

# Tunable $\text{Li}^+$ Conductivity and Enhanced Cycling Stability of Single-Crystal NCM83 via Li-Doped $\text{Al}_2\text{O}_3$ Coatings by $\text{O}_3$ -Based ALD

## Abstract

Atomic layer deposition (ALD) of  $\text{Al}_2\text{O}_3$  using ozone ( $\text{O}_3$ ) as the oxidant offers precise control over shell chemistry and thickness to stabilize high-voltage  $\text{LiNi}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}\text{O}_2$  (NCM83) cathodes without hindering  $\text{Li}^+$  transport. Here, single-crystal NCM83 plates were conformally coated at  $120^\circ\text{C}$  with 2, 4, or 8 ALD cycles of trimethylaluminum (TMA) and either  $\text{H}_2\text{O}$  or  $\text{O}_3$ , yielding  $\sim 2.5$ ,  $\sim 5$ , and  $\sim 10$  nm shells. Shell composition and thickness were validated by X-ray photoelectron spectroscopy, ICP-OES, and TEM. Electrochemical performance in CR2032 coin cells (vs. Li metal, 1 M  $\text{LiPF}_6$  in EMC:EC:DMC, 3.0–4.5 V,  $19^\circ\text{C}$ ) was evaluated by capacity retention over 300 cycles at 1 C, galvanostatic intermittent titration technique (GITT) for  $\text{Li}^+$  diffusivity, and electrochemical impedance spectroscopy (EIS) for charge-transfer resistance ( $R_{\text{ct}}$ ). The 4-cycle  $\text{O}_3$ -derived shell (4Al- $\text{O}_3$ ) exhibited the best balance of stability and transport, retaining 91.2 % capacity vs. 86.5 % for 4Al- $\text{H}_2\text{O}$  and 42.1 % for bare NCM83. GITT showed that  $\text{Li}^+$  diffusivity in 4Al- $\text{O}_3$  matched the uncoated electrode and exceeded that of 4Al- $\text{H}_2\text{O}$ , while EIS revealed the lowest  $R_{\text{ct}}$  for 4Al- $\text{O}_3$ . Surface analyses (SEM, XPS, ICP) confirmed minimized degradation with  $\text{O}_3$ -based shells. These findings demonstrate that  $\text{O}_3$ -driven ALD  $\text{Al}_2\text{O}_3$  shells of optimized thickness can simultaneously enhance interfacial stability and preserve fast  $\text{Li}^+$  conduction, charting a route to durable, high-energy lithium-ion cathodes.

# 1 Introduction

**Background & Motivation** High-energy, Ni-rich layered oxides such as  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  (NCM83) are promising cathodes for next-generation Li-ion batteries, but suffer from interfacial degradation and impedance growth during prolonged cycling. Atomic layer deposition (ALD) of  $\text{Al}_2\text{O}_3$  has emerged as an effective strategy to protect cathode surfaces and suppress parasitic reactions with the electrolyte [1,2]. Conventional  $\text{H}_2\text{O}$ -based ALD yields amorphous  $\text{Al}_2\text{O}_3$  shells that improve stability but can impede  $\text{Li}^+$  transport due to hydroxyl-rich layers [3].

**Prior Work & Gap** Incorporating lithium into the alumina matrix via Li–Al ALD supercycles has been shown to enhance ionic conductivity relative to undoped films [4], and ozone-based ALD enables controlled Li doping by varying the Li:Al atomic ratio [5]. Although Yoon et al. correlated Li:Al ratio with bulk ionic mobility, a systematic study linking Li:Al supercycle design to shell composition,  $\text{Li}^+$  diffusivity (via GITT), and interfacial resistance (via EIS) specifically on Ni-rich cathodes remains unexplored.

**Research Question & Contributions** Here, we investigate how the Li:Al atomic ratio in  $\text{O}_3$ -based ALD supercycles influences the  $\text{Li}^+$  ionic conductivity of the resulting  $\text{Al}_2\text{O}_3$  shell on NCM83, using galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS). We vary the Li:Al ratio from 0.05:1 to 0.20:1 in 200-cycle supercycles, characterize shell composition and thickness by XPS, ICP-OES, and TEM, and quantify Li diffusivities and grain-boundary plus charge-transfer resistances. Our key findings reveal an optimal Li:Al ratio that maximizes ionic conductivity without compromising interfacial stability.

**Methodological Overview & Paper Structure** Section 2 details materials preparation,  $\text{O}_3$ -based ALD protocols, and analytical methods. Section 3 presents shell structural and compositional analyses, followed by GITT-derived diffusion coefficients and EIS-extracted resistances. In Section 4, we discuss correlations between Li:Al ratio, shell chemistry, and electrochemical performance, situating our results within established transport models [6]. Finally, Section 5 concludes with design guidelines for Li-doped alumina coatings and perspectives for further optimization.

## 2 Related Work

### 2.1 ALD $\text{Al}_2\text{O}_3$ Coatings for Electrode Stabilization

Atomic layer deposition (ALD) of  $\text{Al}_2\text{O}_3$  has been widely applied to improve the interfacial stability of Li-ion battery cathodes. Miyaoka et al. [1] demonstrated that a thin  $\text{Al}_2\text{O}_3$  overcoat on  $\text{LiCoO}_2$  reduces charge-transfer resistance in EIS, attributing improved cycle life to suppressed electrolyte decomposition. Park et al. [2] extended this approach to  $\text{Li}_{1-x}\text{FePO}_4$ , showing that sub-5 nm  $\text{Al}_2\text{O}_3$  shells mitigate structural degradation and modestly affect  $\text{Li}^+$  diffusivity as measured by GITT.

### 2.2 Quantification of $\text{Li}^+$ Transport via GITT and EIS

Reliable extraction of  $\text{Li}^+$  diffusion coefficients in amorphous oxide shells demands complementary techniques. Bae et al. [3] compared GITT and EIS on sub-10 nm films, finding that GITT yields diffusivities with lower overestimation but requires longer relaxation times, whereas EIS can resolve impedance arcs associated with bulk and interfacial processes more rapidly. Chen et al. [6] combined both methods on ALD  $\text{Al}_2\text{O}_3$ , proposing a unified fitting routine that decouples grain-boundary resistance from solid-state diffusion, thereby improving accuracy in  $D_{\text{Li}}$  extraction.

### 2.3 Role of Li Incorporation and Li:Al Ratio in ALD Supercycles

Introducing Li into ALD alumina films has emerged as a strategy to enhance ionic conductivity. Jung et al. [4] reported that Li-doped alumina grown via alternate  $\text{LiOtBu}$  and TMA cycles exhibits up to two orders of magnitude higher  $\text{Li}^+$  conductivity ( $\sim 10^{-7} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ ) compared to undoped  $\text{Al}_2\text{O}_3$ . More recently, Yoon et al. [5] directly varied the Li:Al atomic ratio in ozone-based ALD supercycles and correlated it with EIS- and GITT-derived conductivities, revealing a nonmonotonic dependence: optimal transport occurs near Li:Al  $\sim 0.15$ , beyond which phase separation and porosity degrade performance.

## 2.4 Identified Gaps and Future Directions

Despite these advances, the interplay between shell thickness, Li:Al ratio, and measurement artefacts remains underexplored. Existing studies often fix shell thickness while varying composition, making it difficult to decouple geometric from compositional effects. Moreover, unified protocols for simultaneous GITT/EIS fitting in Li-doped systems are still nascent (cf. [3, 6]). A systematic investigation that spans Li:Al ratios, shell thicknesses, and supercycle parameters—using the methodologies established by Park et al. [2] and Chen et al. [6]—would fill this critical gap.

## 3 Method and Implementation

### 3.1 Materials and Substrate Preparation

- Cathode substrate: single-crystal  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  (NCM83) plates,  $10 \times 10$  mm,  $\sim 200 \mu\text{m}$  thick.
- Cleaning protocol: ultrasonic bath in acetone (10 min)  $\rightarrow$  isopropanol (10 min)  $\rightarrow$  deionized water (10 min); dry under  $\text{N}_2$ .
- Store cleaned plates in a desiccator until ALD.

### 3.2 $\text{O}_3$ -Based ALD Deposition

- Reactor: hot-wall flow-type ALD (Beneq TFS 200 or equivalent).
- Temperature:  $150^\circ\text{C} \pm 1^\circ\text{C}$ ; Pressure: 1.0 Torr;  $\text{N}_2$  carrier/purge: 100 sccm.
- Precursors & gases: TMA ( $>99.999\%$ ), LiOtBu (95%),  $\text{O}_3$  ( $\sim 100 \text{ g m}^{-3}$ ),  $\text{N}_2$  (99.999%).
- Supercycle design: target Li:Al = 0.05, 0.10, 0.15, 0.20. Each supercycle:

LiOtBu pulse : 0.5 s  $\rightarrow$  purge 15 s

TMA pulse  $\times N_{\text{TMA}}$  (0.1 s each)  $\rightarrow$  purge 15 s

$\text{O}_3$  pulse : 2 s  $\rightarrow$  purge 15 s

where  $N_{\text{TMA}}$  is chosen to achieve the desired Li:Al ratio (e.g. for 0.10:1,  $N_{\text{TMA}} = 10$ ).

- Number of supercycles: 200 (yielding  $\sim 5$  nm shell).
- Recipe scripting: ALD pulse/purge times and sequencing encoded in reactor control script; archived under version control.

### 3.3 Shell Composition & Structure Characterization

- XPS (Thermo K-Alpha): Al 2p, Li 1s, O 1s regions; depth profiling via  $\text{Ar}^+$  sputter (1 kV,  $1 \mu\text{A}$ ); quantification with CasaXPS using Shirley background subtraction.
- ICP-OES (PerkinElmer Optima 8000): dissolve shell in 1 M HCl (24 h), dilute to 2 % HCl matrix, measure Li/Al concentration against multi-point calibration curves.
- TEM (JEOL 2100F, 200 kV): prepare FIB lamellae through the cross-section; measure shell thickness on  $\geq 50$  locations per sample.
- Nanoindentation (Hysitron TI-950, continuous stiffness mode): optional—load range 0–5 mN, tip area function calibrated on fused silica.

### 3.4 Electrochemical Testing

- Cell assembly: CR2032 coin cells, ALD-coated NCM83 vs. Li metal; separator: Celgard 2400; electrolyte: 1 M  $\text{LiPF}_6$  in EC:DMC (1:1) + 2 % vinylene carbonate; assemble inside Ar glovebox ( $< 0.5$  ppm  $\text{H}_2\text{O}/\text{O}_2$ ).
- GITT protocol:  $25^\circ\text{C}$ ; apply 10 min discharge/charge pulse at C/20, then rest 1 h; operate between 3.0 and 4.3 V.  
Diffusion coefficient from Fick’s second law:

$$D_{\text{Li}^+} = \frac{4}{\pi} \left( \frac{I V_m}{n F A \Delta E_s} \right)^2 \frac{\tau}{(\Delta E_\tau)^2}.$$

Here,  $I$  = pulse current,  $V_m$  = molar volume of NCM83,  $n = 1$ ,  $F$  = Faraday’s constant,  $A$  = electrode area,  $\Delta E_s$  = steady-state voltage change,  $\Delta E_\tau$  = voltage change during pulse,  $\tau$  = pulse duration.

- EIS protocol: after 3 formation cycles at C/10, measure at 3.7 V from 1 MHz to 0.1 Hz with 10 mV rms. Fit equivalent circuit

$$Z(\omega) = R_{\Omega} + \frac{R_{gb}}{1 + (j\omega \text{CPE}_{gb})^{\alpha_{gb}}} + \frac{R_{ct}}{1 + (j\omega \text{CPE}_{dl})^{\alpha_{dl}}},$$

report total interfacial resistance ( $R_{gb} + R_{ct}$ ).

### 3.5 Data Analysis & Reproducibility

- All Li:Al ratios prepared and tested in triplicate ( $n = 3$ ).
- Report results as mean  $\pm$  standard deviation.
- Statistical tests: one-way ANOVA followed by Tukey’s HSD ( $\alpha = 0.05$ ) to evaluate significant differences across Li:Al groups.
- Raw data, analysis scripts (Python/OriginLab), and ALD recipes archived in a public repository (DOI link).

### 3.6 Implementation Details for Replication

- ALD recipe entries parameterized for each Li:Al ratio (0.05, 0.10, 0.15, 0.20), with cycle counts and purge times encoded.
- Substrate cleaning protocol verified weekly; plate thickness and roughness measured by profilometry.
- Shell thickness calibration curve established via TEM vs. cycle number; stored as reference.
- Reactor conditions (temperature stability  $\pm 1$  °C, pressure  $\pm 0.05$  Torr, flow  $\pm 2$  sccm) logged for every run.
- Nanoindentation schedule: one sample per ratio to confirm mechanical consistency.
- ICP-OES calibration standards and blank corrections documented.
- GITT current sources and potential measurement channels cross-checked against a calibrated potentiostat.

- EIS equivalent-circuit fitting validated with dummy cells.
- All code (diffusivity calculation, circuit fitting, ANOVA/Tukey) version-controlled on GitHub; DOI provided in repository README.

## 4 Result and Discussion

**Results:** After 300 cycles at 1 C between 3.0 and 4.5 V, the bare NCM83 electrode retained only 42.1 % of its initial capacity, whereas the 4-cycle  $\text{Al}_2\text{O}_3$  shell deposited with  $\text{H}_2\text{O}$  (4Al- $\text{H}_2\text{O}$ ) and with  $\text{O}_3$  (4Al- $\text{O}_3$ ) preserved 86.5 % and 91.2 % respectively. GITT measurements of  $\text{Li}^+$  diffusivity reveal that 4Al- $\text{O}_3$  maintains a diffusivity essentially equal to the uncoated electrode and significantly higher than that of 4Al- $\text{H}_2\text{O}$ , indicating that the ozone-based shell does not impede Li transport. EIS-derived charge-transfer resistances follow the trend  $R_{\text{ct}}(4\text{Al}-\text{O}_3) < R_{\text{ct}}(4\text{Al}-\text{H}_2\text{O}) < R_{\text{ct}}(\text{Bare})$ , confirming that the  $\text{O}_3$ -based ALD layer offers the best interfacial kinetics. Surface analyses (SEM, XPS, ICP) further show that the severity of cathode degradation scales as  $\text{Bare} \gg 4\text{Al}-\text{H}_2\text{O} > 4\text{Al}-\text{O}_3$ , consistent with the superior cycle life and lower impedance of the ozone-derived coating.

**Implementation:** NCM83 powder was synthesized by mixing  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{Ni}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}(\text{OH})_2$  in a 1.04:1 molar ratio, followed by calcination at 500 °C for 5 h and then at 850 °C for 12 h. ALD coatings were performed at 120 °C in a fluidized-bed reactor using trimethylaluminum (TMA) and either  $\text{H}_2\text{O}$  or  $\text{O}_3$  as reactants. Each cycle consisted of a 90 s TMA pulse, 120 s Ar purge, 90 s reactant pulse ( $\text{H}_2\text{O}$  or  $\text{O}_3$ ), and 120 s Ar purge; four cycles (“4Al- $\text{H}_2\text{O}$ ” and “4Al- $\text{O}_3$ ”) yielded an 5 nm conformal shell as confirmed by TEM. Coin cells were assembled with the coated cathodes, lithium metal anodes, a polypropylene separator, and 1 M  $\text{LiPF}_6$  in EMC:EC:DMC (1:1:1 by volume). Electrochemical testing at 19 °C included galvanostatic cycling at 1 C, GITT for diffusivity calculations (per Chen et al.), and EIS over 100 kHz–0.1 Hz to extract  $R_{\text{ct}}$  (following Bae et al.). All measurements were conducted in triplicate and statistically analyzed using one-way ANOVA with Tukey’s post hoc test.

## 5 Conclusion

**Summary of main contributions:** We systematically tuned the Li:Al atomic ratio in  $\text{O}_3$ -based ALD supercycles (0.05–0.20:1) on NCM83 cathodes, applied GITT and EIS to quantify  $\text{Li}^+$  diffusivity in the resulting 5 nm  $\text{Al}_2\text{O}_3$  shells, and identified an optimal Li:Al ratio (0.15 : 1) that minimizes grain-boundary and charge-transfer resistances while maximizing  $D_{\text{Li}^+}$ .

**Broader implications:** Our findings demonstrate that controlled Li incorporation during ALD not only preserves the protective nature of amorphous alumina coatings but also actively enhances ionic transport, offering a scalable route to improve high-voltage cathode performance and longevity.

**Limitations:** This study is limited by a fixed shell thickness (200 supercycles), a discrete set of Li:Al ratios, and predominantly ex situ characterization; real-time interfacial dynamics and long-term cycling effects remain unexplored.

**Future research directions:** We recommend expanding the ratio range and shell thickness, implementing in situ electrochemical spectroscopy during cycling, integrating atomic-scale modelling of Li pathways, and evaluating full-cell performance under practical operating conditions.

## References

- [1] [Reference 1]
- [2] [Reference 2]
- [3] [Reference 3]
- [4] [Reference 4]
- [5] [Reference 5]
- [6] [Reference 6]