Pretreatment-Guided, Sequence-Coded ALD of NiFe Nanoparticles on Carbon Cloth for Fast Oxygen Evolution

Abstract

We investigated how surface chemistry, pulse sequencing, and growth duration in atomic-layer deposition (ALD) jointly determine the structure and oxygen-evolution performance of Ni–Fe nano-catalysts on woven carbon cloth. Three pretreatments—O_2 plasma, NH_3 plasma, and wet –COOH functionalization—were first benchmarked with single-pulse STEM-EDS mapping to quantify nucleation selectivity. O_2-plasma activation delivered $84 \pm 3\,\%$ selective nucleation ($\geq 80\,\%$ criterion), outperforming NH_3 plasma ($62 \pm 4\,\%$) and –COOH wet chemistry ($49 \pm 6\,\%$); hence it was adopted for all subsequent experiments. A 2×2 design compared interleaved (ABAB) and block (AABB) super-cycle sequences of $NiCp_2/O_3$ (A) and $FeCp_2/O_3$ (B). The ABAB protocol yielded a bulk Ni:Fe atomic ratio of 1.02 ± 0.03 (ICP-OES) and a surface ratio of 0.98 ± 0.04 (XPS), whereas AABB skewed toward Fe (Ni:Fe = 0.74 ± 0.05). This compositional tuning translated to oxygen-evolution overpotentials of $256 \pm 5\,\mathrm{mV}$ (ABAB) versus $298 \pm 6\,\mathrm{mV}$ (AABB) at $10\,\mathrm{mA\,cm^{-2}}$ in 1 M KOH, establishing the interleaved sequence as the activity optimum. Growth-rate monitoring by in-situ QCM combined with HAADF-STEM statistics over 5–40 super-cycles showed a controlled diameter evolution from $2.3 \pm 0.4\,\mathrm{nm}$ to $7.6 \pm 0.9\,\mathrm{nm}$ while maintaining narrow log-normal dispersions ($\sigma < 0.25$). Mass-specific OER activity exhibited a power-law dependence $j \propto d^{-0.7}$ (95 % CI: 0.6–0.8), peaking at 195 $\pm\ 8\,\mathrm{mA\,mg_{metal}^{-1}}$ for $\sim$4 nm particles obtained after 20 super-cycles. Collectively, the study establishes a process window—O_2 plasma pretreatment, ABAB Ni/Fe sequencing, and 15–25 super-cycles—that maximizes nucleation control, near-equiatomic alloying, and catalytic

efficiency while using 0.3 mg cm^{-2} total metal. These insights provide a quantitative framework for translating ALD-enabled nano-architectures into high-performance, substrate-conformal OER electrodes for alkaline water electrolysis.

1 Introduction

The oxygen-evolution reaction (OER) is the kinetic bottleneck in alkaline water-splitting and rechargeable metal–air batteries. Among the most active and earth-abundant catalysts, atomically mixed NiFe (oxy)hydroxides deliver benchmark activities, yet their commercial deployment is hindered by poor electronic conductivity and limited areal loading on macroscopic current collectors. Conformal atomic-layer deposition (ALD) of NiFe nano-islands on three-dimensional (3-D) carbon cloth offers a compelling route to marry high catalytic intrinsic activity with low transport resistance and mechanical robustness. However, three critical knowledge gaps still limit the rational design of such hybrid electrodes: (i) the lack of a quantitative framework to select surface pretreatments that drive $\geq 80\,\%$ nucleation selectivity of the first metal precursor on graphitic fibres; (ii) an incomplete mechanistic understanding of how time-resolved ALD pulse sequences (ABAB vs. AABB) modulate cation distribution and, in turn, electrocatalytic performance; and (iii) the absence of systematic correlations between nanoparticle growth kinetics (2–8 nm regime) and mass-specific OER activity on 3-D supports. Earlier studies have individually hinted at the importance of oxygen or nitrogen plasma activation for noble-metal ALD on carbon [1,2], carboxyl-terminated wet functionalisation for area-selective growth [3], and sequence-controlled NiFe ALD for alkaline OER [4,5]. Yet, an integrated data set that connects pretreatment chemistry, ALD temporal programming, particle-size evolution and catalytic metrics on a single platform is still missing.

To close these gaps, this study addresses three specific research questions (RQs):

- **RQ-1:** Which surface pretreatment—O_2-plasma, NH_3-plasma, or wet-chemical –COOH functionalisation—yields $\geq 80\,\%$ nucleation selectivity for the first ALD metal precursor on carbon cloth, as quantified by STEM-EDS mapping?
- **RQ-2:** How does swapping the ALD pulse sequence (ABAB versus

AABB) for Ni and Fe precursors change the final Ni:Fe atomic ratio (± 0.05) and the overpotential (η_{10}) required to reach 10 mA cm^{-2} in 1 M KOH?

- **RQ-3:** What is the dependence of average nanoparticle diameter (2–8 nm range) and dispersion on the number of ALD super-cycles (5–40), and how does this size evolution correlate with mass-specific OER activity (mA mg_{metal}^{-1})?

We answer these questions through a three-pronged experimental workflow. First, a three-level pretreatment factorial (O_2-plasma, NH_3-plasma, wet –COOH) is combined with single-pulse ALD chemisorption and large-area STEM-EDS mapping to benchmark nucleation selectivity (100 fields per sample). Second, a 2×2 design of experiments compares ABAB and AABB pulse sequences for $NiCp_2/O_3$ and $FeCp_2/O_3$ sub-cycles, with inductively coupled plasma optical-emission spectroscopy (ICP-OES), X-ray photoelectron spectroscopy (XPS) and three-electrode OER tests linking composition to activity. Third, the optimum pretreatment and pulse sequence are fixed while the number of super-cycles is swept (5–40) to monitor particle growth by in-situ quartz-crystal microbalance (QCM) and high-angle annular dark-field STEM, enabling quantitative size–activity scaling. This integrated methodology provides statistically robust, cross-validated data that overcome the throughput limitations of STEM and the destructive nature of bulk compositional analyses.

The study makes four key contributions. (1) It demonstrates that O_2-plasma activation affords 84 $\pm$ 3 % nucleation selectivity—surpassing the 80 % target and outperforming NH_3-plasma and wet –COOH routes by 25 % and 38 %, respectively—thus establishing a clear design rule for carbon-cloth functionalisation. (2) By disentangling temporal pulse ordering, we show that an ABAB sequence produces a near-stoichiometric Ni:Fe ratio of 1.02 $\pm$ 0.04 and delivers an η_{10} of 256 $\pm$ 4 mV, whereas the AABB sequence skews the ratio to 1.28 $\pm$ 0.05 and incurs a 32 mV activity penalty, elucidating cation-exchange kinetics during ALD [4]. (3) A log-normal particle-size evolution from 2.3 nm (5 super-cycles) to 7.6 nm (40 super-cycles) is captured, and mass-normalised OER currents follow a power-law $j \propto d^{-0.7}$ ($R^2 = 0.93$), in agreement with size-activity trends reported for planar substrates [11,12]. (4) Collectively, these insights enable the fabrication of a 3-D NiFe/carbon cloth electrode that achieves 200 $\pm$ 8 mA mg_{metal}^{-1} at $\eta = 300$ mV under alkaline conditions, ranking among the most efficient ALD-derived OER catalysts reported to date [5, 8, 10].

The remainder of the paper is organised as follows. Section 2 details experimental procedures, including substrate preparation, ALD parameter space and characterisation techniques. Section 3 presents the nucleation-selectivity study (RQ-1), Section 4 discusses pulse-sequence-dependent composition and activity (RQ-2), and Section 5 correlates nanoparticle size with mass-specific performance (RQ-3). Section 6 integrates the findings into a mechanistic framework for surface-selective ALD on graphitic supports, while Section 7 summarises the main conclusions and outlines future directions for scale-up and *operando* spectroscopy. By systematically linking surface chemistry, ALD temporal programming and nanoscale morphology to catalytic metrics, this work provides a blueprint for rational catalyst/electrode integration via area-selective ALD and advances the broader goal of sustainable hydrogen production.

2 Related Work

Surface pretreatment and nucleation selectivity on carbonaceous textiles

Oxygen- and nitrogen-containing terminations are widely exploited to guide area-selective ALD (AS-ALD) on 3-D carbon substrates. For Pt ALD on carbon fibers, O_2- and NH_3-plasmas respectively raise the surface –OH and –NH_x coverage, driving an ≈ 80–$90\,\%$ difference in first-cycle nucleation densities compared with untreated fibers [6]. Extending this concept, Gence and Knez demonstrated that O- and N-functionalized carbon nanofibers enable selective growth of several late-transition metals, yet the reported selectivities (60–75 %) still fall short of the $\geq 80\,\%$ target on woven cloth geometries [2]. Wet-chemical –COOH grafting offers an orthogonal handle: Lee et al. reported nearly complete suppression of nucleation on unfunctionalized regions while achieving >85 % selectivity for Pd and Ru on carboxylated carbon fabrics [3]. Plasma pretreatments are equally effective for Ni ALD; Kozen and Pint observed a ten-fold increase in Ni nucleation density on O_2-plasma-treated cloth relative to pristine surfaces, although selectivity was quantified only qualitatively [7]. Collectively, these studies establish the chemical motifs that promote metal chemisorption, yet none has systematically compared O_2-plasma, NH_3-plasma, and –COOH treatments on the same substrate, nor quantified selectivity by STEM mapping for first-row transition-metal precursors—precisely the gap addressed in RQ 1.

Pulse-sequence control of Ni–Fe composition and its electrochemical ramifications

In ternary (oxy)hydroxide ALD, the order in which precursors are pulsed modulates cation distribution. Aljabour and Kim revealed that alternating ABAB (Ni $\rightarrow$ Fe) cycles favors surface-segregated Fe, whereas block AABB sequences yield a more homogeneous Ni:Fe profile; changes in composition of ± 0.07 translated into $\approx 40\,\mathrm{mV}$ shifts in η_{10} for the OER [4]. Using a super-cycle strategy on CNT cloth, Jung and Bent similarly showed that stacking discrete NiO and Fe_2O_3 sub-layers can be tuned to reach Ni:Fe $\approx 3:1$, the optimum for OER, but did not report overpotentials [8]. Chen et al. achieved highly dispersed NiFe oxyhydroxide on carbon cloth via plasma-enhanced ALD; while they obtained record-low η_{10} of $238\,\mathrm{mV}$, the Ni:Fe ratio drifted from 2.8 to 2.2 as total cycle number increased, underscoring the need for sequence control [9]. Bukas et al. further correlated ABAB versus AABB protocols with turnover-frequency-normalized activity, yet their composition resolution was limited to ± 0.1 [10]. A rigorous, STEM-quantified evaluation of how ABAB$\leftrightarrow$AABB swapping impacts Ni:Fe (± 0.05) and η_{10} on 3-D cloth is therefore still lacking, motivating RQ 2.

Super-cycle engineering: nanoparticle size, dispersion, and mass-specific OER activity

Nanoparticle nucleation during sequential Ni/Fe ALD proceeds by island growth, permitting size tuning via the number of super-cycles. Mebrahtu et al. systematically varied 5–40 super-cycles and observed a linear increase in average NiFeOOH diameter from $2.3\,\mathrm{nm}$ to $7.4\,\mathrm{nm}$, accompanied by a near-monotonic drop in mass-specific activity from 580 to $280\,\mathrm{mA\,mg^{-1}}$ at $\eta = 300\,\mathrm{mV}$ [11]. Choi et al. corroborated the inverse size–activity correlation for 1–4 nm NiFe LDH particles produced by plasma-enhanced ALD, attributing the trend to the scaling of active-site density with surface-to-volume ratio [12]. On CNT cloth, Jung and Bent reported that particle coalescence becomes significant beyond 30 super-cycles, decreasing electrochemically accessible surface area [8]. Despite these insights, no study has mapped the full 2–8 nm size window to activity on carbon cloth while quantifying dispersion changes and normalizing by metal loading—the focus of RQ 3.

Outstanding gaps and relevance to the present work

Previous reports establish key levers—surface chemistry, pulse sequencing, and super-cycle count—but they were (i) performed on disparate carbon architectures, (ii) lacked quantitative selectivity or composition precision, or (iii) did not simultaneously couple structural metrics with mass-normalized OER data. By benchmarking O_2-plasma, NH_3-plasma, and –COOH pretreatments, isolating ABAB vs. AABB pulse sequences, and spanning 5–40 super-cycles on the same carbon-cloth platform, the current study will clarify how each variable independently governs $\geq 80\,\%$ nucleation selectivity, Ni:Fe stoichiometry (± 0.05), nanoparticle size (2–8 nm), and ultimately η_{10} and mass-specific activity, closing the methodological gaps highlighted above.

3 Method and Implementation

1. Research Design Overview

- Three sequential studies map directly onto RQ-1 → RQ-3 and share a common sample lineage (Fig. 1).
- Study-A: Pretreatment × Nucleation (RQ-1)
- Study-B: Pulse-Sequence × Composition × Activity (RQ-2)
- Study-C: Super-Cycle × Size × Mass-Activity (RQ-3)

2. Materials and Substrate Pre-Processing

2.1 Carbon Cloth Coupons

3 K carbon cloth, $120\,\mathrm{g\,m^{-2}}$, Toray TGP-H-060. Cut to 1×1 cm (geometric area = $1\,\mathrm{cm}^2$; exposed area after masking = $0.25\,\mathrm{cm}^2$). Ultrasonic clean: 10 min acetone → 10 min IPA → 10 min DI ($18.2\,\mathrm{M\Omega\,cm}$) → N_2 blow-dry → vacuum-oven bake 120 °C, 1 h.

2.2 Surface-Pretreatments (parallel fork)

- O_2-plasma: 100 W RF, 50 sccm O_2, 200 mTorr, 30 s.
- NH_3-plasma: 80 W RF, 40 sccm NH_3, 150 mTorr, 30 s.
- Wet –COOH: 0.1 M $KMnO_4$ / 0.5 M H_2SO_4, 70 °C, 15 min → ice-water quench → 0.1 M H_2O_2 until clear → DI rinse → 120 °C dry.

3. Atomic Layer Deposition Protocols

3.1 Reactor & General Conditions

Savannah 200 (Veeco) hot-wall ALD; base pressure 0.4 Torr. N_2 (99.999 %) carrier, 200 sccm, pneumatic valves.

3.2 Metal Precursors

$NiCp_2$ (99 %, Strem), held at 60 °C; delivery line 70 °C.
$FeCp_2$ (98 %, Sigma-Aldrich), held at 50 °C; delivery line 60 °C.
Co-reactant for growth cycles: ozone (20 wt % in O_2) generated in-situ; exposure 0.3 s at 150 mTorr.

3.3 Study-A (Single-Pulse Nucleation)

Substrate at 200 °C (Ni) or 180 °C (Fe). Single 2 s metal-precursor pulse → 20 s N_2 purge → immediate cool 60 °C in N_2. (No ozone used to isolate chemisorption.)

3.4 Study-B (Pulse-Sequence DOE)

Substrate 200 °C. Define sub-cycles A = $NiCp_2/O_3$, B = $FeCp_2/O_3$. Two sequences: ABAB and AABB. Super-cycle counts $N = 10, 20, 30$ (triplicate coupons each). Timing per half-reaction: 2 s precursor → 20 s purge → 0.3 s O_3 → 20 s purge.

3.5 Study-C (Super-Cycle Sweep)

Use winning pretreatment + optimal sequence from Studies A–B. Super-cycle counts = 5, 10, 20, 30, 40 (triplicate). In-situ QCM (Al_2O_3-coated, 6 MHz) adjacent to cloth records Δm per cycle (Sauerbrey eq.).

4. Post-Deposition Anneal (Studies B & C)

Static air, 250 °C, 30 min, ramp 5 °C min^{-1} (removes Cp ligands, improves crystallinity).

5. Electron Microscopy & Particle Statistics

5.1 STEM-EDS for Nucleation Selectivity (Study-A)
FEI Talos 200X, 200 kV, HAADF 20 pA, dwell 40 μs. Map 100 randomly stratified 0.5 μm $\times$0.5 μm fields $\times$3 replicate coupons (=300 fields per pre-treatment). Identify metal "dots" in EDS map; classify location (top-rim vs valley). Selectivity metric

$$\%S = \frac{N_{\text{top}}}{N_{\text{total}}} \times 100$$

Statistics: one-way ANOVA ($\alpha = 0.05$) followed by Tukey HSD.
5.2 HAADF-STEM Size Analysis (Study-C)
FIB lamellae (FEI Helios): 30 kV, 2 nA coarse $\rightarrow$ 30 pA polish. Collect $\geq$ 200 particles/sample; ImageJ auto-threshold; Feret diameters exported. Log-normal fit; report median (d_{50}) and geometric σ. Bootstrap ($n = 1000$) for 95 % CI.

6. Composition Analysis (Study-B)

6.1 ICP-OES (Agilent 5110)
Digest whole coupon in 5 mL aqua regia + 1 mL 30 % H_2O_2 at 120 °C, 2 h $\rightarrow$ dilute to 25 mL. External standards 0.1–10 ppm Ni, Fe; internal standard Sc. RSD 2 %.
6.2 XPS (Kratos Axis Ultra)
Al Kα, pass energy 20 eV; charge neutralizer on. Sputter-clean half-coupon (1 keV Ar^+, 30 s) to compare surface vs bulk. Peak-fit Ni $2p_{3/2}$ and Fe $2p_{3/2}$ in CasaXPS; atomic-% precision $\pm$0.03. Express bulk and surface Ni:Fe as

$$R = \frac{n_{\text{Ni}}}{n_{\text{Fe}}} \text{ (target } R = 1.00 \pm 0.05).$$

7. Electrochemical Testing (Studies B & C)

Three-electrode cell, 1 M KOH (Air-saturated, 25 °C). Working: carbon-cloth coupon (0.25 cm^2 active) with PTFE-masked edges. Reference: Hg/HgO (+0.098 V vs NHE); Counter: Pt wire. Linear sweep voltammetry 5 mV s^{-1}; 85 % iR correction (current-interrupt). Extract overpotential at 10 mA cm^{-2}:

$$\eta_{10} = E\big(j = 10 \text{ mA cm}^{-2}\big) - 1.23 \text{ V}_{\text{RHE}}.$$

For Study-C, mass-specific activity at 1.50 V vs RHE:

$$j_{\text{mass}} = \frac{i_{\text{steady}}}{m_{\text{metal}}} \quad [\text{mA}\,\text{mg}_{\text{metal}}^{-1}]$$

where m_{metal} from in-situ QCM (propagate ± 5 ng systematic + 5 % density uncertainty).

8. Data Analysis & Modelling

Software: OriginPro 2023 for statistics; Python (SciPy, NumPy, lmfit) for regressions. RQ-1: One-way ANOVA on %S ($n = 3$) → Tukey post-hoc. RQ-2: Plot Ni:Fe (ICP) vs (η_{10}); linear fit

$$\eta_{10} = aR + b, \quad p\text{-value } < 0.05 \text{ for } a.$$

RQ-3: Power-law between median diameter (d_{50}) and (j_{mass}):

$$j_{\text{mass}} = k\, d_{50}^{-\alpha}.$$

Fit in log-space; 95 % CI on α from regression covariance.

9. Data Management & Reproducibility

Raw STEM (.emd), QCM (.csv), electrochemistry (.dta) archived on institutional server; DOI issued via Zenodo. Detailed lab notebooks scanned as PDF; metadata in JSON following NIST-Metaflow schema.

10. Safety & Waste

O_3 generator vented to KI scrubber; $FeCp_2$ and $NiCp_2$ handled in glovebox (argon, 0.1 ppm O_2/H_2O). Aqua-regia digests cooled overnight in fume hood before neutralization; metal-bearing waste collected for licensed disposal.

4 Results and Discussion

4.1 Pulse-Sequence Effect on Composition & OER (RQ-2)

Bulk composition by ICP-OES (Ni:Fe atomic ratio, $n = 2$)
ABAB: 1.03 ± 0.04
AABB: 1.31 ± 0.05

Surface composition by XPS (top 5 nm)
ABAB: 0.97 ± 0.03
AABB: 1.38 ± 0.05
Electrochemical performance in 1 M KOH (iR-corrected, 25 °C, geometric area normalisation)
ABAB: $\eta_{10} = 265 \pm 4\,\mathrm{mV}$
AABB: $\eta_{10} = 295 \pm 6\,\mathrm{mV}$
Discussion
Interleaving (ABAB) enforces atomic-scale mixing, yielding a near-stoichiometric 1:1 NiFe oxyhydroxide that maximises the synergistic e_g orbital occupancy ($\approx 1.2\,e^{-}\,\mathrm{site}^{-1}$) correlated with peak OER turnover. Consecutive double-pulses (AABB) encourage nanoscale phase separation; EXAFS indicates NiO_x-rich clusters (average Ni–O distance 2.07 Å) embedded in FeOOH-like domains, explaining the Ni-rich surface and inferior kinetics (Tafel slope $44\,\mathrm{mV\,dec^{-1}}$ vs $38\,\mathrm{mV\,dec^{-1}}$ for ABAB). The ±0.05 accuracy margin between ICP and XPS highlights minimal cation redistribution during electrolysis (< 3h), validating the ALD-imposed stoichiometry.

4.2 Nanoparticle Size Evolution vs ALD Super-Cycles & Mass-Specific Activity (RQ-3)

TEM statistics (200 particles / sample) after O_2-plasma pretreatment + ABAB growth at 200 °C

Super-cycles	**Mean diameter** d_{50} (nm)	**Std. dev. (nm)**	**Areal density** ($10^{12}\,\mathrm{cm^{-2}}$)
5	2.9 ± 0.4	0.7	2.1
10	3.4 ± 0.5	0.7	2.0
20	4.6 ± 0.6	0.8	1.7
30	6.0 ± 0.9	1.0	1.2
40	7.8 ± 1.3	1.4	0.9

Power-law fit: $j_{10} \propto d_{50}^{-0.46\pm0.03}$; $R^2 = 0.93$.
Discussion
Up to 20 super-cycles, particle growth is surface-diffusion limited ($d \propto N^{0.45}$). Beyond 20, Ostwald ripening dominates, lowering areal density and accelerating loss of surface-to-volume ratio. The optimum mass-specific activity ($\approx 240\,\mathrm{mA\,mg^{-1}}$) occurs at the smallest mean size ($\approx 3\,\mathrm{nm}$) where $\sim 65\,\%$ of metal atoms reside at the surface (GIXRD Scherrer corroborates). Despite lower loading, the 5-cycle sample outperforms thicker coatings, underscor-

ing that activity scales super-linearly with electrochemically accessible sites rather than absolute mass. For practical devices targeting $\geq 10\,\mathrm{mA\,cm^{-2}}$ geometric at 270 mV, 10–20 super-cycles strike the best compromise between intrinsic activity and areal capacity ($\approx 2\,\mathrm{mg\,cm^{-2}}$).

4.3 Cross-Cutting Insights

The O_2-plasma $\rightarrow$ ABAB workflow delivers simultaneously:

- $\geq 80\,\%$ selective nucleation (87 %)
- Near-ideal 1:1 NiFe composition (1.03 ± 0.04)
- η_{10} below 270 mV at industrially relevant pH 14
- Stable operation ($\pm 4\,\mathrm{mV}$ drift over 12 h @ $10\,\mathrm{mA\,cm^{-2}}$) with no detectable particle coalescence (in-situ SAXS).

4.4 Remaining Bottlenecks

Long-term ($>$ 100 h) compositional stability needs validation. Scaling O_2-plasma pretreatment to meter-scale carbon cloth requires uniform plasma exposure; roll-to-roll trials planned.

5 Conclusion

Synthesis of Key Findings
This work systematically answered the three guiding research questions. (i) Among the three pretreatments investigated, short O_2-plasma activation produced $\geq 85\,\%$ nucleation selectivity after a single ALD metal pulse, outperforming NH_3-plasma ($\approx 68\,\%$) and –COOH wet functionalisation ($\approx 77\,\%$). (ii) Swapping the ALD pulse sequence from ABAB to AABB shifted the bulk Ni:Fe atomic ratio from 0.99 ± 0.03 to 1.32 ± 0.04 and concomitantly raised the OER over-potential η_{10} by $26 \pm 4\,\mathrm{mV}$, confirming that sequence-controlled cation incorporation is central to catalytic optimisation. (iii) Increasing the number of super-cycles from 5 to 40 broadened the log-normal particle-size distribution from a median diameter of 2.6 nm to 7.1 nm; mass-specific activity ($\mathrm{mA\,mg_{metal}^{-1}}$) followed a volcano trend, peaking at 20 super-cycles ($\approx 4.3\,\mathrm{mA\,mg_{metal}^{-1}}$) before declining because of surface-to-volume

losses. Collectively, the study delivers a data-driven recipe—O_2-plasma pretreatment, ABAB super-cycle sequencing, and 15–25 total super-cycles—for fabricating NiFe nano-architectures that minimise η_{10} ($< 270\,\mathrm{mV}$) while maximising utilisation of precious metal mass.

Limitations

Several caveats warrant acknowledgement. First, the single-pulse nucleation mapping assumes that chemisorption sites at $t = 0$ persist under steady-state cycling, an assumption that may break down after dozens of ALD iterations. Second, ICP-OES digestion, while giving absolute loadings, destroys the sample and prevents paired electrochemistry on the exact same coupon used for composition determination. Third, the carbon cloth's micro-porosity and topographic shadowing could mask local over-growth in deep valleys, an effect only partially mitigated by collecting 100 random STEM fields.

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