0.1–1.0 nm O_3-ALD Al_2O_3 on NMC-83-12-05: Rate–Impedance Trade-offs and Comparison to H_2O-ALD

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 $P[\Delta R_{ct}(50) \leq 0.30] \geq 0.9$ 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

2.1 Ultrathin ALD Al_2O_3 on layered cathodes

Foundational work demonstrated that conformal, ultrathin Al_2O_3 deposited by ALD on layered oxides stabilizes the surface against electrolyte attack and transition-metal dissolution, improving cycling stability with minimal initial impedance penalty when coatings remain sub- to few-nanometers; it also established rate and EIS benchmarking practices widely followed in later NMC811 studies [5]. Comprehensive reviews summarize ALD process chemistry, typical Al_2O_3 thickness ranges used in batteries, and performance metrics linking rate capability and interfacial resistance [2,3].

2.2 Thickness–performance trade-off

Across layered oxide cathodes, the consensus is that there is a narrow thickness window where Al_2O_3 is thick enough to passivate parasitic reactions yet thin enough to limit added charge-transfer resistance; beyond roughly the sub-nm to low-nm regime, impedance growth and rate loss become pronounced [2,3,5]. Reviews emphasize that optimized coatings often lie in the Ångström-to-subnanometer range for high-rate performance, whereas thicker films can suppress side reactions but degrade 5C/0.2C capacity ratios via increased interfacial resistance [2,3].

2.3 Oxidant choice (H_2O vs O_3) and film properties

ALD Al_2O_3 grown with TMA/H_2O typically exhibits higher –OH content and lower density than TMA/O_3 at comparable temperatures; O_3-grown films are denser and contain fewer impurities, which can improve chemical robustness but may increase intrinsic resistivity if the film is too thick [4,6]. These chemistry–property differences suggest that the optimal O_3-grown Al_2O_3 thickness for fast Li^+ transport may shift thinner than the optimal H_2O-grown thickness to avoid excess impedance while preserving passivation [2–4].

2.4 Ni-rich NMC with ALD Al_2O_3: benefits and constraints

For Ni-rich NMC, ALD Al_2O_3 is frequently reported to suppress electrolyte-driven surface reconstruction and metal dissolution, leading to improved capacity retention and moderated R_{ct} growth, provided the coating remains ultrathin; excessive thickness can elevate R_{ct} and impair high-rate capacity retention [3,7]. Studies using TMA/H_2O commonly identify sub-nm to ~ 1 nm as a practical window balancing CEI stabilization and rate capability; head-to-head rate/EIS analyses typically track ΔR_{ct} over tens of cycles and compare high-rate to low-rate baselines [3,5,7].

2.5 Comparative oxidant studies and implications

While many NMC811 coating studies have used TMA/H_2O, comparative ALD oxidant works show that TMA/O_3 yields denser, less hydroxylated Al_2O_3 with lower impurity levels on oxides, correlating with improved chemical passivation but potentially reduced defect-mediated Li^+ transport at higher thickness [4,6]. The "sweet spot" thickness for O_3-grown Al_2O_3 may thus be at the lower end of the ultrathin regime [2,3].

2.6 Gaps relative to the present question

Direct determination of the optimal O_3-ALD Al_2O_3 thickness within 0.1–1.0 nm on NMC-83-12-05 that maximizes 5C capacity (relative to 0.2C) while constraining $\Delta R_{ct} \leq 30\%$ after 50 cycles at 25°C (2.8–4.3 V), and a head-to-head comparison to H_2O-ALD at matched thickness under identical protocols, appears insufficiently resolved in the literature. Methodological precedents exist [5], yet targeted O_3-vs-H_2O, sub-nm mapping on NMC811 remains a clear opportunity [3,6].

3 Method and Implementation

3.1 Objective and factors

Objective: Identify the O_3-ALD Al_2O_3 thickness on $LiNi_{0.83}Co_{0.12}Mn_{0.05}O_2$ (NMC-83-12-05) in 0.1–1.0 nm that maximizes 5C rate capability relative to 0.2C, subject to $\Delta R_{ct}(50) \leq 30\%$ at 25°C, 2.8–4.3 V; compare O_3-ALD vs H_2O-ALD at matched thickness.
   Factors and levels:

- Oxidant: O_3 vs H_2O

- Thickness: 0.1–1.0 nm (8 levels) + uncoated

- Cell format: Half-cell primary; full-cell validation subset

3.2 Cell formats, electrodes, electrolyte

- Half-cells (primary): Li||NMC; 10–12 mg cm^{-2} loading

- Full cells (validation): Graphite∥NMC; 12–14 mg cm^{-2}; N/P=1.07–1.15

- Cathode: 94:3:3 (NMC–PVDF–Super P) at ∼35% porosity

- Electrolyte: 1 M LiPF$_6$ in EC/EMC (3:7) + 2% VC

- Formation: 3 cycles at C/10 to 4.3 V with CV to C/50

3.3 ALD processing

- Platform: Powder ALD primary (fluidized-bed or rotary); electrode-level ALD subset optional

- Temperature: 120°C for both TMA/O$_3$ and TMA/H$_2$O

- TMA/O$_3$: O$_3$ in O$_2$ (80–150 g/Nm^3), TMA dose 0.10 s, O$_3$ dose 1–3 s

- TMA/H$_2$O: H$_2$O dose 0.10 s

- Thickness matched by SE/XRR, not just cycle count

3.4 Rate and EIS testing

- Rate test: 0.2C→5C (charge=discharge), rests ≥ 15 min, 0.2C recovery every 5 cycles

- EIS: 1 MHz–10 mHz, 5–10 mV, at 50% SOC after formation and after cycles 10, 25, 50

- Temperature: 25.0 ± 0.5°C

- $\Delta R_{ct}(50) = [R_{ct,50} - R_{ct,0}]/R_{ct,0}$

3.5 Bayesian modeling and desirability

We adopt a Bayesian hierarchical model for $Q_{5C}/Q_{0.2C}$ and $\Delta R_{ct}(50)$, factoring in replicate cells, batch, day, operator. A desirability function D combines rate performance and ΔR_{ct} constraint ($\leq 30\%$ at cycle 50). We estimate the thickness t^* for O$_3$-ALD that maximizes $Q_{5C}/Q_{0.2C}$ subject to P[$\Delta R_{ct}(50) \leq 0.30$] ≥ 0.9 and compare it to H$_2$O-ALD at matched thickness.

3.6 Analysis workflow

Below is a high-level UML-like overview. In practice, we would embed or run plantuml or equivalent for diagrams, but we show them in verbatim form here:

```
@startuml
start
:Pre-dry NMC powders (120C, vacuum, overnight);
if (ALD oxidant) then (O3)
  :Powder ALD: TMA/O3 @120C;
else (H2O)
  :Powder ALD: TMA/H2O @120C;
endif
:Post-ALD bake (90C, Ar/vac, 2h);
:SE/XRR on Si; compute GPC & density;
:TEM/EELS + XPS subset on coated powders;
:Electrode fabrication (94:3:3; calender to 35%±5% porosity);
:Cell assembly (Li||NMC primary; subset Graphite||NMC);
:Formation (3× C/10 to 4.3V, CV to C/50; rest 2h);
:Baseline EIS @50% SOC;
:0.2C baseline cycles ×3;
:Rate test 0.5C->1C->2C->5C with rests and 0.2C recovery;
:EIS @ cycles 10, 25, 50;
:Post-mortem: ToF-SIMS/XPS, ICP-OES (subset);
:Data QC (KK tests, outlier flags);
:Bayesian modeling & desirability optimization;
:Report t* and O3 vs H2O comparison;
stop
@enduml

@startuml
actor Operator
participant Cycler
participant Chamber
participant EIS
participant DB as Database
Operator -> Cycler: Formation (3x C/10 to 4.3V; CV to C/50)
Operator -> Chamber: Set 25.0±0.5C; wait stabilize
Cycler -> Cycler: 0.2C baseline cycles x3
Operator -> EIS: Baseline EIS @50% SOC (1MHz-10mHz)
loop Rate steps with recovery
  Cycler -> Cycler: 0.5C -> 1C -> 2C -> 5C ...
  alt Scheduled EIS
    Operator -> EIS: EIS after cycles 10, 25, 50
  end
end
Cycler -> DB: Upload raw cycling + metadata
EIS -> DB: Upload spectra + fits
@enduml

@startuml
```

```
class ALDCondition {
  +condition_id
  +oxidant (O3|H2O)
  +thickness_nm
  +batch_id
  +gpc_A_per_cycle
  +notes
}
class Cell {
  +cell_id
  +format (half|full)
  +loading_mg_cm2
  +porosity_frac
  +electrolyte
  +condition_id
  +assembly_day
  +operator
  +temperature_C
}
class Measurement {
  +cell_id
  +cycle_idx
  +soc
  +Q_mAh_g
  +R_s_ohm
  +R_ct_ohm
  +W_params
  +temp_C
  +flags
}
class ModelSpec {
  +formulas
  +priors
  +margins
  +desirability_weights
}
class Results {
  +posteriors
  +t_star_nm
  +decisions
  +diagnostics
}
ALDCondition "1" <-- "many" Cell
Cell "1" <-- "many" Measurement
ModelSpec "1" --> "1" Results
```

```
@enduml

@startuml
package Instruments {
  [Cycler]
  [EIS]
  [SE/XRR]
  [XPS]
  [TEM]
  [ToF-SIMS]
  [ICP-OES]
}
[Raw Data Store]
[QC/Validation]
[Tidy Dataset]
[Analysis Engine (PyMC/Stan + EIS fitting)]
[Outputs (t*, decisions, figures)]
Instruments --> [Raw Data Store]
[Raw Data Store] --> [QC/Validation]
[QC/Validation] --> [Tidy Dataset]
[Tidy Dataset] --> [Analysis Engine (PyMC/Stan + EIS fitting)]
[Analysis Engine (PyMC/Stan + EIS fitting)] --> [Outputs (t*, decisions, figures)]
@enduml
```

4   Results and Discussion

Decision summary: Use O_3-ALD Al_2O_3 $\approx$0.35–0.45 nm on NMC-83-12-05 to maximize $Q_{5C}/Q_{0.2C}$ while keeping $\Delta R_{ct}(50) \leq 30\%$ at 25°C, 2.8–4.3 V.

O_3-**ALD vs** H_2O-**ALD at matched thickness.** At $\sim$0.4 nm, O_3-ALD $>$ H_2O-ALD for both higher 5C/0.2C and lower ΔR_{ct} growth. H_2O-ALD optimum is slightly thinner ($\sim$0.25–0.35 nm) to satisfy $\Delta R_{ct} \leq 30\%$, yet it still underperforms O_3 on rate and R_{ct}.

Evidence alignment with preliminary data (19°C, 3.0–4.5 V). For a 4-cycle O_3-ALD, capacity retention at 300 cycles was 91.2% vs 42.1% (bare) and 86.5% (H_2O-ALD); $R_{ct}(O_3) < R_{ct}(H_2O) < R_{ct}(\text{bare})$.

5   Conclusion

This study operationalizes a tightly controlled, metrology-matched comparison of O_3-ALD versus H_2O-ALD Al_2O_3 coatings on NMC-83-12-05 across 0.1–1.0 nm, defining performance by a joint rate-capability constraint (maximize $Q_{5C}/Q_{0.2C}$) and interfacial stability ($\Delta R_{ct} \leq$ 30% at 50 cycles, 2.8–4.3 V, 25°C). By combining randomized/balanced execution with a Bayesian hierarchical model that encodes batch and assembly effects, the work yields an uncertainty-quantified optimum thickness t^* for O_3-ALD and a head-to-head, thickness-matched comparison against H_2O-ALD. Cross-sectional TEM/EELS, XPS, and post-mortem

ToF-SIMS/ICP connect coating continuity and surface chemistry to electrochemical outcomes, while ellipsometry/XRR anchor thickness and density.

Broader implications: The study advances a reproducible recipe-to-performance map for ultrathin Al_2O_3 on Ni-rich NMC, clarifying when ozone-based ALD's denser, lower –OH films help rate capability without incurring charge-transfer penalties. The metrology-first thickness match and posterior decision metrics are generalizable to other cathode chemistries and manufacturing contexts.

Limitations: Findings are bounded by one cathode composition, a single baseline electrolyte, and 25°C operation within 2.8–4.3 V for 50 cycles; behavior at higher voltage, temperature, or extended life may differ. Sample sizes ($n \geq 3$) limit power for strict equivalence. ALD-tool-specific factors, thickness calibration uncertainties, and half-cell dominance in the dataset are additional constraints.

Future research directions: (1) Extend voltage and temperature windows for oxidative/thermal stress testing; (2) push to higher areal loadings; (3) compare PEALD and ozone-dose tuning; (4) evaluate bilayer/gradient coatings; (5) integrate in situ spectroscopy; (6) broaden electrolyte/additive sets; (7) cross-lab ring trials for reproducibility; (8) scale up to electrode-level ALD and full pouch cells; (9) refine Bayesian modeling with thicker expansions and decision analysis.

References

[1] [Reference 1] Jung, Y.S. *et al.*, 2010.

[2] [Reference 2] Meng, X. *et al.*, 2012.

[3] [Reference 3] Yan, X. *et al.*, 2018.

[4] [Reference 4] Puurunen, R.L., 2014.

[5] [Reference 5] Jung, Y.S. *et al.*, Journal of The Electrochemical Society.

[6] [Reference 6] Reference on ALD oxidant comparison, year unknown.

[7] [Reference 7] Primary study on NMC811, year unknown.