 'Results

Plotting reaction current density:

Variable name: tcd.IIMag

The variable name can be found in 'Component 1' > 'Tertiary Current Distribution, Nernst-Plank'

Detailed procedure of electrode current density simulation in COMSOL and the corresponding parameters

Step1: Units setup

Length unit: nm

Angular unit: radians

Step2: Parameter definitions

Name	Expression	Description
v_a	0[V]	anode potential vs RHE
rp_electrolyte	78	Relative permittivity of electrolyte
rp_metal	1	Relative permittivity of metal
ec_electrolyte	5.8 [S/m]	Electric conductivity of electrolyte
ec_metal	45.6e6[S/m]	Electric conductivity of metal
I_ave	100[mA/cm^2]	1000 A/m ²

The parameters required in the simulation should be defined in advance for convenience. These pre-defined parameters can then be used in subsequent simulations, avoiding entering these values and equations repeatedly.

Step3: Geometry modelling

Import the pre-built geometry file using 'import' function;

The model was constructed in electric field simulation in COMSOL saved as a .mphbin file, which can be imported into COMSOL for reaction current density simulation by using 'import' function.

Step4: Material Setup

Add materials from built-in material bank in COMSOL

Water(liquid)

Gold(solid)

Step5: Defining domains and boundary conditions for the model

1. cathode surface boundary
2. anode surface boundary
3. nanostar surface boundary

In this step, the boundaries and domains used in the simulation are defined in advance for the purpose of convenience.

Step 6: 'Electric Current' interface setup

Electric potential anode: v_a

Normal current density: I_{ave}

Step 7: 'Mesh' setup

Size 1 Max: 10 [nm] Min:1 [nm]

Free Triangular

There are two options of the mesh for 2D simulation in COMSOL: 'Free triangular' and 'Mapped'. Here, Free triangular mesh is applied as an example.

Step 8: 'Study' setup

Study type: Stationary

A stationary analysis solves for stationary displacements or a steady-state condition;

Run the study

Hit 'Compute';

Depending on how detailed the model is, the run time can vary from min to hours;

Step 9: Plotting 'Results'

Plotting electrode current density:

Variable name: ec.normJ

The variable name can be found in 'Component 1' > 'Electric Current' > 'Currents and charge'

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