

Supplementary Information:

Mathematical Modeling of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$
Reaction on a Nickel Rotating Disk Electrode: A
Foundation for Studying Organic Electrooxidation

Jessica Ortega-Ramos^{1,2}, Daniela Ferreira-Garcia^{1,2}, Gerardine G. Botte^{1,2*}

1. Institute for Sustainability & Circular Economy, Texas Tech University, Lubbock, TX 79409
2. Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409

Corresponding author information

*Gerardine G. Botte –Institute for Sustainability and Circular Economy, Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409, United States, Email: gerri.botte@ttu.edu

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S1. Summary of Model Equations

Table S1. Summary of model equations for the Layer Model.

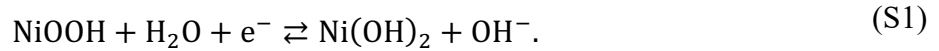
Region	Equations	
$y = -a$	$C_{OH} = 0$	(A.1)
	$C_{Na} = 0$	(A.2)
	$D_{s,v} c_{v,max} \frac{\partial \theta_v}{\partial y} = 0$	(A.3)
	$\phi_2 = 0$	(A.4)
	$\phi_1 = V_d$	(A.5)
$-a < y < 0$	$C_{OH} = 0$	(A.6)
	$C_{Na} = 0$	(A.7)
	$\frac{\partial \theta_v}{\partial t} = D_{s,v} \frac{\partial^2 \theta_v}{\partial y^2}$	(A.8)
	$\phi_2 = 0$	(A.9)
	$\frac{\partial}{\partial y} \left(\sigma \frac{\partial \phi_1}{\partial y} \right) = 0$	(A.10)
$y = 0$	$\frac{s(OH)}{n_F} i + N_{OH} = 0$	(A.11)
	$\frac{s(Na)}{n_F} i + N_{Na} = 0$	(A.12)
	$\frac{s(\theta_v)}{n_F} i + N_{\theta_v} = 0$	(A.13)
	$z(Na)c_{b,Na}C_{Na} + z(OH)c_{b,OH}C_{OH} = 0$	(A.14)
	$-\sigma \frac{\partial \phi_1}{\partial y} = i$	(A.15)
$0 < y < 2\delta$	$c_{b,OH} \frac{\partial C_{OH}}{\partial t} = -\frac{dN_{OH}}{dy}$	(A.16)
	$c_{b,Na} \frac{\partial C_{Na}}{\partial t} = -\frac{dN_{Na}}{dy}$	(A.17)
	$\theta_v = 0$	(A.18)
	$z(Na)c_{b,Na}C_{Na} + z(OH)c_{b,OH}C_{OH} = 0$	(A.19)
	$\phi_1 = 0$	(A.20)
$y = 2\delta$	$C_{OH} = 1$	(A.21)
	$C_{Na} = 1$	(A.22)
	$\theta_v = 0$	(A.23)
	$\phi_2 = 0$	(A.24)
	$\phi_1 = 0$	(A.25)

Table S2. Summary of model equations for the Surface Model.

Region	Equations	
$y = 0$	$\frac{s(OH)}{nF} i + N_{OH} = 0$	(B.1)
	$\frac{s(Na)}{nF} i + N_{Na} = 0$	(B.2)
	$c_{v,max} \frac{d\theta_v}{dt} = -\frac{s(\theta_v)}{nF} i$	(B.3)
	$z(Na)c_{b,Na}C_{Na} + z(OH)c_{b,OH}C_{OH} = 0$	(B.4)
$0 < y < 2\delta$	$c_{b,OH} \frac{\partial C_{OH}}{\partial t} = -\frac{dN_{OH}}{dy}$	(B.5)
	$c_{b,Na} \frac{\partial C_{Na}}{\partial t} = -\frac{dN_{Na}}{dy}$	(B.6)
	$\theta_v = 0$	(B.7)
	$z(Na)c_{b,Na}C_{Na} + z(OH)c_{b,OH}C_{OH} = 0$	(B.8)
$y = 2\delta$	$C_{OH} = 1$	(B.9)
	$C_{Na} = 1$	(B.10)
	$\theta_v = 0$	(B.11)
	$\phi_2 = 0$	(B.12)

S2. Current Density Equation Derivation

The current density expression is based on the Butler-Volmer equation [1, 2], assuming a single-electron transfer, as shown in equation (S1).



For the reaction in equation (S1), the rate expressions for the oxidation (r_a) and reduction (r_c) at a certain applied potential V are presented in equations (S2) and (S3), respectively.

$$r_a = k_a c_{\text{Ni(OH)}_2} c_{\text{OH}}^\alpha \exp\left[\frac{nF}{RT}(1 - \beta)V\right], \quad (\text{S2})$$

$$r_c = k_c c_{\text{NiOOH}} \exp\left[-\frac{nF}{RT}\beta V\right]. \quad (\text{S3})$$

where k_a and k_c are the kinetic constants of the oxidation and reduction reactions, respectively; c_i is the concentration of species i in mol cm⁻³ (or mol cm⁻² for Ni(OH)₂ and NiOOH in the FPD model); α is the partial order of OH⁻ for the reaction in equation (S1) (α would be 1 if equation (S1) was an elementary step); n is the number of electrons transferred; F is the Faraday constant; R is the ideal gas constant; T is the temperature; and β is the symmetry factor.

The total current is defined in equation (S4).

$$i = r_a - r_c,$$

$$i = k_a c_{Ni(OH)_2} c_{OH}^\alpha \exp \left[\frac{nF}{RT} (1 - \beta) V \right] - k_c c_{NiOOH} \exp \left[-\frac{nF}{RT} \beta V \right]. \quad (S4)$$

At equilibrium, $r_a = r_c$, $i = 0$, and $V = U$, where U is the equilibrium potential:

$$k_a c_{Ni(OH)_2} c_{OH}^\alpha \exp \left[\frac{nF}{RT} (1 - \beta) U \right] = k_c c_{NiOOH} \exp \left[-\frac{nF}{RT} \beta U \right]. \quad (S5)$$

Solving for the equilibrium potential in equation (S5), we obtain the expression in equation (S6).

$$U = \frac{RT}{nF} \ln \left[\frac{k_c c_{NiOOH}}{k_a c_{Ni(OH)_2} c_{OH}^\alpha} \right]. \quad (S6)$$

If we define the overpotential as $\eta = V - U$ and solve for V , we obtain equation (S7).

$$V = \eta + \frac{RT}{nF} \ln \left[\frac{k_c c_{NiOOH}}{k_a c_{Ni(OH)_2} c_{OH}^\alpha} \right]. \quad (S7)$$

Substituting equation (S7) in equation (S4) and simplifying the expression, we obtain equation (S8).

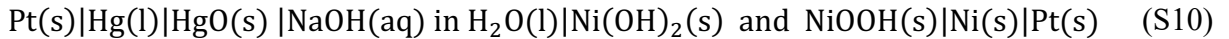
$$i = nF \left(\frac{k_a c_{Ni(OH)_2} c_{OH}^\alpha}{k_c c_{NiOOH}} \right)^\beta k_c c_{NiOOH} \left\{ \exp \left[\frac{(1 - \beta)nF}{RT} \eta \right] - \exp \left[\frac{-\beta nF}{RT} \eta \right] \right\}. \quad (S8)$$

Finally, substituting the variables for their dimensionless counterparts: $c_{Ni(OH)_2} = (1 - \theta) c_{v,max}$, $c_{NiOOH} = \theta c_{v,max}$, and $c_{OH} = C_{OH} c_{b,OH}$, we obtain equation (S9).

$$i = nF \left(\frac{k_a (1 - \theta) C_{OH}^\alpha c_{b,OH}^\alpha}{k_c \theta} \right)^\beta k_c \theta c_{v,max} \left\{ \exp \left[\frac{(1 - \beta)nF}{RT} \eta \right] - \exp \left[\frac{-\beta nF}{RT} \eta \right] \right\}. \quad (S9)$$

S3. Equilibrium Potential Equation Derivation

The equilibrium potential, U , of the nickel hydroxide electrode relative to a Hg/HgO reference electrode, whose cell diagram (with the different phases indicated with Greek letters above) is presented in equation (S10):

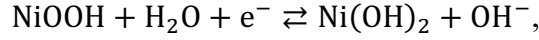


can be defined in terms of the electrochemical potential of the electrons in the platinum leads according to equation (S11):

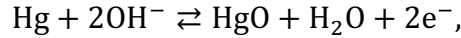
$$nFU = -nF(\Phi^\varepsilon - \Phi^{\varepsilon'}) = \mu_e^\varepsilon - \mu_e^{\varepsilon'}, \quad (S11)$$

where Φ^i is the electric potential in the phase i , and μ_i^j is the electrochemical potential of species i in the phase j .

At equilibrium, the electrochemical and chemical potentials of the species participating in the reaction on each side of the cell are related according to equations (S12) and (S13).



$$\mu_{\text{NiOOH}}^{\zeta} + \mu_{\text{H}_2\text{O}}^{\xi} + \mu_{\text{e}^-}^{\varepsilon'} = \mu_{\text{Ni(OH)}_2}^{\zeta} + \mu_{\text{OH}^-}^{\xi}, \quad (\text{S12})$$



$$\mu_{\text{Hg}}^{\rho} + 2\mu_{\text{OH}^-}^{\xi'} = \mu_{\text{HgO}}^{\pi} + \mu_{\text{H}_2\text{O}}^{\xi'} + 2\mu_{\text{e}^-}^{\varepsilon}. \quad (\text{S13})$$

Solving for $\mu_{\text{e}^-}^{\varepsilon'}$ and $\mu_{\text{e}^-}^{\varepsilon}$ in equations (S12) and (S13), and substituting in equation (S11), we obtain equation (S14).

$$\mu_{\text{e}^-}^{\varepsilon} - \mu_{\text{e}^-}^{\varepsilon'} = \frac{1}{2}\mu_{\text{Hg}}^{\rho} + \mu_{\text{OH}^-}^{\xi'} - \frac{1}{2}\mu_{\text{HgO}}^{\pi} - \frac{1}{2}\mu_{\text{H}_2\text{O}}^{\xi'} - \left(\mu_{\text{Ni(OH)}_2}^{\zeta} + \mu_{\text{OH}^-}^{\xi} - \mu_{\text{NiOOH}}^{\zeta} + \mu_{\text{H}_2\text{O}}^{\xi} \right). \quad (\text{S14})$$

Assuming that the internal solution of the Hg/HgO reference electrode and the cell electrolyte are of the same composition, then $\mu_{\text{OH}^-}^{\xi'} = \mu_{\text{OH}^-}^{\xi}$ and $\mu_{\text{H}_2\text{O}}^{\xi'} = \mu_{\text{H}_2\text{O}}^{\xi}$. This assumption yields equation (S15).

$$nFU = \mu_{\text{e}^-}^{\varepsilon} - \mu_{\text{e}^-}^{\varepsilon'} = \frac{1}{2}\mu_{\text{Hg}}^{\rho} - \frac{1}{2}\mu_{\text{HgO}}^{\pi} - \frac{3}{2}\mu_{\text{H}_2\text{O}}^{\xi} - \mu_{\text{Ni(OH)}_2}^{\zeta} + \mu_{\text{NiOOH}}^{\zeta}. \quad (\text{S15})$$

For the species in the solid solution (Ni(OH)_2 and NiOOH), the chemical potential can be defined as in equation (S16).

$$\mu_i = \mu_i^* + RT \ln c_i + RT \ln \gamma_i \quad (\text{S16})$$

where γ_i is the molar activity coefficient, and μ_i^* is the reference chemical potential, whose value depends on the primary and secondary reference state chosen [1].

For pure substances, the chemical potential is just the chemical potential of the pure compound μ_i^0 . For water, the chemical potential of the solvent for a single electrolyte is defined in equation (S17).

$$\mu_i = \mu_i^0 - RTvm\phi M_0 \quad (\text{S17})$$

where $\nu = \nu_+ + \nu_-$ and ν_+ , ν_- are the numbers of cations and anions into which a mole of electrolyte dissociates; m is the molality of the solution (mol kg^{-1}), φ is the osmotic coefficient of the solvent, and M_0 is the molar mass of the solvent.

Applying all these definitions to equation (S15) yields equation (S18).

$$nFU = nFU^\circ + RT \ln \frac{c_{\text{NiOOH}}}{c_{\text{Ni(OH)}_2}} + RT \ln \frac{\gamma_{\text{NiOOH}}}{\gamma_{\text{Ni(OH)}_2}} - 3RTm\varphi M_{\text{H}_2\text{O}}, \quad (\text{S18})$$

where the concentration-independent terms are grouped in the standard potential term FU° defined in equation (S19).

$$nFU^\circ = \frac{1}{2}\mu_{\text{Hg}}^0 - \frac{1}{2}\mu_{\text{HgO}}^0 - \frac{3}{2}\mu_{\text{H}_2\text{O}}^0 + \mu_{\text{NiOOH}}^0 - \mu_{\text{Ni(OH)}_2}^*. \quad (\text{S19})$$

Finally, substituting the variables for their dimensionless counterparts: $c_{\text{Ni(OH)}_2} = (1 - \theta)c_{v,\text{max}}$, and $c_{\text{NiOOH}} = \theta c_{v,\text{max}}$, we obtain equation (S20).

$$U = U^\circ + \frac{RT}{nF} \ln \frac{\theta}{1 - \theta} + \frac{RT}{nF} \ln \frac{\gamma_{\text{NiOOH}}}{\gamma_{\text{Ni(OH)}_2}} - \frac{3RT}{nF} m\varphi M_{\text{H}_2\text{O}}. \quad (\text{S20})$$

The last term on the right in equation (S20) can be estimated to have a constant contribution ≈ 0.00132 V to the total cell voltage (for 1 mol dm^{-3} NaOH solution: $m \approx 1$ mol kg^{-1} , $M_{\text{H}_2\text{O}} = 0.018$ g mol^{-1} , $\nu = 2$, $\varphi = 0.954$ [3]). Therefore, this term can be safely disregarded, and the final equation would be equation (S21).

$$U = U^\circ + \frac{RT}{nF} \ln \frac{\theta}{1 - \theta} + \frac{RT}{nF} \ln \frac{\gamma_{\text{NiOOH}}}{\gamma_{\text{Ni(OH)}_2}}. \quad (\text{S21})$$

S4. Hysteresis of the $\text{Ni(OH)}_2/\text{NiOOH}$ Reaction: Different Standard Equilibrium Potentials

To account for the well-documented, rate-independent hysteresis of the equilibrium potential during the $\text{Ni(OH)}_2/\text{NiOOH}$ transformation [4–6], our first approach was to use different values for the standard equilibrium potential (U°) for the forward and backward scans in the simulated cyclic voltammetry, while keeping the coefficients in the activity expression constant. This produced cyclic voltammograms with perfectly symmetrical anodic and cathodic peaks (same shape and intensity), yet the experimental data showed significant differences between the anodic and cathodic peaks, creating a disparity between simulations and experiments.

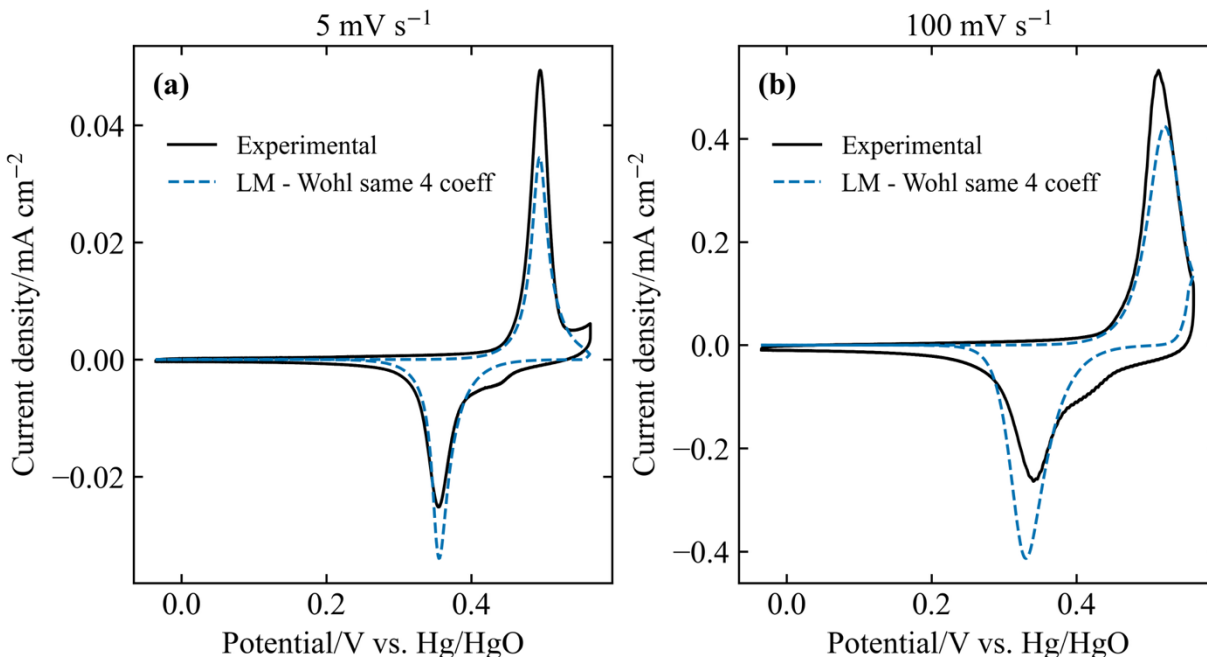


Fig. S1 Results of calibrating the Layer Model (LM) to experimental cyclic voltammograms of the nickel RDE in 0.1 M NaOH at 1000 rpm, and scan rates of 5 mV s⁻¹ and 100 mV s⁻¹ using the four-coefficient Wohl expansion (same self-interaction coefficients for forward and backward scan, labeled “LM – Wohl same 4 coeff”) and distinct standard equilibrium potential (U°) for the forward ($U^\circ = 0.467$ V) and backward ($U^\circ = 0.337$ V) scans. For this particular calibration, the layer thickness was $a = 2 \times 10^{-7}$ cm, and the proton vacancy diffusion coefficient was imposed (not calibrated) as $D_{s,v} = 2.12 \times 10^{-13}$ cm² s⁻¹.

S5. Charge and Discharge Curves of the Nickel RDE

The discharge curve was measured at a low galvanostatic rate (± 1 μ A) to approximate the equilibrium potential as a function of state of charge (SOC), following the approach of Ta and Newman [5], who showed that sufficiently slow galvanostatic cycling allows the voltage–SOC curve to serve as a reasonable approximation of the equilibrium potential. To observe hysteresis, the charge curve was also measured at the same rate. These experiments were performed in 0.10 M NaOH using the nickel RDE at 0 rpm (no rotation).

Following electrode activation, the system was subjected to potentiostatic conditioning at 0.1 V vs. Hg/HgO for 30 min in 0.1 M NaOH to ensure operation within the non-faradaic region prior to measurements. Galvanostatic charge/discharge measurements were subsequently performed in 0.1 M NaOH at ± 1 μ A, with a data sampling interval of 0.1 s. Charging was terminated upon reaching an upper voltage cutoff of 0.55 V vs. Hg/HgO, followed immediately by full galvanostatic discharge.

The equations proposed to describe the equilibrium potential as a function of θ using Wohl, Margules, and van Laar models (see equations (S22) to (S24)) were fitted to the discharge and charge curves to obtain initial estimates of the model coefficients and the standard equilibrium potential U° in each case.

$$U = U^\circ + \frac{RT}{nF} \ln \left(\frac{\theta}{1 - \theta} \right) - \frac{1}{nF} \sum_{k=2}^N \Omega_k k (1 - \theta)^{k-1}, \quad (\text{S22})$$

$$U = U^\circ + \frac{RT}{nF} \ln \left(\frac{\theta}{1 - \theta} \right) - \frac{RT}{2nF} [-2A_0 + 4A_0(1 - \theta) - 2B_0 + 6B_0(1 - \theta) - 3B_0(1 - \theta)^2], \quad (\text{S23})$$

$$U = U^\circ + \frac{RT}{nF} \ln \left(\frac{\theta}{1 - \theta} \right) - \frac{RT}{nF} \left\{ \frac{A'[B'(1 - \theta)^2 - 1 + 2(1 - \theta) - (1 - \theta)^2]}{[\theta + B'(1 - \theta)]^2} \right\}, \quad (\text{S24})$$

Fig. S2 shows the equilibrium potential as a function of θ for the experimental charge (left side) and discharge (right side), and the theoretical curves using equations (S22)-(S24) with the calibrated coefficients for each experiment.

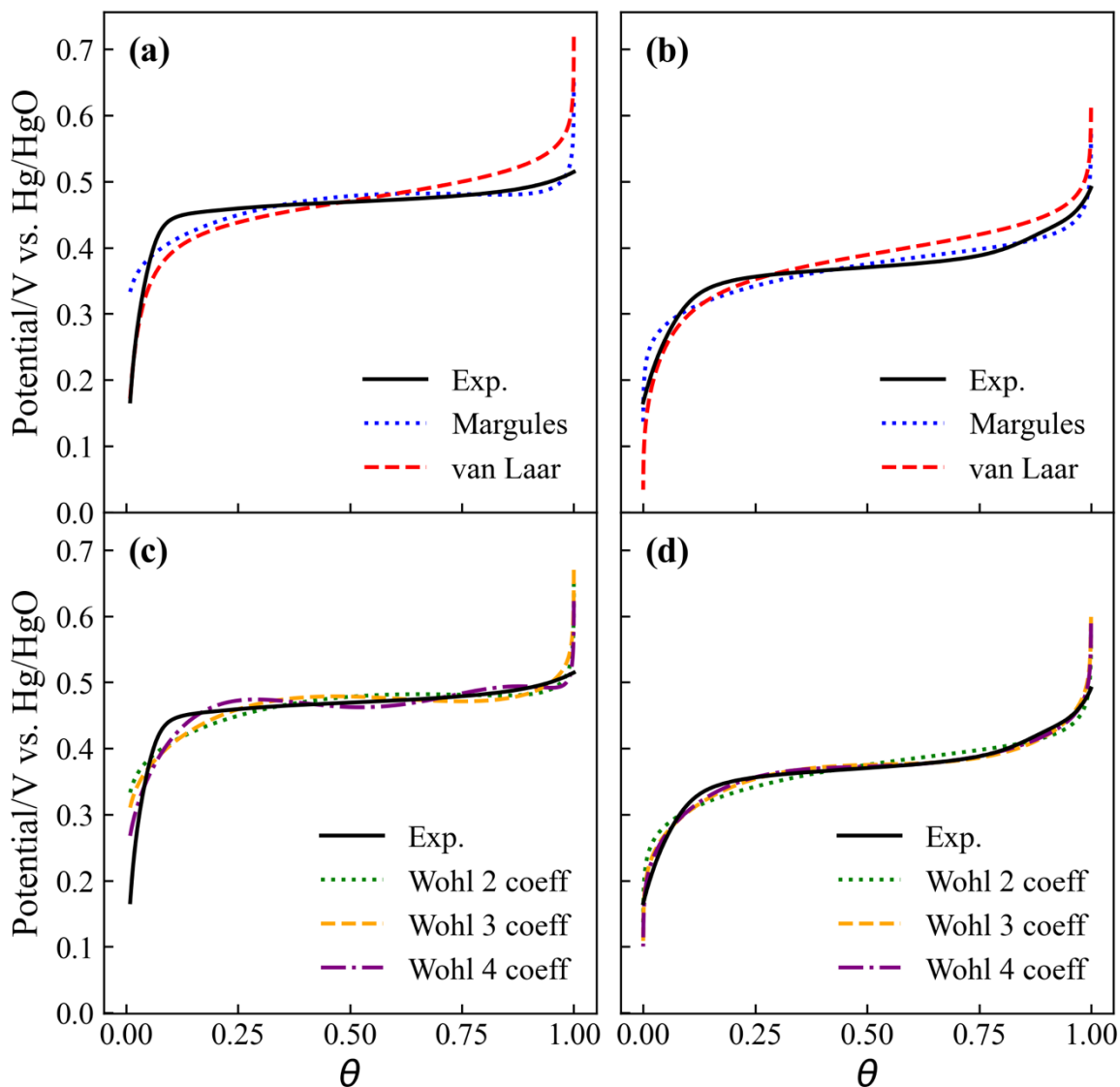


Fig. S2 Experimental ('Exp.') and simulated charge and discharge curves in 0.1 M NaOH and at 0 rpm (no rotation) using the nickel RDE. The top panels show the performance of the Margules and van Laar models for simulating the charge (a) and discharge (b) curves. The bottom panels show the performance of the Wohl expansion with different numbers of coefficients for simulating the charge (c) and discharge (d) curves.

The calibrated coefficients for each model (Wohl, Margules, and van Laar) and experiment (charge and discharge) are shown in **Table S3**.

Table S3. Calibrated coefficients of the Wohl expansion, Margules, and van Laar models for the charge and discharge experiments in 0.1 M NaOH and at 0 rpm (no rotation) using the nickel RDE.

	Charge	Discharge
Wohl expansion		
With N = 3 (2 coefficients)		
U^0 (V vs. Hg/HgO)	0.4017	0.3528
Ω_2/F (V)	-0.129	-0.043
Ω_3/F (V)	-0.069	-0.0283
With N = 4 (3 coefficients)		
U^0 (V vs. Hg/HgO)	0.4244	0.3798
Ω_2/F (V)	0.009	0.118
Ω_3/F (V)	0.163	0.242
Ω_4/F (V)	-0.117	-0.135
With N = 5 (4 coefficients)		
U^0 (V vs. Hg/HgO)	0.382	0.3698
Ω_2/F (V)	-0.421	0.031
Ω_3/F (V)	-1.14	-0.007
Ω_4/F (V)	1.42	0.1501
Ω_5/F (V)	-0.622	-0.1132
Margules model		
U^0 (V vs. Hg/HgO)	0.4608	0.3679
A_0	3.07	1.61
B_0	-5.38	-2.20
Van Laar model		
U^0 (V vs. Hg/HgO)	0.4610	0.3795
A'	0.42	0.5
B'	0.042	0.10

In **Table S3**, for the Wohl expansion, only the values for $N = 3$ (two coefficients) were used as initial guesses in the calibration with the cyclic voltammograms. For $N > 3$, we used the estimated values for Ω_2/F and Ω_3/F resulting from the first calibration with the cyclic voltammograms, while 0.001 was used for higher-order coefficients (Ω_4/F , Ω_5/F , Ω_6/F , and Ω_7/F). This approach was adopted because using the values from **Table S3** directly would produce an additional anodic peak that had no physical meaning.

S6. Spatial Grid Convergence Study

A spatial grid convergence study was conducted by systematically discretizing and solving the governing PDE system on a sequence of successively refined grids, with the number of nodes approximately doubling at each step (126 to 64,001 nodes total across the oxide and diffusion layers in the Layer Model, or just the diffusion layer in the Surface Model). For the Layer Model, the root-mean-square error (RMSE) in the dimensionless vacancy concentration profile was computed for each grid relative to a reference solution obtained on the finest grid evaluated (100,001 nodes). As shown in **Fig. S3**, RMSE decreases with increasing node count until it plateaus at approximately 6×10^{-8} , a floor consistent with the nonlinear solver's convergence tolerance. A grid was considered sufficient once its RMSE fell below 1.0×10^{-7} . This criterion was satisfied at 2,001 nodes, which was therefore used across all Layer Model simulations reported in this work.

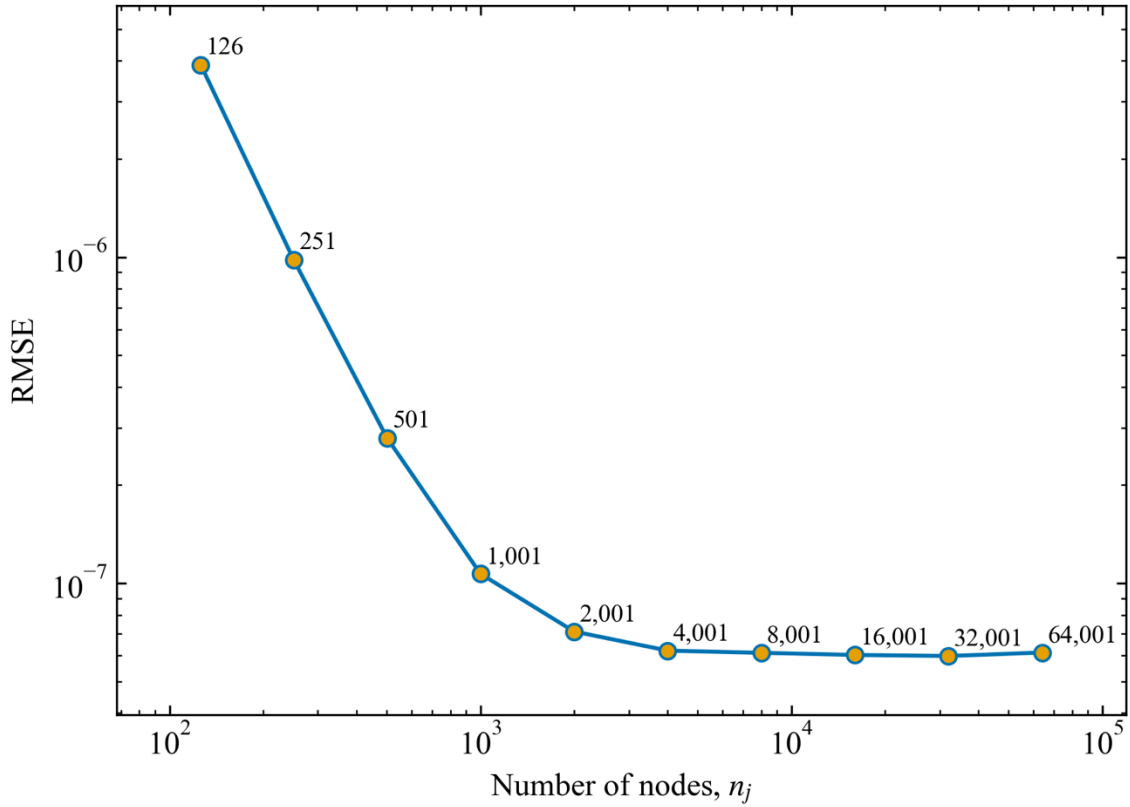


Fig. S3 Root Mean Square Error (RMSE) of the dimensionless vacancy concentration profile, computed for different numbers of nodes (n_j) relative to a reference simulation with $n_j = 100,001$.

For the Surface Model, the root-mean-square error (RMSE) in the dimensionless OH^- concentration profile was computed for each grid relative to a reference solution obtained on the finest grid evaluated (100,001 nodes). As shown in **Fig. S4**, RMSE decreased monotonically with increasing node count but did not plateau over the range evaluated, instead following an apparent power-law decay ($\text{RMSE} \sim N^{-0.5}$) with no evidence of an asymptotic floor up to 64,001 nodes.

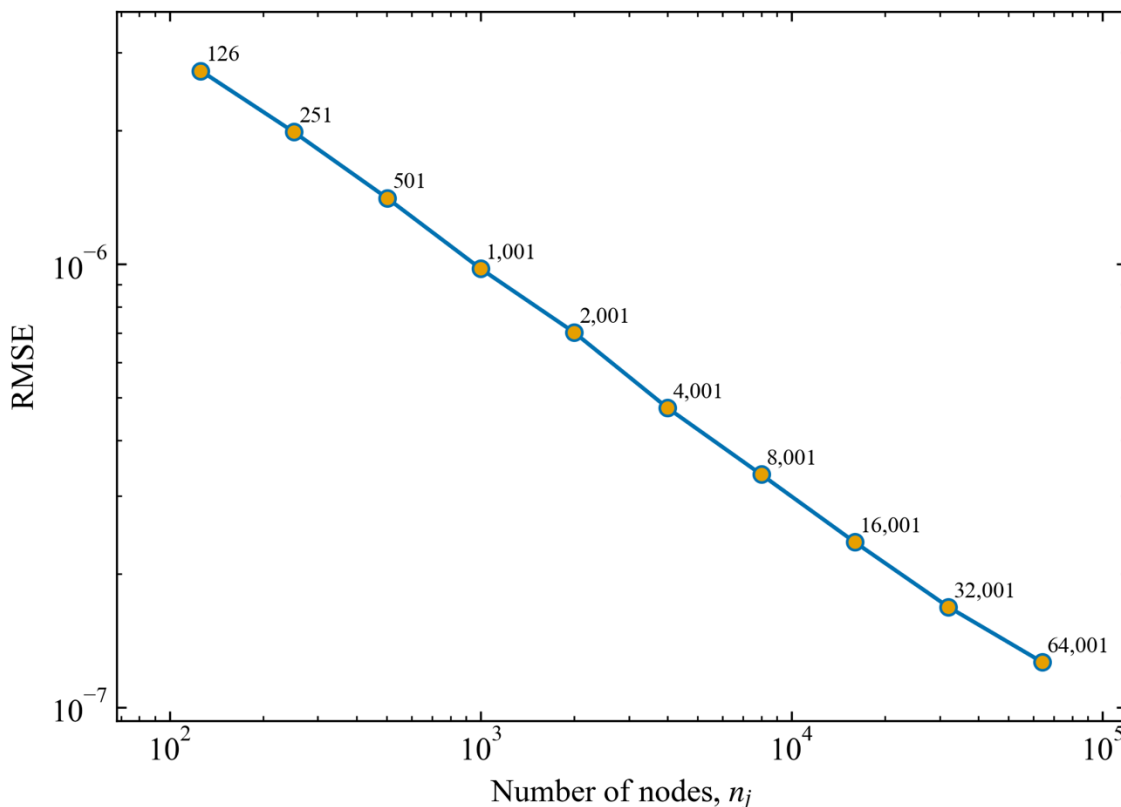


Fig. S4 Root Mean Square Error (RMSE) of the dimensionless OH^- concentration profile, computed for different numbers of nodes (n_j) relative to a reference simulation with $n_j = 100,001$.

Since the internal OH^- concentration profile did not reach a numerical plateau over the range of grids evaluated (see above), grid sufficiency for production simulations was instead assessed based on the current density–potential curve, which is the quantity directly compared to experimental data during parameter estimation. The RMSE between the simulated current density curve at each grid and the reference solution (100,001 nodes) was uniformly on the order of 10^{-10} mA/cm² across all grids tested (126 to 64,001 nodes), corresponding to a relative error of $\sim 10^{-7}$ % of the peak current density, which is consistent with the floating-point noise floor. This result indicates the current density curve is fully grid-independent at all resolutions evaluated, including the coarsest (126 nodes). Therefore, a grid of 1,001 nodes was used for all Surface Model production simulations, providing substantial margin above this noise floor while remaining computationally efficient. At this resolution, the internal concentration is not identical to the 100,001-node reference, but it deviates only by 0.174% at the most mass-transport-limited condition evaluated (the reduction-peak potential), which is well within the precision relevant to the fitted quantities reported in this work.

S7. Raw Simulation Results without Smoothing the Current Spike

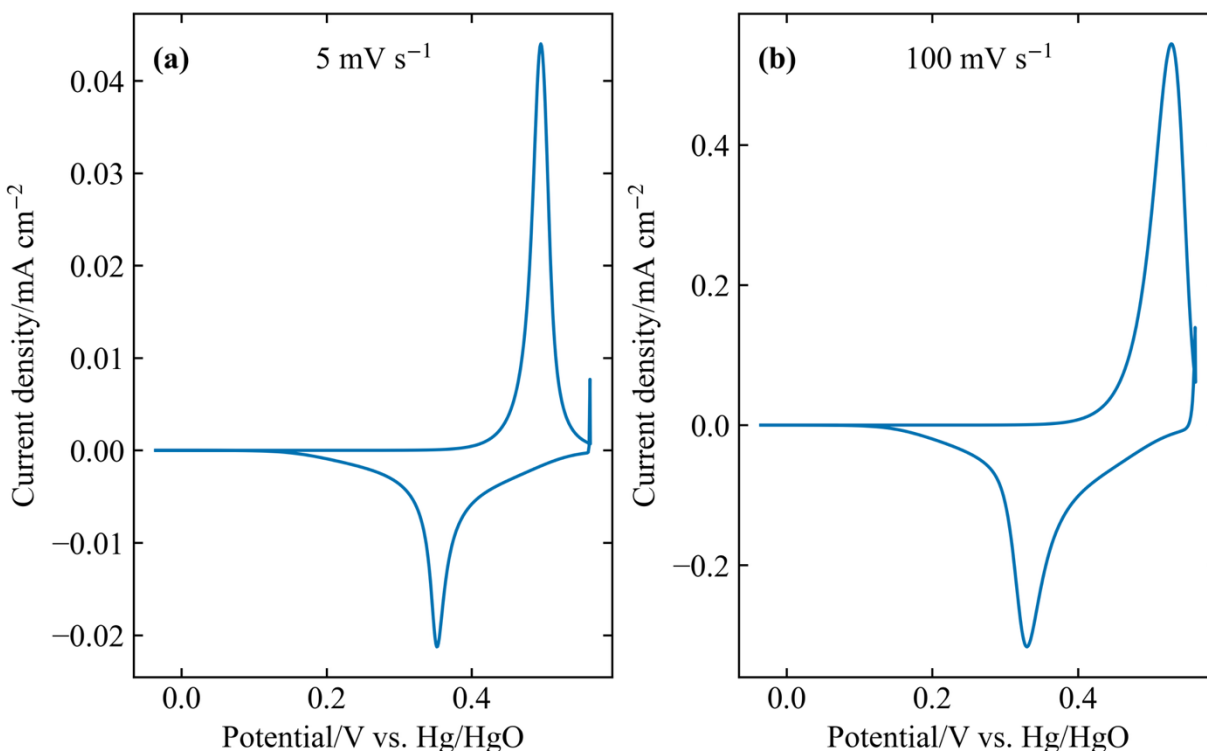
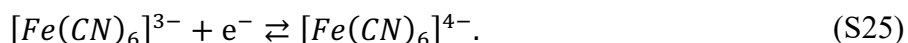


Fig. S5 Raw simulations of the nickel RDE in 0.1 M NaOH at 1000 rpm, and scan rates of (a) 5 mV s⁻¹ and (b) 100 mV s⁻¹.

S8. Model Benchmarking

S8.1 Diffusion-Limited Reaction: Ferrocyanide/Ferricyanide in KNO₃

To validate the rotating disk electrode (RDE) modeling framework independently of the Ni(OH)₂/NiOOH system, the model was applied to the one-electron ferrocyanide/ferricyanide redox couple, whose reaction is shown in equation (S25).



This is a well-characterized system with known diffusion coefficients and quasi-reversible kinetics, making it a standard benchmark for RDE mass-transport models.

The model solves the one-dimensional, transient Nernst–Planck equations for the four species present in solution: [Fe(CN)₆]⁴⁻, [Fe(CN)₆]³⁻, and the supporting NO₃⁻ and K⁺ ions, within the hydrodynamic diffusion boundary layer of thickness δ adjacent to the disk surface ($0 \leq y \leq 2\delta$). **Table S4** summarizes the full set of governing equations, boundary conditions, and closure relations.

Table S4. Summary of model equations for the Ferrocyanide/Ferricyanide Model.

Region	Equations	
$y = 0$	$\frac{s([Fe(CN)_6]^{4-})}{nF}i + N_{[Fe(CN)_6]^{4-}} = 0$	(C.1)
	$\frac{s([Fe(CN)_6]^{3-})}{nF}i + N_{[Fe(CN)_6]^{3-}} = 0$	(C.2)
	$\frac{s(NO_3^-)}{nF}i + N_{NO_3^-} = 0$	(C.3)
	$\frac{s(K^+)}{nF}i + N_{K^+} = 0$	(C.4)
	$z([Fe(CN)_6]^{4-})c_{b,[Fe(CN)_6]^{4-}}C_{[Fe(CN)_6]^{4-}} +$ $z([Fe(CN)_6]^{3-})c_{b,[Fe(CN)_6]^{3-}}C_{[Fe(CN)_6]^{3-}} + z(NO_3^-)c_{b,NO_3^-}C_{NO_3^-} + z(K^+)c_{b,K^+}C_{K^+} =$ 0	(C.5)
$0 < y < 2\delta^a$	$c_{b,[Fe(CN)_6]^{4-}} \frac{\partial C_{[Fe(CN)_6]^{4-}}}{\partial t} = - \frac{dN_{[Fe(CN)_6]^{4-}}}{dy}$	(C.6)
	$c_{b,[Fe(CN)_6]^{3-}} \frac{\partial C_{[Fe(CN)_6]^{3-}}}{\partial t} = - \frac{dN_{[Fe(CN)_6]^{3-}}}{dy}$	(C.7)
	$c_{b,NO_3^-} \frac{\partial C_{NO_3^-}}{\partial t} = - \frac{dN_{NO_3^-}}{dy}$	(C.8)
	$c_{b,K^+} \frac{\partial C_{K^+}}{\partial t} = - \frac{dN_{K^+}}{dy}$	(C.9)
	$z([Fe(CN)_6]^{4-})c_{b,[Fe(CN)_6]^{4-}}C_{[Fe(CN)_6]^{4-}} +$ $z([Fe(CN)_6]^{3-})c_{b,[Fe(CN)_6]^{3-}}C_{[Fe(CN)_6]^{3-}} + z(NO_3^-)c_{b,NO_3^-}C_{NO_3^-} + z(K^+)c_{b,K^+}C_{K^+} =$ 0	(C.10)
$y = 2\delta^a$	$C_{[Fe(CN)_6]^{4-}} = 1$	(C.11)
	$C_{[Fe(CN)_6]^{3-}} = 0$	(C.12)
	$C_{NO_3^-} = 1$	(C.13)
	$C_{K^+} = 1$	(C.14)
	$\phi_2 = 0$	(C.15)

^a δ is a characteristic diffusion length of the system $\delta = 1.805D_{s,j}^{1/3} \nu^{1/6} \omega^{-1/2}$.

Since the exact profile approaches bulk composition only asymptotically, the outer boundary condition must be applied far enough from the electrode that the imposed bulk value does not distort the surface gradient. At $y = \delta$, the true concentration is still only 90.4% of bulk, and truncating there overestimates the limiting current by 10.6%; the error falls to 0.49% at $y = 1.5\delta$ and 0.003% at $y = 2\delta$. The computational domain was therefore extended to $y = 2\delta$, discretized over $n_j = 1001$ nodes. The potential was swept from -0.2 to 0.6 V vs. Ag/AgCl at 0.01 V s⁻¹; all remaining parameters are listed in **Table S5**. Notice that the initial conditions for ferrocyanide and ferricyanide are $C_{[Fe(CN)_6]^{4-}} = 1 - 1 \times 10^{-10}$ and $C_{[Fe(CN)_6]^{3-}} = 1 \times 10^{-10}$, respectively, since the system consists of a 0.1 M KNO₃, 1 mM K₄[Fe(CN)₆] solution (no ferricyanide initially).

Table S5. Model parameters for the Ferrocyanide/Ferricyanide Model.

Symbol	Parameter name	Value	Reference
n_j	Number of nodes in the y dimension for the Surface Model	1001	
T	Temperature (K)	298.15	
n_v	Number of data points (dimensionless)	1000	
ν	Kinematic viscosity (cm ² s ⁻¹)	0.00893	[7]

$D_{s,[Fe(CN)_6]^{4-}}$	Diffusion coefficient of $[Fe(CN)_6]^{4-}$ ($\text{cm}^2 \text{s}^{-1}$)	0.667×10^{-5}	[8]
$D_{s,[Fe(CN)_6]^{3-}}$	Diffusion coefficient of $[Fe(CN)_6]^{3-}$ ($\text{cm}^2 \text{s}^{-1}$)	0.726×10^{-5}	[8]
D_{s,NO_3^-}	Diffusion coefficient of NO_3^- ($\text{cm}^2 \text{s}^{-1}$)	1.902×10^{-5}	[7]
D_{s,K^+}	Diffusion coefficient of K^+ ($\text{cm}^2 \text{s}^{-1}$)	1.957×10^{-5}	[7]
$z([Fe(CN)_6]^{4-})$	Charge number of $[Fe(CN)_6]^{4-}$ (dimensionless)	-4	
$z([Fe(CN)_6]^{3-})$	Charge number of $[Fe(CN)_6]^{3-}$ (dimensionless)	-3	
$z(NO_3^-)$	Charge number of NO_3^- (dimensionless)	-1	
$z(K^+)$	Charge number of K^+ (dimensionless)	1	
$s([Fe(CN)_6]^{4-})$	Stoichiometric coefficient of $[Fe(CN)_6]^{4-}$ (dimensionless)	1	
$s([Fe(CN)_6]^{3-})$	Stoichiometric coefficient of $[Fe(CN)_6]^{3-}$ (dimensionless)	-1	
$s(NO_3^-)$	Stoichiometric coefficient of NO_3^- (dimensionless)	0	
$s(K^+)$	Stoichiometric coefficient of K^+ (dimensionless)	0	
sr	Scan rate (V s^{-1})	0.01	
n_e	Number of electrons transferred (dimensionless)	1	
β	Symmetry factor (dimensionless)	0.5	
$c_{b,[Fe(CN)_6]^{4-}}$	Bulk concentration of $[Fe(CN)_6]^{4-}$ (mol cm^{-3})	1.0×10^{-6}	
$c_{b,[Fe(CN)_6]^{3-}}^a$	Bulk concentration of $[Fe(CN)_6]^{3-}$ (mol cm^{-3})	1.0×10^{-6}	
c_{b,NO_3^-}	Bulk concentration of NO_3^- (mol cm^{-3})	1.0×10^{-4}	
c_{b,K^+}	Bulk concentration of K^+ (mol cm^{-3})	1.04×10^{-4}	
k_{1f}^b	Forward kinetic constant (cm s^{-1})	0.02	[9]
k_{1b}^b	Backward kinetic constant (cm s^{-1})	0.02	[9]
U°	Standard equilibrium potential (V vs. Ag/AgCl, KCl sat.)	0.163	[10]

^a This is the maximum concentration $c_{b,[Fe(CN)_6]^{3-}}$ can reach, but it does not mean that the system starts at this concentration of ferricyanide. Since the initial dimensionless concentration is $C_{[Fe(CN)_6]^{3-}} = 1 \times 10^{-10}$, there is almost no ferricyanide in the system when the experiment starts $c_{[Fe(CN)_6]^{3-}} = c_{b,[Fe(CN)_6]^{3-}} \times C_{[Fe(CN)_6]^{3-}} = 1 \times 10^{-6} \times 1 \times 10^{-10} = 1 \times 10^{-16} \text{ mol cm}^{-3}$.

^b It was assumed that the reaction followed similar kinetics to the system with 0.1 M KCl supporting electrolyte.

Fig. S6 (a) shows simulated voltammograms at six rotation rates from 1 to 4000 rpm. At 1 rpm, where forced convection is weak, the response retains the peak-shaped character of a transient (semi-infinite diffusion) experiment. As the rotation rate increases, the voltammograms become sigmoidal, developing the well-defined mass-transport-limited plateau characteristic of steady-state RDE voltammetry, with the plateau current increasing monotonically with ω .

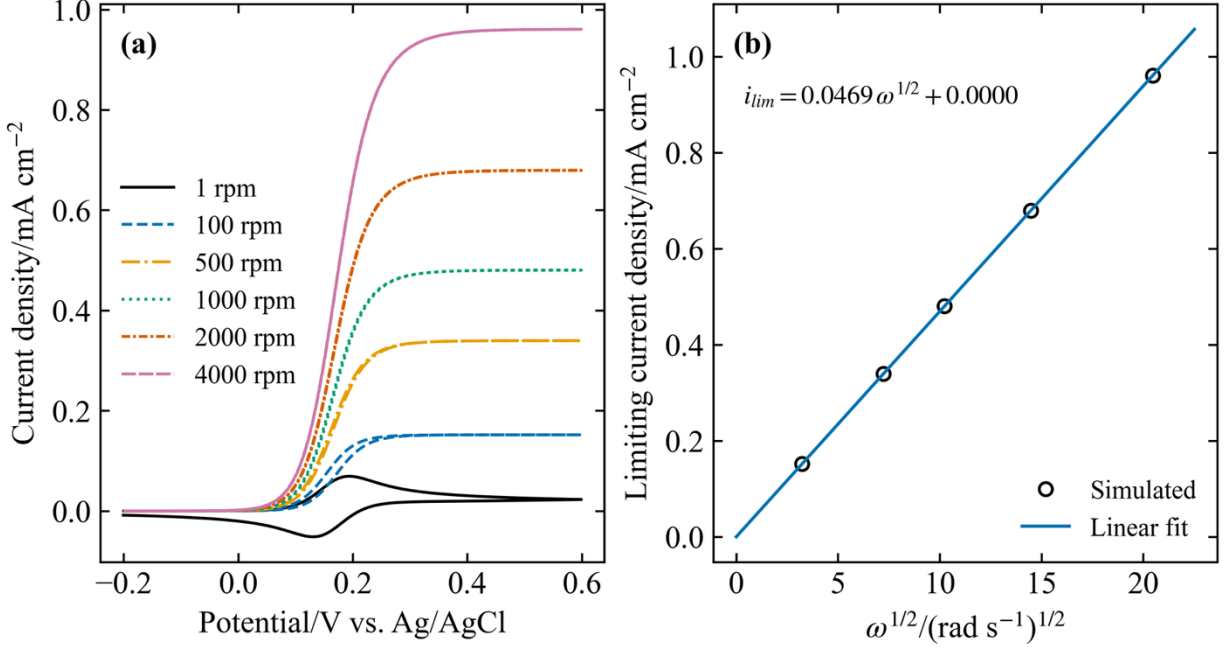


Fig. S6 (a) Simulated cyclic voltammograms of the ferrocyanide/ferricyanide reaction in 0.1 M KNO₃, 1 mM K₄[Fe(CN)₆], at 10 mV s⁻¹ and different RDE rotation speeds. (b) Limiting current density (*i*_{lim}) as a function of the square root of the RDE rotation speed ($\omega^{1/2}$). The simulation at 1 rpm was excluded from the Levich analysis since the concentration profile does not reach steady state, and this response is not diffusion-limited in the Levich sense.

The limiting current densities (*i*_{lim}), extracted at the most positive potential of the sweep, are plotted against $\omega^{1/2}$ in **Fig. S6** (b). The response is linear and passes through the origin: $i_{lim} = 0.0469\omega^{1/2}$. For comparison, the Levich equation (equation (S26)), evaluated with the parameters of **Table S5** ($n_e = 1$, $D_{s,[Fe(CN)_6]^{4-}} = 0.667 \times 10^{-5}$ cm² s⁻¹, $\nu = 0.00893$ cm² s⁻¹, $c_{b,[Fe(CN)_6]^{4-}} = 1.0 \times 10^{-6}$ mol cm⁻³), predicts a slope of 0.04654 mA cm⁻² rad^{-1/2} s^{1/2}. The simulated slope agrees within 0.8%.

$$i_{lim} = 0.620nFD_{s,j}^{2/3}\nu^{-1/6}\omega^{1/2}c_{b,j} \quad (S26)$$

These results confirm that the framework reproduces the qualitative voltammetric behavior expected of an RDE (the transition from transient peak-shaped to steady-state sigmoidal response with increasing rotation) and the quantitative Levich scaling of the diffusion-limited current, supporting its application to the Ni(OH)₂/NiOOH system.

S8.2 Surface-confined Redox Reaction of Adsorbed Species

The ferrocyanide/ferricyanide system validated the transport framework: the Nernst–Planck flux equations, RDE convection, and electroneutrality condition. However, the Ni(OH)₂/NiOOH Surface Model introduces a qualitatively different physical picture: the electroactive species (proton vacancies) are immobile, surface-confined entities whose dynamics are governed entirely by a single ordinary differential equation relating coverage to faradaic current (equation (16) in the main text). Validating this component requires a separate benchmark. The one-electron surface-

confined redox reaction $O + e^- \rightleftharpoons R$ was chosen because it is the closest structural analog to the $\text{Ni}(\text{OH})_2 / \text{NiOOH}$ half-reaction: both are surface-confined, described by Butler–Volmer kinetics written in terms of a fractional coverage θ_O and its complement $(1 - \theta_O)$, use a Nernst-shifted equilibrium potential that carries a logarithm in the coverage ratio, and are subject to the same site-balance constraint $\theta_R + \theta_O = 1$. In the benchmark, activity coefficients are set to unity (ideal Langmuir behavior), isolating the numerical implementation of the coverage ODE, the site balance, and the coverage clamp from the additional complexity introduced by the Wohl expansion in the actual model. Closed-form analytical results for the ideal case are available from Laviron's theory [11, 12], as presented in [10], providing exact targets against which the framework can be evaluated. Model parameters are listed in **Table S6**, while model equations $y = 0$ are shown in equations (S27) and (S28) (model's equations for $y > 0$ are the trivial $\theta_R(j) = \theta(j - 1)$).

Table S6. Model parameters for the one-electron surface-confined (adsorbed) redox reaction.

Symbol	Parameter name	Value
nj	Number of nodes in the y dimension for the Surface Model	5
T	Temperature (K)	298.15
nv	Number of data points (dimensionless)	5001
$s(R)$	Stoichiometric coefficient of R (dimensionless)	1
$s(O)$	Stoichiometric coefficient of O (dimensionless)	-1
n_e	Number of electrons transferred (dimensionless)	1
β	Symmetry factor (dimensionless)	0.5
$c_{b,R}$	Total surface site concentration of R and O (mol cm^{-2})	1.0×10^{-9}
k_s (reversible)	Standard rate constant for the reversible reaction (s^{-1})	1×10^5
k_s (quasi-reversible)	Standard rate constant for the quasi-reversible reaction (s^{-1})	1.0
U°	Standard equilibrium potential (V)	0.0

$$\Gamma_T \frac{d\theta_R}{dt} = -\frac{s(R)}{nF} i \quad (\text{S27})$$

$$\theta_R + \theta_O = 1 \quad (\text{S28})$$

Simulations were performed at a fixed scan rate of 100 mV s^{-1} for five values of the number of output points, nv , ranging from 501 to 10,001 (**Table S7**). The resulting potential step dV decreased from 2.4 mV to 0.12 mV. The anodic peak current density $i_{p,a}$ converged monotonically toward the analytical Laviron value of $0.09389 \text{ mA cm}^{-2}$, with the relative error decreasing as dV^2 , consistent with second-order convergence of the backward-Euler time-stepping scheme. The peak-to-peak splitting ΔE_p equaled exactly $2dV$ at every resolution, confirming it is a pure grid artifact with no physical content in the reversible limit. The width at half maximum converged to 90.576 mV, within 0.13% of the analytical prediction of $3.53RT/nF = 90.69 \text{ mV}$. The integrated anodic charge was invariant to resolution at $Q = 0.09649 \text{ mC cm}^{-2}$, matching the theoretical $nF\Gamma_T$ value to within 0.02%. The $nv = 5,001$ run ($dV = 0.24 \text{ mV}$) was selected for all subsequent validation steps, as it achieves relative errors below 0.001% in $i_{p,a}$.

Table S7. Parameters used to evaluate the numerical convergence of the simulated cyclic voltammograms for a reversible redox reaction ($k_s = 1 \times 10^5 \text{ s}^{-1}$) of surface-confined (adsorbed) species at 100 mV s^{-1} .

nv	$dV \text{ (mV)}^a$	$E_{p,a} \text{ (mV)}$	$E_{p,c} \text{ (mV)}$	Width at half maximum (mV)	$i_{p,a} \text{ (mA cm}^{-2}\text{)}$	$\% \Delta i_{p,a}^b$
501	2.4	2.4	-2.4	90.654	0.09382132	-0.0725
1,001	1.2	1.2	-1.2	90.594	0.09387246	-0.0180
2,001	0.6	0.6	-0.6	90.580	0.09388526	-0.0044
5,001	0.24	0.24	-0.24	90.576	0.09388884	-0.0005
10,001	0.12	0.12	-0.12	90.576	0.09388935	0.0000

^a Median potential step in millivolts, computed directly from the forward branch of the output data.

^b Relative error in $i_{p,a}$ compared to the finest-resolution run (the last row, which is used as the reference), expressed as a percentage: $100 \times (i_{p,a} - i_{p,a}^{ref}) / i_{p,a}^{ref}$. Should approach zero as nv increases and should decrease as dV^2 , i.e., halving dV should reduce this by a factor of four.

The Butler–Volmer kinetics are formulated in terms of the fractional coverage θ of the reduced species R, which enters the equilibrium potential through a Nernst logarithm, $\ln[(1 - \theta_o)/\theta_o]$, and the exchange current density through the product $\theta_o^\beta (1 - \theta_o)^{1-\beta}$. Both expressions are singular at $\theta_o = 0$ and $\theta_o = 1$, so the coverage is clamped to the interval $[\varepsilon, 1 - \varepsilon]$ with $\varepsilon = 10^{-10}$ throughout the simulation. The clamp activates whenever the Nernstian equilibrium coverage at the applied potential falls below ε , which occurs for $|V_d - U^\circ| > (RT/nF) \ln(1/\varepsilon) = 0.592 \text{ V}$ at 298.15 K . Within the $\pm 0.3 \text{ V}$ potential window used here, the equilibrium coverage at the window endpoints is approximately 3.5×10^{-9} (anodic limit) and $1 - 3.5 \times 10^{-9}$ (cathodic limit), both well above ε . Accordingly, all validation runs recorded zero clamp activations. When the window exceeds the 0.592 V threshold, the clamp pins θ above its equilibrium value at the window edge, sustaining a spurious residual current that grows as ε increases; charge integration is the first diagnostic affected, while peak-shape metrics remain accurate until the window is considerably wider. For the potential windows used in applications to the $\text{Ni(OH)}_2/\text{NiOOH}$ system, the clamp threshold was verified against the applied window prior to parameter estimation.

Simulations were performed at scan rates spanning three decades ($1\text{--}3,000 \text{ mV s}^{-1}$) at the same fixed dV . For the reversible case (**Fig. S7** (a)–(b)), the anodic peak current density was proportional to scan rate over the entire range, with a fitted slope of $0.9389 \text{ mA cm}^{-2} \text{ V}^{-1} \text{ s}$ and an intercept indistinguishable from zero ($R^2 = 1.000$). This confirms the expected $i_{p,a} \propto sr$ scaling, which distinguishes surface-confined reactions from diffusional ones ($i_{p,a} \propto sr^{1/2}$). The integrated anodic charge remained constant at $nF\Gamma_T$ across all scan rates, verifying that the site balance is conserved regardless of the time step.

To verify that the model correctly captures the transition from reversible to irreversible kinetics, given that the $\text{Ni(OH)}_2/\text{NiOOH}$ is not perfectly reversible, we repeated simulations at the same scan rates with k_s reduced to 1.0 s^{-1} (**Fig. S7** (c)–(d)). At low scan rates, the peak potentials were scan-rate independent, consistent with reversible behavior ($\Lambda = RTk_s/nFsr \gg 1$), while at high scan rates both $E_{p,a}$ and $E_{p,c}$ shifted linearly with $\ln(sr)$. Linear regression of the high-scan-rate tail yielded slopes of $+0.0472 \text{ V}$ and -0.0472 V for the anodic and cathodic branches, respectively,

approximately 8% below the Laviron predictions of $RT/[(1 - \beta)nF]$ and $-RT/(\beta nF)$ for $\beta = 0.5$. (± 0.05138 V at 298.15 K). This underestimate arises because the regression spans the transition region, where scan rates at the lower end of the fitted range have not yet reached the fully irreversible asymptote, pulling the fitted slope below its limiting value. The fitted intercepts (± 0.1546 V) agree with the Laviron prediction (± 0.1525 V) to within 1.4% and were equal in magnitude and opposite in sign, consistent with the expected symmetry. These results confirm that the framework reproduces both the reversible limit and the quasi-irreversible Laviron trumpet, with the transition occurring at the theoretically predicted $\Lambda \approx 1$.

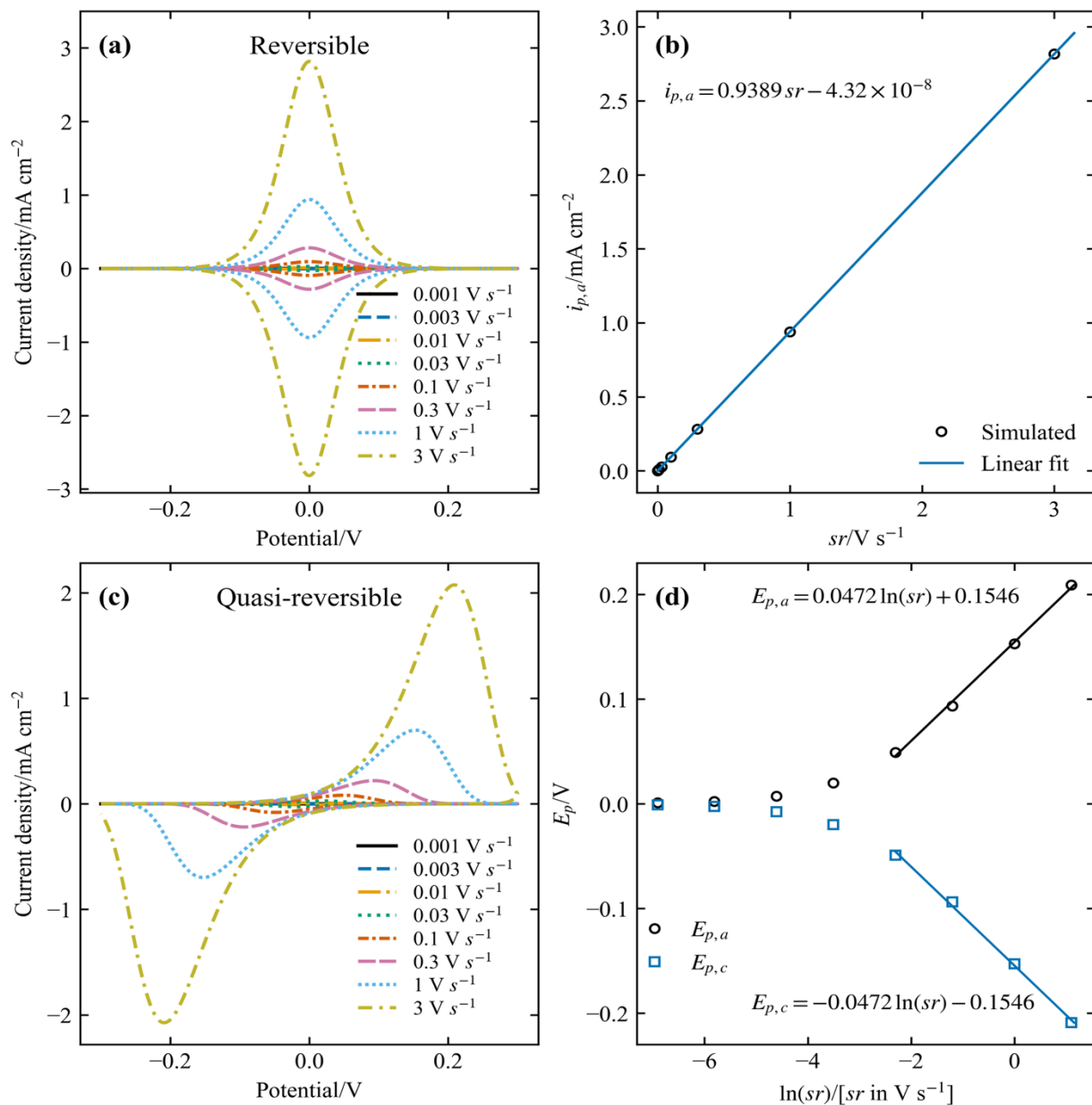


Fig. S7 (a) Simulated cyclic voltammograms for a reversible redox reaction ($k_s = 1 \times 10^5 \text{ s}^{-1}$) of surface-confined (adsorbed) species at different scan rates. (b) Anodic peak current densities ($i_{p,a}$) as a function of the scan rate for the

cyclic voltammograms shown in (a). (c) Simulated cyclic voltammograms for a quasi-reversible redox reaction ($k_s = 1.0 \text{ s}^{-1}$) of surface-confined (adsorbed) species at different scan rates. (d) Anodic and cathodic peak potentials (E_p) as a function of the logarithm of the scan rate ($\ln(sr)$).

Collectively, these results confirm that the numerical framework correctly reproduces the reversible limit, the $i_{p,a} \propto sr$ scaling, and the quasi-irreversible Laviron trumpet for a surface-confined redox couple. The one structural feature not exercised here (the Wohl expansion activity coefficients) enters only through the equilibrium potential U and does not change the time-stepping; its contribution to the simulated voltammogram can therefore be isolated from numerical artifacts. Any discrepancy between the simulated and experimental $\text{Ni(OH)}_2/\text{NiOOH}$ cyclic voltammograms that is not reproduced by the ideal Laviron relations is attributable to the non-ideal activity coefficients rather than to the framework itself.

S9. Sensitivity Analysis of the Value for the Symmetry Factor (β)

The Butler–Volmer kinetic expression used in the Surface Model requires a value for the symmetry (charge-transfer) factor, β , which is fixed at 0.5 in the main-text calibration while the remaining ten thermodynamic parameters (the forward- and backward-scan standard potentials (U°) and Wohl coefficients (Ω_2 – Ω_5)) are left free. Because anodic/cathodic peak asymmetry in the CV response can in principle arise either kinetically ($\beta \neq 0.5$) or thermodynamically (asymmetric forward/backward Ω_k), fixing β at a conventional value raises the possibility that the fitted Ω_k are partly compensating for a kinetic asymmetry that the model is not otherwise permitted to express. To assess this, we re-estimated the full parameter set of the Surface Model (with the 4-coefficient Wohl expansion) with β fixed at 0.3 and 0.7, and separately with β treated as a freely adjustable parameter bounded between 0.3 and 0.7. In each case, k_0 , U° , and Ω_2 – Ω_5 were re-optimized against the same 5 and 100 mV s^{-1} cyclic voltammetry data used elsewhere in this study. Results are summarized in **Table S8**.

Table S8. Estimated parameters and RMSE (5 and 100 mV s^{-1}) for the simulations based on the Surface Model with the Wohl expansion (4 coefficients) using different values of the symmetry factor (β).

Parameters	$\beta = 0.3$	$\beta = 0.7$	$\beta = 0.5$ (this work)	β adjustable ($\beta = 0.561$) ^{a,b}
k_0 ($\text{s}^{-1} \text{ cm}^{3/2} \text{ mol}^{-1/2}$)	29.0 ± 0.3	$2,080 \pm 20$	266 ± 2	500 ± 30
<i>Forward scan</i>				
U° (V vs. Hg/HgO)	0.4284 ± 0.0005	0.4268 ± 0.0004	0.4453 ± 0.0008	0.4424 ± 0.0006
Ω_2/F (V)	-0.1767 ± 0.0005	-0.1494 ± 0.0004	-0.072 ± 0.003	-0.080 ± 0.002
Ω_3/F (V)	-0.382 ± 0.002	-0.2332 ± 0.0006	-0.064 ± 0.008	-0.071 ± 0.005
Ω_4/F (V)	0.464 ± 0.002	0.2059 ± 0.0006	0.051 ± 0.008	0.052 ± 0.005
Ω_5/F (V)	-0.2091 ± 0.0005	-0.0696 ± 0.0001	-0.015 ± 0.003	-0.013 ± 0.002
<i>Backward scan</i>				
U° (V vs. Hg/HgO)	0.421 ± 0.002	0.414 ± 0.002	0.424 ± 0.001	0.416 ± 0.002
Ω_2/F (V)	0.123 ± 0.006	0.103 ± 0.005	0.131 ± 0.003	0.110 ± 0.004
Ω_3/F (V)	-0.003 ± 0.008	-0.02 ± 0.01	0.023 ± 0.008	-0.012 ± 0.007
Ω_4/F (V)	0.25 ± 0.01	0.23 ± 0.01	0.19 ± 0.01	0.218 ± 0.009
Ω_5/F (V)	-0.180 ± 0.009	-0.158 ± 0.007	-0.138 ± 0.006	-0.153 ± 0.005

RMSE, 5 mV s ⁻¹ (mA cm ⁻²)	0.00234	0.00192	0.00147	0.00144
RMSE, 100 mV s ⁻¹ (mA cm ⁻²)	0.02071	0.01234	0.01109	0.01048

^a β was bounded between 0.3 and 0.7 in the calibration, converging at the optimum value of 0.561.

^b The correlation coefficient between k_0 and β in this regression is 0.99. k_0 and β are therefore not independently resolved: the relative uncertainty in k_0 increases from 3–5% in the fixed- β cases to approximately 23% here. The marginal RMSE reduction relative to $\beta = 0.5$ reflects this trade-off rather than an independent improvement in either parameter, and k_0 and β from this column should not be interpreted as independent point estimates.

RMSE at both scan rates is minimized among the fixed- β cases at $\beta = 0.5$, and increases substantially at either extreme tested ($\beta = 0.3$ and $\beta = 0.7$). When β is adjustable, the optimization converges to $\beta = 0.561$, inside the tested bounds rather than at either boundary, with an RMSE only marginally lower than the $\beta = 0.5$ case (approximately 2–5% lower depending on scan rate). However, this marginal improvement should be interpreted with caution. In the β -adjustable regression, the correlation coefficient between k_0 and β is 0.99, indicating that the two parameters are effectively collinear in the vicinity of the optimum; no other parameter pair involving β shows comparable correlation ($|r| < 0.21$ in all other cases). Consistent with this, the relative uncertainty on k_0 increases from approximately 3–5% in any of the fixed- β cases to approximately 23% when β is fit simultaneously. The small reduction in RMSE therefore reflects k_0 and β trading off along a shallow ridge in the objective function rather than either parameter being more precisely resolved, and k_0 and β obtained from the adjustable- β regression should not be treated as independently meaningful point estimates.

The Wohl coefficients obtained at $\beta = 0.5$ and at the freely optimized $\beta = 0.561$ agree closely in both sign and magnitude for all five terms on both scan branches. Moving to the tested extremes ($\beta = 0.3$ or $\beta = 0.7$), however, several coefficients change substantially in magnitude, and Ω_3 for the backward (reduction) scan changes sign (+0.023 at $\beta = 0.5$ versus -0.003 at $\beta = 0.3$ and -0.02 at $\beta = 0.7$, with the latter two not distinguishable from zero within uncertainty). This sensitivity does not bear on the structural conclusion drawn from the expansion order itself (more than three coefficients are needed), but it compounds the caveat already placed on the individual coefficient values in the main text: in addition to being jointly constrained by correlation among themselves at fixed β , they are also conditioned on the assumed value of β , and their magnitudes should be interpreted accordingly.

These results also bear on whether the fitted Ω_k are absorbing kinetic asymmetry that the fixed value of β cannot express. Two observations argue against this. First, in the β -adjustable regression, β correlates strongly only with k_0 ($r = 0.99$). This means that, near the optimum, a shift in β is compensated almost entirely by an offsetting shift in k_0 , not by the Ω_k : were the true kinetic value of β to differ from the assumed 0.5, that mismatch would be expected to bias the fitted k_0 rather than distort the fitted Ω_k . Second, the unconstrained optimization converges to $\beta = 0.561$,

close to the assumed value of 0.5, rather than drifting toward either tested extreme, which is the behavior expected if a substantial hidden kinetic asymmetry were being masked by fixing $\beta = 0.5$.

On this basis, $\beta = 0.5$ was retained for the calibration reported in the main text since it gives an RMSE not meaningfully distinguishable from the unconstrained optimum and it avoids the k_0 - β identifiability problem introduced when β is treated as a freely adjustable parameter. Finally, the correlation structure of the unconstrained fit indicates that the fitted Ω_k are not compensating for a suppressed kinetic asymmetry.

S10. Determination of the Maximum Concentration of Proton Vacancies

The maximum concentration of proton vacancies was determined from the average cathodic charge density (Q_c) of the experimental cyclic voltammograms at different scan rates. For each scan rate, the forward (anodic) and reverse (cathodic) branches of the CV trace were separated at the point of maximum applied potential, $V_{\max}$. Within a fixed integration window (0.10–0.565 V vs. Hg/HgO), the current density was integrated with respect to potential using the trapezoidal rule, and the resulting integral was divided by the scan rate, sr , to convert the potential-integrated quantity into a time-integrated charge density (see equation (S29)).

$$Q_j = \frac{1}{sr} \int_{V_{start}}^{V_{end}} idV. \quad (S29)$$

We also calculated the anodic charge density, Q_a , from the forward branch traversed in the direction of increasing potential. The cathodic charge density, Q_c , was computed from the reverse branch, with the potential array reordered to increasing V_d prior to integration so that both charges were evaluated over the same window and with the same sign convention. No baseline subtraction was applied; the reported charge densities therefore reflect the total integrated current density over the window. Here, we assumed the capacitive current contribution to the total charge was negligible (less than 10%), so the calculated charge directly reflects the total amount of electroactive species oxidized and reduced. The result of this integration is illustrated in **Fig. S8**.

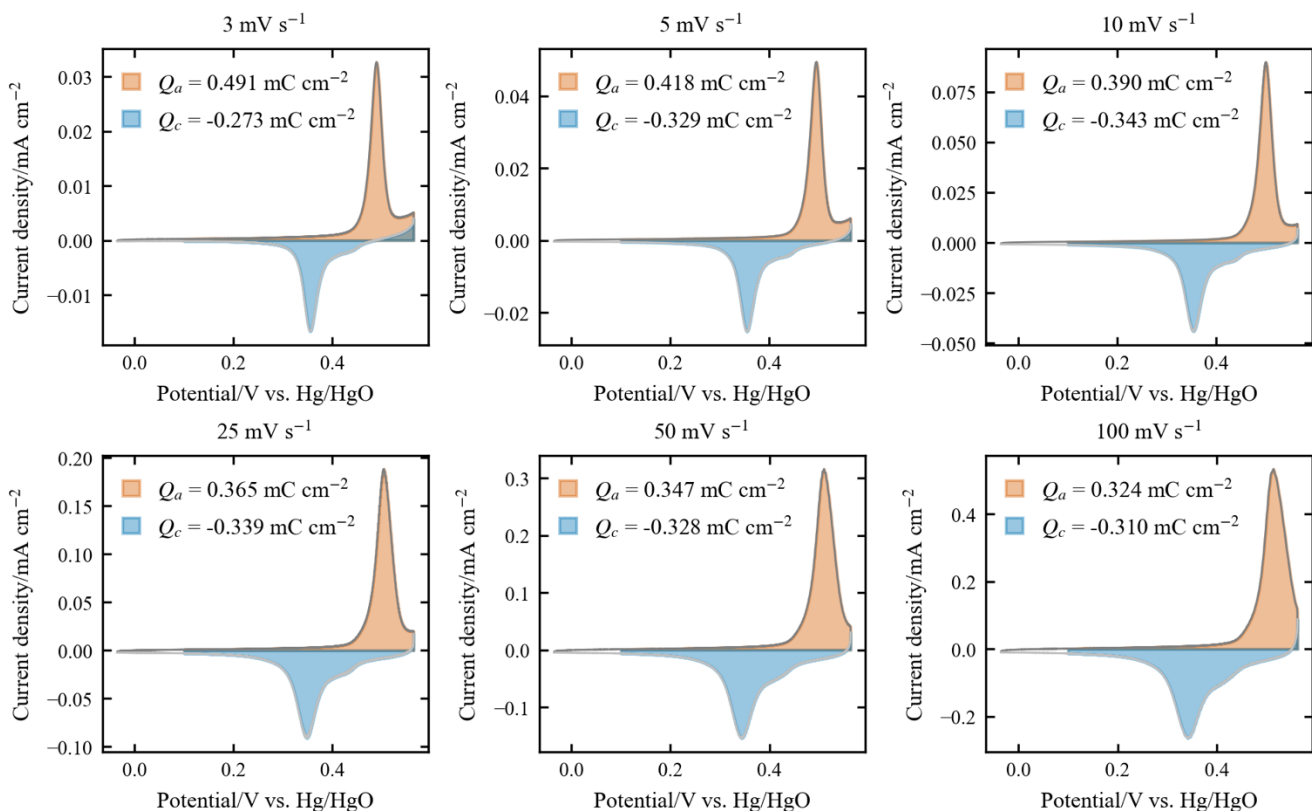


Fig. S8 Estimation of the cathodic and anodic charge densities (Q_c and Q_a) of the experimental cyclic voltammograms at different scan rates in the potential window of 0.10 to 0.565 V vs. Hg/HgO without baseline correction.

The cathodic charge density was related to the number of moles of electrons transferred using the Faraday constant, and this quantity (in mol cm⁻²) was directly related to the surface concentration of NiOOH, which is equivalent to the maximum concentration of proton vacancies in the system for the Surface Model ($c_{v,max}(SM)$), assuming one mol of proton vacancies per mol of NiOOH (see equation (S30)).

$$\frac{Q_c}{F} = c_{e^-} = c_{NiOOH} = c_{v,max}(SM). \quad (S30)$$

To calculate the maximum concentration of proton vacancies in the Layer Model (in mol cm⁻³), $c_{v,max}(SM)$ was divided by the Ni(OH)₂ layer thickness.

S11. Analysis of the OER Contribution

Across all six scan rates, integration of the experimental cyclic voltammograms over the chosen window (0.10–0.565 V vs. Hg/HgO, no baseline correction; **Fig. S8**) yields an anodic charge density, Q_a , that exceeds the magnitude of the cathodic charge density, $|Q_c|$ (**Table S9**). For a fully reversible, surface-confined redox couple, Q_a and $|Q_c|$ are expected to be equal and independent of scan rate, since the total charge corresponds to a fixed quantity of interconverted

Ni(OH)₂/NiOOH. The systematic excess observed here, together with its pronounced scan-rate dependence, is inconsistent with this idealized picture and instead suggests a contribution from the irreversible oxygen evolution reaction (OER) occurring within the integration window.

Table S9. Anodic and cathodic charge densities, their ratio, and percent deviation from unity, computed by direct integration of the cyclic voltammograms in **Fig. S8** (0.10–0.565 V, no baseline correction).

Scan rate (mV s ⁻¹)	Q_a (mC cm ⁻²)	Q_c (mC cm ⁻²)	$Q_a/ Q_c $	% deviation from 1.0
3	0.4906	-0.2728	1.7988	80
5	0.4178	-0.3290	1.2699	27
10	0.3895	-0.3435	1.1341	13
25	0.3649	-0.3395	1.0749	7
50	0.3473	-0.3280	1.0589	6
100	0.3244	-0.3101	1.0461	5

The ratio $Q_a/|Q_c|$ decreases from 1.80 at 3 mV s⁻¹ to 1.05 at 100 mV s⁻¹, corresponding to a decrease in the percent deviation from unity from 80% to 5%. This behavior parallels the mechanistic picture established for thin-film Ni(OH)₂ electrodes by Ta and Newman [5], who explicitly decomposed the total anodic current in their cyclic voltammograms into intercalation and OER components as a function of sweep rate. They found that OER comprised a minor fraction of the anodic charge at their fastest sweep rate (1 mV s⁻¹) but dominated it at their slowest (0.01 mV s⁻¹), because the intercalation current is capacity-limited while OER is not. This is noted only as a qualitative comparison; differences in electrode configuration (RDE vs. static thin film) and in the range of scan rates examined preclude a quantitative transfer of the OER kinetic parameters reported by Ta and Newman (their Table I) to the present system.

Overall, the scan-rate dependence of $Q_a/|Q_c|$ and the precedent established by Ta and Newman support the interpretation that a portion of the anodic charge integrated over the 0.10–0.565 V window is attributable to OER rather than to the Ni(OH)₂/NiOOH intercalation reaction, with the contribution becoming more significant at slower scan rates. Q_a should accordingly be regarded as an upper bound on the true intercalation charge, particularly at the slower end of the scan-rate range examined.

This distinction is directly relevant to the parameter calibration performed in this work, which used cyclic voltammetry data at 5 and 100 mV s⁻¹. At 100 mV s⁻¹, the estimated OER contribution to the anodic charge is comparatively small (5% deviation from unity), whereas at 5 mV s⁻¹ the estimated contribution is substantially larger (27%) and should not be treated as negligible. Still, we do not attempt a quantitative deconvolution of the OER and intercalation charge in the present work. Explicit treatment of the oxygen evolution side reaction, following the approach of Ta and Newman [5], is identified as a direction for future refinement of the model and is beyond the framework-level scope of the present study.

S12. Non-identifiability Problem: Proton Vacancy Diffusion Coefficient ($D_{s,v}$) and the Solid Oxide Layer Thickness (a)

In the Layer Model, the proton vacancy diffusion coefficient ($D_{s,v}$) governs the rate of proton vacancy transport through the solid oxide layer to the electrode surface. Because this parameter and the layer thickness (a) were not known a priori, PEST calibration of $D_{s,v}$ was performed independently at different a values spanning the range reported in the literature for this system (2–10 nm) [13–19]. The calibrated value of $D_{s,v}$ increased consistently with a , from $2.40 \times 10^{-13} \text{ cm}^2/\text{s}$ at $a = 2 \text{ nm}$ to $5.51 \times 10^{-12} \text{ cm}^2/\text{s}$ at $a = 10 \text{ nm}$, as shown in **Table S10**.

Table S10. Estimated proton vacancy diffusion coefficient ($D_{s,v}$) and 95% Confidence Interval (CI) for each layer thickness (a). The simulation used the two-coefficient Wohl expansion.

a (nm)	$D_{s,v}$ ($\text{cm}^2 \text{ s}^{-1}$)	$D_{s,v}$ 95% CI ($\text{cm}^2 \text{ s}^{-1}$)	RMSE, 5 mV s^{-1} (mA cm^{-2})	RMSE, 100 mV s^{-1} (mA cm^{-2})
2	2.401×10^{-13}	$[5.32 \times 10^{-15}, 1.08 \times 10^{-11}]$	0.00143793	0.018563
4	9.075×10^{-13}	$[3.33 \times 10^{-13}, 2.47 \times 10^{-12}]$	0.00145267	0.0184066
6	2.540×10^{-12}	$[1.56 \times 10^{-12}, 4.13 \times 10^{-12}]$	0.00143355	0.0187279
8	3.607×10^{-12}	$[2.61 \times 10^{-12}, 4.99 \times 10^{-12}]$	0.0014238	0.0191076
10	5.513×10^{-12}	$[4.32 \times 10^{-12}, 7.03 \times 10^{-12}]$	0.0014215	0.0191594

The precision with which $D_{s,v}$ could be determined was strongly dependent on a . At $a = 2 \text{ nm}$, the 95% confidence interval spanned more than three orders of magnitude ($[5.32 \times 10^{-15}, 1.08 \times 10^{-11}] \text{ cm}^2 \text{ s}^{-1}$), whereas at $a = 10 \text{ nm}$ the interval narrowed to within a factor of 1.6 ($[4.32 \times 10^{-12}, 7.03 \times 10^{-12}] \text{ cm}^2 \text{ s}^{-1}$). This progressive narrowing was consistent across the full range tested (**Table S10**), indicating that $D_{s,v}$ becomes increasingly well constrained by the experimental data as the assumed layer thickness increases, and is essentially unidentifiable at the thinner end of the literature-reported range.

Despite this pronounced variation in parameter identifiability, model fit quality was comparatively insensitive to a : RMSE varied by only 2.2% across the 5 mV/s scans and 3.9% across the 100 mV/s scans over the entire tested range, as shown in **Table S10** and **Fig. S9**. Notably, the two scan rates showed different trends: RMSE at 5 mV/s was lowest at $a = 8\text{--}10 \text{ nm}$, while RMSE at 100 mV/s was lowest at $a = 2\text{--}4 \text{ nm}$ (see **Fig. S9**), favoring opposite ends of the tested range. Because no single value of a simultaneously minimizes RMSE for both scan rates, $a = 6 \text{ nm}$ was selected as an intermediate value that avoids over-optimizing the fit to either scan rate individually, yielding RMSE of $0.00143 \text{ mA cm}^{-2}$ (5 mV/s) and $0.0187 \text{ mA cm}^{-2}$ (100 mV/s), both close to the minimum observed for their respective scan rates across the tested range. This confirms that the overall agreement between simulated and experimental voltammograms does not meaningfully discriminate between the tested values of a .

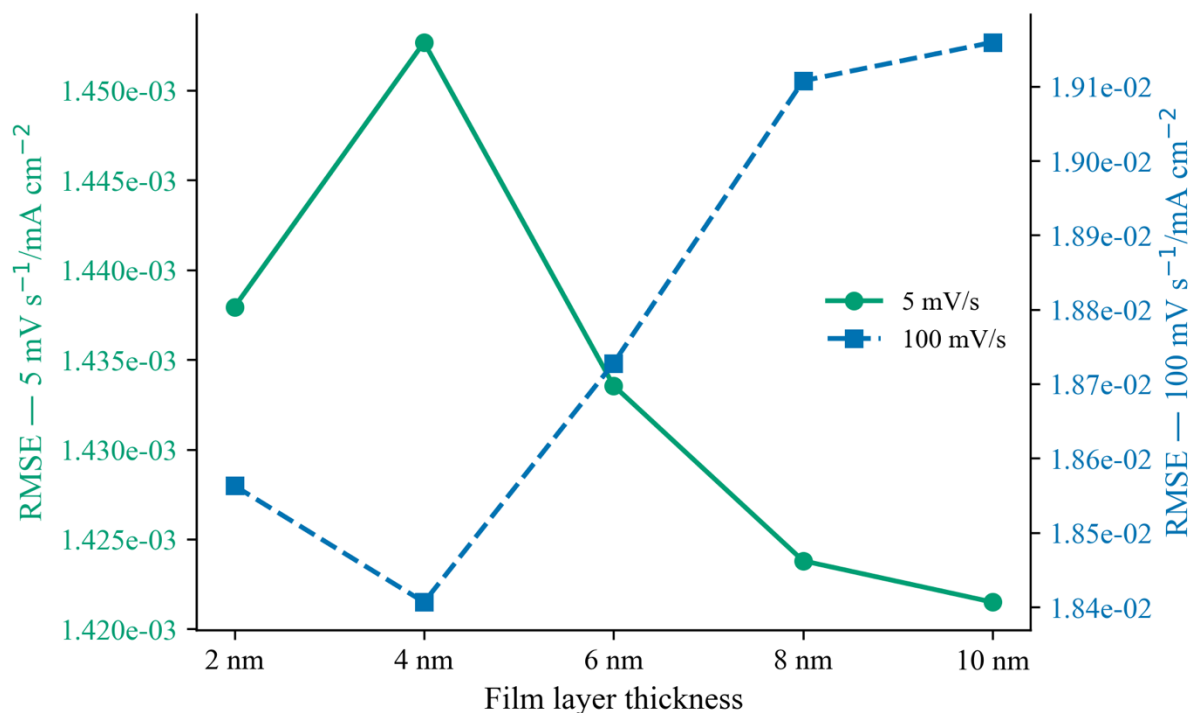


Fig. S9 Root Mean Squared Errors (RMSEs) of the calibrations with different layer thicknesses, where the left y-axis represents the RMSEs for the 5 mV s⁻¹ cyclic voltammogram and the right y-axis represents the RMSEs for the 100 mV s⁻¹ cyclic voltammograms.

This dependence on the assumed thickness is not confined to $D_{s,v}$. **Table S11** shows the calibrated kinetic and thermodynamic parameters obtained at each value of a using the two-coefficient Wohl expansion. The apparent kinetic constant, k_0 , increased 5-fold across the tested range (6.2×10^{-5} to 3.1×10^{-4} s⁻¹ cm^{5/2} mol^{-1/2}), consistent with the coupling between the kinetic and mass-transport terms in the model. The thermodynamic parameters were comparatively less sensitive to a : the standard equilibrium potentials, U° , varied by no more than 1.4% across the range, while the Wohl coefficients (Ω_2/F , Ω_3/F) drifted by up to 10%. One coefficient, Ω_3/F for the forward scan, changed sign across the tested range (+0.0005 at $a = 2$ nm to -0.0007 at $a = 10$ nm); given its small magnitude, this is consistent with the parameter being poorly resolved from zero rather than indicating a physically meaningful change in sign.

Table S11. Estimated kinetic and thermodynamic parameters for each layer thickness (a). The simulation was done using the two-coefficient Wohl expansion.

Parameter	2 nm	4 nm	6 nm	8 nm	10 nm
k_0 (s ⁻¹ cm ^{5/2} mol ^{-1/2})	6.2×10^{-5}	1.3×10^{-4}	1.8×10^{-4}	2.5×10^{-4}	3.1×10^{-4}
<i>Forward scan</i>					
U° (V vs. Hg/HgO)	0.4557	0.4554	0.4559	0.4541	0.4540
Ω_2/F (V)	-0.0351	-0.0353	-0.0348	-0.0372	-0.0374
Ω_3/F (V)	0.0005	0.0005	0.0006	-0.0005	-0.0007
<i>Backward scan</i>					
U° (V vs. Hg/HgO)	0.4085	0.4077	0.4080	0.4030	0.4027
Ω_2/F (V)	0.0745	0.0735	0.0742	0.0678	0.0675

Ω_3/F (V)	0.0478	0.0469	0.0478	0.0448	0.0446
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Overall, these results show that the choice of a and $D_{s,v}$ affects the estimated kinetic parameter and, to a lesser extent, the coefficients in the Wohl expansion, but does not significantly affect the quality of the fit to the experimental data or the estimated standard equilibrium potentials.

S13. Initial Values for the Dependent Variables in the Models

Table S12. Initial values for the dependent variables in the model.

Variable	Initial value		
	$-a \leq y < 0$	$y = 0$	$0 < y \leq 2\delta$
C_{OH}	0	1	1
C_{Na}	0	1	1
θ_v	1×10^{-10}	1×10^{-10}	0
ϕ_2	0	0	0
ϕ_1	0	0	0

S14. Experimental Methods

S14.1 Reagents and Instrumentation

All inorganic and organic reagents were used as received unless otherwise stated. Sodium hydroxide (NaOH, 1 M standard solution, Lot: 250243), hydrochloric acid (HCl, trace metal grade, Lot: 23040119), nitric acid (HNO₃, ACS grade), acetone (HPLC grade), and isopropanol (Optima grade) were purchased from Fisher Chemical. Nickel(II) nitrate hexahydrate [Ni(NO₃)₂·6H₂O, 98%] was obtained from Thermo Scientific. Alumina polishing suspensions (5, 0.3, and 0.05 μ m particle size, respectively) were obtained from Allied High Tech Products, Inc. All solutions were prepared using ultrapure water (18.2 M Ω ·cm, Elga Purelab Ultra) unless otherwise specified.

Electrochemical experiments employed a three-electrode configuration. The working electrode was a nickel disk insert (5.00 mm OD $\times$ 4.00 mm thick; Pine Research Instrumentation, Part No. AFED050P040NI). The counter electrode was a platinum foil (0.005 in. thickness, 3N5 purity; ESPI Metals, Lot No. Q20825). The reference electrode was a Hg/HgO electrode with 1 M NaOH internal solution (MTX Labs).

All electrochemical measurements were performed using a Squidstat Plus potentiostat (Admiral Instruments inc). Rotating disk electrode (RDE) experiments were conducted using an MSR electrode rotator (Pine Research Instrumentation, Model No. AFMSRCE) with a borosilicate glass RDE cell (Pine Research Instrumentation) compatible with $\sim$ 8 mL of electrolyte.

S14.2 Electrolyte Purification

Sodium hydroxide (NaOH) electrolyte solutions at concentrations of 1, 0.5, and 0.1 M were prepared for the electrochemical characterization of nickel in alkaline media. To ensure the absence of iron (Fe) impurities in all electrolyte solutions, a purification procedure was carried out prior to

use, following the protocol described by Marquez et al. (2023) [20]. The resulting Ni(OH)_2 precipitate effectively scavenged trace Fe contaminants from the solution, yielding an Fe-free electrolyte. The purified solution was subsequently filtered with a $0.22\ \mu\text{m}$ syringe filter prior to use in all electrochemical experiments. Unless otherwise specified, all solutions were degassed for 30 min using a Branson 2800 ultrasonic processor operating in degas mode immediately prior to each measurement to minimize dissolved oxygen content.

S14.3 Electrode and Glassware Cleaning Protocol

The electrochemical response of the system is highly sensitive to contamination introduced by any component of the electrochemical cell. To ensure a reproducible system, a rigorous preparation protocol was applied to all cell components prior to each experiment. The nickel disk electrode was mechanically polished for 60 cycles on polishing cloths progressing from coarse to fine (1500, 2000, 3000, and 5000 grit). Initial polishing was carried out on a 1500-grit cloth with ultrapure water, followed by successive polishing steps with alumina suspensions of decreasing particle size (5, 0.3, and $0.05\ \mu\text{m}$) on 2000-, 3000-, and 5000-grit cloths, respectively. Following mechanical polishing, the electrode was sonicated in 0.5 M HCl and 20% isopropanol solutions for 10 min each using a Branson 2800 ultrasonic sonicator. The electrode was subsequently rinsed with acetone and used immediately to minimize surface oxidation upon air exposure. All glassware components, including the electrochemical cell, electrode holders, and capillaries, were subjected to a two-step cleaning protocol. First, all glassware was submerged in a 3:1 HNO_3 :HCl solution for 30 min to remove organic contaminants and manufacturing residues. Subsequently, all components were sonicated in ultrapure water for 30 min.

S14.4 Electrode Activation

Following the cleaning protocol, the nickel electrode was immersed in 1 M NaOH in a three-electrode electrochemical cell, consisting of a mercury–mercury oxide (Hg/HgO , 1 M NaOH) reference electrode positioned via a Luggin capillary filled with the corresponding electrolyte concentration, and a platinum (Pt) foil as the counter electrode. The electrode was electrochemically activated by cycling the potential between 0.0 and 0.6 V vs. Hg/HgO for 500 cycles at $100\ \text{mV s}^{-1}$, thereby promoting the formation of a stable $\text{Ni(OH)}_2/\text{NiOOH}$ overlayer. Activation was considered complete when the anodic peak current density reached a stable value of $1\ \text{mA cm}^{-2}$ in the last cycle, confirming a reproducible and fully developed $\text{Ni(OH)}_2/\text{NiOOH}$ active layer. The electrolyte was subsequently replaced with fresh electrolyte solution before kinetic analysis was performed.

S15. Calculation of the Liquid Junction Potential

The liquid junction potential between the electrolyte (solution A, $0.1\ \text{mol dm}^{-3}$ NaOH) and the internal solution of the reference electrode (solution B, $1.0\ \text{mol dm}^{-3}$ NaOH) was estimated using the Henderson equation (equation (S31)) [21, 22].

$$E_{LJP} = \frac{RT}{F} \left[\frac{(U_A - V_A) - (U_B - V_B)}{(U'_A + V'_A) - (U'_B + V'_B)} \right] \ln \left[\frac{U'_A + V'_A}{U'_B + V'_B} \right], \quad (\text{S31})$$

where:

$$U = \sum c_+ \lambda_+^0,$$

$$V = \sum c_- \lambda_-^0,$$

$$U' = \sum c_+ \lambda_+^0 |z_+|,$$

$$V' = \sum c_- \lambda_-^0 |z_-|.$$

where E_{LJP} is the liquid junction potential, c_+ is the cation concentration (in mol dm⁻³), c_- is the anion concentration (in mol dm⁻³), λ_+^0 is the limiting cationic conductivity (S cm² mol⁻¹), λ_-^0 is the limiting anionic conductivity (S cm² mol⁻¹), and z_i is the ion valence. For Na⁺ and OH⁻, the limiting ionic conductivities are 50.08 and 198 S cm² mol⁻¹ [7], respectively. Using these values yields $E_{LJP} = 0.0353$ V, which was subtracted from the measured potential for experiments performed at 0.1 M NaOH. For the experiment at 0.5 M NaOH, $E_{LJP} = 0.0106$ V was subtracted from the measured potential.

S16. Electrochemically Active Surface Area Determination

The electrochemically active surface area (EASA), determined to be 1.1564 cm² (roughness factor of 5.9), was calculated from the double-layer capacitance (C_{dl}) using equation (S32) derived from the cyclic voltammetry in the non-Faradaic potential window of 0.00 to 0.16 V vs. Hg/HgO in 1 M NaOH electrolyte.

$$EASA = \frac{C_{dl}}{C_s}, \quad (\text{S32})$$

where C_s is the specific capacitance of a smooth planar surface at a given OH⁻ concentration.

Cyclic voltammograms were recorded at scan rates of 10, 25, 50, 75, and 100 mV s⁻¹, and the anodic and cathodic currents were extracted at the midpoint potential (0.08 V vs. Hg/HgO). The average capacitive current ($\Delta I = (I_a - I_c) / 2$) was plotted as a function of scan rate, and C_{dl} was obtained from the slope of the linear fit (see Fig. S10).

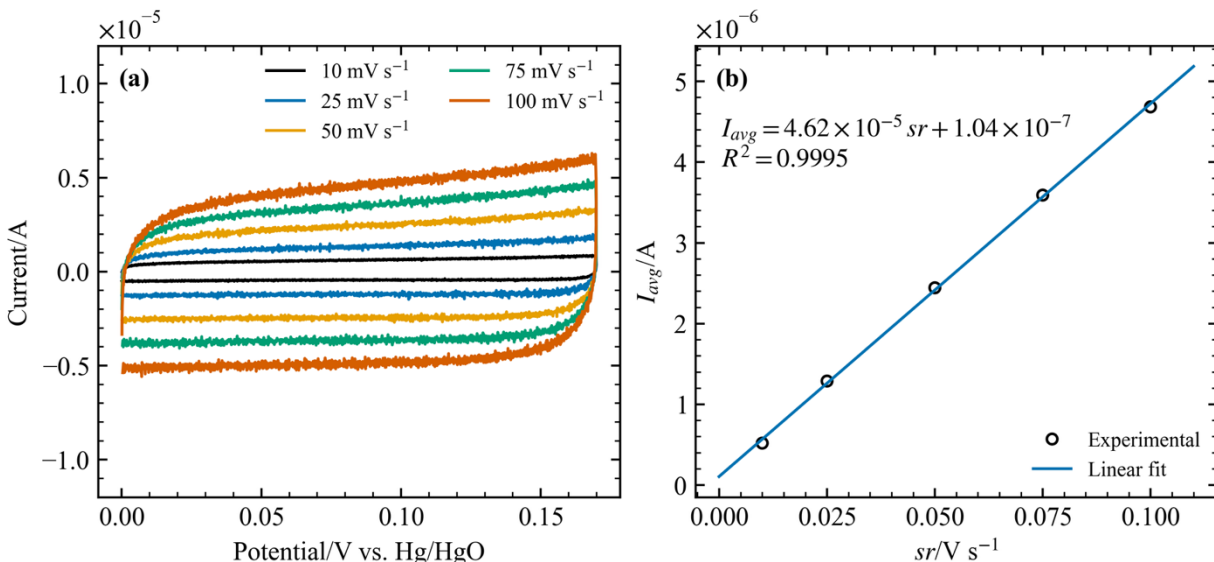


Fig. S10 (a) Cyclic voltammograms in the non-Faradaic potential window of 0.00 to 0.16 V vs. Hg/HgO in 1 M NaOH electrolyte. (b) Average capacitive current as a function of the scan rate and linear fit of the experimental data points.

Reported C_s values in NaOH solutions range from 0.022 to 0.130 mF cm^{-2} [23], with 0.040 mF cm^{-2} being the most widely adopted value for 1 M NaOH electrolyte solutions [23–26], and therefore employed in this work (through all the NaOH concentrations studied). However, the associated uncertainty in the estimated EASA can be as large as a factor of 7, as reported by McCrory et al. 2013 [23], in part due to pseudocapacitance contributions that increase the C_{dl} and may originate from ion adsorption and intercalation. Therefore, in the next section, we show that the estimated kinetic and thermodynamic parameters were insensitive to the EASA value used to calculate the current density.

S17. Estimation of Kinetic and Thermodynamic Parameters Considering EASA Uncertainty

To test the effect of the selected EASA, we ran calibrations by fitting the Surface Model with the four-coefficient Wohl expansion to the experimental data, using EASA values seven times smaller and seven times larger than the value calculated in this work (1.1564 cm^2) to compute the current density. The estimated parameters for both calibrations are shown in **Table S13**.

Table S13. Estimated kinetic and thermodynamic parameters for the Surface Model with the four-coefficient Wohl expansion for experimental current density scaled to seven times smaller and larger.

Parameter	Calculated EASA	7×Smaller EASA	7×Larger EASA
k_0 ($\text{s}^{-1} \text{cm}^{3/2} \text{mol}^{-1/2}$)	266 ± 2	268 ± 2	267 ± 2
<i>Forward scan</i>			
U° (V vs. Hg/HgO)	0.4453 ± 0.0008	0.4443 ± 0.0008	0.4447 ± 0.0008
Ω_2/F (V)	-0.072 ± 0.003	-0.074 ± 0.003	-0.074 ± 0.003
Ω_3/F (V)	-0.064 ± 0.008	-0.065 ± 0.008	-0.065 ± 0.007
Ω_4/F (V)	0.051 ± 0.008	0.050 ± 0.009	0.051 ± 0.008
Ω_5/F (V)	-0.015 ± 0.003	-0.014 ± 0.004	-0.014 ± 0.003
<i>Backward scan</i>			
U° (V vs. Hg/HgO)	0.424 ± 0.001	0.423 ± 0.001	0.422 ± 0.002
Ω_2/F (V)	0.131 ± 0.003	0.130 ± 0.003	0.130 ± 0.003
Ω_3/F (V)	0.023 ± 0.008	0.023 ± 0.008	0.023 ± 0.008
Ω_4/F (V)	0.19 ± 0.01	0.19 ± 0.01	0.19 ± 0.01
Ω_5/F (V)	-0.138 ± 0.006	-0.139 ± 0.006	-0.139 ± 0.006

In **Table S13**, the variation in the kinetic and thermodynamic parameters between the different EASA values is negligible (no more than 7%). Therefore, these parameters are insensitive to the specific EASA used to calculate the current densities. The parameter that does change with the EASA is the calculated maximum concentration of proton vacancies ($c_{v,max}$) for the Surface Model and Layer Model.

S18. Results of the Surface Model Calibrations Using Different Expressions for the Activity Coefficients

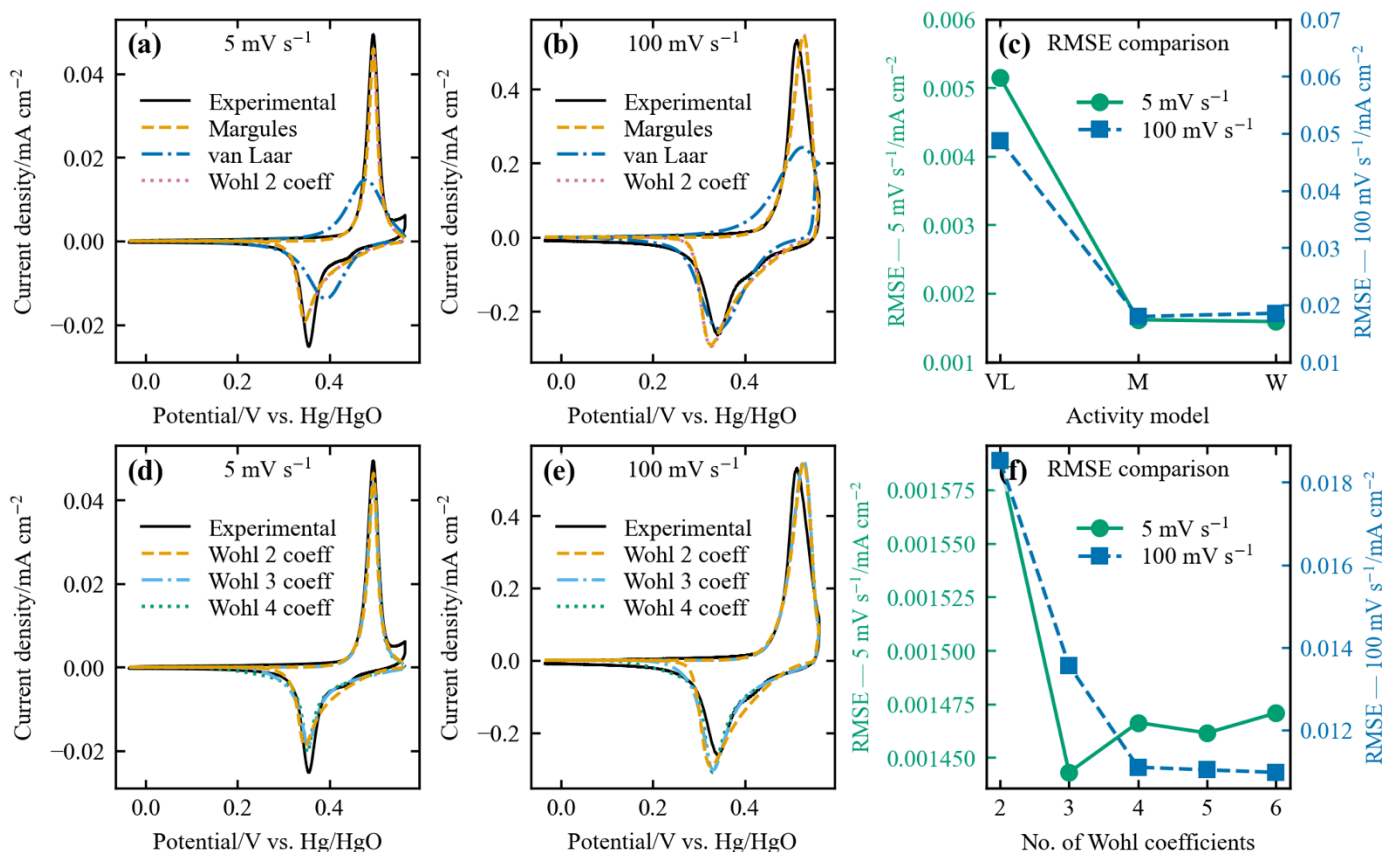


Fig. S11 Results of calibrating the Surface Model (SM) to experimental cyclic voltammograms of the nickel RDE in 0.1 M NaOH at 1000 rpm, and scan rates of 5 mV s⁻¹ and 100 mV s⁻¹ using different expressions for the activity coefficients in the equilibrium potential equation, based on the two-parameter Margules, van Laar, and two-coefficient Wohl expansion (“Wohl 2 coeff”) models ((a) and (b)). The calibration results are also shown using the Wohl expansion with 2, 3, and 4 coefficients (panels (d) and (e)). The Root Mean Squared Error (RMSE) of the calibrations is compared between van Laar (“VL”), Margules (“M”), and the two-coefficient Wohl (“W”) in (c), and across different numbers of coefficients in the Wohl expansion in (f).

S19. Estimated Kinetic and Thermodynamic Parameters for the Surface Model and Layer Model Using Different Expressions for the Activity Coefficients

Table S14 and **Table S15** list the estimated parameters and BIC values for the Layer Model (LM) and Surface Model (SM), respectively, using each activity-coefficient expression considered. For the LM, the BIC decreases monotonically from two through five coefficients and rises at six, supporting the four-coefficient choice adopted in the main text, especially when parameter constrainability is also considered. The SM sequence is less regular: the five-coefficient calibration gives a higher BIC (−26,591) than both its four- (−26,939) and six-coefficient (−27,048) counterparts. Since the Wohl expansion is nested, the five-coefficient model's feasible parameter space contains the four-coefficient optimum, so its objective function cannot exceed the four-

coefficient value at a true optimum; the complexity penalty for the two additional parameters is $2\ln(n) = 2\ln(2000) \approx 15$, setting the maximum possible BIC increase. The observed rise of 348 units is 23 times this ceiling and implies an objective function 18% higher than the four-coefficient calibration (confirmed directly by the PEST run record for that calibration), indicating an incompletely converged fit rather than a genuine information-criterion signal. Taken at face value, the SM BIC would favor six coefficients. In that calibration, however, Ω_4/F through Ω_7/F are indistinguishable from zero on both scan branches (forward: -0.004 ± 0.1 , 0.01 ± 0.2 , 0.01 ± 0.1 , and -0.01 ± 0.03 V; backward: 0.03 ± 0.2 , 0.01 ± 0.3 , -0.01 ± 0.3 , and -0.04 ± 0.08 V), so the apparent improvement is not accompanied by any gain in parameter identifiability. Four coefficients were therefore retained for both models.

Table S14. Estimated kinetic and thermodynamic parameters, and Bayesian Information Criterion (BIC) for the Layer Model using different expressions for the activity coefficients.

Parameters	Margules	van Laar	Wohl 2 coeff.	Wohl 3 coeff.	Wohl 4 coeff.	Wohl 5 coeff.	Wohl 6 coeff.
k_0 ($\text{s}^{-1} \text{cm}^{5/2} \text{mol}^{-1/2}$)	$(1.77 \pm 0.02) \times 10^{-4}$	$(1.8 \pm 0.3) \times 10^{-4}$	$(1.78 \pm 0.05) \times 10^{-4}$	$(1.82 \pm 0.02) \times 10^{-4}$	$(1.81 \pm 0.02) \times 10^{-4}$	$(1.81 \pm 0.02) \times 10^{-4}$	$(1.81 \pm 0.02) \times 10^{-4}$
<i>Forward scan</i>							
U° (V vs. Hg/HgO)	0.4902 ± 0.0002	0.461 ± 0.008	0.4559 ± 0.0003	0.4454 ± 0.0004	0.4416 ± 0.0005	0.4431 ± 0.0006	0.4434 ± 0.0009
Ω_2/F (V) or A_0 or A'	-1.27 ± 0.03	0.4 ± 0.3	-0.03481 ± 0.0004	-0.066 ± 0.001	-0.082 ± 0.002	-0.072 ± 0.004	-0.070 ± 0.008
Ω_3/F (V) or B_0 or B'	-0.19 ± 0.04	0.04 ± 0.03	0.0006 ± 0.0002	-0.040 ± 0.002	-0.073 ± 0.004	-0.04 ± 0.01	-0.04 ± 0.04
Ω_4/F (V)				0.0194 ± 0.0009	0.053 ± 0.005	0.004 ± 0.03	0.004 ± 0.09
Ω_5/F (V)					-0.013 ± 0.002	0.03 ± 0.02	0.01 ± 0.1
Ω_6/F (V)						-0.013 ± 0.008	0.005 ± 0.08
Ω_7/F (V)							-0.007 ± 0.03
<i>Backward scan</i>							
U° (V vs. Hg/HgO)	0.3876 ± 0.0002	0.461 ± 0.008	0.408 ± 0.002	0.458 ± 0.003	0.430 ± 0.001	0.419 ± 0.002	0.410 ± 0.002
Ω_2/F (V) or A_0 or A'	-2.94 ± 0.06	0.5 ± 0.2	0.074 ± 0.002	0.227 ± 0.006	0.135 ± 0.003	0.125 ± 0.009	0.11 ± 0.01
Ω_3/F (V) or B_0 or B'	4.6 ± 0.1	0.10 ± 0.03	0.048 ± 0.001	0.240 ± 0.005	0.007 ± 0.003	0.05 ± 0.04	0.05 ± 0.05
Ω_4/F (V)				-0.089 ± 0.002	0.216 ± 0.006	0.06 ± 0.07	0.03 ± 0.2
Ω_5/F (V)					-0.151 ± 0.004	0.03 ± 0.07	0.02 ± 0.2
Ω_6/F (V)						-0.08 ± 0.02	-0.005 ± 0.2
Ω_7/F (V)							-0.05 ± 0.05
BIC	-25,892	-20,710	-26,550	-26,716	-27,023	-27,036	-27,026

Table S15. Estimated kinetic and thermodynamic parameters, and Bayesian Information Criterion (BIC) for the Surface Model using different expressions for the activity coefficients.

Parameters	Margules	van Laar	Wohl 2 coeff.	Wohl 3 coeff.	Wohl 4 coeff.	Wohl 5 coeff.	Wohl 6 coeff.
k_0 (s ⁻¹ cm ^{3/2} mol ^{-1/2})	266 ± 3	90 ± 6	268 ± 3	272 ± 2	266 ± 2	268 ± 2	266 ± 2
<i>Forward scan</i>							
U° (V vs. Hg/HgO)	0.4907 ± 0.0003	0.461 ± 0.007	0.4551 ± 0.0004	0.4493 ± 0.0005	0.4453 ± 0.0008	0.4463 ± 0.0009	0.447 ± 0.001
Ω ₂ /F (V) or A ₀ or A'	-1.35 ± 0.03	0.4 ± 0.2	-0.03616 ± 0.0005	-0.056 ± 0.001	-0.072 ± 0.003	-0.065 ± 0.005	-0.06 ± 0.01
Ω ₃ /F (V) or B ₀ or B'	-0.02 ± 0.04	0.04 ± 0.02	-0.0006 ± 0.0004	-0.029 ± 0.002	-0.064 ± 0.008	-0.03 ± 0.01	-0.03 ± 0.05
Ω ₄ /F (V)				0.014 ± 0.001	0.051 ± 0.008	0.003 ± 0.03	-0.004 ± 0.1
Ω ₅ /F (V)					-0.015 ± 0.003	0.03 ± 0.03	0.01 ± 0.2
Ω ₆ /F (V)						-0.013 ± 0.009	0.01 ± 0.1
Ω ₇ /F (V)							-0.01 ± 0.03
<i>Backward scan</i>							
U° (V vs. Hg/HgO)	0.3844 ± 0.0007	0.380 ± 0.005	0.412 ± 0.002	0.444 ± 0.003	0.424 ± 0.001	0.412 ± 0.002	0.404 ± 0.002
Ω ₂ /F (V) or A ₀ or A'	-2.59 ± 0.07	0.5 ± 0.1	0.076 ± 0.002	0.214 ± 0.007	0.131 ± 0.003	0.12 ± 0.02	0.10 ± 0.02
Ω ₃ /F (V) or B ₀ or B'	4.0 ± 0.1	0.10 ± 0.03	0.045 ± 0.001	0.243 ± 0.008	0.023 ± 0.008	0.06 ± 0.06	0.06 ± 0.09
Ω ₄ /F (V)				-0.098 ± 0.003	0.19 ± 0.01	0.05 ± 0.1	0.03 ± 0.2
Ω ₅ /F (V)					-0.138 ± 0.006	0.02 ± 0.1	0.01 ± 0.3
Ω ₆ /F (V)						-0.07 ± 0.03	-0.01 ± 0.3
Ω ₇ /F (V)							-0.04 ± 0.08
BIC	-25,587	-21,251	-25,395	-26,338	-26,939	-26,591	-27,048

S20. Parameter Correlation Coefficient Matrix

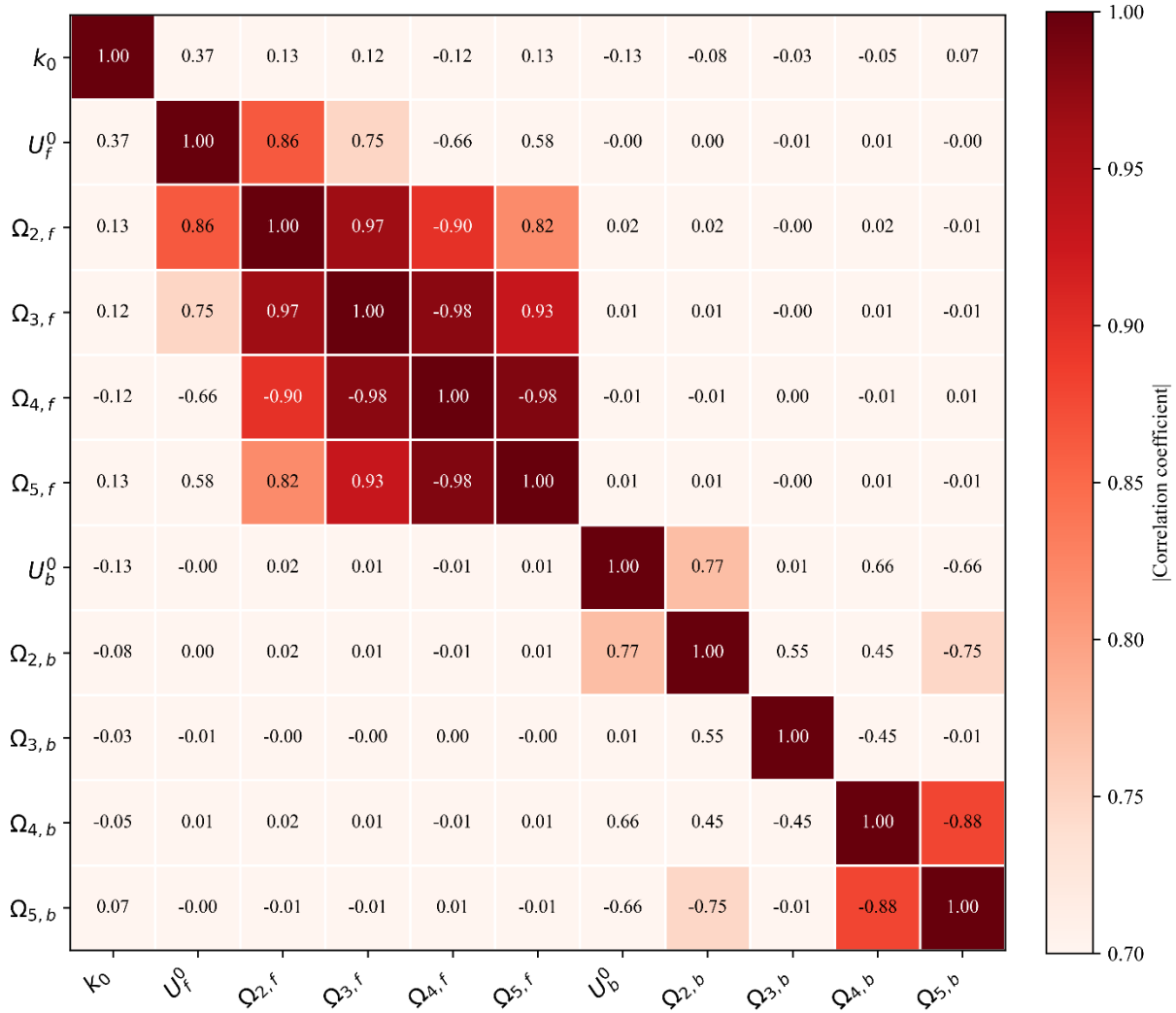


Fig. S12 Parameter correlation coefficient matrix for the calibration of the Layer Model with the four-coefficient Wohl expansion with the experimental data. The subscript “f” means forward, while “b” means backward.

S21. Assumptions Not Met for Wilks and Williams Test

Standard statistical tests for comparing how well two models fit a dataset, including the classical Wilks (1946) and Williams (1959) test [27–29], assume the fitting errors behave in a specific, well-behaved way: each error should be unrelated to its neighbors, should follow a bell-curve (normal) distribution, and should be roughly the same size everywhere in the dataset. We checked whether the Layer Model (LM) and Surface Model (SM) errors meet these conditions and found that they do not, in three distinct ways (see **Fig. S13**).

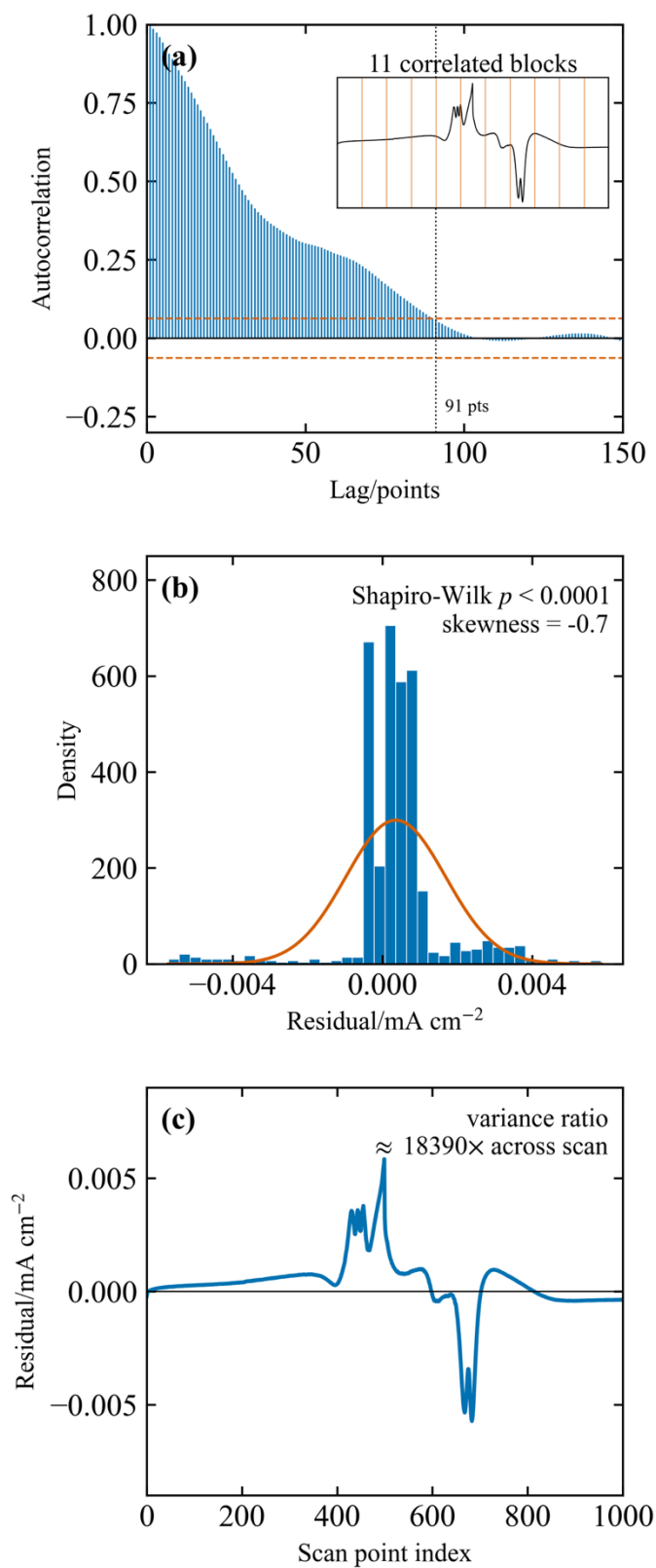


Fig. S13 Three signs that the model residuals violate the assumptions required by classical statistical tests. All panels show the Layer Model's residuals (predicted minus measured current) at 5 mV s^{-1} . (a) Autocorrelation stays well above

the range expected by chance (dashed red band) out to a lag of ~91 points, meaning nearby residuals are not independent; the inset shows the resulting 11 correlated blocks across the scan. Here, lag refers to how similar residuals are to other residuals a given number of points away (b) The residual distribution (blue) is far more sharply peaked and heavy-tailed than the bell-shaped curve (orange) expected under normality (Shapiro-Wilk $p < 0.0001$). (c) Error size is not constant across the scan: residuals spike sharply near the voltammetric current peaks, with variance differing by a factor of roughly 18,390 between the calmest and noisiest regions.

First, because the comparison points come from a single continuous voltammetric sweep rather than independent repeated measurements, consecutive errors are correlated with one another rather than providing fully independent information (**Fig. S13 (a)**). Second, formal statistical tests for a bell-curve shape strongly rejected that assumption for both models at both scan rates (Shapiro-Wilk and D'Agostino-Pearson tests, $p < 0.0001$ in all cases): the errors had noticeably heavier tails than a bell curve would predict, meaning a handful of unusually large errors were common rather than rare (**Fig. S13 (b)**). Third, the size of the errors was far from uniform across the scan: a formal test for unequal variance (Levene's test) confirmed that error size varied enormously depending on where in the sweep a point fell: up to several hundred-fold at 100 mV s^{-1} and several thousand-fold at 5 mV s^{-1} between the calmest and noisiest regions of the scan (**Fig. S13 (c)**). This pattern is physically sensible: a small mismatch between model and experiment in potential produces a small error where the current-potential curve is flat, but a large error where the curve is steep, such as near a voltammetric peak. Thus, errors cluster where the curve is steepest, not evenly across the sweep.

Since all three conditions were violated, we used a block permutation test instead, which makes none of these assumptions and works directly from the measured data.

S22. Block Permutation Test for Comparing Layer Model and Surface Model Fit Quality

S22.1 How the Test Works

For each comparison point, we compare how far off each model's prediction was from the experimental value, and combine these into one overall number: the total difference in squared error between the two models. Formally, for comparison point j , the paired squared-residual difference is shown in equation (S33).

$$d_j = r_{SM,j}^2 - r_{LM,j}^2 = (i_j - \hat{i}_{SM,j})^2 - (i_j - \hat{i}_{LM,j})^2, \quad (\text{S33})$$

where i_j is the experimental current density value and $\hat{i}_{SM,j}$, $\hat{i}_{LM,j}$ are the Surface Model's and Layer Model's predictions at that point j . Summing this over all points gives the overall test statistic, shown in equation (S34).

$$T_{obs} = \sum_{j=1}^n d_j = RSS_{SM} - RSS_{LM}, \quad (\text{S34})$$

The logic of the test is simple: if the two models were truly equivalent, it shouldn't matter which one happened to be closer to the experiment at any particular point (that outcome is essentially a coin flip), meaning d_j and $-d_j$ are equally likely under the null hypothesis. This is the assumption of independent and symmetric errors (ISE), one of two possible formal foundations for permutation-style inference [30]. We chose ISE deliberately over the alternative, exchangeable errors (EE), which underlies ordinary block-shuffling approaches, because EE additionally requires homogeneous error variance across all comparison points, a condition our own heteroscedasticity diagnostics above rule out directly. ISE tolerates exactly this kind of heteroscedasticity, provided the sign of d_j remains an unbiased coin flip.

We can therefore ask: if we repeatedly and randomly re-flip the sign of d_j , and recompute the total T each time (called $T_{\text{permutation}}$), how often does this random reshuffling produce a gap as large as, or larger than, what we actually observed? If our real result is unusual compared to these random reshuffles, that is evidence of a genuine difference between the models. If it looks like a typical outcome of random reshuffling, the models cannot be reliably distinguished.

One adjustment was needed to make this reshuffling valid for our data specifically: because nearby points in the scan are correlated rather than independent, reshuffling individual points one at a time would overstate how much independent evidence each point contributes. Instead, we reshuffled points in contiguous groups ("blocks") along the scan (see inset in **Fig. S13** (a)), so neighboring points were always flipped together rather than independently, preserving their natural relationship while still generating a valid random comparison. The size of each block was chosen based on how far the correlation between neighboring errors actually extends in the real data, following established block-resampling approaches for correlated measurements [31, 32] and specifically block permutation approaches used for correlated data in other fields facing this same problem [30, 33].

S22.2 Exact Inference

With k blocks, there are exactly 2^k possible ways to flip the blocks' signs. When this number was small enough to enumerate directly ($2^k \leq 2^{20} \approx 1$ million; equivalently, $k \leq 20$ blocks), we computed the p-value exactly by checking every one of the 2^k possible sign combinations, rather than estimating it from a random sample of reshuffles. This removes simulation noise from the reported result entirely: an exact p-value is a fixed proportion of a fully enumerated population, not an estimate that varies from run to run. Both scan rates fell within this range (11 blocks at 5 mV s⁻¹, 2,048 sign patterns; 9 blocks at 100 mV s⁻¹, 512 sign patterns), so all p-values reported below are exact.

S22.3 Robustness of Block Length

Because the block length is estimated from the data's autocorrelation structure, we assessed its sensitivity by repeating the test with the block length halved and doubled, holding everything else fixed. At both scan rates, the conclusion was unchanged across this threefold range of block

lengths: no p-value approached the 0.05 threshold in either direction (5 mV s⁻¹: p = 0.25–0.69 across half/base/double block length; 100 mV s⁻¹: p = 0.24–0.63). This indicates that the non-significant result is not an artifact of the particular block length chosen. Given the calibration limitation identified below is anti-conservative, it would inflate the rate of false rejections of the null hypothesis (no significant difference); therefore, the fact that we still could not reject the null hypothesis consistently across block lengths reinforces the conclusion that there is no significant difference between the models.

S22.4 Where the Evidence Concentrates

Breaking T_{obs} down block by block showed that, at both scan rates, its value is dominated by one or two blocks rather than distributed evenly across the scan: at 5 mV s⁻¹, three adjacent blocks together account for essentially the entire observed statistic (101% of T_{obs} , with partial internal cancellation); at 100 mV s⁻¹, two adjacent blocks account for it (100%). In both cases, these blocks coincide with the forward and reverse voltammetric current peaks, consistent with the physical expectation described in the previous section that model discrepancies concentrate where the current-potential curve is steepest. Away from these peak regions, individual comparison points modestly favor the Layer Model (negative d_j at 83% of points at 5 mV s⁻¹ and 57% at 100 mV s⁻¹), consistent with the small overall RMSE advantage reported in the main text. This concentration means the test's effective resolution at each scan rate is smaller than the nominal block count suggests, a point returned to below.

S22.5 Verifying the Symmetry Assumption

Because the ISE assumption underlying this test requires that d_j be governed by a symmetric, unbiased process, we checked this directly. A naive check, pooled skewness of d_i across all 1,000 points, found strong apparent asymmetry at both scan rates (skewness 6.4 - 7.5; skewtest $p \approx 10^{-190}$ – 10^{-213} ; confirmed by a two-sample Kolmogorov–Smirnov test comparing d_j against $-d_{ji}$ and by a Wilcoxon signed-rank test, both $p < 10^{-4}$). Taken at face value, this would suggest the symmetry assumption is severely violated. However, this diagnostic implicitly assumes something close to homogeneous variance to compute its significance, an assumption this data violates by construction, for the same reasons a permutation test was chosen over a classical parametric one in the first place. We therefore constructed a more appropriate check: a synthetic null dataset using the real data's own local error amplitude (smoothed, but otherwise exactly the true heteroscedastic shape, including the peak-driven pattern described above), with both models' errors drawn independently and symmetrically by construction, guaranteeing ISE holds by design. Across 300 such replicates per scan rate, pooled skewness as extreme as, or more extreme than, what the real data showed occurred purely by chance 10% of the time at 5 mV s⁻¹ and 36% of the time at 100 mV s⁻¹, which is a routine consequence of this level of heteroscedasticity, not a rare or alarming event. More directly, the actual test's false-positive rate under this matched, guaranteed-true null stayed close to its nominal 5% target at both scan rates (3.7% and 4.0%). We conclude that the

heteroscedasticity of magnitude and shape in the real data does not, on its own, threaten the test's validity, and that the naive skewness diagnostic would be misleading.

S22.6 An Important Limitation: Calibration Under High Autocorrelation

A separate check targeted a different assumption dimension: whether blocks behave as effectively independent units when autocorrelation is high relative to sample size, as in this dataset. Using synthetic residuals with autocorrelation matched to two regimes (moderate persistence and higher persistence, chosen to reproduce block counts (9–11) comparable to the real data), we found the test calibrated correctly under moderate persistence (false-positive rate 5.0%, from 300 independent trials) but not under the higher, more representative persistence level (11.3%). Because this could plausibly reflect insufficient burn-in in the synthetic generator rather than a genuine limitation, we repeated the check with a properly stationary construction (burn-in of at least twenty times the process's relaxation time); the false-positive rate remained elevated, in fact rising further (17.0–29.0% across three persistence levels chosen to bracket the real data's observed block counts), ruling out non-stationarity as the explanation. This reflects a known limitation of block-based resampling and permutation methods when the underlying dependence range is long relative to sample size [31]. Because this bias is anti-conservative, it inflates the likelihood of falsely detecting a difference; it does not undermine the non-significant result reported here ($p = 0.69$, $p = 0.29$); on the contrary, a properly calibrated test would be expected to yield p -values at least as large. We report this limitation for transparency rather than because it affects the study's conclusions, and note that it is unrelated to, and unaffected by, the symmetry check described above.

S22.7 Power to Detect a Physically-Localized Difference

Section S22.4 found that the observed test statistic was concentrated almost entirely in the blocks coinciding with the voltammetric current peaks, the region where a genuine difference between the Layer Model's and Surface Model's diffusion-layer treatments would plausibly emerge. We therefore first evaluated the test's power against a difference confined to that same region, using the real-envelope synthetic construction described above, with a systematic difference injected only within the dominant peak-region blocks. Detection power rose sharply with effect size: a localized difference of 20% relative amplitude was detected in 79–99% of trials across the two scan rates, and 30% or greater was detected in 98–100% of trials.

S22.8 Confirming the Test Works Correctly

We also checked the test's more general behavior under conditions resembling our real residuals: errors that are correlated, heavy-tailed, and unevenly sized across the scan, generated synthetically so the "correct" answer was known in advance. Under moderate persistence, with no true difference between two models built into the synthetic data, the test incorrectly flagged a significant difference in 15 of 300 independent trials (5.0%), matching the intended 5% false-positive rate closely, and correctly detected a real, deliberately introduced difference (this time distributed uniformly across the scan, rather than concentrated as above) in 95.5–98.5% of trials,

depending on how large the difference was. Under the higher-persistence regime described above, power against this more diffuse alternative fell accordingly, from 95.5–98.5% under moderate persistence to 47.5% and 80.5% at the smaller and larger injected effect sizes, respectively, alongside the elevated false-positive rate, consistent with a test that is simultaneously less discriminating and more prone to spurious rejections under strong dependence, both effects of the same underlying limitation. Overall, these two checks indicate that while the test's power against a small, diffuse difference is limited under the autocorrelation present in this data, its power against a difference concentrated where LM and SM's mechanistic assumptions would actually be expected to diverge is considerably stronger.

S23. Variation of the Partial order of OH⁻ to Reproduce Changes in OH⁻ concentration

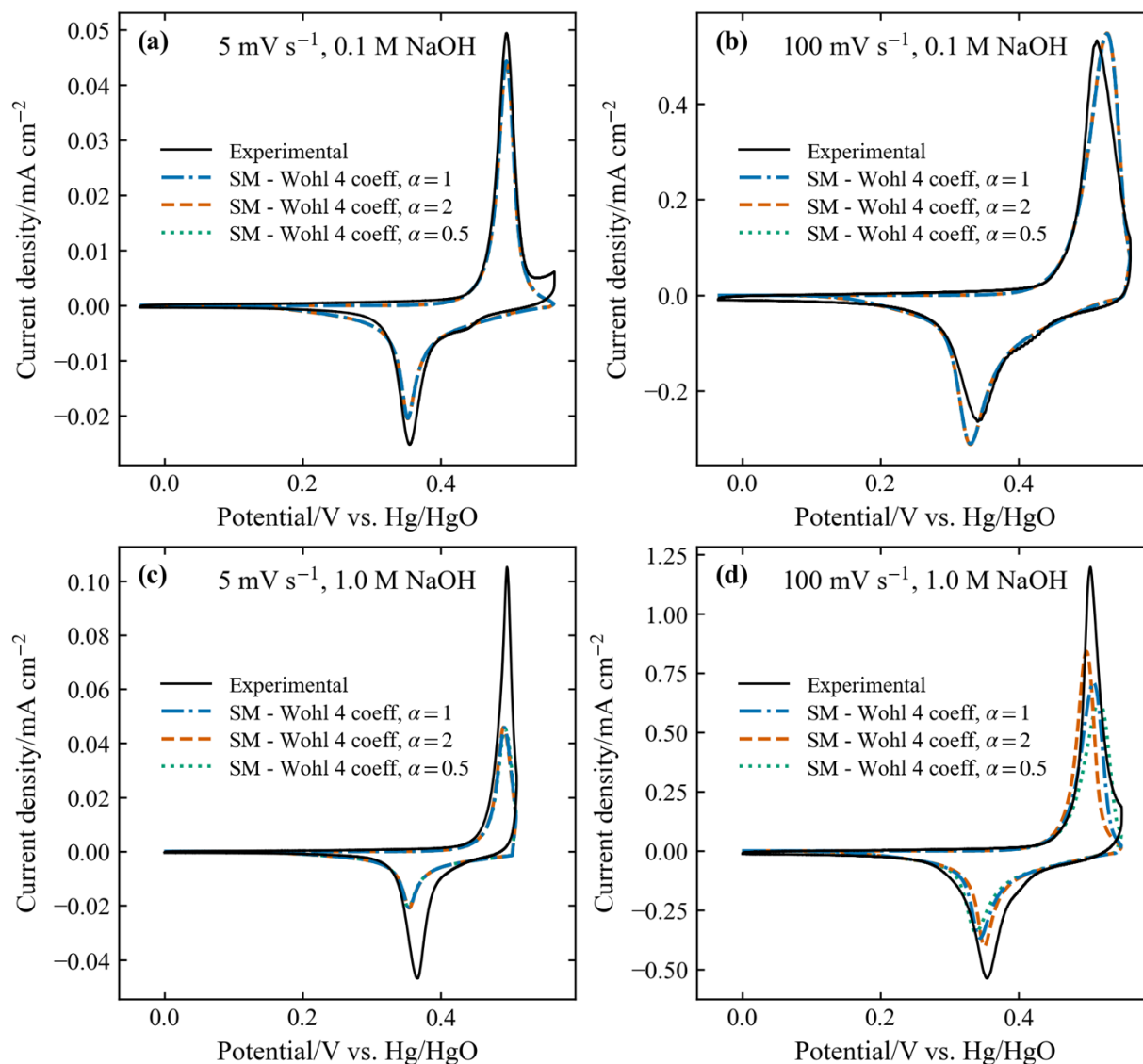


Fig. S14 Simulated cyclic voltammograms using different partial orders of OH⁻ in the exchange current density expression for the nickel RDE in 0.1 M NaOH ((a) and (b)) and 1.0 M NaOH ((c) and (d)) at scan rates of 5 mV s⁻¹ and 100 mV s⁻¹, and 1000 rpm.

S24. Experimental Cyclic Voltammograms at Different NaOH Concentrations

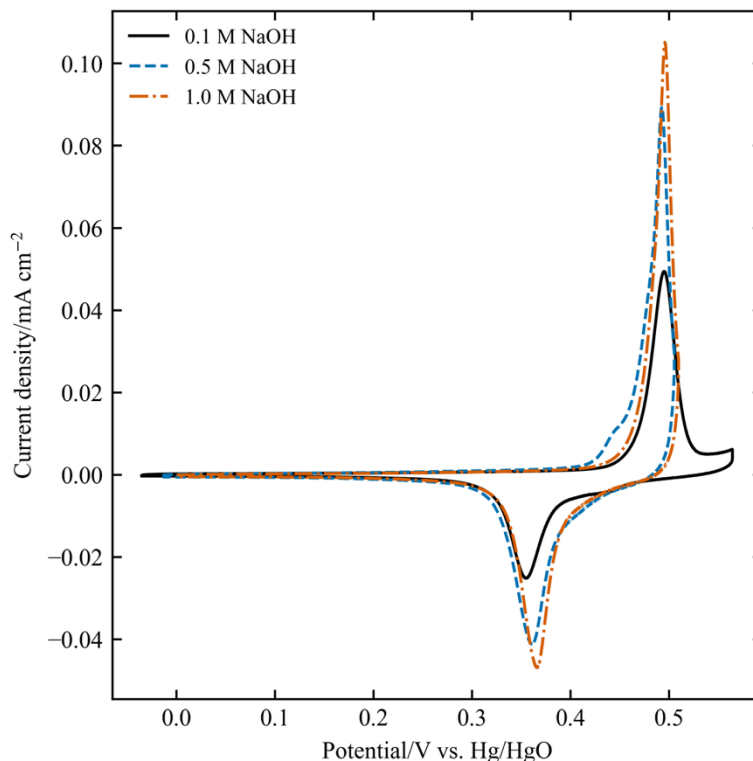


Fig. S15 Experimental cyclic voltammograms at NaOH concentrations of 0.1, 0.5, and 1.0 M.

S25. Screening Candidate Functional Forms for the Fraction of Electrochemically Active Proton Vacancies, $\Theta(c_{OH})$

To justify the functional form adopted for $\Theta(c_{OH})$ in equation (28) of the main text, we compared several candidate saturating and non-saturating functions of c_{OH} against an independent set of $c_{v,max}$ estimates. We obtained these estimates by calibrating $c_{v,max}$ separately at three NaOH concentrations (0.1, 0.5, and 1 M; 5 mV/s scan rate) via single-parameter PEST calibrations, summarized in **Table S16**.

Table S16. Calibrated maximum concentration of proton vacancies ($c_{v,max}$) for each OH^- concentration (c_{OH}).

c_{OH} (mol L ⁻¹)	$c_{v,max}$ (mol cm ⁻²)
0.1	$(3.84 \pm 0.02) \times 10^{-9}$
0.5	$(6.17 \pm 0.04) \times 10^{-9}$
1.0	$(6.37 \pm 0.06) \times 10^{-9}$

We fit each candidate function of the form $c_{v,max} = c_{v,total} \times \Theta(c_{OH})$, with $c_{v,total} = 2.65 \times 10^{-8}$ mol cm⁻² fixed, using weighted nonlinear least squares (weights = $1/\sigma_i$), where σ_i is the standard deviation of the calibrated $c_{v,max}$. Candidate functions are summarized in **Table S17** and shown in **Fig. S16**.

Table S17. Candidate functions of the fraction of electrochemically active proton vacancies ($\Theta(c_{OH})$) and adjusted parameters. In these equations, the OH^- concentration is in mol cm^{-3} . χ^2 is the weighted sum of squared residuals.

Function	$\Theta(c_{OH})$	Adjusted parameters	χ^2	Weighted R^2
Linear	$K \cdot c_{OH}$	$K = 409 \pm 2$	3.86×10^4	-6.88
Simple Langmuir	$\frac{K \cdot c_{OH}}{K \cdot c_{OH} + 1}$	$K = 745 \pm 4$	2.54×10^4	-4.18
Power Law	$K \cdot c_{OH}^\xi$	$K = 1.47 \pm 0.04$ $\xi = 0.251 \pm 0.003$	200.7	0.959
tanh saturation	$K \cdot \tanh[\xi \cdot c_{OH}]$	$K = 0.235 \pm 0.001$ $\xi = 7170 \pm 60$	7.85	0.998
Exponential saturation (equation (28))	$K[1 - \exp(-\xi \cdot c_{OH})]$	$K = 0.237 \pm 0.001$ $\xi = 9500 \pm 100$	4.51	0.999

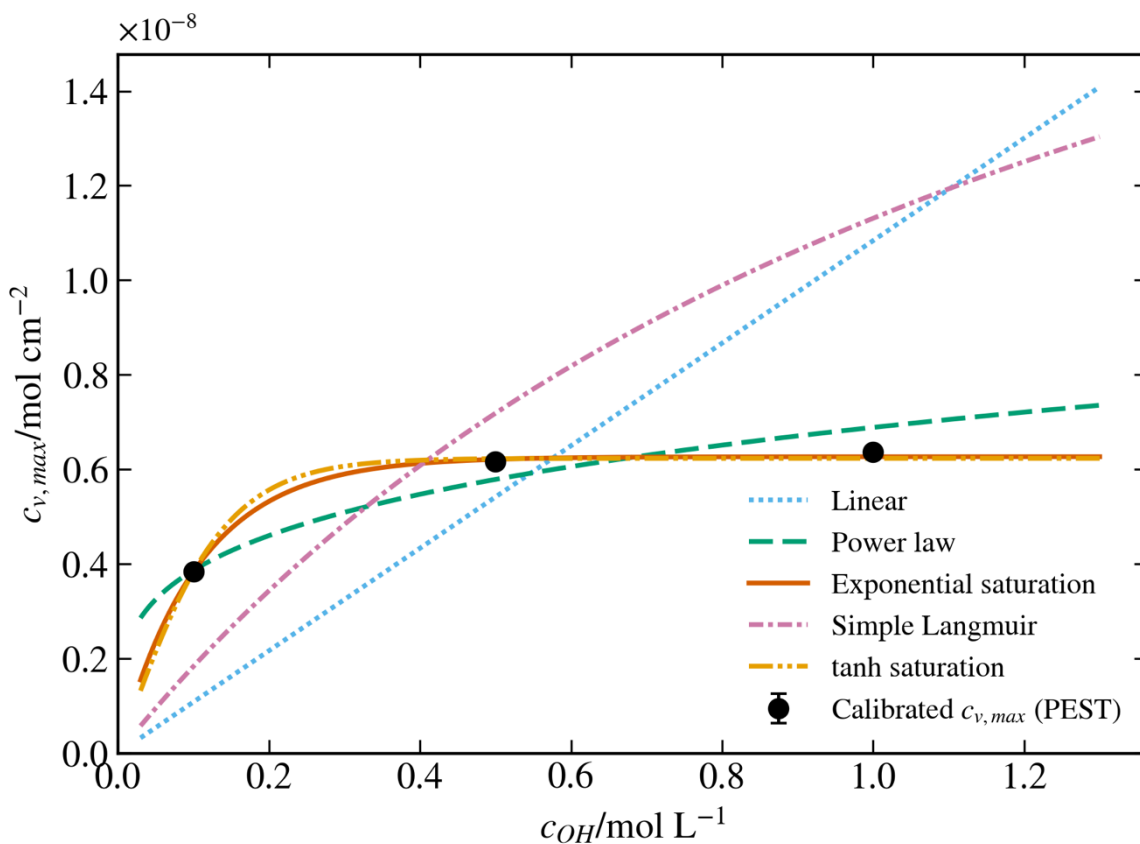


Fig. S16 Candidate functions of the fraction of electrochemically active proton vacancies ($c_{v,max} = c_{v,total} \times \Theta(c_{OH})$) and calibrated $c_{v,max}$ at different OH^- concentrations.

The linear and simple-Langmuir forms are clearly inadequate: both substantially overpredict $c_{v,max}$ at 1 M NaOH (weighted $R^2 < 0$), confirming that a single adjustable parameter cannot simultaneously capture the initial rise and the approach to a plateau observed in the data. The

power-law form fits the three points reasonably well but has no finite asymptote as $c_{OH} \rightarrow \infty$, which is physically inconsistent with the finite active-site density motivating equation (28), and is therefore excluded on those grounds despite its acceptable χ^2 . The exponential-saturation and *tanh* forms both reproduce the data closely and are statistically difficult to distinguish given only three concentrations ($\Delta\chi^2 = 3.3$ with one degree of freedom per fit); we selected the exponential-saturation form because it gave the marginally better fit and is the form reported in equation (28).

We note that this comparison is intended only to screen among candidate shapes for $\Theta(c_{OH})$ and uses $c_{v,max}$ values calibrated independently at each concentration for that purpose. The calibration constants K and ξ reported for equation (28) in the main text are instead obtained by simultaneous, direct calibration of the full continuum model against the experimental cyclic voltammograms at 0.1 and 1 M NaOH, 5 and 100 mV s⁻¹, and differ from the illustrative values in **Table S17** above as a result.

Given the limited number of NaOH concentrations available (three), this screening should be regarded as qualitative rather than statistically rigorous; it rules out functions with the wrong asymptotic behavior but does not uniquely establish the exponential-saturation form over other saturating alternatives such as *tanh*.

S26. Reproducibility Study of the Experimental Cyclic Voltammograms

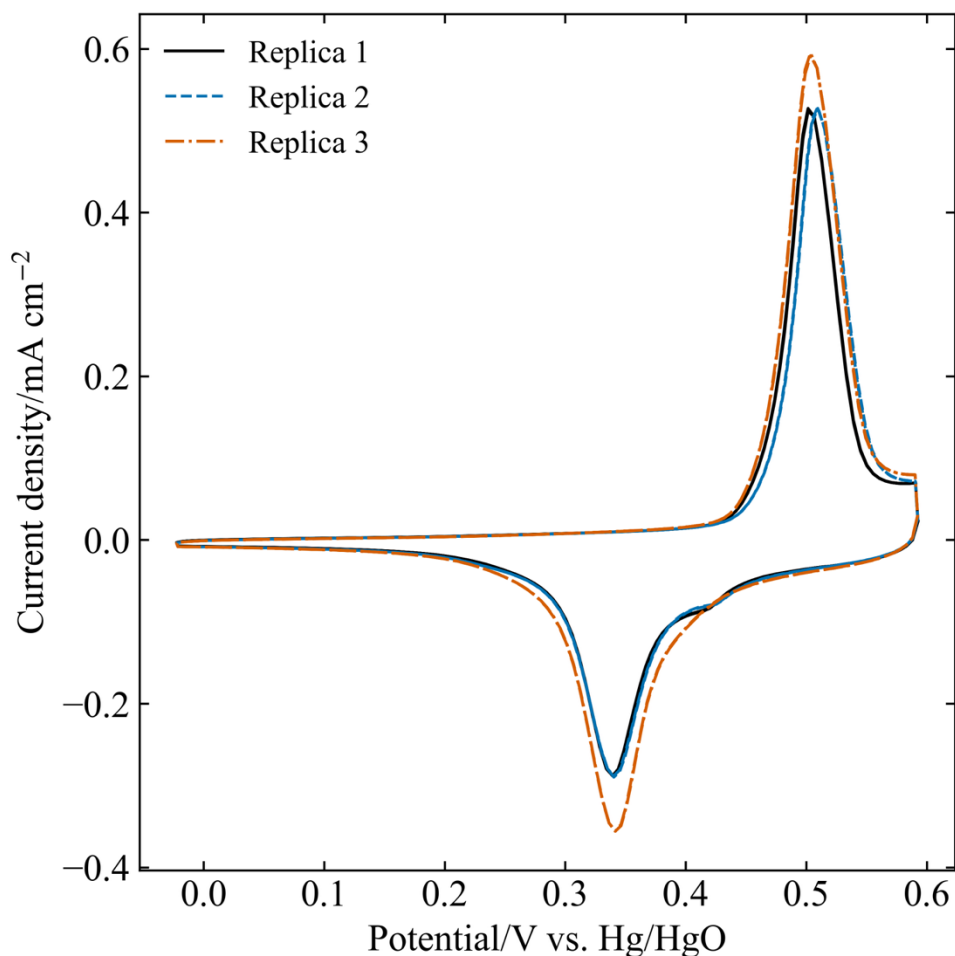


Fig. S17 Comparison of three replicas of the cyclic voltammetry of the nickel RDE in 0.2 M NaOH at 100 mV s⁻¹ and 0 rpm.

Table S18. Comparison of the anodic and cathodic peak current densities and potentials for three replicas of the cyclic voltammetry of the nickel RDE in 0.2 M NaOH at 100 mV s⁻¹ and 0 rpm.

Quantity	Average	Standard deviation	Percentage different between highest and lowest
Anodic peak current density (mA cm ⁻²)	0.5503	0.0387	12.8%
Cathodic peak current density (mA cm ⁻²)	-0.3113	0.0387	19.0%
Anodic peak potential (V)	0.5049	0.0042	1.6%
Cathodic peak potential (V)	0.3404	0.0011	0.6%

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