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Research Article

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Posted Date: October 13th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10943146/v1>

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Additional Declarations: No competing interests reported.

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

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Abstract

Nickel is a low-cost, widely available metal well suited to large-scale applications such as wastewater treatment, sensors, and electrosynthesis, where the electrochemically active species is a thin $\text{Ni(OH)}_2/\text{NiOOH}$ surface layer. Existing models are largely battery-oriented, limiting their transferability across these applications. Here, the $\text{Ni(OH)}_2/\text{NiOOH}$ reaction was modeled on a nickel rotating disk electrode (RDE) to simulate cyclic voltammetry, combining species conservation equations, Butler–Volmer kinetics, and a Nernst expression with composition-dependent activity coefficients, with kinetic and thermodynamic parameters fitted to experimental data. Hysteresis between oxidation and reduction was captured by assigning distinct equilibrium-potential parameters to the forward and reverse scans. A kinetics-limited Surface Model was compared to a proton-diffusion-limited Layer Model using a block permutation test, which found no statistically significant difference in fit quality; the Surface Model was therefore preferred for its simpler structure and better-constrained parameters. The dominant factor in reproducing experimental voltammograms was the description of the activity coefficients in the equilibrium-potential expression; among several candidates, a Wohl expansion using four proton–proton self-interaction coefficients was selected. Model predictions were extended across 0.1–1.0 M NaOH by introducing an empirical correction that made the maximum concentration of electroactive material depend on surface OH^- concentration. Simulated and experimental voltammograms were both insensitive to rotation speed, indicating that OH^- transport does not limit the reaction at 100 mV s^{-1} . Because the RDE geometry defines mass transport unambiguously, the model provides a foundation, extensible to organic substrates, for mathematical modeling of organic electrooxidation on nickel electrodes.

Keywords

$\text{Ni(OH)}_2/\text{NiOOH}$ electrocatalysis, Cyclic voltammetry simulation, Rotating disk electrode, Activity coefficients, Equilibrium potential hysteresis

1. Introduction

For more than a century, nickel hydroxide has been recognized as a valuable electrode material for rechargeable alkaline battery systems [1], and more recently, it has been used in electrocatalysis [2], electrosynthesis [3], electrochemical sensors [4], supercapacitors [5], and electrochromic devices [6]. In all these applications, the seemingly reversible transformation from nickel hydroxide (Ni(OH)_2) to nickel oxyhydroxide (NiOOH) plays a central role, which has driven the need to not only understand but also predict its behavior to optimize performance in each application. However, this reaction has proven difficult to characterize experimentally and theoretically due to the structural complexity of the electroactive material (including different polymorphs, structural disorder, and impurities), which significantly affects catalytic activity and solid-state transport properties [7].

From a theoretical perspective, early macroscopic models of the $\text{Ni(OH)}_2/\text{NiOOH}$ reaction primarily focused on battery applications, where the high concentrations of OH^- in the cell (1 to 8 M) and the challenges posed by the electrode's porous structure necessitated the use of concentrated solution theory [8–11] and porous electrode theory [11–14]. Micka and Rousar [15, 16], among the first to apply porous-electrode theory to nickel hydroxide electrodes, developed a 1-D model based on known electrochemical behavior and transport equations, which enabled only limited prediction of theoretical discharge characteristics because the voltage curves could not be satisfactorily fitted by assuming an ideal solid-phase solution. Fan and White [17, 18] refined these predictions by modifying the expression for the open-circuit potential of the reaction according to the non-ideal solid-phase solution theory presented by Barnard et al. [19], in which the activities of the oxidized and reduced nickel species are considered rather than their mole fractions. Still, these modifications were insufficient to accurately predict the percent utilization of the active material as a function of current. More details about these contributions and related work can be found in the excellent reviews by Srinivasan et al. [20] and Gomadam et al. [21].

Although existing macroscopic models of $\text{Ni(OH)}_2/\text{NiOOH}$ have been refined to accurately reproduce and explain charge/discharge behavior in battery systems, their reliance on concentrated-solution and porous-electrode theories makes them poorly suited for fundamental studies of organic oxidation on nickel electrodes, which are critical for the design, optimization, and scale-up of cost-effective nickel-based electrolyzers and sensors. A representative case is the electrochemical conversion of biosolids into circular fertilizers [22–25] and value-added products [26], in which the Ni(II)/Ni(III) couple mediates the oxidation of chemically complex organic substrates in dilute alkaline media. Because such processes are operated at low applied potentials to maximize selectivity toward the target product, the potential window of practical interest is precisely the one in which the $\text{Ni(OH)}_2/\text{NiOOH}$ transformation, rather than oxygen evolution, governs the current. These systems instead feature lower OH^- concentrations (0.1 to 1 M), mass-transport limitations of the substrate [27–29] or of OH^- [30] from the bulk solution, and, in some cases, impurities that may interfere with the electrochemical response [31–33]. Therefore, these distinct experimental conditions require a separate theoretical treatment.

Cyclic voltammetry is particularly well suited to this task, as it resolves electron-transfer steps and distinguishes direct from mediated catalytic oxidation routes [34–38]. Ta and Newman [39] treated cathodically deposited Ni(OH)_2 (10–40 nm) as a 1-D thin-film intercalation electrode including proton diffusion and oxygen evolution, reproducing the general electrode behavior across cyclic, potentiostatic, and galvanostatic waveforms, but only at 0.01–1 mV s^{-1} . Koshel' and Kostyrya [40] added proton migration, a state-of-charge-dependent diffusion coefficient, and a battery-type activity-coefficient correction to the Nernst equation; this model is more sophisticated thermodynamically and transport-wise, but was developed for an idealized single crystal rather than validated against voltammograms from a defined electrode geometry.

Seghioeur et al. [41] proposed a mathematical model for the $\text{Ni(OH)}_2/\text{NiOOH}$ reaction over a nickel disk based on the rate of phase transformation in the solid state. The authors assumed rapid proton diffusion through the bulk of the deposit and considered the contribution of the oxygen evolution reaction (OER) to the total current. The exchange current density of $\text{Ni(OH)}_2/\text{NiOOH}$ (j_0) and OER (j_{0,O_2}), and the equilibrium potential of the $\text{Ni(OH)}_2/\text{NiOOH}$ reaction (E_{eq}) were adjusted to obtain the best fit with the experimental curves, resulting in only general agreement between the anodic and cathodic peak positions but not the shapes. Finally, Medrano-Banda et al. [42] developed a simple $\text{Ni(OH)}_2/\text{NiOOH}$ model to study glucose oxidation on electrodeposited nickel electrodes and to understand the effects of glucose concentration and scan rate on cyclic voltammetry. The authors assumed that the $\text{Ni(OH)}_2/\text{NiOOH}$ reaction occurs only at the nickel electrode surface and follows the Langmuir isotherm, neglecting the oxide layer's 3D nature. The OER was also not considered. The standard potential of the reaction (E^0) and the charge-transfer kinetic constant

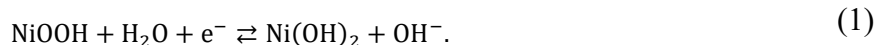
(k_1) were fitted to the experimental cyclic voltammetry. Only semi-quantitative agreement was achieved since the simulated voltammograms showed broader peaks than the experimental ones.

A common feature of the models proposed by Seghioer et al. [41] and Medrano-Banda et al. [42] is that they are generally simpler than those proposed for nickel-based batteries or by Ta and Newman [39] and Koshel' and Kostyrya [40], because proton diffusion is not considered (or is assumed to be fast) and the equilibrium potential is assumed to be constant. Further, across all four studies, the effect of OH^- concentration on the kinetics and shape of the cyclic voltammetry remains unaddressed. These remarks raise the question of how detailed or complex the model must be to accurately predict $\text{Ni}(\text{OH})_2/\text{NiOOH}$ cyclic voltammetry, which considerations are most important, and how OH^- concentration can be included in the proposed model.

In this work, a mathematical model was developed for the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ transformation within the oxide layer that forms on a nickel RDE in alkaline media. Kinetic and thermodynamic parameters were obtained by fitting simulated cyclic voltammograms to experimental data, with the equilibrium potential expressed using composition-dependent activity coefficients, and several activity-coefficient models were compared. Two mechanistic approaches were evaluated: one in which proton diffusion through the oxide layer limits the rate (Layer Model), and one in which diffusion is fast and the kinetics are set by charge transfer at the oxide/electrolyte interface (Surface Model). Under the conditions studied, neither model reproduces the experimental voltammograms unless the equilibrium potential is described by a four-coefficient Wohl expansion with distinct parameters for the oxidation and reduction sweeps. An empirical dependence of the active proton-vacancy fraction on surface OH^- concentration extends the Surface Model to 0.1–1.0 M NaOH. The resulting framework is deliberately tractable and constitutes a first step toward modeling organic electrooxidation on nickel electrodes, for which the rotating disk geometry already supplies a well-defined description of substrate mass transport.

2. Model description

Our goal is to derive well-defined, robust mathematical equations that simulate proton intercalation and deintercalation in the presence of OH^- ions during the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ reaction shown in equation (1), which occurs in a thin film at the surface of a nickel electrode. Equation (1) was considered without specifying the phases involved ($\alpha\text{-Ni}(\text{OH})_2/\gamma\text{-NiOOH}$ or $\beta\text{-Ni}(\text{OH})_2/\beta\text{-NiOOH}$). Thus, the estimated parameters from this model are a function of the specific phase distribution, hydration level, and structural disorder of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ layer.



The development of the mathematical models was broken down into four subsections, starting with presenting the two approaches to model the system: the Layer Model (LM) and Surface Model (SM); followed by the equations describing the material balances in each model, the kinetics considerations based on the Butler-Volmer equation, and finally the treatment of the system thermodynamics is discussed.

2.1 Modelling approaches

For the bare nickel RDE, two possible 1-D models can be proposed, as illustrated in **Fig. 1**. The first, called “Layer Model,” follows the classical view of the reaction mechanism previously developed for battery systems [43–45], in which the reaction rate is limited by proton diffusion through the nickel hydroxide layer of characteristic thickness a . The second model, a simplified version of the first called “Surface Model,” assumes that a is relatively small, resulting in a short proton diffusion path, so the process is faster than proton/electron transfer at the nickel hydroxide/electrolyte interface. This approach implies that $\text{Ni}(\text{OH})_2$ and NiOOH exist only at the electrode/electrolyte interface as a few molecular layers. The solution domain extends up to 2δ , where δ is a characteristic diffusion length of the system $\delta = 1.805D_{s,j}^{1/3}v^{1/2}\omega^{-1/2}$.

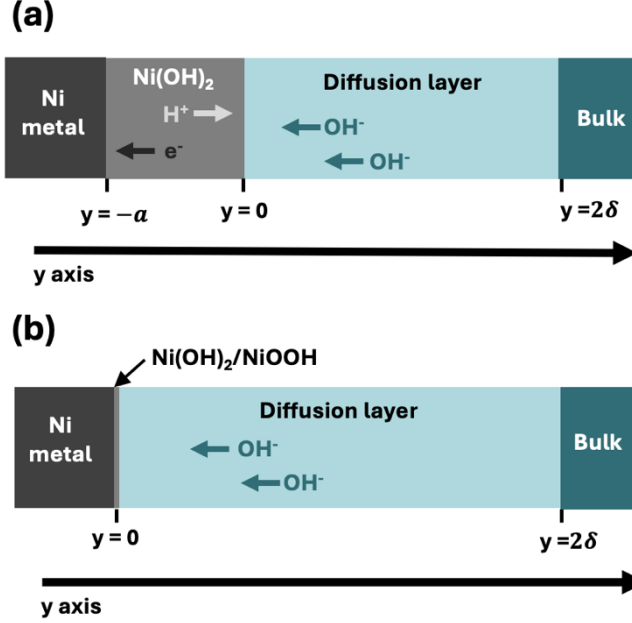


Fig. 1 Schematics of a nickel electrode in alkaline media for the (a) Slow proton diffusion and (b) Fast proton diffusion one-dimensional models. δ is a characteristic diffusion length of the system $\delta = 1.805 D_{s,j}^{1/3} \nu^{1/6} \omega^{-1/2}$.

A common aspect of both models is that the focus will be on proton vacancies rather than on the protons themselves, since the vacancy mole fraction is directly proportional to the NiOOH mole fraction. This species is of special interest because it has been shown to mediate the electro-oxidation of organic compounds in alkaline media [2, 3, 46].

2.2 Transport phenomena

The mass transport in the electrolyte is described using the theory of dilute solutions [11], and the electrolyte is assumed to consist solely of hydroxide ions (OH^-), sodium ions (Na^+), and water (H_2O). Given the characteristics of the RDE system [47], only diffusion near the electrode and in the direction normal to the disk surface (y -direction) needs to be considered. Therefore, the material balance of species j in the y -direction is defined in equation (2).

$$\frac{\partial c_j}{\partial t} = -\frac{\partial N_j}{\partial y} + R_j, \quad (2)$$

where c_j is the concentration in mol cm^{-3} , N_j is the molar flux in $\text{mol cm}^{-2} \text{s}^{-1}$, and R_j is the net generation rate by homogeneous chemical reactions of species j . The R_j is equal to zero since there is no homogeneous reaction occurring in the system, while N_j is affected by ionic migration, diffusion, and convection [11], as shown in equation (3).

$$N_j = -z(j) \frac{D_{s,j} F c_j}{RT} \frac{\partial \phi_2}{\partial y} - D_{s,j} \frac{\partial c_j}{\partial y} + v_y c_j, \quad (3)$$

where $z(j)$ is the charge number, $D_{s,j}$ is the diffusion coefficient of species j , F is the Faraday constant, R is the ideal gas constant, T is the temperature, and ϕ_2 is the potential in the solution. For the RDE system, the convection is governed by the flow velocity towards the electrode surface and in the y -direction, v_y , defined in equation (4) [47].

$$v_y = -0.51 \omega^{\frac{3}{2}} \nu^{-\frac{1}{2}} y^2, \quad (4)$$

where ω is the angular velocity of rotation, ν is the kinematic viscosity, and y is the distance from the RDE surface.

The variation of the potential in the solution, ϕ_2 , in the electrolyte can be specified by considering the electroneutrality condition, shown in equation (5) [11].

$$\sum_j z(j) c_j = 0. \quad (5)$$

For the Layer Model, inside the solid nickel hydroxide layer, the mass transport of the proton vacancies (or protons) is assumed to be purely diffusional and only in the y-direction, illustrated in **Fig. 1**, obeying Fick's second law as shown in equation (6).

$$\frac{\partial c_v}{\partial t} = D_{s,v} \frac{\partial^2 c_v}{\partial y^2}, \quad (6)$$

where c_v is the concentration of proton vacancies in mol cm⁻³ and $D_{s,v}$ is the diffusion coefficient of proton vacancies in the solid phase, which is assumed to be equal to the diffusion coefficient of protons (D_{s,H^+}) in the same phase.

Within the solid layer, there is no distributed reaction because it is assumed that all Faradaic current enters only at the nickel hydroxide-electrolyte interface and flows in the y-direction, while proton diffusion and electron transfer occur simultaneously. Therefore, by conservation of charge, the divergence of the current density must be zero inside the solid layer, as shown in the 1-D case by equation (7).

$$\frac{\partial i}{\partial y} = \frac{\partial}{\partial y} \left(\sigma \frac{\partial \phi_1}{\partial y} \right) = 0, \quad (7)$$

where σ is the conductivity of the solid in S cm⁻¹, ϕ_1 is the potential in the solid phase in V, and i is the current density circulating through the system in A cm⁻². The conductivity of the solid phase depends on the fractions of Ni(OH)₂ and NiOOH present, as NiOOH has been reported to have significantly higher conductivity than Ni(OH)₂ [7, 48, 49]. However, no single value has been reported for the conductivity of either material, given that it depends on their hydration level and other microstructural characteristics, details that are presumably unknown for the specific conditions chosen in this work. Thus, the functional relationship presented in equation (8) was chosen to describe the conductivity as a function of the fraction of proton vacancies (defined in equation (11)) because it has been successfully used in previous models of the Ni(OH)₂/NiOOH system [45] and yields reasonable values for Ni(OH)₂ ($\sigma = 2.51 \times 10^{-5}$ S cm⁻¹) and NiOOH ($\sigma = 0.1185$ S cm⁻¹).

$$\sigma = 0.1185 \exp[-8.459(1 - \theta_v)^4], \quad (8)$$

Critically, with these values for the σ , the ohmic drop across the solid layer would be negligible for very thin Ni(OH)₂ layers (< 10 μm). However, we still consider this phenomenon, so the mathematical framework developed here is extensible to systems with thicker Ni(OH)₂ layers.

To facilitate calculations and the visualization of concentration profiles, dimensionless species concentrations are defined in equations (9)-(11) in terms of the bulk or maximum concentration of chemical species.

$$C_{OH} = \frac{c_{OH}}{c_{b,OH}} \quad (9)$$

$$C_{Na} = \frac{c_{Na}}{c_{b,Na}} \quad (10)$$

$$\theta_v = \frac{c_v}{c_{v,max}} \quad (11)$$

where $c_{b,OH}$ and $c_{b,Na}$ are the bulk concentrations of OH⁻ and Na⁺, respectively, and $c_{v,max}$ is the maximum concentration of proton vacancies (or protons) available in the nickel hydroxide layer. The dimensionless concentration θ_v can be regarded as the mole fraction of proton vacancies, and it is related to the mole fraction of protons (θ_{H^+}) as shown in equation (12).

$$\theta_v + \theta_{H^+} = 1. \quad (12)$$

The distance, time, current density, and potential remained dimensional variables to allow direct comparison with experimental data. Furthermore, the range of scan rates studied and the different modeling approaches spanned many characteristic time and length scales, so imposing a single normalization could have obscured rather than simplified the simulation results.

To solve the mass balances presented previously, the following boundary conditions are defined:

- At the interface between the nickel metal and the nickel hydroxide ($y = -a$), the concentrations of Na^+ and OH^- are zero, there is no flux of proton vacancies (equation (13)), and the potential in the solid is equal to the applied potential, V_d .

$$D_{s,v} c_{v,max} \frac{\partial \theta_v}{\partial y} = 0. \quad (13)$$

- At the interface between the nickel hydroxide and the electrolyte ($y = 0$), the molar flux of species j (OH^- , Na^+ , and proton vacancies) equals the rate of their consumption or production, as shown in equation (14). The potential in the solution is defined by the electroneutrality condition (equation (5)), while the potential in the solid follows Ohm's law (equation (15)).

$$\frac{s(j)}{nF} i + N_j = 0. \quad (14)$$

$$i = -\sigma \frac{\partial \phi_1}{\partial y}. \quad (15)$$

where $s(j)$ is the stoichiometric coefficient of species j and n is the number of electrons transferred.

- At the bulk of the electrolyte ($y = 2\delta$), the concentrations of OH^- and Na^+ are equal to the bulk concentrations, and the mole fraction of proton vacancies and the potential (both in the solution and the solid) are equal to zero.

In the Surface model, the system extends from the electrode surface to the solution bulk, as shown in **Fig. 1**. Therefore, only the governing equations on the electrolyte side are considered (neglecting the potential in the solid state since it is irrelevant in this system), and the boundary conditions at $y = 0$ are the same except for the mole fraction of proton vacancies, which is now defined by equation (16).

$$c_{v,max} \frac{d\theta_v}{dt} = -\frac{s(\theta_v)}{nF} i. \quad (16)$$

Similarly, the boundary conditions previously defined for $y = 2\delta$ apply to this approach. A summary of the model equations is presented in **Tables S1** and **S2**.

2.3 Kinetics

The kinetics of the electrochemical reaction in equation (1) is assumed to follow the Butler-Volmer equation (equation (17)), which relates the current density, i , and the overpotential, η .

$$i = i_0 \left\{ \exp \left[\frac{(1 - \beta)nF}{RT} \eta \right] - \exp \left[\frac{-\beta nF}{RT} \eta \right] \right\}, \quad (17)$$

where i_0 is the exchange current density and β is the symmetry factor. The exchange current density, shown in equation (18), is a function of the mole fraction of proton vacancies (θ_v) and depends on the kinetic constants of the oxidation (k_a) and reduction (k_c) reactions, the OH^- concentration at the electrode surface (c_{OH}), and the maximum concentration of proton vacancies ($c_{v,max}$), which would be a volumetric concentration in mol cm^{-3} for the Layer Model and a surface concentration in mol cm^{-2} for the Surface Model. It is assumed that the maximum concentration of proton vacancies in NiOOH equals the maximum concentration of protons available to react within Ni(OH)_2 , even though the volumes of Ni(OH)_2 and NiOOH are not necessarily the same.

$$i_0 = nF k_a^\beta k_c^{1-\beta} c_{v,max} (c_{b,OH}^\alpha)^\beta (C_{OH}^\alpha)^\beta (1 - \theta_v)^\beta \theta_v^{1-\beta}. \quad (18)$$

Since k_a and k_c cannot be estimated separately with reasonable precision, they were consolidated into a single kinetic parameter (apparent kinetic constant): $k_a^\beta k_c^{1-\beta} = k_0$. Additionally, the partial order of the OH^- concentration in the rate equation (α) is initially assumed to be 1, with equation (1) treated as an elementary reaction (see Section S2 of the **Supplementary Information**).

The overpotential is defined in equation (19).

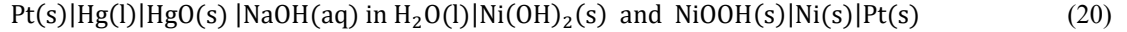
$$\eta = \phi_1 - \phi_2 - U(\theta_v), \quad (19)$$

where ϕ_1 is the potential in the solid, ϕ_2 is the potential in the solution, and $U(\theta_v)$ is the equilibrium potential that depends on the mole fraction of proton vacancies. In the Surface Model, the potential in the solid equals the applied potential ($\phi_1 = V_d$), as the potential drop inside the solid phase is neglected. V_d , ϕ , and $U(\theta_v)$ are reported in V vs. Hg/HgO reference electrode.

Although the oxygen evolution reaction (OER) has previously been regarded as an important parasitic reaction [50], its contribution to the total current in the potential range of the $Ni(OH)_2/NiOOH$ reaction has been reported to be minor in Fe-free electrolytes [51–53]. This is consistent with the applications motivating this work, which target potentials where charge is preferentially directed toward the $Ni(OH)_2/NiOOH$ couple rather than lost to oxygen evolution [22–26]. However, we found that OER contributions to the total anodic charge might be scan-rate dependent in our own data, remaining small at the faster scan rates used for model calibration but more appreciable at the slowest rate examined (**Supplementary Information**, Section S11). Still, explicitly treating the OER as a competing reaction is beyond the scope of the present framework; the model instead describes the potential window over which the $Ni(OH)_2/NiOOH$ couple is treated as the dominant current-carrying process.

2.4 Thermodynamics

The equilibrium potential, U , of the nickel hydroxide electrode relative to a Hg/HgO reference electrode, whose cell diagram is presented in equation (20):



can be defined according to equation (21):

$$U = U^\circ + \frac{RT}{nF} \ln \left(\frac{\theta_v}{1 - \theta_v} \right) + \frac{RT}{nF} \ln \left(\frac{\gamma_v}{\gamma_{H^+}} \right), \quad (21)$$

where U° is the standard reduction potential of the reaction in equation (1) vs. Hg/HgO and γ_j is the molar activity coefficient of species j (protons and proton vacancies). In equation (21), it was assumed that the reference electrode's internal solution and the electrolyte have the same composition and concentration (liquid junction is ignored), and that the relative activity of water was approximately one. This assumption about solution composition holds experimentally since the measured potentials were post-corrected for the liquid junction potential when the external and internal solutions differed in composition (Section S15 of the **Supplementary Information**). Consequently, in this Hg/HgO reference scale, U is independent of OH^- activity. The full derivation of equation (21) is presented in Section S3 of the **Supplementary Information**.

Several expressions for the activity coefficients in equation (21) have been derived in the literature for intercalation electrodes [54, 55], which differ in how the molar excess Gibbs free energy G^E is defined relative to an ideal solution and with respect to the chosen reference state. In the case of lithium intercalation/deintercalation [54], and making an analogous derivation in this work, the reference states are defined to satisfy the conditions in equations (22) and (23).

$$\gamma_{H^+} \rightarrow 1 \text{ as } \theta_{H^+} \rightarrow 0 \quad (22)$$

$$\gamma_v \rightarrow 1 \text{ as } \theta_v \rightarrow 1. \quad (23)$$

Considering the reference states selected, the deviations from the ideal solution can only be due to the interactions between intercalated protons. If the non-vanishing G^E relative to an ideal dilute proton solution is expressed by a series expansion in θ_{H^+} , as proposed by Verbrugge and Koch [54], the equilibrium potential takes the form of equation (24).

$$U = U^\circ + \frac{RT}{nF} \ln \left(\frac{\theta_v}{1 - \theta_v} \right) - \frac{1}{nF} \sum_{k=2}^N \Omega_k k (1 - \theta_v)^{k-1}, \quad (24)$$

where Ω_k is the k th self-interaction coefficient characterizing proton-proton interaction. In this work, self-interaction coefficients from Ω_2 through Ω_N were considered, where N ranges from 3 to 7; an expansion truncated at Ω_N is referred to throughout as an "N-1 coefficient" model.

Other works [19, 55] consider Ni(OH)_2 and NiOOH as distinct, non-dissociated components of a solid solution, analogous to mixtures of non-ionic organic liquids. In this case, G^E was described by the Two-Parameter Margules and van Laar models, resulting in the expressions for the equilibrium potential shown in equations (25) and (26) [55], respectively.

$$U = U^\circ + \frac{RT}{nF} \ln \left(\frac{\theta_v}{1 - \theta_v} \right) - \frac{RT}{2nF} [-2A_0 + 4A_0(1 - \theta_v) - 2B_0 + 6B_0(1 - \theta_v) - 3B_0(1 - \theta_v)^2], \quad (25)$$

$$U = U^\circ + \frac{RT}{nF} \ln \left(\frac{\theta_v}{1 - \theta_v} \right) - \frac{RT}{nF} \left\{ \frac{A'[B'(1 - \theta_v)^2 - 1 + 2(1 - \theta_v) - (1 - \theta_v)^2]}{[\theta_v + B'(1 - \theta_v)]^2} \right\}, \quad (26)$$

where A_0 and B_0 are the two parameters in Margules model, and A' and B' are the two parameters in van Laar model. The three expressions shown in equations (24), (25), and (26) were considered candidates for describing the equilibrium potential of the reaction.

An important phenomenon regarding the equilibrium potential that the equations above do not capture is its robust, rate-independent hysteresis: its value depends on whether the potential at a given electrode composition was approached from higher or lower potentials. Ta and Newman [56] investigated this feature and attributed the consistent ~95 mV separation between oxidation and reduction current-density peaks in cyclic voltammetry (independent of scan rate at scan rates lower than 1 mV s⁻¹) to hysteresis in the charging and discharging cycles. The authors reproduced this peak separation in cyclic voltammetry using an empirical expression for the equilibrium potential that shifts by an offset of ±46 mV, depending on whether the scan is forward (oxidation, +46 mV) or backward (reduction, -46 mV). However, following this approach yields cyclic voltammogram simulations with perfectly symmetrical anodic and cathodic peaks (see **Fig. S1**), whereas experimental anodic and cathodic peaks vary considerably in shape and intensity.

Srinivasan et al. [57] further investigated this hysteresis behavior, explaining it with a domain model in which the electrode is treated as an ensemble of domains, each with a critical potential for proton extraction during oxidation and a distinct critical potential for proton insertion during reduction; the oxidation and reduction boundary curves arise from two separate distributions of these critical potentials across the domain population. Consistent with this framework and following the precedent of fitting distinct empirical parameter sets to the oxidation and reduction boundary curves [57], each adjustable coefficient in equations (24)–(26), including the activity-coefficient parameters and the standard equilibrium potential, was assigned separate values for the forward (oxidation) and backward (reduction) scans. The initial values for these adjustable parameters (except Ω_4/F through Ω_7/F) were obtained by fitting equations (24)–(26) to the charge and discharge curves at relatively low current density (See **Fig. S2**), which served as a rough approximation of how the equilibrium potential varies with the fraction of proton vacancies or state of charge. The initial values for Ω_4/F through Ω_7/F were arbitrarily set to 0.001.

3. Mathematical methods

The systems of nonlinear partial differential equations were discretized numerically using the control-volume formulation (or finite-volume method) [58] in the spatial dimension to ensure mass conservation, with implicit time-stepping in the temporal dimension. The volumes were centered at the node points, and dependent-variable values at those points were obtained assuming a piece-wise linear profile (PLP) [58]. Spatial grid independence for both models was confirmed via RMSE convergence analysis (see **Supplementary Information**, Section S6), yielding grid resolutions of 2,001 (Layer Model) and 1,001 (Surface Model) nodes for all simulations. Uniform spacing was employed within the solid oxide and electrolyte diffusion layer, but a much finer spacing was used in the oxide layer (1001 nodes over $a = 6$ nm) than in the electrolyte (1000 nodes over $2\delta = 61.6$ μm).

The discretized nonlinear equations were linearized using the Newton-Raphson method (the Jacobians were computed via symbolic differentiation in Maple 2024), and solved using the BAND J [11, 59, 60], which employs the lower-upper decomposition method subroutines, adapted from FORTRAN scripts developed by Botte [61, 62]. Additionally, a subroutine was used to post-correct the simulated current by smoothing the current spike at the transition between the forward and backward scans via interpolation (see **Fig. S5**). This spike arose from the sudden change in the equilibrium potential parameters (and thus the overpotential) at this transition point in the cyclic voltammogram. Furthermore, to prevent a mathematical singularity when $\theta_v = 1$ and $\theta_v = 0$ in equation (21), θ_v was constrained between 1×10^{-10} and $1 - 1 \times 10^{-10}$. Finally, the validity of the proposed modeling framework as well as the numerical solutions was tested against well-characterized systems (Section S8 of the **Supplementary Information**).

The unknown parameters in each model were estimated using the PEST (“Parameter ESTimation”) software package. PEST adjusts model parameters to minimize the sum of squared residuals between model outputs (numerical simulations) and observations (experimental data) via an iterative Gauss–Levenberg–Marquardt algorithm [63]. The simulations were fitted simultaneously to the experimental cyclic voltammograms at 5 and 100 mV s^{-1} to constrain the adjustable parameters. This approach prevents the fitted parameters from being biased toward the dynamics dominant at a single timescale, since the scan rate governs the relative timescales of interfacial kinetics and mass transport. The values of the known parameters and transport properties are presented in **Table 1** and were used for the simulations unless stated otherwise. The initial values for the dependent variable are presented in **Table S12**.

Table 1. Fixed model parameters.

Symbol	Parameter name	Value
n_j (SM)	Number of nodes in the y dimension for the Surface Model	1001
n_j (LM)	Number of nodes in the y dimension for the Layer Model	2001
T	Temperature (K)	298.15
ω	Disk rotation speed (rpm)	1000
nv^a	Number of data points (dimensionless)	1000
$\nu_{0.1}^b$	Kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$) for the 0.1 M NaOH	0.00909
$\nu_{0.5}^b$	Kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$) for the 0.5 M NaOH	0.00967
$\nu_{1.0}^c$	Kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$) for the 1 M NaOH	0.01054
D_{s,OH^-}^d	Diffusion coefficient of OH^- ($\text{cm}^2 \text{s}^{-1}$)	5.273×10^{-5}
D_{s,Na^+}^d	Diffusion coefficient of Na^+ ($\text{cm}^2 \text{s}^{-1}$)	1.334×10^{-5}
$D_{s,v}$	Diffusion coefficient of proton vacancies ($\text{cm}^2 \text{s}^{-1}$)	2.54×10^{-12}
a	Solid $\text{Ni}(\text{OH})_2$ thickness (cm)	6.0×10^{-7}
$z(\text{Na}^+)$	Charge number of Na^+ (dimensionless)	1
$z(\text{OH}^-)$	Charge number of OH^- (dimensionless)	-1
$s(\text{Na}^+)$	Stoichiometric coefficient of Na^+ (dimensionless)	0
$s(\text{OH}^-)$	Stoichiometric coefficient of OH^- (dimensionless)	1
$s(\theta_v)$	Stoichiometric coefficient of NiOOH /proton vacancies (dimensionless)	-1
sr	Scan rate (V s^{-1})	0.005 and 0.1
n_e	Number of electrons transferred (dimensionless)	1
β^c	Symmetry factor (dimensionless)	0.5

$c_{b,OH}$ and $c_{b,Na}$	Bulk concentration of OH^- and Na^+ (mol cm^{-3})	1×10^{-4} , 5×10^{-4} , and 1×10^{-3}
$c_{v,max}$ (LM) ^f	Maximum concentration of proton vacancies in the Layer Model (mol cm^{-3})	5.5391×10^{-3}
$c_{v,max}$ (SM) ^f	Maximum concentration of proton vacancies in the Surface Model (mol cm^{-2})	3.3235×10^{-9}
$\rho_{Ni(OH)_2}$ ^d	Density of $Ni(OH)_2$ (g cm^{-3})	4.1

^a The number of experimental points was reduced from its original size (7299 and 9119 points at 5 and 100 mV s^{-1} , respectively) by linear interpolation of potential and current onto a uniformly spaced grid of scan indices spanning the original data range. This was done to speed up calculations while keeping the same number of data points.

^b Kinematic viscosities were calculated from dynamic viscosities, estimated using the Jones–Dole equation, $\eta = \eta_0(1 + A\sqrt{c_{NaOH}} + Bc_{NaOH})$, with $A = 0.0036 \text{ dm}^{3/2} \text{ mol}^{-1/2}$ and $B(NaOH) = B(Na^+) + B(OH^-) = 0.085 + 0.122 = 0.207 \text{ dm}^3 \text{ mol}^{-1}$ [64]. $\eta_0 = 0.8904 \text{ mPa s}$ for water at 25 °C. However, the equation is strictly valid below $\sim 0.5 \text{ M}$; the estimate at 0.5 M is used in the absence of measured values at 25 °C and is consistent with the small sensitivity of the results to ν (which enters δ as $\nu^{1/6}$). Density values were computed using the Laliberté–Cooper model [65] with NaOH coefficients from the Supporting Information of [66]. Kinematic viscosity was calculated as $\nu = \eta/\rho$.

^c Calculated from the dynamic viscosity and density reported in [67].

^d Data obtained from [68]. Diffusion coefficients are for infinitely dilute solutions.

^e Since the experimental anodic/cathodic peak asymmetry could be produced kinetically ($\beta \neq 0.5$) rather than thermodynamically (different forward/backward equilibrium potential parameters), a sensitivity analysis was performed (Section S9 of the **Supplementary Information**), which established 0.5 as the optimal value.

^f See Section S10 of the **Supplementary Information**.

Although the layer thickness (a) and the diffusion coefficient of proton vacancies ($D_{s,v}$) were not known a priori, they were treated as fixed rather than adjustable parameters because they were not identifiable from the cyclic voltammetry data alone. Thus, the layer thickness was chosen from the literature-reported range of 2 to 10 nm for this system [69–75], and the diffusion coefficient was then estimated using that thickness (for more details, see Section S12 of the **Supplementary Information**). Although the specific combination of a and $D_{s,v}$ affected the values of the estimated kinetic parameter and, to a lesser extent, the coefficients in the activity expressions, it did not significantly affect the quality of the fit to the experimental data, nor the estimated standard equilibrium potentials.

Model selection among nested formulations (i.e., Layer Model variants with different numbers of Wohl self-interaction coefficients) was based on the Bayesian information criterion (BIC) [76], which penalizes additional parameters that do not meaningfully improve the fit. Comparisons among competing, non-nested regression equations are conventionally assessed using the Wilks test, originally developed by Wilks [77] and described by Williams [78], following the presentation given by Himmelblau [79]: the method poses the comparison in terms of the homogeneity of the residual sums of squares among equations, coupled with a t-test on the resulting combination weights. This procedure assumes normally distributed, independent, and homoscedastic residuals, conditions that do not hold for the comparison between the Layer Model and Surface Model (**Supplementary Information**, Section S21). We instead assessed this comparison with a nonparametric block permutation test (**Supplementary Information**, Section S22). Finally, the root-mean-square error (RMSE) was also considered when initially assessing model suitability.

4. Experimental methods

Cyclic voltammetry (CV) measurements were conducted over a potential window of 0 to $\sim 0.6 \text{ V}$ vs. Hg/HgO, with the upper limit adjusted based on the electrolyte concentration. Measurements were performed at multiple scan rates (3, 5, 10, 25, 50, and 100 mV s^{-1}) and electrode rotation speeds (500, 1000, 2000, and 5000 rpm). Fresh electrolyte solution was used for each scan rate to ensure consistent, reproducible experimental conditions, unless otherwise specified (see reproducibility assessment in Section S26 of the **Supplementary Information**). All current densities in this work are reported with respect to the electrochemically active surface area (EASA), and the applied potential (E) was manually post-corrected for 85% of the uncompensated solution resistance (R_u) estimated by electrochemical impedance spectroscopy (EIS). Additionally, the applied potential was corrected for the liquid junction potential (E_{LJP}) for measurements in 0.1 and 0.5 M NaOH [80]. Thus, the reported applied potential (V_d) was determined as $V_d = E - 0.85 R_u i - E_{LJP}$. For more details regarding the reagents and instrumentation, electrolyte purification protocol, electrode activation, and calculation of the E_{LJP} and EASA (and evaluation of the EASA uncertainty effect over the estimated parameters), see Sections S14–S17 of the **Supplementary Information**.

5. Results and discussion

5.1 Activity expressions for the equilibrium potential

The results of the Layer Model calibrations with the 5 mV s^{-1} and 100 mV s^{-1} experimental cyclic voltammograms using different expressions for the activity coefficients in the equilibrium potential expression (equation (21)) are shown in **Fig. 2**, along with comparisons of the RMSE, which was used to evaluate the model's goodness of fit. The panels (a), (b), and (c) focus on comparing activity expressions using two coefficients (Wohl expansion was truncated to the second term in equation (24)), while panels (d), (e), and (f) compare the same activity expression based on Wohl expansion with different numbers of coefficients. The Surface Model calibrations show a similar trend and are shown in **Fig. S11**.

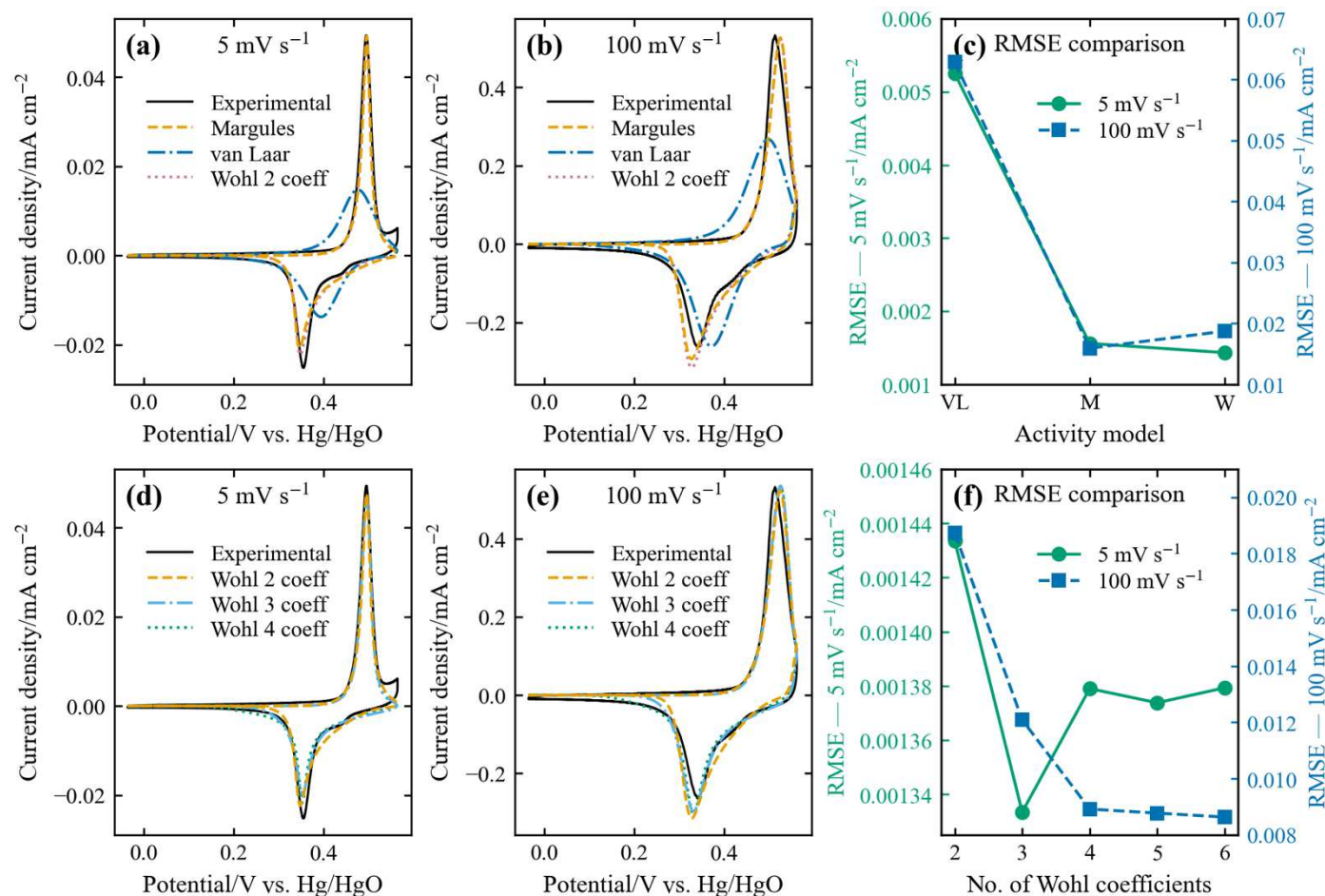


Fig. 2 Results of calibrating the Layer Model (LM) to experimental cyclic voltammograms of the nickel RDE in 0.1 M NaOH at 1000 rpm, and scan rates of 5 mV s^{-1} and 100 mV s^{-1} using different expressions for the activity coefficients in the equilibrium potential equation (equation (21)), based on 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 the van Laar (“VL”), Margules (“M”), and two-coefficient Wohl (“W”) in (c), and between different numbers of coefficients in the Wohl expansion in (f).

The calibration with the highest RMSE at both 5 mV s^{-1} and 100 mV s^{-1} used the activity-coefficient expression based on van Laar's model (equation (26)), and the major discrepancies between the corresponding simulation and the experimental data are evident in panels (a) and (b) of **Fig. 2**. The calibration results for the simulations using Margules and the two-coefficient Wohl expansion (with Ω_2 and Ω_3) had comparable RMSEs, as expected, since both are relatively simple, low-order descriptions of the excess Gibbs energy. Increasing the number of coefficients in Wohl's

activity expression (equation (24)) produces a systematic improvement in agreement between the experimental data and the simulation beyond that of the two-coefficient expression. Although not visible in panels (d) and (e) of **Fig. 2**, this trend is reflected in the RMSEs in panel (f). Even when the RMSE increases after three coefficients for the 5 mV s⁻¹ cyclic voltammograms, the difference between the lowest and highest RMSE (relative to the highest) is only 7%; this is small compared with the corresponding difference at 100 mV s⁻¹, where the reduction in RMSE from two to four coefficients is 52%.

The BIC in **Table 2** supports this choice for the Layer Model: it decreases substantially from two to four coefficients (-26,550 to -27,023, with the largest single improvement of -307 between three and four), then changes only marginally from four to five (-13) and increases from five to six (+10). Beyond four coefficients, several higher-order Ω_k values have standard errors comparable to or exceeding their fitted magnitude (e.g. $\Omega_5/F = 0.03 \pm 0.07$ V for five coefficients, backward scan), indicating they are no longer constrained by the data. The Surface Model's BIC sequence is less regular and would nominally favor six coefficients (**Table S15**), but its additional coefficients are likewise unresolved from zero. Therefore, four coefficients were retained for both models, with the Surface Model BIC discussed further in Section S19 of the **Supplementary Information**. Notice, however, that the improvement is modest in absolute terms, since the RMSE falls from approximately 3% of the peak current density with two coefficients at 100 mV s⁻¹ to approximately 1.5% with four, so a two-coefficient calibration may remain a reasonable, more economical choice where high precision is not required.

Table 2. Estimated parameters and Bayesian Information Criterion (BIC) for the simulation based on the Layer Model with the Wohl expansion (equation (24)) using different numbers of coefficients.

Parameter	2 coefficients	3 coefficients	4 coefficients	5 coefficients	6 coefficients
k_0 (s ⁻¹ cm ^{5/2} mol ^{-1/2})	$(1.78 \pm 0.05) \times 10^{-4}$	$(1.82 \pm 0.02) \times 10^{-4}$	$(1.81 \pm 0.02) \times 10^{-4}$	$(1.81 \pm 0.02) \times 10^{-4}$	$(1.81 \pm 0.02) \times 10^{-4}$
<i>Forward scan</i>					
U° (V vs. Hg/HgO)	0.4559 ± 0.0003	0.4454 ± 0.0004	0.4416 ± 0.0005	0.4431 ± 0.0006	0.4434 ± 0.0009
Ω_2/F (V)	-0.03481 ± 0.0004	-0.066 ± 0.001	-0.082 ± 0.002	-0.072 ± 0.004	-0.070 ± 0.008
Ω_3/F (V)	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)	0.408 ± 0.002	0.458 ± 0.003	0.430 ± 0.001	0.419 ± 0.002	0.410 ± 0.002
Ω_2/F (V)	0.074 ± 0.002	0.227 ± 0.006	0.135 ± 0.003	0.125 ± 0.009	0.11 ± 0.01
Ω_3/F (V)	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	-26,550	-26,716	-27,023	-27,036	-27,026

Having established four coefficients as the best-supported calibration, it is worth considering what this result indicates about the underlying thermodynamics. In the Wohl expansion, taken relative to an ideal dilute proton solution, each successive coefficient k characterizes interactions among a progressively larger number of protons [54, 81]; the improved agreement obtained once three and four coefficients are included therefore indicates that interactions beyond the ternary level (Ω_3) are needed to describe the non-ideal behavior of the equilibrium state of the system. However, the specific numerical values obtained for each coefficient should not be over-interpreted as precisely determined measures of self-interaction energies: with eleven adjustable parameters across both scan directions, a high correlation between some of the coefficients was observed (see **Fig. S12**), and the fitted values are better understood as jointly

constrained by the overall voltammogram shape than as independently resolved quantities. This non-ideality is specific to the solid solution of protons and vacancies; the electrolyte is treated as a dilute solution, decoupled from this behavior because the equilibrium potential is independent of OH^- activity on the Hg/HgO scale, and the surface OH^- concentration varies by less than 0.1% during a scan (Section 5.5).

The remaining calibrated parameters in **Table 2** are worth examining individually. The apparent kinetic constant lacks a straightforward interpretation because it combines information from both the anodic and cathodic reactions, which cannot be deconvoluted. The estimated standard equilibrium potentials for the forward and backward scans are close to the reported formal potential (U°) of 0.4428 V vs. Hg/HgO by Barnard et al. [82] for the transformation of activated $\beta\text{-Ni}(\text{OH})_2/\beta\text{-NiOOH}$, supporting the physical consistency of the calibrated model with independently reported thermodynamic data. However, a direct comparison is not possible because this formal potential depends on the activity of protons and proton vacancies, which vary continuously during potential cycling, highlighting the importance of the activity-based treatment developed in this work over a fixed formal-potential approach. Furthermore, the estimated parameters for this model are highly sensitive to experimental factors that can alter the shape of the cyclic voltammogram, such as electrode composition and history, activation method, and electrolyte composition. This sensitivity reflects the genuine complexity of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ system, and the mathematical framework developed here provides a consistent, physically grounded structure within which the effects of such conditions can be located and compared, rather than left as purely qualitative differences between voltammograms. This framework, which closely agrees with experimental data across scan rates, provides a foundation for quantitatively testing reaction mechanisms in the electrocatalytic oxidation of organic compounds on nickel electrodes. Work in progress applies it to the mediated oxidation of organic substrates relevant to biosolids valorization [22–26], where the well-defined mass transport of the rotating disk geometry allows substrate transport and $\text{Ni}(\text{OH})_2/\text{NiOOH}$ surface kinetics to be separated in the analysis.

5.2 Model approach comparison

Fig. 3 compares the calibration results for the Layer Model (LM) and the Surface Model (SM) at 5 mV s^{-1} and 100 mV s^{-1} . Although not apparent, the differences in agreement with the experimental data between the two model approaches are evident in the RMSE values at 5 mV s^{-1} and 100 mV s^{-1} in **Table 3**. At both scan rates, the LM RMSEs are lower than those of the SM.

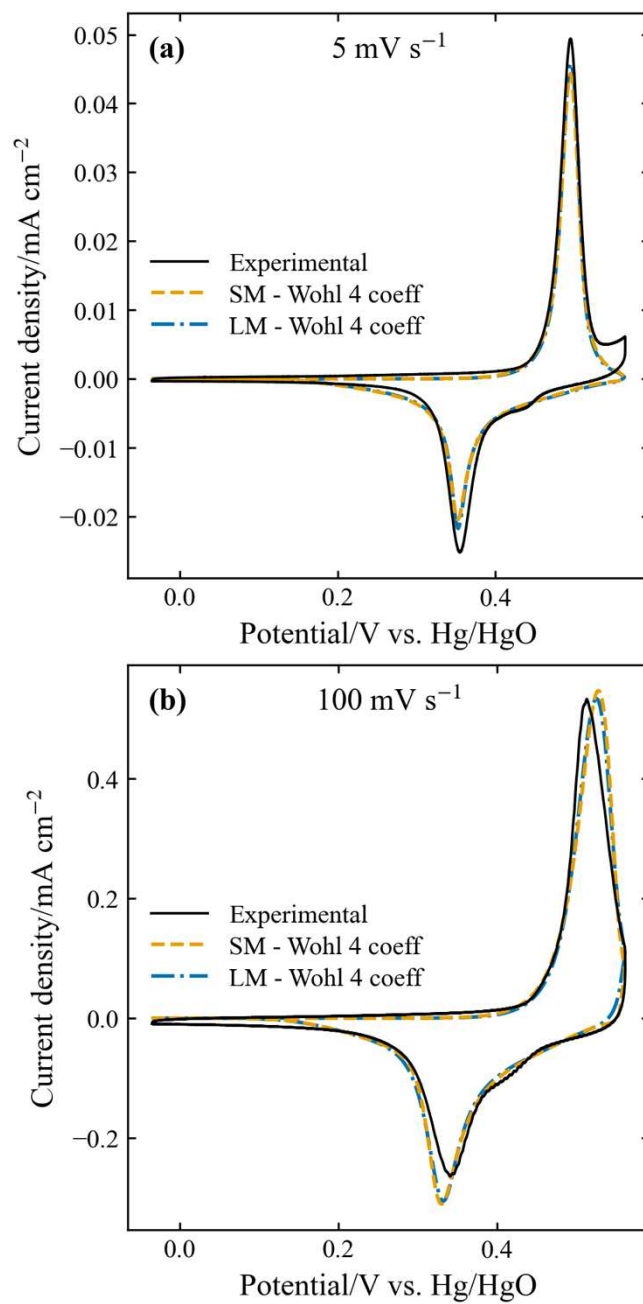


Fig. 3 Results of calibrating the Layer Model (LM) and Surface Model (SM) to experimental cyclic voltammograms of the nickel RDE in 0.1 M NaOH at 1000 rpm and scan rates of 5 mV s⁻¹ **(a)** and 100 mV s⁻¹ **(b)** using four-coefficient Wohl expansion (“Wohl 4 coeff”) to define the activity coefficients in the equilibrium potential expression (equation (21)).

Table 3. Comparison of the Surface Model (SM) and the Layer Model (LM) performance at 5 mV s⁻¹ and 100 mV s⁻¹ using RMSE and the block permutation test.

Parameter	5 mV s ⁻¹	100 mV s ⁻¹
RMSE for the SM (mA cm ⁻²)	0.00147	0.01109
RMSE for the LM (mA cm ⁻²)	0.00138	0.00892
Number of points (n)	1000	1000
Block length (points) ^a	91	117
Number of blocks (n _{blocks})	11	9
$T_{obs} = RSS_{SM} - RSS_{LM}$ (mA ² cm ⁻⁴)	2.486×10 ⁻⁴	4.368×10 ⁻²
Unique permutations evaluated (2 ^{n_{blocks}}) ^b	2,048	512
p-value (two-sided) ^{b,c}	0.687	0.293

^a Block length chosen as the longer of the Layer Model's and Surface Model's residual correlation lengths, to preserve local autocorrelation structure during permutation. The result was stable to halving and doubling this value (p = 0.25–0.69 and 0.24–0.63 across the range tested; **Supplementary Information**, Section S22.3).

^b With this small number of blocks, the null distribution of sign-flip outcomes was small enough to enumerate exactly rather than estimate by simulation; the p-value is therefore an exact result. See **Supplementary Information**, Section S22.2.

^c A calibration check (**Supplementary Information**, Section S22.6) found this test can be anti-conservative under the level of autocorrelation present in this data, meaning the true p-values may be even larger (i.e., even less significant) than reported here.

Beyond the simple RMSE comparison, a block permutation test was used to assess whether the difference in fit quality between the Layer Model and the Surface Model exceeds what would be expected from the data's own variability [83]. The null hypothesis (H₀) was that the two models fit the data equally well, so that any difference between them reflects only random variability; the alternative hypothesis (H₁) was that one model fits systematically better than the other. For the test, the total difference between the residual sum of squares (RSS_k) of the Surface Model and the Layer Model, $T_{obs} = RSS_{SM} - RSS_{LM}$, was compared with the range of values expected by chance if neither model fit better. This chance-level range was generated by randomly flipping the sign of the difference between the residuals ($r_{k,j}$) squared of the Surface Model and the Layer Model ($d_j = r_{SM,j}^2 - r_{LM,j}^2$) within contiguous blocks of the scan and computing the sum, $T_{permutation} = \sum_{j=1}^n d_j$ (see further details in Section S22 of the **Supplementary Information**). The p-value is the proportion of these permuted sums ($T_{permutation}$) that are at least as extreme as the observed value (T_{obs}), that is, the probability of a difference this large arising by chance alone if H₀ were true.

Table 3 shows the parameters and results of this test. At both scan rates, the observed difference in fit quality was not significantly different from what would be expected by chance (5 mV s⁻¹: p = 0.69; 100 mV s⁻¹: p = 0.29), indicating no statistically significant difference between the Layer Model's and Surface Model's ability to fit the experimental data at either scan rate. Furthermore, the Layer Model's and Surface Model's predicted currents are highly correlated at both scan rates (Pearson correlation coefficient: $r = 0.9992$ and 0.9984 at 5 and 100 mV s⁻¹, respectively), consistent with the two models producing largely indistinguishable predictions despite differing mechanistic assumptions about solid-layer diffusion structure. Therefore, the modestly lower RMSE observed for the Layer Model at both scan rates, most notably at 100 mV s⁻¹, should be interpreted as a numerical trend rather than as statistically robust evidence that the Layer Model outperforms the Surface Model.

The insignificant difference in fit quality between the two models is expected given the relatively thin solid-layer thickness assumed here (6 nm), which does not allow a substantial concentration gradient to develop, as shown in the predicted proton vacancy fraction profiles in **Fig. 4**. This can be understood quantitatively in terms of the dimensionless finite-diffusion parameter, $w = n_e F a^2 sr / RT D_{s,v}$ [84], which compares the characteristic timescale for proton diffusion across the solid layer ($a^2 / D_{s,v}$) to that of the potential sweep ($RT / n_e F sr$, where “sr” is the scan rate). Using our calibrated $D_{s,v} = 2.54 \times 10^{-12}$ cm² s⁻¹ and $a = 6$ nm, $w = 0.028$ at 5 mV s⁻¹ and $w = 0.55$ at 100 mV s⁻¹, both far below the value ($w > 10$) at which semi-infinite, strongly diffusion-limited behavior would be expected [84]. The predicted profiles of the proton vacancy fraction across the solid layer, which are essentially flat at 5 mV s⁻¹ (**Fig. 4** (a) and (b)), and with a barely perceptible slope at 100 mV s⁻¹ (**Fig. 4** (c) and (d)), are consistent with w remaining well below the diffusion-dominated regime at both scan rates.

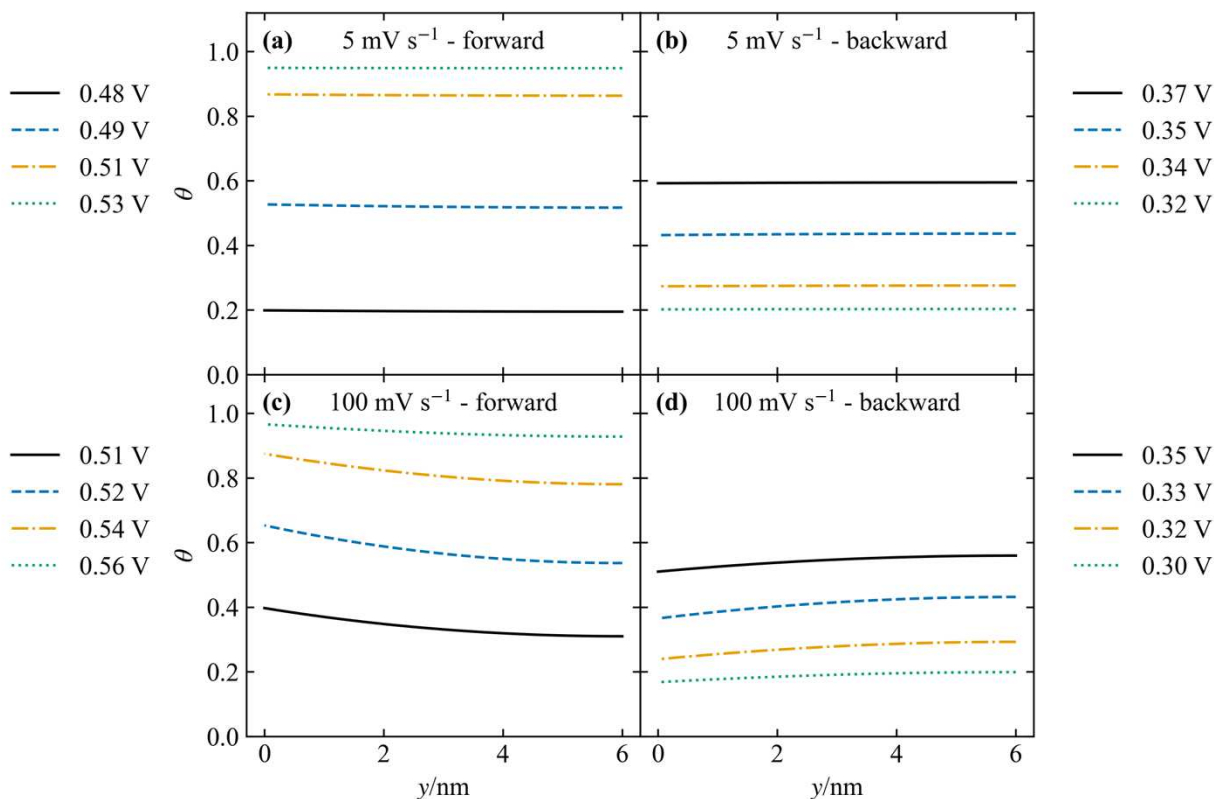


Fig. 4 Predicted proton vacancy fraction (θ) profiles at different potentials during the cyclic voltammetry at 5 mV s^{-1} ((a) forward and (b) backward scans) and 100 mV s^{-1} ((c) forward and (d) backward scans).

Although there is no statistical difference between the Layer Model's and the Surface Model's ability to fit the experimental data, the Surface Model offers a practical advantage: its single-region diffusion-layer formulation. This feature can be decisive when the electrocatalytic reaction of interest on the nickel electrode involves a complex mechanism with many participating species and intermediates: coupling such a mechanism to multiple regions increases computational cost and complicates parameter identifiability. This issue is already present in the Layer Model, given the non-identifiability of the diffusion coefficient and layer thickness for this system (Section S12, **Supplementary Information**). Accordingly, the Surface Model offers clear practical value for studying the electro-oxidation of organic compounds and will be used for the rest of this work.

5.3 Model evaluation at different scan rates

The simulated cyclic voltammograms generated by the Surface Model using the four-coefficient Wohl expansion at different scan rates are compared with the experimental data in **Fig. 5**. The simulated and experimental cyclic voltammograms agree well at scan rates of 25 and 50 mV s^{-1} , both within the 5 to 100 mV s^{-1} range over which the model was calibrated. The Surface Model also performs well at scan rates outside the 5 to 100 mV s^{-1} range, as shown in panel (a) of **Fig. 5** for a 3 mV s^{-1} cyclic voltammogram.

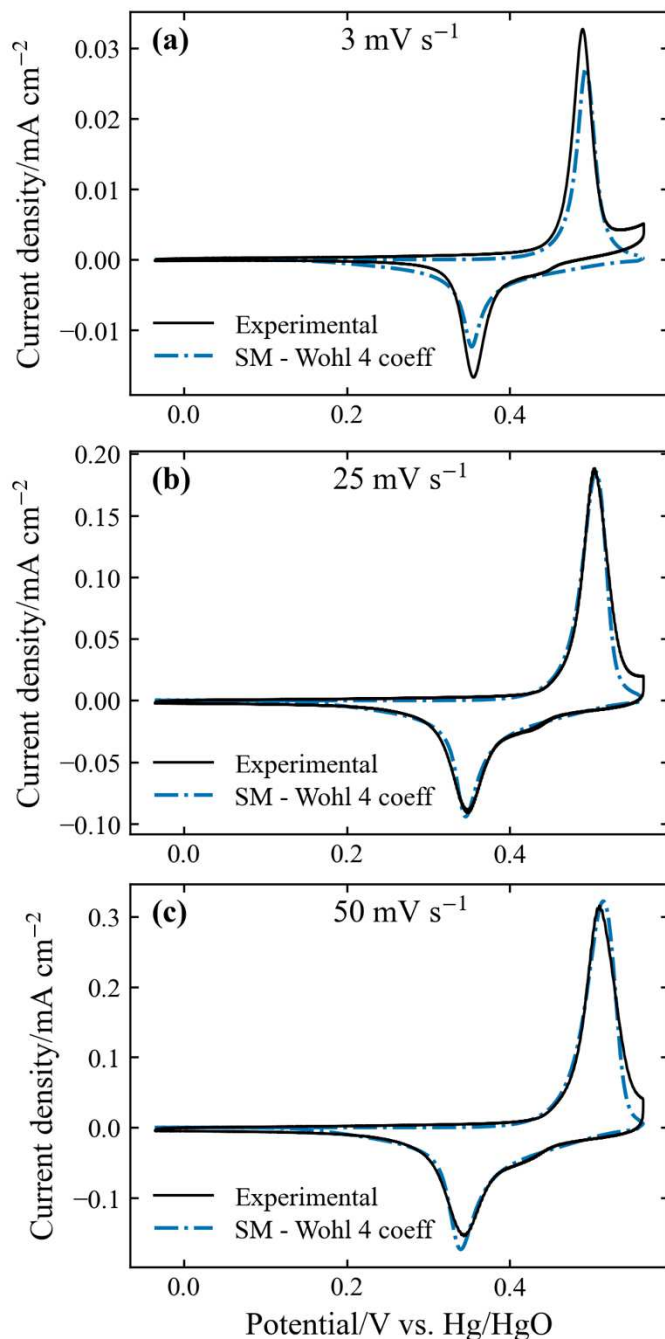


Fig. 5 Comparison of the Surface Model’s simulation (using the four-coefficient Wohl expansion, labeled “SM – Wohl 4 coeff”) with the experimental cyclic voltammograms of the nickel RDE in 0.1 M NaOH at scan rates of 3 mV s⁻¹ (a), 25 mV s⁻¹ (b), and 50 mV s⁻¹ (c), and at 1000 rpm.

5.4 Effect of OH⁻ concentration

Organic electrooxidation on nickel electrodes is strongly modulated by electrolyte pH (or OH⁻ concentration) through competition for substrate adsorption [85, 86] and reaction-pathway selectivity [46]. These effects are intertwined with the underlying Ni(OH)₂/NiOOH pH-dependent electrochemistry [87, 88]. Therefore, isolating the substrate’s specific contribution requires a model that first accurately captures how OH⁻ concentration affects the Ni(OH)₂/NiOOH reaction in the absence of substrate.

Experimentally, the effect of OH^- concentration on the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ cyclic voltammetry has been well documented [88–90], with the most notable change being an increase in the intensities of the anodic and cathodic peaks as the hydroxyl concentration increases, while the peak potentials remain unchanged in iron-free solutions [87]. However, the proposed model cannot reproduce these changes, even when the partial order of OH^- in the rate law is changed from the initial assumption of $\alpha = 1$ (see **Fig. S14**). Since U is independent of OH^- activity on the Hg/HgO reference scale, the only available handle for the OH^- concentration effect on the current density is the exchange current density expression (equation (18)), specifically the maximum proton vacancy concentration ($c_{v,max}$). Therefore, we modified the model to reproduce the experimental trend by introducing an empirical correction to this variable. The *maximum* proton vacancy concentration used in this work represents only a fraction of the *total* proton vacancies available on the $\text{Ni}(\text{OH})_2$ layer ($c_{v,total}^L$), which is a property of the material and can be calculated using equation (27).

$$c_{v,total}^L = \frac{\rho_{\text{Ni}(\text{OH})_2}}{M_{\text{Ni}(\text{OH})_2}}, \quad (27)$$

where $\rho_{\text{Ni}(\text{OH})_2}$ is the density of $\text{Ni}(\text{OH})_2$ in g cm^{-3} and $M_{\text{Ni}(\text{OH})_2}$ is the molecular mass of $\text{Ni}(\text{OH})_2$ in g mol^{-1} . From equation (27), the total proton vacancy concentration is $0.0442 \text{ mol cm}^{-3}$ in the Layer Model, while in the Surface Model it is $c_{v,total}^S = 2.653 \times 10^{-8} \text{ mol cm}^{-2}$ (considering a layer thickness of $a = 6 \text{ nm}$ and $c_{v,total}^S = c_{v,total}^L \times a$). Based on the trends reported [91] and observed in our experiments (**Fig. S15**), we propose that only a fraction of this total amount ($c_{v,total}^L$ or $c_{v,total}^S$) is electrochemically active during the reaction, and this fraction (Θ) increases with the surface OH^- concentration and approaches a plateau, following the saturating exponential form given in equation (28).

$$\Theta = \frac{c_{v,max}}{c_{v,total}^S} = K \left[1 - \exp \left(-\xi \cdot \frac{c_{b,\text{OH}} c_{\text{OH}}}{c_{\text{OH},ref}} \right) \right], \quad (28)$$

where $c_{\text{OH},ref}$ is an OH^- reference concentration taken as $c_{\text{OH},ref} = 1 \text{ mol cm}^{-3}$.

The expression in equation (28) captures two limiting behaviors consistent with the trends observed experimentally: at low OH^- concentration, only a small fraction of the total proton vacancy inventory in the film participates in the redox reaction, and this fraction grows with OH^- concentration; at sufficiently high OH^- concentration, the fraction approaches a plateau value $K < 1$, reflecting that only a finite fraction of the total site density in the film becomes electrochemically active. We selected this functional form from several candidate saturating functions of OH^- concentration based on fit quality, as detailed in the **Supplementary Information** (Section S25). The parameters K and ξ are treated as empirical parameters that set, respectively, the saturation level and the rate at which the active fraction approaches that level with increasing OH^- concentration; both are determined by fitting to experimental cyclic voltammograms at two OH^- concentrations (0.1 and 1.0 M) and scan rates (5 and 100 mV s^{-1}) while keeping the rest of the electrochemical parameters (kinetic constant and thermodynamic parameters) estimated for the 0.1 M case fixed.

The results of calibrating K and ξ in the modified Surface Model (mSM) using the four-coefficient Wohl expansion against experimental cyclic voltammograms at 5 and 100 mV s^{-1} in 0.1 and 1.0 M NaOH are shown in **Fig. 6**. From this calibration, $K = 0.197 \pm 0.001$ and $\xi = 10,200 \pm 100$ were obtained.

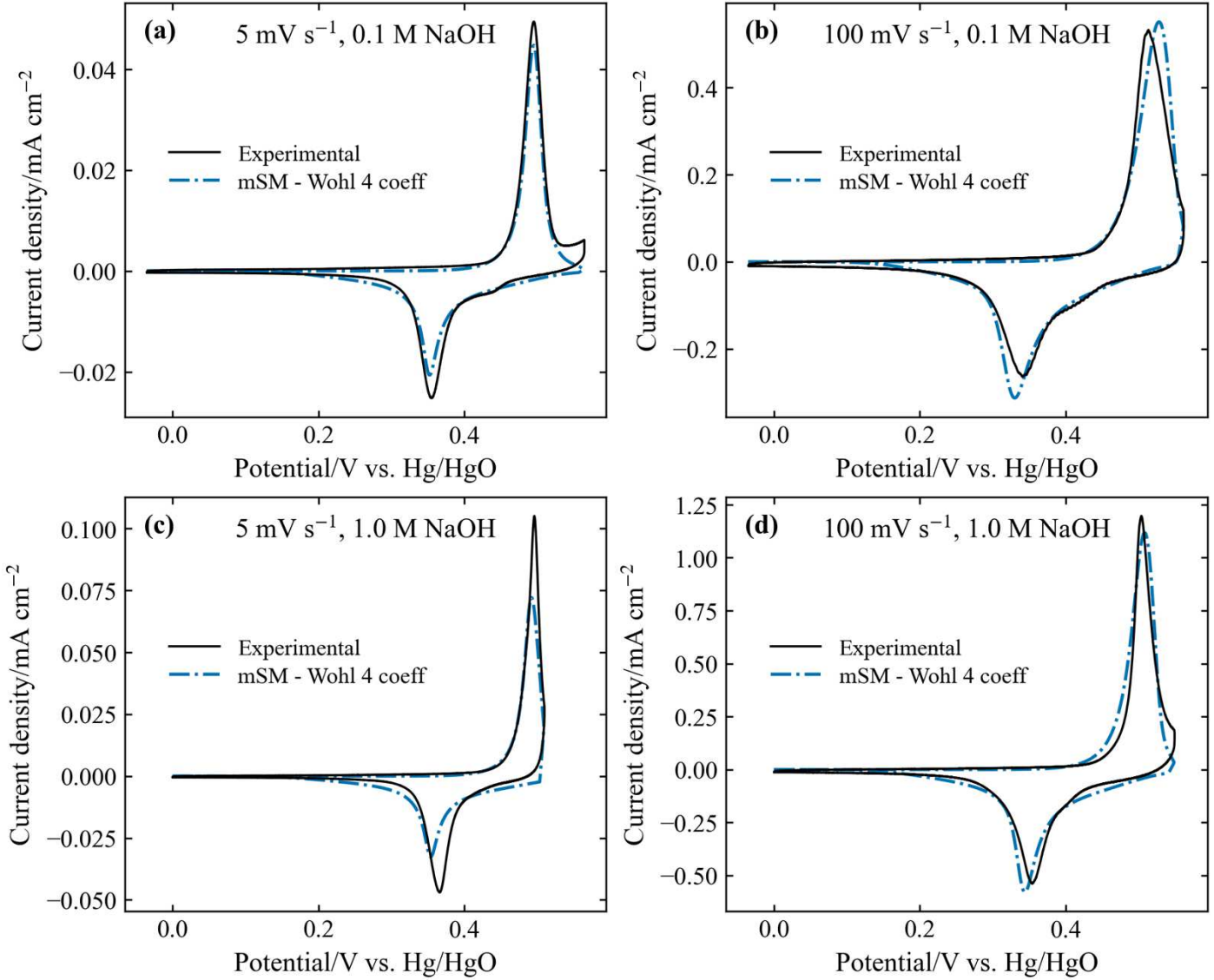


Fig. 6 Results of calibrating the modified Surface Model (mSM) (using the four-coefficient Wohl expansion) to experimental cyclic voltammograms of the nickel RDE in 0.1 M NaOH ((a) and (b)) and 1.0 M NaOH ((c) and (d)) at scan rates of 5 mV s⁻¹ and 100 mV s⁻¹, and 1000 rpm. The 1.0 M NaOH cyclic voltammograms show reasonable agreement, with most parameters estimated from the 0.1 M NaOH experiments.

It is worth noting that K and $c_{v,total}^S$ are not independently constrained by this calibration because both depend on the assumed layer thickness $a = 6$ nm. Only their product, which is the absolute surface concentration of electrochemically active proton vacancies ($c_{v,abs}^S = K \times c_{v,total}^S = 5.226 \times 10^{-9}$ mol cm⁻²), is determined directly by fitting. Since $K \leq 1$ by definition, this product sets a lower bound on the admissible layer thickness: $a_{min} = c_{v,abs}^S / c_{v,total}^L K = 1.2$ nm, corresponding to full utilization of the proton-vacancy inventory. This lower bound lies below the 2–10 nm range reported for anodically formed oxide layers on nickel [69–75], suggesting the true thickness is close to, though not precisely at, this bound and that the 6 nm assumption overestimates it.

In contrast, the fraction of K (i.e., saturation) reached at each tested OH⁻ concentration depends only on ξ and is independent of the assumed layer thickness: 63.9% of saturation is reached at 0.1 M NaOH, and 100.0% (99.996%) at 1.0 M, confirming that the two calibration concentrations bracket the transition from partially to fully active film. However, we would expect ξ to depend on the Ni(OH)₂ synthesis method and the activation protocol, given that Figure

8 of [91] shows peak current increasing with $[\text{OH}^-]$ up to roughly 2.0–2.5 M, beyond which further increases in concentration produce comparatively little additional change in peak current. Consequently, the NaOH concentration at which the electrode reaches ~100% saturation will vary with experimental conditions.

In **Fig. 6**, the simulations and experimental data agree reasonably well at 1.0 M NaOH for peak shapes and positions. However, at 1.0 M NaOH and 5 mV s^{-1} (**Fig. 6 (c)**), the model underestimates the peak current densities by 25–30%. This discrepancy affects the anodic and cathodic peaks in similar proportion, suggesting it reflects the total amount of electroactive material accessed over the scan rather than a faradaic process acting on one branch only. One plausible contributor is that at slow scan rates the system has sufficient time to undergo concentration-dependent structural changes in the film, including changes in hydration state and oxide restructuring [7], that increase the accessible inventory beyond what the empirical correction predicts. Because the correction conflates all such contributions into a single concentration-dependent term, it cannot be expected to reproduce the full scan-rate dependence of the experimental response. Resolving this limitation would require explicit treatment of each concentration-dependent physical process, which is beyond the scope of this investigation and is left for future work.

The robustness of the resulting modified Surface Model was tested by comparing the simulation with the experiment at a concentration different from those used for calibration. The comparison is shown in **Fig. 7** at a concentration of 0.5 M NaOH. The peak shapes and positions agree, but the simulation underpredicts the peak current densities, consistent with the scan-rate-dependent underprediction observed at 1.0 M NaOH (**Fig. 6 (c)**). The model therefore captures the qualitative behavior across concentrations but is expected to underpredict peak currents at slow scan rates, a limitation attributed to scan-rate-dependent structural changes in the film that the empirical correction cannot resolve.

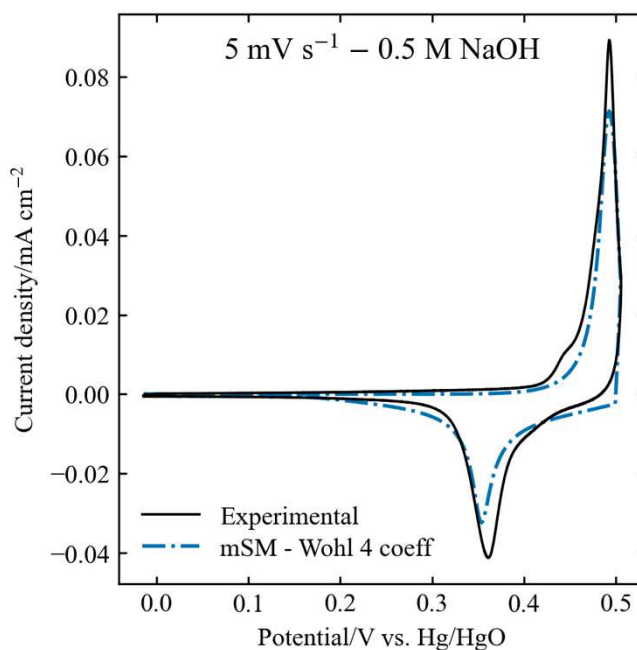


Fig. 7 Comparison of the modified Surface Model simulation (using the four-coefficient Wohl expansion, labeled “mSM – Wohl 4 coeff”) with the experimental cyclic voltammograms of the nickel RDE in 0.5 M NaOH at 5 mV s^{-1} and 1000 rpm.

5.5 Model evaluation at different rotation speeds

Having established that the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ reaction depends on the OH^- concentration at the electrode surface, it is important to verify that this concentration is not itself limited by OH^- transport from the bulk solution. If the reaction were transport-limited, the experimental cyclic voltammograms (and thus, the simulated ones) would be expected to vary systematically with rotation speed. **Fig. 8** compares simulated cyclic voltammograms from the modified Surface Model with the four-coefficient Wohl expansion to experimental data in 0.1 M NaOH at rotation speeds of 500, 1000, 2000, and 5000 rpm and at 100 mV s^{-1} . The shapes and peak potentials closely agree (**Fig. 8 (b), (c), (e), and (f)**), yet

the peak current densities in the experimental cyclic voltammograms are 4-9% higher. This discrepancy is consistent with electrode-to-electrode variability in the thickness of the electrochemically active nickel hydroxide layer arising from differences in polishing, activation history, and cumulative cycling time; a reproducibility study under comparable conditions (**Fig. S17** and **Table S18**) found peak-current differences as large as 19% between independently prepared electrodes.

In **Fig. 8** (a) and (d), the simulated and experimental cyclic voltammograms are insensitive to rotation speed at 100 mV s^{-1} . Experimentally, this trend is consistent with what Carbonio et al. [92] reported for thin (~ 13 nm) $\text{Ni}(\text{OH})_2$ layers deposited on Pt in a 0.01 M NaOH and 0.33 M Na_2SO_4 electrolyte. At the simulation level, this result reveals a key characteristic of the model: it predicts that the surface concentration of hydroxyl ions changes little from its bulk value during cyclic voltammetry (less than 0.1%). Therefore, the reaction is not even partially limited by the supply of hydroxyl ions to the electrode surface at 0.1 M NaOH, and changes in the convection regime do not matter.

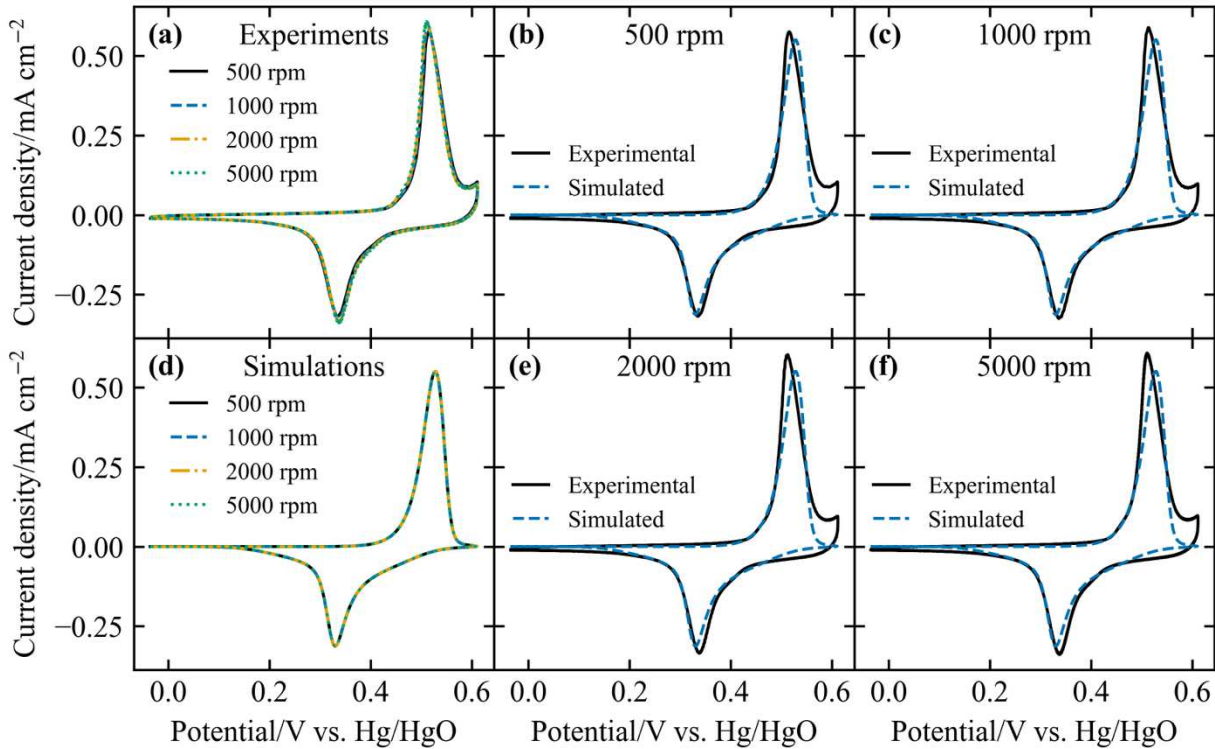


Fig. 8 Experimental (a) and simulated (d) cyclic voltammograms of the nickel RDE in 0.1 M NaOH at 100 mV s^{-1} and rotation speeds of 500, 1000, 2000, and 5000 rpm. The simulations were based on the modified Surface Model simulation using the four-coefficient Wohl expansion. Experimental and simulated cyclic voltammograms are also compared at each rotation speed: 500 rpm (b), 1000 rpm (c), 2000 rpm (e), and 5000 rpm (f).

Theoretically, if the mass transport of the hydroxyl ions were limiting the reaction, the resulting limiting current density can be calculated using the Levich equation (equation (29) [47]).

$$i_{lim} = 0.62nFD_{OH^-}^{\frac{2}{3}}\omega^{\frac{1}{2}}\nu^{-\frac{1}{6}}c_{OH^-}. \quad (29)$$

Plugging in the OH^- diffusion coefficient of $5.27 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [68], bulk NaOH concentration of $1 \times 10^{-4} \text{ mol cm}^{-3}$, solution kinematic viscosity of $0.00909 \text{ cm}^2 \text{ s}^{-1}$ [68], and a rotation speed of 1000 rpm ($104.72 \text{ rad s}^{-1}$) into equation (29), we obtain a current density of 188 mA cm^{-2} . Compared to the order-of-magnitude current densities measured in this work (relative to the geometric surface area), around 3.54 mA cm^{-2} at 100 mV s^{-1} and 0.1 M NaOH, the measured current density is only 2% of the theoretical limiting current. This result supports the model's prediction that hydroxyl-ion transport does not limit the reaction, even at a relatively low concentration of 0.1 M NaOH.

6. Conclusions

A mathematical model was developed to simulate the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ reaction on a nickel RDE, based on conservation equations, Butler-Volmer kinetics, and the Nernst expression with composition-dependent activity coefficients. Hysteresis between oxidation and reduction was captured by assigning distinct equilibrium-potential parameters to the forward and reverse scans. Two mechanistic approaches were evaluated: the Layer Model and the Surface Model, and several expressions for the activity coefficients of protons and proton vacancies were tested. The choice of the activity-coefficient expression was found to be critical for achieving close agreement between the simulated and experimental cyclic voltammograms. Among these expressions, the one based on the Wohl series expansion improved the fit systematically as more proton-proton self-interaction coefficients were included, up to a total of four; beyond that, additional coefficients were not well constrained by calibration with the experimental data. This result suggests that interactions among up to five protons should be considered to accurately describe the system's equilibrium state.

A block permutation test, an approach not commonly applied in electrochemical model discrimination, revealed no statistically significant difference in how well the Layer Model and Surface Model reproduce the experimental cyclic voltammogram. This result is consistent with the extremely thin $\text{Ni}(\text{OH})_2$ solid layer (2-10 nm) reported for this system ($\text{Ni}(\text{OH})_2/\text{NiOOH}$ anodically formed over Ni electrodes) [69–75], where a significant concentration gradient in the solid layer will not fully develop over such a short path. Although the two models performed equivalently, the simpler Surface Model has high practical value for simulating cyclic voltammograms of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ reaction during organic electrooxidation, as it requires only one region to describe the system and is less prone to identifiability problems related to the proton vacancy diffusion coefficient and oxide layer thickness, which are not easily determined independently for the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ anodically formed over Ni electrodes.

Regarding the effect of OH^- concentration, the model must include a saturating exponential dependence on the surface OH^- for the fraction of active proton vacancies to achieve reasonable agreement with experimental data for NaOH concentrations in the range 0.1-1.0 M. This modification changes the total amount of electroactive material participating in the reaction according to the surface OH^- concentration. To the best of our knowledge, this is the first explicit relationship linking OH^- concentration to the electroactive proton/proton-vacancy inventory in a voltammetric model of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ reaction, successfully capturing the overall changes in cyclic voltammograms across different NaOH concentrations and opening the door to mechanistic studies of the pH effect in the mediated electro-oxidation of organic compounds over nickel electrodes through mathematical modeling. This modification could be further refined to account for the underprediction of peak current densities at slower scan rates, such as 5 mV s^{-1} . The deficit affects the anodic and cathodic peaks in similar proportion. Because oxygen evolution contributes anodic current only, it cannot account for a deficit that appears on both branches, and the symmetry of the deficit further suggests that OER contribution in the peak region is limited, even if it is more appreciable over the full 0.10–0.565 V integration window.

In terms of OH^- transport limitations, it was confirmed experimentally, and then accurately simulated, that the cyclic voltammograms of Ni RDE in 0.1 M NaOH at 100 mV s^{-1} are insensitive to the rotation speed, suggesting that OH^- transport does not limit the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ reaction under these experimental conditions. This result supports using the RDE as a well-characterized mass-transport environment for future studies extending this model to substrate oxidation.

Finally, this framework is currently being extended to the mediated electrooxidation of organic substrates on nickel, beginning with model compounds representative of the biosolids conversion chemistry that motivated this study [22–26]. Because the rotating disk geometry supplies a well-defined description of substrate mass transport, and because the parameters governing the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ transformation itself have been established here independently of any substrate, the kinetics of the surface-mediated oxidation step can be isolated and tested against candidate mechanisms rather than inferred from the overall voltammetric response. The same approach should extend to other organic substrates oxidized through the $\text{Ni}(\text{II})/\text{Ni}(\text{III})$ couple in alkaline media.

7. Declarations

7.1 Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

7.2 Funding

This work was supported by the National Science Foundation Engineering Research Center for Advancing Sustainable and Distributed Fertilizer Production (CASFER), award number 2133576.

7.3 Acknowledgment

This material is based upon financial support by the National Science Foundation, EEC Division of Engineering Education and Centers, NSF Engineering Research Center for Advancing Sustainable and Distributed Fertilizer Production (CASFER), NSF 20-553 Gen-4 Engineering Research Centers award # 2133576. Any opinions, findings, conclusions, or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

7.4 Data availability

Data will be made available upon reasonable request to the corresponding author.

7.5 Author contributions

Jessica Ortega-Ramos: Formal analysis, software, investigation, visualization, writing – original draft.

Daniela Ferreira-Garcia: Data curation, validation, investigation, visualization, writing – original draft.

Gerardine G. Botte: Conceptualization, formal analysis, funding acquisition, project administration, supervision, resources, writing – review and editing.

7.6 Generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work, the author(s) used Claude.ai to prepare scripts for the simulations, data analysis, and visualization, brainstorm ideas, and double-check consistency and clarity of the writing. After using this service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the published article.

8. List of symbols

a	Thickness of the solid oxide layer, in cm.
A	Coefficient in the Jones–Dole equation, in $\text{dm}^{3/2} \text{mol}^{-1/2}$.
B	Coefficient in the Jones–Dole equation, in $\text{dm}^3 \text{mol}^{-1}$.
A_0, B_0	Margules model parameters, dimensionless.
A', B'	van Laar model parameters, dimensionless.
c_j	Concentration of species j , in mol cm^{-3} .
$c_{b,j}$	Bulk concentration of species j , in mol cm^{-3} .
$c_{j,ref}$	Reference concentration of species j , in mol cm^{-3} .
$c_{v,max}$	Maximum concentration of proton vacancies, in mol cm^{-2} (Surface Model) or mol cm^{-3} (Layer Model).
$c_{v,abs}^S$	Absolute surface concentration of electrochemically active proton vacancies, in mol cm^{-2} .
$c_{v,total}^L$	Total proton vacancies concentration, in mol cm^{-3} .
$c_{v,total}^S$	Total proton vacancies surface concentration, in mol cm^{-2} .
C_j	Dimensionless concentration of species j .
C_{dl}	Double-layer capacitance, in F.
C_s	Specific capacitance of a smooth planar surface, in F cm^{-2} .
d_j	Difference of squared residuals of the Surface Model and the Layer Model at point j , in $\text{mA}^2 \text{cm}^{-4}$.
$D_{s,j}$	Diffusion coefficient of species j , in $\text{cm}^2 \text{s}^{-1}$.
E	Raw applied potential (before iR and LJP corrections), in V.
E_{LJP}	Estimated liquid junction potential, in V.
$EASA$	Electrochemically active surface area, in cm^2 .
F	Faraday constant, in C mol^{-1} .
G^E	Molar excess Gibbs free energy, in J mol^{-1} .
i	Current density, in mA cm^{-2} .

i_0	Exchange current density, in mA cm ⁻² .
i_{lim}	Mass transport limiting current density, in mA cm ⁻² .
I	Current, in A.
k_0	Apparent kinetic constant, in s ⁻¹ cm ^{5/2} mol ^{-1/2} (Layer Model) or s ⁻¹ cm ^{3/2} mol ^{-1/2} (Surface Model).
k_a	Kinetic constant of the oxidation, in cm ⁴ mol ⁻¹ s ⁻¹ (Layer Model) or cm ³ mol ⁻¹ s ⁻¹ (Surface Model).
k_c	Kinetic constant of the reduction, in cm s ⁻¹ (Layer Model) or s ⁻¹ (Surface Model).
M_j	Molecular mass of species j , in g mol ⁻¹ .
n	Number of data points used in the statistical test.
n_{blocks}	Number of blocks used in the block permutation test.
n_e	Number of electrons transferred, dimensionless.
N_j	Molar flux of species j , in mol cm ⁻² s ⁻¹ .
n_j	Number of nodes in the s in the y dimension, dimensionless.
nv	Number of data points, dimensionless.
Q_a	Total anodic charge density, in mC cm ⁻² .
Q_c	Total cathodic charge density, in mC cm ⁻² .
r	Pearson correlation coefficient.
$r_{k,j}$	Residual (experimental data - model prediction) at point j for a model k .
R	Ideal gas constant, in J mol ⁻¹ K ⁻¹ .
R_j	Net generation rate by homogeneous chemical reactions of species j , in mol cm ⁻³ s ⁻¹ .
R_u	Estimated uncompensated solution resistance, in Ω .
RSS_k	Residual sum of squares for a particular modeling approach k .
$s(j)$	Stoichiometric coefficient of species j , dimensionless.
sr	Scan rate, in V s ⁻¹ .
t	Time, in s.
T	Temperature, in K.
T_{obs}	Observed test statistic, in mA ² cm ⁻⁴ .
$T_{permutation}$	Permuted test statistic, in mA ² cm ⁻⁴ .
U	Equilibrium potential, in V.
U°	Standard equilibrium potential, in V vs. Hg/HgO.
v_y	Flow velocity towards the electrode surface, in cm s ⁻¹ .
V_d	Applied potential, in V vs. Hg/HgO.
w	Dimensionless finite-diffusion parameter.
y	Spatial distance, in cm.
$z(j)$	Charge number of species j , dimensionless.

Greek letters

α	Partial order of OH ⁻ in the rate law of the Ni(OH) ₂ /NiOOH reaction, dimensionless
β	Symmetry factor, dimensionless.
γ_j	Activity coefficient of species j , dimensionless.
δ	Characteristic diffusion thickness, $\delta = 1.805 D_{s,j}^{1/3} \nu^{1/2} \omega^{-1/2}$, in cm.
η	Overpotential, in V. Also, dynamic viscosity, in mPa s.
K, ξ	Calibration empirical constants, dimensionless.
ν	Kinematic viscosity, in cm ² s ⁻¹ .
Ω_k	Coefficient k of the Wohl series expansion, in J mol ⁻¹ .
ω	Angular velocity of rotation of the RDE, in rad s ⁻¹ .
ϕ_1	Potential in the solid, in V.
ϕ_2	Potential in the solution, in V.
ρ_j	Density of species j , in g cm ⁻³ .
σ	Conductivity of the solid, in S cm ⁻¹ .
θ_{H^+}	Mole fraction of protons or Ni(OH) ₂ , dimensionless.
θ_v	Mole fraction of proton vacancies or NiOOH, dimensionless.
Θ	Fraction of electrochemically active proton vacancies in the film, dimensionless.

Subscripts and superscripts

<i>a</i>	Anodic.
<i>b</i>	Property of the bulk of the solution.
<i>c</i>	Cathodic.
<i>H⁺</i>	Property of protons.
<i>j</i>	General chemical species.
<i>Na</i>	Property of sodium ion.
<i>OH</i>	Property of hydroxyl ion.
<i>v</i>	Proton vacancy.
<i>y</i>	In the y-direction.
$\circ$	Standard property.
$\circ$	Reference property, apparent property.

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