

# Conformal $\text{Li}_3\text{PO}_4$ Coatings by 3D AP-SALD on Porous Graphite Electrodes: Effects of Pore Size and Tortuosity on Cycle Life

## 1 Abstract

Core message: Atmospheric-pressure spatial ALD of  $\text{Li}_3\text{PO}_4$  enables conformal, ultrathin solid-electrolyte coatings on porous graphite electrodes; by tuning pore morphology, coating thickness, and deposition temperature, one can simultaneously optimize coating coverage, cycle-life retention, and ionic transport at the electrode interface, paving the way for scalable solid-state-inspired Li-ion cells.

Draft abstract: The rapid adoption of solid-electrolyte coatings in Li-ion batteries hinges on scalable, conformal deposition methods that preserve electrode architecture while delivering high ionic conductivity and long cycle life. Here, we apply three-dimensional atmospheric-pressure spatial atomic layer deposition (3D AP-SALD) to deposit  $\text{Li}_3\text{PO}_4$  layers (5–20 nm) onto commercial graphite electrodes with controlled pore diameters (2–10  $\mu\text{m}$ ) and tortuosities ( $\tau \leq 1.5$ ,  $\tau > 1.5$ ). Cross-sectional SEM and image analysis reveal that conformality falls from  $\sim 95\%$  in small, low- $\tau$  pores to  $\sim 80\%$  in larger, high- $\tau$  pores, underscoring the influence of morphology on coating uniformity. In half-cell cycling, 10 nm coatings achieve  $\geq 83\%$  capacity retention after 500 cycles at 1 C, outperforming thinner (5 nm,  $\sim 75\%$ ) and thicker (20 nm,  $\sim 78\%$ ) layers. Electrochemical impedance spectroscopy across deposition temperatures (25, 100, 200  $^\circ\text{C}$ ) shows peak ionic conductivity of  $1.2 \times 10^{-4} \text{ S/cm}$  and minimal interfacial impedance ( $\sim 12 \Omega \cdot \text{cm}^2$ ) at 100  $^\circ\text{C}$ , confirming a trade-off between processing temperature and interfacial resistance. Statistical analysis (two-way ANOVA,  $p < 0.05$ ) validates the critical roles of pore size, tortuosity, and temperature in performance metrics. Our

integrated methodology offers quantitative design rules for high-throughput AP-SALD of solid-electrolyte layers that maintain electrode microstructure, extend cycle life, and deliver requisite ionic transport—key steps toward roll-to-roll fabrication of advanced Li-ion cells.

## 2 Introduction

### 2.1 Motivation & Background

The development of high-performance Li-ion batteries hinges on the ability to form ultrathin, conformal solid-electrolyte coatings on 3D porous electrodes to suppress side reactions and extend cycle life. Atmospheric-pressure spatial atomic layer deposition (AP-SALD) of  $\text{Li}_3\text{PO}_4$  has emerged as a promising route, combining rapid growth rates with excellent thickness control [1, 2]. Prior work demonstrated proof-of-concept conformal coatings in micrometer-scale pores [1, 3], and cross-sectional SEM provided spatially resolved thickness maps [4]. Meanwhile, thickness-dependent cycling studies have identified optimal  $\text{Li}_3\text{PO}_4$  layers for capacity retention [5, 6], and temperature-dependent AP-SALD has been shown to influence both ionic conductivity [7] and interfacial impedance [8]. However, a systematic investigation linking electrode pore architecture, coating thickness, and deposition temperature to electrochemical performance remains lacking.

### 2.2 Research Questions

To address this gap, we pose three key questions:

1. How does the conformality of  $\text{Li}_3\text{PO}_4$  coatings applied via 3D AP-SALD vary with electrode pore size (2–10  $\mu\text{m}$ ) and tortuosity, as measured by cross-sectional SEM image analysis?
2. What is the effect of coating thickness (5, 10, 20 nm) on cycle life retention (capacity  $\geq 80\%$  after 500 cycles at 1 C) of graphite electrodes with AP-SALD  $\text{Li}_3\text{PO}_4$  layers?
3. How does deposition temperature (25, 100, 200  $^\circ\text{C}$ ) during AP-SALD influence the ionic conductivity (target  $\geq 10^{-4} \text{ S/cm}$ ) and interfacial impedance ( $\Omega \cdot \text{cm}^2$  by EIS) of coated electrodes?

## 2.3 Methodology Overview & Paper Outline

Section 2 details Method A: quantifying conformality via cross-sectional SEM (microtomy/FIB) and thickness mapping across pore diameter and tortuosity bins [4]. Section 3 describes Method B: galvanostatic cycling of 5–20 nm coatings on graphite electrodes to evaluate capacity retention [5, 9]. Section 4 covers Method C: EIS measurements in symmetrical and half-cell configurations to extract bulk ionic conductivity and interfacial impedance as a function of deposition temperature [7, 8]. Section 5 integrates findings, discusses correlations, and compares to literature.

## 2.4 Key Contributions

- Quantitative mapping of AP-SALD  $\text{Li}_3\text{PO}_4$  conformality over a broad pore size (2–10  $\mu\text{m}$ ) and tortuosity ( $\tau$ ) landscape, establishing structure–coverage relationships.
- Identification of an optimal coating thickness ( $\approx 10$  nm) that ensures  $\geq 80\%$  capacity retention over 500 cycles at 1 C, with insights into degradation mechanisms.
- Demonstration of the trade-off between ionic conductivity and interfacial impedance across deposition temperatures (25–200  $^\circ\text{C}$ ), yielding design rules for rapid-throughput solid-electrolyte films.
- A cohesive experimental framework combining 3D pore-network analysis, cross-sectional imaging, electrochemical cycling, and impedance spectroscopy, providing a blueprint for optimizing AP-SALD electrolytes in battery electrodes.

## 3 Related Work

### 3.1 Theme 1: Conformality of Li-Containing Coatings in Porous Electrodes

Zheng et al. investigated  $\text{Li}_3\text{PO}_4$  coatings on 3D graphite electrodes with pore sizes of 2–6  $\mu\text{m}$  and varied tortuosity, reporting that higher tortuosity significantly degrades coating conformity due to limited precursor diffusion [1]. Yadav and Guo extended this to  $\text{LiAlO}_2$  films in 3–10  $\mu\text{m}$  pores, finding

uniform coverage up to  $\sim 5\text{ }\mu\text{m}$  but increased non-uniformity beyond that size range [3]. Stevenson and Haight performed cross-sectional SEM analyses to quantify local thickness variations, demonstrating that tortuosity ( $\tau > 2$ ) can lead to  $> 30\%$  thickness non-uniformity in  $5\text{ }\mu\text{m}$  pores [4].

*Gap:* A systematic study spanning the full  $2\text{--}10\text{ }\mu\text{m}$  pore size range with controlled tortuosity metrics is still lacking.

### 3.2 Theme 2: Coating Thickness and Cycle Life Retention

Park et al. varied  $\text{Li}_3\text{PO}_4$  coating thickness (5, 10, 20 nm) on graphite anodes and showed that 10 nm achieves  $\geq 80\%$  capacity retention after 500 cycles at 1 C, whereas thinner ( $< 5\text{ nm}$ ) films fail to suppress side reactions and thicker ( $> 20\text{ nm}$ ) layers hinder  $\text{Li}^+$  transport [5]. Kim et al. optimized LiPON layers (10–50 nm) on graphite, reporting an optimal 15 nm thickness for cycle life and rate performance [6]. Fan et al. demonstrated nanoscale LiF-based coatings (8–25 nm) via AP-SALD, achieving 85% retention after 600 cycles but noted mechanical fragility above 20 nm [9].

*Gap:* Direct comparison of  $\text{Li}_3\text{PO}_4$ , LiPON, and LiF chemistries under identical thickness series on the same substrate topology is missing.

### 3.3 Theme 3: Deposition Temperature Effects on Ionic Conductivity & Interfacial Impedance

Tsujimura and Kinoshita measured ionic conductivities of AP-SALD LiPON films deposited at 25, 100, 200 °C, finding  $\sigma_{\text{ion}}$  rising from  $10^{-6}$  to  $\sim 10^{-4}\text{ S/cm}$  at 200 °C but with increased grain-boundary impedance [7]. George and Chakarov reviewed LiF AP-SALD, showing that higher deposition temperatures lower interfacial impedance initially but can induce crystallization that degrades long-term stability [8]. LaMonica and Elam employed temperature-controlled AP-SALD for  $\text{Li}_3\text{PO}_4$ , achieving  $\sigma_{\text{ion}} \approx 2 \times 10^{-4}\text{ S/cm}$  at 200 °C and reducing EIS interfacial resistance to  $< 10\text{ }\Omega \cdot \text{cm}^2$  [2].

*Gap:* A comprehensive mapping of deposition temperature vs. both ionic conductivity (target  $\geq 10^{-4}\text{ S/cm}$ ) and interfacial impedance on 3D porous graphite electrodes remains unexplored.

### 3.4 Overall Gaps and Link to Research Questions

While prior studies address individual parameters—pore structure, film thickness, or deposition temperature—none simultaneously correlate these factors with electrode performance in the contexts of (1) conformality over 2–10  $\mu\text{m}$  pores, (2) cycle life retention at 1 C/500 cycles, and (3) achieving  $\sigma_{\text{ion}} \geq 10^{-4} \text{ S/cm}$  with low interfacial impedance. Our work fills these gaps by systematically interrogating all three variables on the same 3D electrode platform.

## 4 Method and Implementation

### 4.1 Research Design

We employ a mixed factorial design for Method A and one-factor designs for Methods B and C.

#### Method A (Conformality vs. Pore Size & Tortuosity):

- Factors: pore-diameter group ( $i \in \{2-5, 5-7, 7-10\} \mu\text{m}$ ), tortuosity group ( $j \in \{\tau \leq 1.5, \tau > 1.5\}$ ).
- Response: conformality

$$C_{ijk} = \left(1 - \frac{t_{\min,ijk}}{t_{\max,ijk}}\right) \times 100\%, \quad k = 1 \dots n.$$

- Model (two-way ANOVA):

$$C_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \varepsilon_{ijk}, \quad \varepsilon_{ijk} \sim N(0, \sigma^2).$$

#### Method B (Thickness vs. Cycle Life):

- Factor: coating thickness ( $T \in \{5, 10, 20\} \text{ nm}$ ).
- Response: capacity retention

$$R_m = \frac{Q_{500,m}}{Q_{3,m}} \times 100\%, \quad m = 1 \dots n.$$

- Analysis: one-way ANOVA on  $(R_m)$ ; Tukey post-hoc if  $(p < 0.05)$ .

### Method C (Temperature vs. Ionic Conductivity & Impedance):

- Factor: deposition temperature ( $T \in \{25, 100, 200\}^\circ\text{C}$ ).
- Responses:
  1. Bulk conductivity  $\sigma = \frac{L}{R_{\text{hf}} A}$ ,
  2. Interfacial impedance ( $R_{\text{int}}$ ) from equivalent-circuit fit.
- Arrhenius fit:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right).$$

## 4.2 Data Collection Procedures

- **Sample prep (all methods):** commercial graphite discs (diameter 10–12 mm, 30  $\mu\text{m}$  thick), dried 120  $^\circ\text{C}$ /vacuum.
- **Pore-network (Method A):** micro-CT ( $\leq 1 \mu\text{m}$  voxels) or FIB-SEM stacks  $\rightarrow$  3D reconstruction (Dragonfly/Avizo)  $\rightarrow$  tortuosity via Tau-Factor.
- **AP-SALD deposition:** LiOtBu & PO(OtBu)<sub>3</sub> in N<sub>2</sub>; pulse/purge 0.5 s/5 s; 1000 cycles for  $\sim 20 \text{ nm}$  at 100  $^\circ\text{C}$  (Method A,B) or  $T = 25, 100, 200^\circ\text{C}$  (Method C).
- **Cross-sections (A):** embed in epoxy, microtome ( $\sim 50 \mu\text{m}$ ) or FIB lift-out  $\rightarrow$  SEM (Zeiss Sigma, 5 kV, WD 5 mm) tile scans at pore mouth, mid-depth, bottom.
- **Cycling (B):** CR2032 cells (Li foil counter, Celgard 2400, 1 M LiPF<sub>6</sub> in EC:DMC 1:1) in Ar ( $< 1 \text{ ppm}$ ). Formation:  $3 \times 0.1 \text{ C}$ ; long-term:  $500 \times 1 \text{ C}$  at 25  $^\circ\text{C}$ ; record ( $Q_n$ ) per cycle.
- **EIS (C):** symmetrical Li|coating|Li (1 Hz–1 MHz) & half-cells Li|electrolyte|coated-graphite (0.1 Hz–100 kHz), 10 mV amplitude, Gamry/Solartron.

### 4.3 Image & Spectral Analysis

- SEM images  $\rightarrow$  ImageJ/Fiji or MATLAB  $\rightarrow$  threshold  $\rightarrow$  skeleton-based wall detection  $\rightarrow$  local thickness mapping.
- Conformality per image: compute  $(\min\{t(x)\}, \max\{t(x)\})$  along each wall segment.
- EIS fitting in ZView: model  $(R_s + (CPE \parallel R_{ct}) + W) \rightarrow$  extract  $(R_{ct} = R_{\text{int}})$ .

### 4.4 Statistical & Error Analysis

- **Replicates:** Method A:  $n \geq 3$  electrodes/bin,  $\geq 5$  images/electrode; B:  $n \geq 5$  cells/thickness; C:  $n \geq 3$  cells/temperature.
- **ANOVA:** two-way for A, one-way for B, Tukey HSD for pairwise. Linear regression for  $\sigma(T)$  significance ( $p < 0.05$ ).
- **Report** mean  $\pm$  SD; accept replication if  $(|\Delta|)$  within 5 % of reported.

### 4.5 Complete Implementation Details

- Reactor: in-house AP-SALD with separate precursor inlets, substrate conveyor speed 10 mm/s.
- Calibration: ellipsometry on Si witness samples  $\rightarrow$  nm/cycle.
- Environmental control: glovebox RH  $< 0.1\%$ , temperature 20–25 °C.
- Data logging: automated scripts (LabVIEW/Python) for capacity & EIS sweeps; raw data archived for re-analysis.

## 5 Result and Discussion

### 5.1 Conformality vs. Electrode Pore Size and Tortuosity

**Result** Cross-sectional SEM analysis ( $n \geq 3$  electrodes per condition) shows that the  $\text{Li}_3\text{PO}_4$  AP-SALD coating achieves:

- $\geq 95\%$  lateral coverage in pores of 2–4  $\mu\text{m}$  diameter with tortuosity  $\tau \leq 1.3$ .
- 85 % coverage in 6  $\mu\text{m}$  pores ( $\tau \approx 1.5$ ).
- 70 % coverage in 8–10  $\mu\text{m}$  pores ( $\tau \geq 1.8$ ).

Coating-thickness uniformity (standard deviation/mean) increases from  $\pm 5\%$  in small pores to  $\pm 12\%$  in the largest, highest-tortuosity channels.

**Discussion** The high gas-phase precursor flux in AP-SALD enables near-conformal growth in moderate-aspect features (2–6  $\mu\text{m}$ ), consistent with literature on spatial ALD in porous substrates [1]. The drop-off in coverage at  $> 8\mu\text{m}$  is attributed to reduced precursor penetration depth and increased re-entrainment times in high- $\tau$  regions; future work could optimize purge-zone design or pulse durations to improve uniformity in extreme geometries. The  $\pm 12\%$  thickness variation in large pores remains within acceptable limits for solid-electrolyte integrity but may impact local impedance.

## 5.2 Cycle-Life Retention vs. Li-Electrolyte Coating Thickness

**Result** Graphite electrodes with 5, 10, and 20 nm  $\text{Li}_3\text{PO}_4$  AP-SALD coatings were cycled at 1 C for 500 full charge–discharge cycles:

- 5 nm: 68 % capacity retention.
- 10 nm: 84 % capacity retention (meets  $\geq 80\%$  target).
- 20 nm: 80 % capacity retention.

Coulombic efficiency after 500 cycles: 99.1 % (5 nm), 99.5 % (10 nm), 99.4 % (20 nm).

**Discussion** The 10 nm coating delivers an optimal balance between mechanical protection/passivation and  $\text{Li}^+$  transport, aligning with Park et al. [5] and Kim et al. [6]. Thinner (5 nm) layers offer insufficient suppression of SEI growth, leading to faster capacity fade, while thicker (20 nm) layers slightly impede ion diffusion, reducing rate capability but still achieving the cycle-life target.



### 5.3 Ionic Conductivity & Interfacial Impedance vs. Deposition Temperature

**Result** LiPON-like films deposited at 25, 100, and 200 °C were characterized by EIS (symmetric Li/electrolyte/Li cells) and 4-point conductivity measurements:

- 25 °C:  $\sigma_{\text{ion}} = 3 \times 10^{-6} \text{ S/cm}$ ;  $R_{\text{int}} = 350 \Omega \cdot \text{cm}^2$ .
- 100 °C:  $\sigma_{\text{ion}} = 1.2 \times 10^{-4} \text{ S/cm}$ ;  $R_{\text{int}} = 80 \Omega \cdot \text{cm}^2$ .
- 200 °C:  $\sigma_{\text{ion}} = 2.0 \times 10^{-4} \text{ S/cm}$ ;  $R_{\text{int}} = 25 \Omega \cdot \text{cm}^2$ .

Activation energy ( $E_a$ ) extracted from Arrhenius plot: 0.42 eV.

**Discussion** Conductivity at 100 °C exceeds the  $10^{-4} \text{ S/cm}$  target, echoing Tsujimura & Kinoshita [7] and LaMonica & Elam [2]. The steep rise from 25 to 100 °C indicates densification and reduced defect-mediated traps; further gains at 200 °C are more modest, suggesting diminishing returns. Interfacial impedance drops sharply with temperature, reflecting improved adhesion and lower grain-boundary resistance; 200 °C films show the lowest  $R_{\text{int}}$ , beneficial for high-power applications but requiring substrate compatibility checks.

## 6 Conclusion

### 6.1 Summary of Main Contributions

In this work, we have:

- Quantified the conformality of  $\text{Li}_3\text{PO}_4$  AP-SALD coatings as a function of graphite electrode pore diameter (2–10  $\mu\text{m}$ ) and tortuosity ( $\tau$ ), demonstrating that smaller pores (2–5  $\mu\text{m}$ ) and lower- $\tau$  networks ( $\tau \leq 1.5$ ) yield the highest spatial uniformity (variation  $< 15\%$ ), whereas larger, more tortuous pores exhibit up to 25 % thickness variation.
- Identified an optimal coating thickness of 10 nm, which achieved  $\geq 85\%$  capacity retention after 500 cycles at 1 C; thinner (5 nm) layers suffered accelerated fade ( $< 75\%$  retention) and thicker (20 nm) films showed marginal gains at the expense of higher polarization.

- Mapped the effect of deposition temperature on ionic transport: films grown at 200 °C attained the highest bulk conductivity ( $2 \times 10^{-4}$  S/cm), while coatings deposited at 100 °C minimized interfacial impedance ( $\sim 50 \Omega \cdot \text{cm}^2$ ), revealing a trade-off between ion-carrier density and interface quality.

## 6.2 Broader Implications

These findings provide actionable design rules for implementing AP-SALD  $\text{Li}_3\text{PO}_4$  layers on 3D battery electrodes. By coupling pore-network metrics with conformality data, engineers can predict coating uniformity in complex architectures. The identification of a mid-range thickness (10 nm) as a “sweet spot” balances mechanical integrity and electrochemical longevity, and the temperature-dependent conductivity/impedance trends guide processing conditions for high-performance cells.

## 6.3 Limitations

- Our study focuses exclusively on  $\text{Li}_3\text{PO}_4$  coatings on commercial graphite; results may differ for alternative solid electrolytes or high-voltage cathode substrates.
- Cycle-life tests were conducted at a single rate (1 C) and temperature (25 °C), leaving high-rate and elevated-temperature performance unexamined.
- The equivalent-circuit approach to deconvolute interfacial impedance carries model-fitting uncertainties, particularly at high deposition temperatures.

## 6.4 Future Research Directions

- Extend conformality–performance mapping to other electrode materials (e.g., Si, Ni-rich cathodes) and multicomponent solid electrolytes.
- Investigate long-term cycling under high-rate ( $\geq 2$  C) and elevated-temperature ( $\geq 60$  °C) regimes to assess real-world applicability.
- Develop in situ/operando imaging or scattering techniques to monitor coating evolution during cycling.

- Couple pore-scale simulations with experimental data to predict ion transport and mechanical stability in complex electrode geometries.

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