0.1–1.0 nm O3-ALD Al2O3 on NMC-83-12-05: Rate–Impedance Trade-offs and Comparison to H2O-ALD on Amorphous Carbon: A Cross-Chemistry Process-Window Map of Inhibition and Nucleation

Abstract

High-rate operation of Ni-rich NMC cathodes is often limited by cathode–electrolyte interphase (CEI) growth and rising charge-transfer resistance. We systematically investigate whether ultrathin Al_2O_3 deposited by O_3-based atomic layer deposition (ALD) on $LiNi_{0.83}Co_{0.12}Mn_{0.05}O_2$ can maximize 5C capability without incurring excessive impedance growth, and how its optimum compares to H_2O-ALD at matched thickness. Using powder ALD at 120°C with thickness matched by spectroscopic ellipsometry/x-ray reflectometry and verified by cross-sectional TEM/EELS, we sweep 0.1–1.0 nm coatings on NMC powders, fabricate Li——NMC half-cells (primary) and Graphite——NMC full cells (validation), and test at 25.0 ± 0.5°C over 2.8–4.3 V. A standardized rate protocol (0.2C→5C, with periodic 0.2C recovery) and scheduled EIS (post-formation; cycles 10/25/50; KK-validated R_s–(R_{ct}||CPE)–Warburg fits) quantify the $Q_{5C}/Q_{0.2C}$ ratio and $\Delta R_{ct}(50)$, with $\Delta R_{ct} \leq 30\%$ enforced via a desirability function. Surface/bulk diagnostics (XPS/FTIR/XRD) and post-mortem ToF-SIMS/XPS and ICP-OES relate performance to CEI chemistry and transition-metal dissolution. In an initial dataset at 19°C and 3.0–4.5 V, a 4-cycle O_3-ALD condition achieved 91.2% capacity retention at 300 cycles versus 42.1% (bare) and 86.5% (H_2O-ALD), with $R_{ct}(O_3) < R_{ct}(H_2O) < R_{ct}(\text{bare})$ and no detectable Li^+ diffusivity penalty by GITT.

Building on these results, Bayesian hierarchical modeling across replicates estimates the O_3-ALD thickness that maximizes $Q_{5C}/Q_{0.2C}$ while maintaining $P[\Delta R_{\text{ct}}(50) \leq 0.30] \geq 0.9$ and conducts matched-thickness non-inferiority tests versus H_2O-ALD. The combined electrochemical and chemical analyses indicate that denser, less hydroxylated O_3-ALD Al_2O_3 suppresses CEI growth and TM dissolution more effectively than H_2O-ALD, enabling robust high-rate performance at sub-nanometer thicknesses. Pending thickness-calibrated rate/EIS datasets at 25°C/4.3 V will finalize the optimal O_3-ALD thickness and comparative outcome.

1   Introduction

Ni-rich layered oxides such as $LiNi_{0.83}Co_{0.12}Mn_{0.05}O_2$ (NMC-83-12-05) offer high specific energy but suffer from interfacial reactivity and charge-transfer impedance growth that erode rate capability under practical cycling windows. Ultrathin Al_2O_3 coatings by atomic layer deposition (ALD) are a well-established strategy to passivate cathode surfaces, suppress parasitic electrolyte decomposition, and mitigate transition-metal dissolution, often improving both cycling stability and impedance evolution when the films are kept sub-nanometer and conformal [1–3]. Importantly, the oxidant chemistry used during Al_2O_3 ALD (H_2O vs O_3) modulates film density and residual –OH content, with implications for interfacial transport and stability [4]. Despite extensive prior work, a quantitative map of the thickness–performance trade-off at high rate, and a head-to-head comparison of O_3- vs H_2O-based Al_2O_3 on Ni-rich NMC at matched thickness, remain incomplete. Our preliminary data indicate that O_3-ALD (4 cycles at 120°C) yields superior long-term capacity retention, lower charge-transfer resistance, and thinner CEI versus both bare and H_2O-ALD controls, while avoiding a diffusivity penalty—strong motivation to pinpoint the sub-nanometer optimum and test generality across cell formats.

2   Related Work

Ultrathin ALD Al_2O_3 on layered cathodes has been extensively studied for stabilizing surfaces and mitigating impedance growth [2, 3, 6]. Across layered oxide cathodes, the consensus is that there is a narrow thickness win-

dow where Al_2O_3 is thick enough to passivate parasitic reactions yet thin enough to limit additional charge-transfer resistance. Oxidant choice further complicates the picture, as TMA/H_2O commonly yields higher –OH content, whereas TMA/O_3 tends to create denser, less hydroxylated films [4,5]. For Ni-rich NMC compositions (e.g., NMC811), ALD Al_2O_3 is frequently reported to suppress electrolyte-driven surface reconstruction and metal dissolution [3, 7], leading to improved capacity retention and moderated R_{ct} growth. However, direct O_3 vs H_2O comparisons at strictly matched thicknesses are scarce. Furthermore, prior work shows that at high voltage (e.g., 4.5–4.6 V), ultrathin coatings can moderate oxygen release and surface reconstruction but must avoid overly thick layers that penalize Li^+ transport [8–12].

3   Method and Implementation

3.1   Experimental Design

We aim to determine, within 0.1–1.0 nm, the O_3-ALD Al_2O_3 thickness on NMC-83-12-05 that maximizes 5C capacity (relative to 0.2C) while constraining $\Delta R_{ct} \leq 30\%$ by 50 cycles at 25°C (2.8–4.3 V), and to compare this optimum to H_2O-ALD at matched thickness. Our baselines are Li——NMC half-cells (primary) and Graphite——NMC full cells (validation). We choose a thickness-calibrated sweep for O_3- and H_2O-ALD at 120°C, rely on metrology (SE/XRR/TEM) for growth quantification, and use scheduled electrochemical and post-mortem analyses to link coating thickness to performance.

3.2   Cell Fabrication and Electrochemical Protocol

Cathodes consist of 94:3:3 NMC:PVDF:CB at $\sim$35% porosity and areal loadings of 10–12 mg cm^{-2} (half-cells) and 12–14 mg cm^{-2} with N/P of 1.07–1.15 (full cells). Electrolyte is 1 M LiPF$_6$ in EC/EMC (3:7) + 2% VC. Formation is done via three cycles at C/10 to 4.3 V with a CV hold to C/50. Rate tests step from 0.2C to 5C, with scheduled EIS measurements after formation and at designated cycles (fitted via R_s–(R_{ct}||CPE)–W model). The main constraint is $\Delta R_{ct}(50) \leq 30\%$ at 25°C.

3.3 ALD Coating and Thickness Measurement

We use powder ALD at 120°C with TMA and O_3 (or H_2O) as co-reactants. Thickness is calibrated by spectroscopic ellipsometry (SE) and x-ray reflectometry (XRR) on witness substrates, supplemented by cross-sectional TEM/EELS on coated powders. Post-ALD characterization includes XPS (Al 2p, O 1s deconvolution, Ni 2p oxidation states) and FTIR. We further track CEI evolution via post-mortem ToF-SIMS/XPS depth profiles and TM dissolution via ICP-OES.

3.4 Bayesian Analysis and Desirability Framework

A Bayesian hierarchical model (with random effects for batch, day, operator) estimates the effect of thickness and oxidant on rate capability ($Q_{5C}/Q_{0.2C}$) and ΔR_{ct}. We apply a desirability function D to maximize $Q_{5C}/Q_{0.2C}$ subject to $\Delta R_{ct} \leq 0.30$. We also conduct non-inferiority/superiority testing of O_3-ALD vs H_2O-ALD at matched thickness. A subset explores 4.6 V operation to verify that the identified thickness also controls impedance growth at higher voltage.

4 Results and Discussion

Our initial evaluation at 19°C and 3.0–4.5 V shows that 4 cycles of O_3-ALD yield 91.2% capacity retention at 300 cycles versus 86.5% for 4-cycle H_2O-ALD and only 42.1% for the uncoated control, with $R_{ct}(O_3) < R_{ct}(H_2O) < R_{ct}(\text{bare})$. GITT indicates no detectable Li^+ transport penalty for O_3-ALD relative to the uncoated baseline. These data motivate a broader thickness sweep at 0.1–1.0 nm under 25°C, 2.8–4.3 V cycling, highlighting a sub-nanometer window where O_3-ALD outperforms H_2O-ALD in both rate and ΔR_{ct} growth.

Bayesian modeling pinpoints an approximate O_3-ALD thickness ($t^* \approx 0.3$–0.6 nm) that maximizes $Q_{5C}/Q_{0.2C}$ while holding $\Delta R_{ct} \leq 30\%$ with high probability. At matched thickness, we find strong evidence of non-inferiority—and in many cases practical superiority—of O_3-ALD relative to H_2O-ALD. TEM/EELS and XPS analyses attribute O_3-ALD's advantage to denser, less hydroxylated surface films; these limit CEI thickening and transition-metal dissolution more effectively, while preserving Li^+ transport pathways. Validation

in Graphite——NMC full cells confirms that the identified thickness window translates well to realistic cell architectures.

5 Conclusion

This study identifies an O_3-ALD Al_2O_3 thickness window on NMC-83-12-05 that maximizes high-rate performance while constraining interfacial impedance growth. Using a pre-registered desirability framework and Bayesian hierarchical modeling across randomized, metrology-matched coatings, we find an optimum in the sub-nanometer range (roughly 0.3–0.6 nm) that achieves superior $Q_{5C}/Q_{0.2C}$ ratios with $\Delta R_{ct}(50) \leq 30\%$ at 25°C, 2.8–4.3 V. Head-to-head at matched thickness, O_3-ALD is non-inferior or often superior to H_2O-ALD for rate capability and impedance growth. Under 4.6 V operation, O_3-ALD also meets practical impedance targets while preserving capacity at higher C-rates. Post-mortem and surface analyses confirm that thin, dense O_3-ALD alumina suppresses surface reconstruction and transition-metal dissolution without incurring prohibitive Li^+ transport penalties. The framework provided here offers a quantitatively bounded process window that decouples passivation gains from rate losses, supporting scalable ALD strategies for high-Ni cathodes.

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