

ALD Pathways Program Oxygen Vacancies and eg Occupancy in NiFe (Oxy)hydroxides

Abstract

Understanding how lattice oxygen vacancies modulate the electronic structure of active metal sites during the oxygen evolution reaction (OER) is central to rational catalyst design. Here we construct a depth-reconciled, multimodal framework to quantify the relationship between oxygen-vacancy indicators—the O 1s XPS vacancy fraction and the O K-edge pre-edge area—and the operando eg occupancy of Ni and Fe sites in ALD-tailored Ni-Fe oxyhydroxide thin films under OER at 1.60–1.65 V_{RHE} . We deploy a locked ALD matrix (Ni:Fe = 100:0–25:75; 2–10 nm; n=3) and a standardized electrochemical protocol (EIS-based iR correction, preconditioning, steady-state criterion, temperature logging), and acquire O K-edge TEY/TFY spectra with step-normalized 528–531 eV integration, ARXPS O 1s angle series with adsorbate removal for vacancy-fraction extraction, and operando Ni/Fe K-edge XAS for pre-edge/white-line and $\Delta\mu$ analysis converted to eg(Ni) and eg(Fe) using calibrated standards. A depth-weighting scheme reconciles probe sensitivities across TEY/TFY, XPS, and K-edges. We fit Models A/B via OLS with HC3 errors and bootstrap confidence intervals, report slopes, intercepts, R^2 , and VIF at 1.60 and 1.65 V_{RHE} , and assess robustness with Deming/robust regressions, alternative normalizations, and Ni-only vs. Ni+Fe subsets. Residuals are cross-correlated with Raman OH/OOH intensity, composition, thickness, and roughness to identify latent variables. This integrated approach delivers statistically rigorous slopes and explained variance linking vacancy descriptors to eg occupancy, clarifying defect–electronic-structure coupling under operating biases and informing defect engineering strategies for advanced OER catalysts.

1 Introduction

Despite decades of study, the electronic descriptors that govern oxygen evolution reaction (OER) activity in alkaline media remain under debate for the prototypical Ni–Fe (oxy)hydroxide catalysts. Prior operando X-ray absorption studies established that Fe incorporation into Ni oxyhydroxide dramatically increases OER rates, with the active phase forming under bias and involving changes in metal–oxygen covalency and oxidation states [1–3]. Complementary soft X-ray and ambient-pressure XPS have revealed dynamic oxygen-ligand-hole features and subsurface hydroxyl/oxygen evolution that accompany OER, hinting that oxygen vacancies and ligand holes are intimately coupled to activity [4, 7, 8, 11]. Recent $\Delta\mu$ and pre-edge/white-line analyses at the Ni/Fe K edges further suggest that eg occupancy on the metal sites tracks the formation of active motifs under turnover [6, 9, 10].

What is still missing is a quantitative, depth-aware link between easily accessible oxygen-vacancy indicators at or near the surface and the operando evolution of metal eg occupancy across well-controlled Ni:Fe compositions and thicknesses. Establishing this link would provide a mechanistic bridge between oxygen-sublattice descriptors and metal-centered electronic structure, enabling predictive control via synthesis.

This work addresses that gap by testing whether oxygen vacancy indicators measured ex situ/in situ (O 1s ARXPS vacancy fraction; O K-edge pre-edge area) quantitatively correlate with operando eg occupancy of Ni and Fe sites (derived from K-edge pre-edge/white-line and $\Delta\mu$ analysis) during steady-state OER at 1.60–1.65 V_{RHE} . Specifically, we ask: What is the quantitative relationship between these vacancy/ligand-hole proxies and eg(Ni) and eg(Fe) under OER bias; and what are the slopes and R^2 of these relationships at 1.60 and 1.65 V_{RHE} ? We further examine model form, probe-depth reconciliation, and robustness across Ni-only and Ni–Fe compositions. In doing so, we unify soft XAS, ARXPS, and operando hard XAS within a single regression framework grounded in prior mechanistic insights on active-phase formation and metal–oxygen covalency [2–4, 6, 9].

2 Related Work

The literature on Ni–Fe (oxy)hydroxides under alkaline OER converges on two coupled descriptors of activity: (i) metal-site electronic structure, of-

ten summarized by Ni/Fe eg occupancy or oxidation state inferred from K-edge pre-edge/white-line and $\Delta\mu$ analysis, and (ii) oxygen sublattice properties, probed by O K-edge pre-edge intensity (metal–oxygen covalency/ligand holes) and by O 1s XPS components sometimes interpreted as vacancy/hydroxyl signatures [1–5, 12–17]. Your question targets whether these oxygen descriptors quantitatively track operando eg occupancy at OER-relevant potentials (1.60–1.65 V_{RHE}).

Active Phase and Metal-Site Electronic Structure Under OER

Multiple operando XAS studies indicate that under OER, Ni in NiFe (oxy)hydroxide evolves toward highly oxidized γ -NiOOH-like states, while Fe remains in high-spin octahedral environments with activity contributions that depend on Fe incorporation and local structure [1–3, 5]. K-edge analyses show potential-dependent changes in pre-edge and white-line features that reflect increasing 3d–O2p hybridization and effective oxidation of Ni, often interpreted as decreased eg occupancy at the metal center [3, 5, 16]. $\Delta\mu$ analysis under operando conditions resolves adsorbate-induced perturbations to the metal coordination shell, linking surface intermediates to electronic-structure changes at catalytic potentials [12, 16].

Oxygen Sublattice: Covalency and Ligand-Hole Formation

Operando soft XAS at the O K-edge consistently reports growth of the pre-edge intensity with potential, attributed to enhanced metal–oxygen covalency and the formation of oxygen ligand-hole states in active NiFe oxyhydroxides [13–15, 17]. These changes correlate qualitatively with the transition to the catalytically active phase and with increased charge transfer between O 2p and metal 3d states [13–15].

O 1s XPS “Vacancies” Versus Hydroxyl/Adsorbate Dynamics

Ambient-pressure XPS reveals that the O 1s envelope under OER comprises lattice oxygen, hydroxyls, and chemisorbed/incipient oxygen species, with

substantial potential-dependent redistribution that can be misassigned as oxygen vacancies [4]. Consequently, any quantitative linkage between an “O 1s vacancy fraction” and metal-site eg occupancy must control for adsorbate coverage and probing depth differences [4, 13].

Attempts to Link Oxygen Descriptors to eg Occupancy

Studies that simultaneously track oxygen-sublattice signatures and metal-site electronic structure indicate co-evolution, but explicit statistical regressions relating O 1s vacancy fractions or O K-edge pre-edge areas to eg occupancy are not reported [4, 12–14, 16]. Potential windows vary, and exact alignment to 1.60–1.65 V_{RHE} is not uniformly documented across datasets [3, 12, 13].

Identified Gaps

None of the cited studies report a numerical slope and R² for:

1. O 1s XPS vacancy fraction versus operando Ni/Fe eg occupancy at 1.60–1.65 V_{RHE},
2. O K-edge pre-edge area versus operando Ni/Fe eg occupancy at 1.60–1.65 V_{RHE}.

Such quantitative regressions are missing in the literature, motivating a new synchronized operando protocol.

3 Method and Implementation

Overall Research Design

We aim to quantify the linear relationships between oxygen-vacancy descriptors (O 1s ARXPS vacancy fraction; O K-edge pre-edge area) and eg occupancy (Ni/Fe K-edge XAS) for Ni–Fe (oxy)hydroxides at 1.60–1.65 V_{RHE}. We will:

- Fabricate an ALD matrix (Ni:Fe = 100:0/90:10/75:25/50:50/25:75; thicknesses 2/5/10 nm; n=3),
- Apply a standardized electrochemical protocol (iR compensation, steady-state, temperature logging),

- Acquire O K-edge TEY/TFY spectra, ARXPS O 1s angle series, and operando Ni/Fe K-edge XAS,
- Convert Ni/Fe pre-edge/white-line and $\Delta\mu$ to eg(Ni) and eg(Fe) using calibrated standards,
- Perform depth-weighting to reconcile TEY/TFY/XPS and K-edge sensitivities,
- Fit Models A/B (OLS with HC3 errors and bootstrap CIs), report slopes, intercepts, R^2 , VIF at 1.60 and 1.65 V_{RHE},
- Conduct Deming/robust regression checks and correlate residuals with compositional and vibrational markers.

Atomic Layer Deposition (ALD) Matrix

- Substrates include glassy carbon (RDE), Si(100), Si₃N₄, or FTO for various analyses.
- Precursors for Ni/Fe: suitable organometallic or coordination complexes; co-reactants O₃+H₂O.
- Growth temperature: $\leq 200^\circ\text{C}$ to preserve amorphous oxyhydroxide character.
- Compositions verified by XPS/ICP-MS, thickness by XRR/ellipsometry.

Electrochemical Protocol for OER

- Electrolyte: 1.0 M KOH, N₂-purged, $25.0 \pm 0.5^\circ\text{C}$.
- RDE at 1600 rpm, geometric area 0.196 cm².
- Reference: Hg/HgO or Ag/AgCl, converted to RHE. 90% iR compensation using R_u from high-frequency EIS.
- Precondition: CV cycling and a hold at 1.55 V_{RHE}.
- Steady-state: check $\left| \frac{1}{j} \frac{dj}{dt} \right| < 0.01 \text{ min}^{-1}$ over 5 min.

O K-edge XAS (TEY/TFY/IPFY)

- Beamline with soft XAS capabilities. Calibrate energy to a standard reference.
- Collect TEY/TFY, optionally IPFY to mitigate saturation. Avoid beam damage.
- Integrate pre-edge (528–531 eV) after step normalization: $A_{528-531}$.
- Propagate errors from counting statistics and energy calibration by bootstrapping.

ARXPS O 1s Series for Vacancy-Fraction Extraction

- Measure at angles 15° – 75° , Al $K\alpha$ radiation.
- Remove adventitious C and adsorbates by mild baking or UV/ozone.
- Deconvolute O 1s into lattice/legal definitions, undercoordinated oxygen, hydroxyl, etc.
- Define vacancy fraction $f_{\text{vac}}(\theta) = \frac{A_{\text{vac}}(\theta)}{A_{\text{latt}}(\theta) + A_{\text{vac}}(\theta)}$.
- Model to obtain bulk-equivalent $f_{\text{vac}}^{\text{XPS}}$ adjusted for depth.

Operando Ni/Fe K-edge XAS

- Hard XAS with operando flow or RDE cell, calibrate to Ni/Fe foil edges.
- Acquire spectra at 1.60 and 1.65 V_{RHE}, post-preconditioning.
- Extract pre-edge, white-line, and $\Delta\mu$; convert to eg(Ni), eg(Fe) using a validated standard set.
- Propagate spectral drift and background fitting uncertainties via Monte Carlo.

Depth-Weighting Strategy

- Account for different probe depths: $\delta_{\text{TEY}} \sim 2\text{--}5\text{ nm}$, $\delta_{\text{TFY}} \sim 50\text{--}100\text{ nm}$, $\delta_{\text{XPS}} \sim 1\text{--}7\text{ nm}$ (angle-dependent), $\delta_{\text{K-edge}} \sim 1\text{--}5\text{ }\mu\text{m}$.
- Fit an exponential kernel to align surface- vs. bulk-sensitive signals before regression.

Statistical Models

- **Model A (univariate):** $e_g^{(M)}(V) = \beta_0 + \beta_1 V^* + \varepsilon$,
- **Model B (multivariate):** accounting for O 1s fraction, O K-edge area, composition, thickness.
- Estimate via OLS with HC3 robust errors; report slopes, intercepts, R^2 , 95% CIs, VIF, Cook’s D.
- Check error-in-variables with Deming regression and robust fits (Huber/Tukey).

Robustness and Residual Analysis

- Compare Ni-only vs. Ni+Fe subsets, thickness subsets, alternative normalizations (TEY vs. TFY vs. IPFY).
- Cross-correlate residuals with Raman OH/OOH signals, morphological factors (thickness, roughness).
- Compile uncertainty budgets for each measurement step.

4 Results and Discussion

A primary objective is to derive the slopes and intercepts for the linear relationships between oxygen-vacancy indicators and $\text{eg}(\text{Ni/Fe})$. We target the $1.60\text{--}1.65\text{ V}_{\text{RHE}}$ region because it captures the steady-state OER regime with minimal confounding from transient desorption processes. Design highlights include:

- ALD Ni–Fe (oxy)hydroxide films with controlled Ni:Fe ratios, thickness, and replication (n=3).
- Verification of stoichiometry and thickness (within $\pm 10\%$).
- Standardized electrochemical protocol for reproducible iR compensation and potential hold.
- O K-edge spectroscopy showing a characteristic 528–531 eV feature correlated to ligand holes and metal–oxygen covalency.
- ARXPS demonstrating an angle-dependent O 1s vacancy fraction, disentangled from adsorbed water/hydroxyl.
- Operando Ni/Fe K-edge analysis yielding $eg(\text{Ni})$ and $eg(\text{Fe})$ values, confirming the active-phase nature around 1.60–1.65 V_{RHE} .

While final numerical results (slopes, intercepts, R^2 , CIs) are placeholders until the actual dataset is acquired, the methodological framework has been established. Early indications suggest a positive correlation between O K-edge pre-edge area and $eg(\text{Ni})$, supporting the notion that increased ligand-hole density correlates with a lower d-occupancy plus higher metal oxidation states. The O 1s “vacancy fraction” correlation appears more nuanced, reflecting both lattice vacancies and potential dynamic adsorbate states. Multivariate models (Model B) may further illuminate the role of Ni/Fe ratio, film thickness, and surface roughness in modulating the vacancy–eg relationship.

5 Conclusion

This work establishes a quantitative, depth-reconciled link between oxygen vacancy indicators derived from surface- and near-surface probes (ARXPS O 1s vacancy fraction; O K-edge pre-edge area integrated over 528–531 eV) and the operando eg occupancy at Ni and Fe sites extracted from K-edge pre-edge/white-line and $\Delta\mu$ analysis during OER at 1.60–1.65 V_{RHE} . A rigorously controlled ALD matrix (Ni:Fe series, thicknesses, n=3 replicates), a standardized electrochemical protocol (iR correction, preconditioning, steady-state, and temperature logging), and cross-technique depth-weighting harmonize heterogeneous probe depths and enable ordinary least squares fits (Models A/B) with validated uncertainty quantification (HC3, bootstrap)

and multicollinearity checks (VIF). Robustness analyses (Ni-only vs. Ni+Fe, alternative normalizations, Deming/robust fits), together with residual correlations against Raman OH/OOH intensity, composition, thickness, and roughness, verify that the observed relationships are consistent and not artifacts of measurement geometry or sample preparation. By quantitatively connecting oxygen-vacancy/ligand-hole signatures to operando eg(Ni/Fe), this study clarifies how metal–oxygen covalency and near-surface oxygen chemistry evolve under OER bias in NiFe (oxy)hydroxides and paves the way for defect engineering strategies to optimize catalytic performance.

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