

Predictive Theory of Electrochemical Ostwald Ripening for Electrodeposited Lithium Metal

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Electrode morphology critically determines the stability and efficiency of lithium metal anodes, yet no predictive framework has explained how measurable parameters control deposition. Here we introduce the first theoretical model of electrochemical Ostwald ripening, capturing the competition between electroplating and surface-energy-driven redistribution and identifying it as the governing process behind morphology evolution in the nondendritic regime. The framework explicitly incorporates solid electrolyte interphase (SEI) resistance, electrolyte conductivity, electrode wettability, and current density, revealing the transition from a 2D SEI-limited to a 3D electrolyte-limited growth. The model yields analytical expressions for nucleus size, density, and distribution that quantitatively reproduce independent experimental results and establishes a direct link between plating conditions, morphology, and Coulombic efficiency. By providing experimentally accessible relationships between key parameters and deposition outcomes, the framework enables a predictive understanding of lithium plating and provides a broadly applicable basis for controlling electrodeposition morphology across diverse electrochemical systems.

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I. INTRODUCTION

The morphology of electrodeposited lithium is a critical factor in the Coulombic efficiency (CE) and lifespan of lithium metal batteries [1]. Irregular deposition accelerates solid electrolyte interphase (SEI) degradation, increases electrolyte consumption, and raises the risk of short circuits—all of which contribute to battery failure [1–3]. Conversely, smooth and compact lithium deposits improve cycling stability by reducing side reactions and ensuring uniform lithium utilization. Beyond batteries, metal deposition morphology is also critical in general galvanic coatings, where surface roughness and deposit uniformity influence properties such as corrosion resistance, adhesion strength, and electrical conductivity [4].

Metal deposition can be broadly divided into dendritic and nondendritic regimes. In the dendritic regime, rapid ion depletion near the electrode surface drives growth into needle-like dendrites [5,6], posing immediate safety risks. The nondendritic regime, by contrast, corresponds to practical operating conditions and is the main focus of this work. Here, deposition proceeds more gradually and is generally described as a two-stage process: during

nucleation, new nuclei form and their initial distribution is established; during subsequent growth, existing nuclei expand while little additional nucleation occurs [7,8].

Classical nucleation theory predicts that large nuclei are statistically suppressed due to the $\sim r^{-2}$ dependence of the Zeldovich factor [9], favoring the formation of small initial clusters under low overpotential η . The critical nucleus size for lithium is approximately $r^* \sim \frac{2\sigma V_m}{RT}$ (around 18 nm [10]), where σ is the metal-electrolyte surface energy. Experimentally observed nuclei, however, are often much larger, indicating that growth processes dominate shortly after nucleation under practical conditions [8], highlighting the central role of the growth phase in determining the final deposition morphology.

In classical models, growth is assumed to proceed without dissolution of nuclei, which leads at constant current to a linear increase in volume, $r^3 \sim it$. This simplified picture omits redistribution processes driven by surface energy minimization, commonly known as Ostwald ripening, in which larger nuclei grow at the expense of smaller ones [11,12] (see Fig 1). However, ripening is crucial for two reasons. First, it accounts for the experimentally observed decrease in nucleation density during the early stages of lithium deposition [13,14] and reflects similar observations in other metal systems, including sodium-ion batteries [15–17], where redistribution promotes smoother, denser deposits. Second, the interplay between electroplating and redistribution current proves necessary to explain the roles of key parameters such as SEI and electrolyte resistivity, metal-electrode

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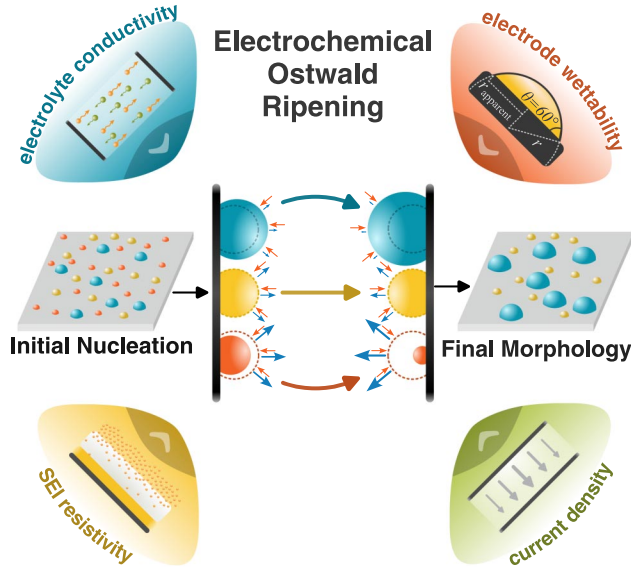


FIG. 1. Ostwald ripening framework mediating the influence of key factors on lithium morphology. The central sequence illustrates the evolution from an initially broad distribution of small nuclei to a final morphology dominated by larger ones, highlighting the growth of larger nuclei at the expense of smaller ones.

interfacial energy, and current density in shaping the final morphology. This addresses an important theoretical gap; although these factors are experimentally known to influence lithium electrodeposition, with lower values generally improving cell life [18–22], the mechanisms by which they exert their effects have remained elusive.

A key implication of deposition morphology is its impact on Coulombic efficiency and battery lifespan [1,23], as a higher surface-to-volume ratio of the lithium deposit accelerates parasitic processes. The morphology at the point of full electrode coverage is particularly decisive, as it defines the subsequent evolution of lithium growth. A simple illustration is provided by the SEI-passivated column model [24], where once the electrode surface is fully covered, further lithium growth proceeds only in the vertical direction, with columns isolated by the SEI retaining their initial diameters at the coverage point. Even when the morphology becomes more complex—for example, when a softer SEI allows partial fusion of neighboring columns and the formation of voids filled with trapped SEI and electrolyte [25]—the initial state still fully determines the subsequent evolution.

In this study, we derive a theoretical framework that explicitly incorporates electrochemical Ostwald ripening into the description of lithium electrodeposition, demonstrating its previously unrecognized yet decisive role in determining plating morphology in the nondendritic regime. The model quantifies how deposition conditions and cell parameters—such as SEI and electrolyte resistances, surface energy, and plating current—govern the

evolution of deposit structure prior to full electrode surface coverage, while the predicted nuclei sizes at this critical point are shown to correlate with CE. Theoretical results closely agree with experimental observations across multiple datasets. Although developed for lithium metal anodes, the framework is broadly applicable to other metal electrodeposition processes, providing a unified basis for understanding and controlling metal morphology across diverse technologies.

II. GENERAL SYSTEM DESCRIPTION

In the classical Ostwald ripening theory of Wagner, Lifshitz, and Slyozov (WLS) [11,12], the governing equations are derived directly from the diffusion equation. For electrochemical systems, however, this approach is less practical [26], as it introduces redundant parameters—particularly for the SEI—that are difficult to measure experimentally. Instead, we adopt a Barton-type formulation [5], which can be directly related to the WLS theory but relies only on experimentally accessible material constants. In our framework, the total overpotential is expressed as the sum of electrodic, diffusive, and surface energy contributions [5]. In the low-current-density regime, the deviation of the nucleus free energy from equilibrium remains small, allowing the electrodic and SEI overpotentials to be linearized and expressed using Ohm’s law [5,26,27]. The total overpotential can then be written as

$$\eta = \frac{i_n RT}{i_0 F} + i_n R_{\text{SEI}} S_{\text{tot}} + \frac{i_n r RT}{DC_{\infty} F^2} + \frac{2\sigma V_m}{\text{Fr}}. \quad (1)$$

Here i_n is the current density at the nucleus surface, i_0 is the exchange current density, and F is the Faraday constant. R_{SEI} is the SEI resistance, and S_{tot} is the total SEI surface area. D and C_{∞} are the lithium ion diffusivity and bulk lithium ion concentration of the electrolyte, respectively. The diffusive overpotential follows from the concentration overpotential in the dilute-solution limit. Using the diffusion-limited current density $i_{\text{lim}} = DC_{\infty} F/r$, the concentration overpotential becomes $\frac{RT}{F} \frac{i_n}{i_{\text{lim}}} = \frac{i_n r RT}{DC_{\infty} F^2}$, which is the form originally introduced by Barton and Bockris [5]. The final term, $\frac{2\sigma V_m}{\text{Fr}}$, accounts for the additional overpotential contribution from the surface energy of the lithium nuclei.

The electrodic and SEI terms can be further combined using a single corrected resistance-area product $\mathfrak{R}/\kappa = \frac{RT}{i_0 F} + R_{\text{SEI}} S_{\text{tot}}$, where $\kappa [\Omega^{-1} \text{m}^{-2}]$ is a free parameter introduced solely for later notational convenience. The SEI term can vary between 10^{-1} and $10^3 \Omega \text{cm}^2$ [21,28,29] and often dominates the smaller electrodic term with high characteristic exchange current density values i_0 on the order of 10^2 – 10^3 A/m^2 [22,30]. Relating the rate of change of the nucleus radius as $i_n = \frac{3Fv}{V_m s} \frac{dr}{dt}$, where $v = \frac{\pi}{3}(2 + \cos\theta)(1 - \cos\theta)^2$ and $s = 2\pi(1 - \cos\theta)$ are the

volumetric and surface shape factors for a hemispherical shape (see Supplemental Material Note 1 [31]) allows Eq. (1) to be rewritten as an evolution equation for the nucleus radius. Introducing the dimensionless variables ($\rho = \frac{RT}{2\sigma V_m} r$, $\rho_s = \frac{RT}{F\eta}$, $\tau = \frac{\kappa(RT)^2}{6\sigma F^2} \frac{s}{v} t$, and $\omega = \frac{2\sigma V_m \kappa}{DC_\infty F^2}$) and collecting the dimensional prefactors yields the dimensionless equation of motion:

$$v_\rho = \frac{d\rho}{d\tau} = \frac{1}{\mathfrak{R} + \omega\rho} \frac{1}{\rho_s} - \frac{1}{\rho} \quad (2)$$

Equation (2) describes the dynamics of the nucleus size evolution. Nuclei smaller than the limiting radius $\rho_s(\tau)$, indicated as yellow nuclei in Fig. 1, dissolve, while nuclei bigger than ρ_s grow. Importantly, the limiting radius $\rho_s(\tau)$ itself is a growing function with time, such that increasingly bigger nuclei start being dissolved as the system evolves. An interesting consequence of Eq. (2) is the emergence of mixed-dimensional behavior in nuclei growth during Ostwald ripening. At early stages (or under high SEI resistivity conditions, $\mathfrak{R} \gg \omega\rho$), the growth dynamics are governed primarily by the effective surface resistivity, which combines charge-transfer and SEI transport contributions, and the system exhibits an effective dimensionality of $n = 2$. In contrast, at later stages (or under low SEI resistivity, $\omega\rho \gg \mathfrak{R}$), the electrolyte-diffusion contribution becomes dominant, and the system transitions to behavior consistent with the $n = 3$ dimensional Ostwald ripening equation of motion. Both limits, by choosing the appropriate κ such that $\mathfrak{R} = 1$ in the two-dimensional case and $\omega = 1$ in the three-dimensional case, can be unified into a generalized form

$$v_\rho = \frac{d\rho}{d\tau} = \frac{1}{\rho^{n-1}} \left(\frac{\rho}{\rho_s} - 1 \right). \quad (3)$$

Following Lifshitz-Slyozov [11], we further introduce the nuclei size distribution function $f(\rho, \tau)$, which fulfills the continuity equation

$$\frac{df}{d\tau} + \frac{d}{d\rho}(f v_\rho) = 0. \quad (4)$$

In the constant current regime, mass conservation is expressed as

$$j = \frac{1}{\tau} \int_0^\infty f(\rho, \tau) \rho^3 d\rho = 3 \int_0^\infty f(\rho, \tau) v_\rho \rho^2 d\rho, \quad (5)$$

where $j = \frac{Fi}{\kappa RT}$ is the dimensionless ion flow. Notably, it is the use of the constant-current assumption in Eq. (5), replacing the constant-volume restriction employed in previous works, that gives rise to the new phenomena explored in this paper (see Supplemental Material Note 2 [31] for the differences).

III. ASYMPTOTIC LIMITS

The solutions of the systems of Eqs. (2)–(5) are discussed in three relevant limiting cases (Fig. 2(a), Supplemental Material Note 2 [31]). First, for high current densities j or high total charge-transfer resistance, the term $\frac{1}{\rho_s}$ becomes dominant in the nucleus growth v_ρ and ripening becomes negligible. In this regime, provided dendritic formation conditions have not been reached, nucleus growth proceeds, conserving the nucleus number density. As a result, the size distribution $f(r, t)$ evolves primarily through a shift of its center—moving toward larger radii, while its shape is approximately preserved [33] (see Fig. 2(a), Supplemental Material Note 2 [31]). In this case, final morphology depends neither on plating current nor on SEI or electrolyte resistivity but is solely determined by initial nucleation density and the total plated lithium volume. We estimate that this no-ripening regime occurs when the total charge-transfer resistance satisfies $(\mathfrak{R} + \omega)/\kappa \gg \frac{RT}{iF} \approx 26 \Omega \cdot \text{cm}^2$ for $i = 1 \text{ mA/cm}^2$ at 300 K, by comparing the surface-energy term with the charge-transfer resistance and assuming a characteristic nucleus size at nucleation of $\rho^* \sim 1$ (or $r^* \sim 18 \text{ nm}$ for lithium). Given that SEI and electrolyte resistance are often relatively low, this suggests that ripening is likely active under most practical conditions and becomes even more prominent at elevated temperatures, which indirectly was observed in Ref. [21].

For the converse limiting case of low or moderate total charge-transfer resistance, the system's behavior critically depends on the dimensionality n . In the second limiting case, the 3D ripening regime (low SEI resistance, $\mathfrak{R} \ll \omega\rho$), the size distribution narrows over time and ultimately collapses into a delta function (see Fig. 2(a), and f_{3D}^∞ in Supplemental Material Note 2 [31]). Simultaneously, the nuclei density N remains constant while the mean nucleus volume grows linearly with time, $\langle \rho^3 \rangle \sim j\tau$ [34]. This behavior has been observed in galvanic metal deposition without SEI [4] and is often described as narrowing of the size distribution at later stages of metal deposition [35].

Finally, for the 2D regime (high SEI resistivity, $\mathfrak{R} \gg \omega\rho$), which is, as will be motivated later, most relevant for lithium batteries, the distribution function takes a self-similar form and becomes independent of the initial distribution:

$$f_{2D}^\infty = 5.19j \frac{\rho}{(\sqrt{2\tau} - \rho)^3} \exp\left(\frac{\sqrt{2\tau}}{\rho - \sqrt{2\tau}}\right) \quad (6)$$

(see also Fig. 2(d) and Supplemental Material Note 2 [31] for the derivation). Interestingly, the emergence of an asymptotic self-similar regime is also consistent with recent numerical studies based on the full nonlinear Butler-Volmer formulation of Ostwald ripening [36]. Similarly, the nuclei density does not depend on the initial

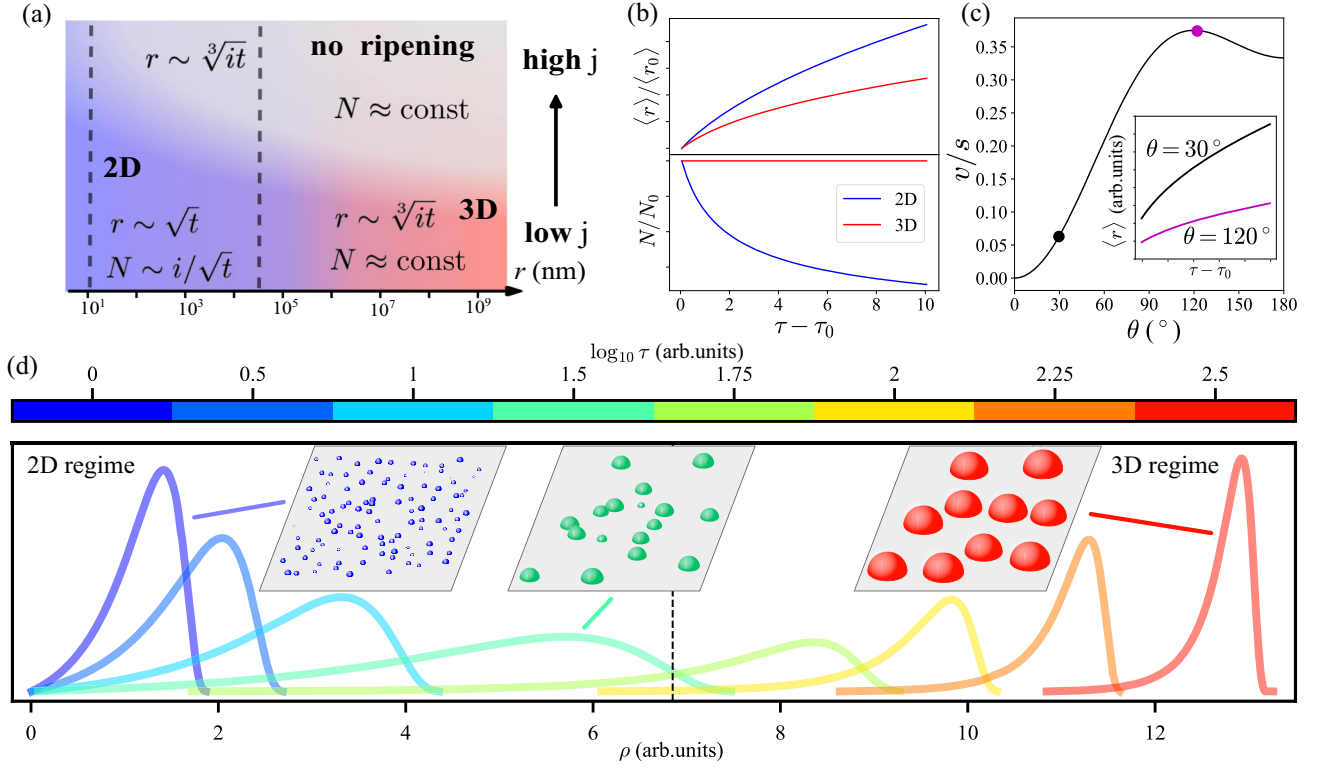


FIG. 2. Comparison of 2D and 3D behavior in constant-current electrochemical Ostwald ripening. (a) Phase diagram showing the 2D/3D and no ripening regimes. The left and right dotted lines mark approximate nuclei sizes at nucleation and at full coverage. (b) Time evolution of average nucleus size ($\langle r \rangle$, top) and nucleation density (N , bottom) in both 2D and 3D regimes. (c) Shape parameter (v/s) as a function of contact angle (θ). Inset: Comparison of $\langle r \rangle$ [in units of $V_m/F\sqrt{\sigma R_{\text{SEI}}S_{\text{tot}}}$ from Eq. (8)] for two different contact angles. (d) Time evolution of the nucleus size distribution: initially following the f_{2D}^∞ profile, the system gradually transitions to a 3D regime with a narrowing distribution. Different time steps are color-coded; insets illustrate the evolving surface coverage.

nucleation density and follows the relation:

$$N \approx 1.35 \frac{j}{\sqrt{\tau}} (\rho/r)^2 \approx 2.48 \frac{F^2}{V_m^2} \left(\frac{R_{\text{SEI}} S_{\text{tot}}}{\sigma} \frac{1}{s} \right)^{\frac{3}{2}} \frac{i\sqrt{v}}{\sqrt{t}}, \quad (7)$$

while the mean nucleus size is given by

$$\langle r \rangle \approx 0.844 \sqrt{\tau} (r/\rho) \approx 0.689 \frac{V_m}{F} \sqrt{\frac{t\sigma}{R_{\text{SEI}} S_{\text{tot}}} \frac{s}{v}}. \quad (8)$$

Importantly, the expected nucleus radius is independent of the current density but is determined by the metal surface energy and R_{SEI} . The nucleation density depends on all three parameters and decreases with time, which at the same current ensures faster growth of the nucleus size r compared to the 3D case [Fig. 2(b)]. Additionally, both nucleation density and growth rate depend on the metal/electrode contact angle θ , which determines the nucleus surface-to-volume ratio. The growth rate reaches its minimal value at $\theta = 120^\circ$ [Fig. 2(c)], as the smaller contact angles ensure denser lithium plating and larger nucleus sizes [18]. Experimentally, the contact angle spans a wide range depending on the substrate material and

surface chemistry. For chemically inert substrates, it varies from strongly lithiophobic surfaces, with contact angles exceeding 130° for materials such as C, Ni, Mo, and Ti [37] to lithiophilic ones, such as Au ($\sim 50^\circ$) [37] or 30° for monolayer amorphous carbon [38]. We remark that, in order to compare with experimental data, the apparent nucleus size should be rescaled as $r_{\text{apparent}} = \alpha r$, where $\alpha = \sin \theta$ for contact angles $\theta < 90^\circ$ and $\alpha = 1$ for $\theta \geq 90^\circ$ (Fig. 1).

As noted above, the system is expected to evolve from a 2D to a 3D regime, during which the nucleus size distribution undergoes a distinct transformation. Initially, in the 2D regime, the distribution broadens, leading to a wide range of nucleus sizes [left part of Fig. 2(d)]. However, as the bulk electrolyte resistivity becomes more dominant compared to the SEI resistivity, the distribution gradually narrows, and in the asymptotic limit, the distribution approaches a δ function, characteristic of classical diffusion-controlled deposition [right part of Fig. 2(d)].

The characteristic moment of regime switching can be estimated from the condition $\rho_{\text{sw}} \omega = \mathfrak{R}$. In lithium batteries, it is estimated to range from $100 \mu\text{m}$ to 10 mm , based on values of R_{SEI} and D from Refs. [13,29,39].

However, this range appears unreasonably large compared to the characteristic feature sizes typically observed in electrode morphology studies (which are usually on the order of $\sim 10^0\text{--}10^1$ μm). As a result, lithium batteries are expected to operate purely in the 2D regime, and growth under ripening proceeds until the electrode surface is nearly fully covered and nuclei can no longer be treated as isolated but rather as a fused, porous medium.

The nucleus size at this full-coverage point (r_{cov}) determines the “weakest point” in the electrode morphology in terms of coverage density, which directly affects battery longevity. In the SEI-passivated column model [24], a simplified approach suggests that the quantity of parasitic side products is approximately proportional to the total exposed metal surface area. As a result, the Coulombic inefficiency, $1 - \text{CE}$, can be estimated as being proportional to the nuclei surface-to-volume ratio, i.e., $\sim 1/r_{\text{cov}}$. The upper limit of r_{cov} can be estimated from dense packing as $\pi\alpha^2 \int_0^\infty f \rho_{\text{cov}}^2 d\rho \approx \frac{\pi}{2\sqrt{3}}$, which in the 2D regime corresponds to the time moment $\alpha^2 \sqrt{\tau_{\text{cov}}} \approx 0.278j^{-1}$. This, in turn, allows us to estimate the characteristic nucleus radius r_{cov} :

$$t_{\text{cov}} \approx 0.0773 \frac{1}{\alpha^4 j^2} (t/\tau) \approx 0.0515 \frac{\sigma}{i^2 R_{\text{SEI}} S_{\text{tot}}} \frac{vs}{\alpha^4},$$

$$\langle r_{\text{cov}} \rangle \approx 0.844 \sqrt{\tau_{\text{cov}}} (r/\rho) \approx 0.156 \frac{\sigma V_m s}{Fi R_{\text{SEI}} S_{\text{tot}} \alpha^2}. \quad (9)$$

We deduce that lower current, SEI resistivity, and contact angle all contribute to a larger $\langle r_{\text{cov}} \rangle$, resulting in lower surface area exposure, higher CE, and better cycling stability—consistent with experimental observations [18,21]. While the initial nucleation stage and its nucleation overpotential (NOP) are often highlighted as key determinants of battery longevity, they do not explicitly appear in our framework. Nevertheless, we imply that the NOP is indirectly governed by nucleus geometry: lower θ results in wider and flatter nuclei and higher electrode surface coverage for the same deposited lithium volume, which reduces local current densities at nuclei surfaces i_n . Lower i_n subsequently decreases the overpotential, promoting the formation of a more conductive SEI and reducing the final SEI resistivity (R_{SEI}) [40,41].

IV. COMPARISON WITH EXPERIMENTS

Our predictions qualitatively align with previous experimental observations, particularly regarding the effects of SEI resistivity on nucleus size, $\langle r_{\text{cov}} \rangle$, and, consequently, battery longevity. In addition, the observed decrease in nucleation density [13] is predicted by our approach but cannot be explained by the standard nucleation-and-growth formalism [34]. To further validate our model quantitatively, we directly compared the predicted average nucleus size, size distribution, and Coulombic efficiency to

experimental data. Unfortunately, there are not many studies that investigate all the aspects required for comparison with the model results. We identified two studies [13,21] that provide extensive experimental data, making quantitative validation possible. Both studies used a 1 M LiTFSI in a DOL/DME electrolyte, with one varying cell temperature [13] and the other varying current density and deposited charges [21].

One of the most challenging aspects of experimental interpretation is determining the correct value of R_{SEI} . Standard electrochemical impedance spectroscopy (EIS) cannot distinguish R_{SEI} from other resistive elements in the equivalent circuit [29], leading to significant discrepancies. The true value of R_{SEI} can be several orders of magnitude lower than the total charge-transfer resistance measured by EIS. For example, in a 1 M LiPF₆ in EC/EMC electrolyte, R_{SEI} measured under blocking conditions is $1.5 \Omega \cdot \text{cm}^2$ [29], whereas conventional EIS reports a total resistance of approximately $100 \Omega \cdot \text{cm}^2$ [28]. To minimize this inconsistency, we assumed that R_{SEI} follows an Arrhenius relation, $R_{\text{SEI}} = A \exp(\frac{E_A}{RT})$, where E_A was fitted to experimental data ($E_A = 32$ kJ/mol, Supplemental Material Note 3 [31]), leaving A as the only free parameter in our model. This approach yielded consistent and reproducible results, independently converging to $R_{\text{SEI}} \approx 0.27 \Omega \cdot \text{cm}^2$ at 300 K [42] for both referenced studies [13,21].

Predicted and experimentally observed average nuclei sizes are in excellent agreement over a wide temperature range (-20°C to 30°C) and plating current densities ($0.1\text{--}5$ mA/cm²) [Fig. 3(a)]. The model also reproduces the size distribution, capturing the characteristic tail in the small-nucleus region [Fig. 3(b)], while the slight mismatch in the large-nucleus tail is likely attributable to coalescence effects [43]. Notably, we emphasize the clear linear correlation between Coulombic inefficiency ($1 - \text{CE}$) and

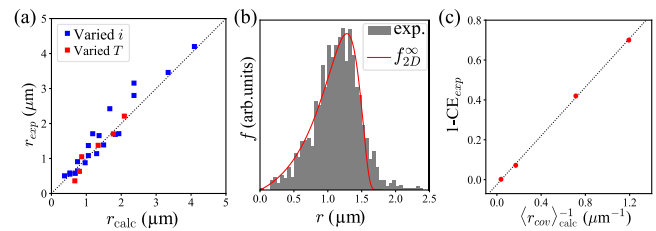


FIG. 3. Comparison of model predictions [Eqs. (7)–(9)] with experimental data. (a) Nucleus radii (r) at different temperatures (T) [21] are shown as red squares. Temperature-dependent variations in R_{SEI} were obtained via Arrhenius fit of measured values (see Supplemental Material Note 3 [31]). Blue squares represent nucleus radii at different current densities (i) and deposited charges [13]. (b) Experimental nucleus size distribution extracted from a large-area SEM image (Fig. S6(a) in Supplemental Material [13,31]) is shown as a bar plot; the red line depicts the theoretical 2D distribution f_{2D}^∞ [see Eq. (6)]. (c) Experimentally measured Coulombic inefficiency ($1 - \text{CE}$) [21] vs calculated $1/r_{\text{cov}}$ [Eq. (9)].

the inverse of the calculated characteristic radius at the point of full electrode coverage, $1/r_{\text{cov}}$ [Fig. 3(c), see the discussion above Eq. (9)]. Overall, the strong correlation between theoretical and experimental results validates the accuracy and predictive power of our model. A detailed discussion about our model's limitation is presented in the Appendix.

V. SUMMARY

In this work, we developed a theoretical framework to describe the evolution of electrode morphology under the competing influences of electroplating and surface-energy-driven redistribution. The analysis reveals three key asymptotic regimes. At high currents and large charge-transfer resistance, ripening is negligible, and nuclei volumes grow uniformly without material redistribution. In contrast, at low charge-transfer resistance and current density, Ostwald ripening dominates: in the surface-resistance-limited 2D regime, this leads to broader size distributions and decreasing nuclei densities, whereas in the bulk-diffusion-controlled 3D regime, the distribution gradually narrows under constant nuclei density. While lithium batteries are expected to operate mainly in the 2D regime, galvanic systems with lower (or without) SEI resistivity are instead well described by the 3D asymptote and may even exhibit the distinct transition from 2D to 3D behavior.

We highlight in particular the analytical expressions derived for the 2D regime. These relations connect nucleus size, size distribution, and density to experimentally accessible parameters such as R_{SEI} , plating current, and electrode wettability. Notably, the framework predicts the characteristic nucleus radius (r_{cov}) and the coverage time (t_{cov}) at which the electrode surface approaches full coverage, the latter correlating directly with Coulombic efficiency (CE), following $1 - \text{CE} \sim 1/r_{\text{cov}}$. Validation of our theoretical predictions against two independent experimental datasets showed excellent agreement. Taken together, our results establish a quantitative link between key experimental variables and lithium plating morphology, CE, and ultimately battery lifetime. In practical terms, this translates into the following relationships:

Electrode wettability, determined by the metal/electrode contact angle θ , controls the nuclei surface-to-volume ratio. Lower θ increases surface coverage for the same deposited charge, reduces effective current density at the nuclei surface, and, in turn, lowers nucleation overpotential and SEI resistivity. While the dependence becomes nonmonotonic for $\theta \geq 90^\circ$, variations in this range have a minor impact compared with the strong improvement observed for $\theta < 90^\circ$, which approaches ideal surface coverage as $\theta \rightarrow 0$.

SEI resistivity (R_{SEI}) and current density (i) jointly determine nuclei sizes and density. Varying both affects the electrode coverage time as $t_{\text{cov}} \sim (i^2 R_{\text{SEI}})^{-1}$. The

morphology at this point has a strong impact on Coulombic efficiency and lifespan and is highly susceptible to increases in current density ($1 - \text{CE} \sim i R_{\text{SEI}}$). After coverage, sensitivity to i decreases, allowing higher currents with less impact on performance. These results provide an analytical framework for optimizing charging protocols and estimating the trade-off between Coulombic efficiency and charging speed.

While our study focused on lithium metal, the underlying principles apply broadly to metal electrodeposition systems where surface morphology plays a critical role. We anticipate that the analytical model presented here will support more precise optimization of battery parameters, ultimately contributing to improved battery performance and lifetime.

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The authors declare no competing interests.

DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

APPENDIX MODEL'S LIMITATION

Our model is constructed under idealized conditions: a flat, homogeneous electrode surface, a uniform SEI layer, and relatively low-current densities that preclude dendrite formation. These assumptions define the principal limitations of our theoretical framework.

The first key limitation is the requirement of relatively low-current density to avoid tip-enhanced growth, which can ultimately lead to dendrite formation. Specifically, the model assumes that ion transport is sufficiently fast to maintain quasiequilibrium over the characteristic size of a growing nucleus. This condition holds when the local current density at the electrode surface remains significantly below the diffusion-limited current density [5,44].

The second limitation arises from SEI inhomogeneity. In practice, the solid electrolyte interphase may exhibit spatial variations in thickness, composition, and ionic conductivity, stemming from initial electrode surface irregularities or from mechanical degradation such as cracking. These variations can lead to uneven local current distribution and nonuniform lithium deposition. Notably, lower initial SEI resistivity has been shown to reduce the likelihood of subsequent SEI disruption [45]. However, it is important to emphasize that if SEI inhomogeneities

occur on a length scale smaller than the typical nucleus size ρ_s (and do not induce dendritic growth), our model remains applicable, subject to corrections to the geometric shape factors s and v .

The third limitation involves substrate inhomogeneity. Even under a spatially uniform electric potential across a metallic substrate, local variations in crystallographic orientation, defects, or grain boundaries can influence the initial SEI formation and lithium nucleation. While these effects can be pronounced during the nucleation stage, their impact on subsequent growth diminishes if the contact angle θ remains uniform across the surface, since the growth phase is determined by nucleus, SEI, and electrolyte properties. In cases of mild initial inhomogeneity, the initial perturbations typically average out during growth, allowing the model to remain applicable. In contrast, in strongly inhomogeneous systems—such as passivated current collectors where lithium nucleation is confined to rare, defective regions of a passivation layer [46]—the initial nucleus density can be extremely low for the ripening process, and the system remains in a non-ripening regime throughout deposition.

The fourth limitation regards the assumption of spherical cap-shaped lithium nuclei. For very small clusters (on the order of ~ 10 nm), faceted geometries such as rhombic dodecahedra are more thermodynamically preferable [47]. Yet as the nuclei grow, the energetic advantage of these faceted shapes over simpler geometries diminishes [26], and their morphology approaches that of truncated spheres defined by the metal-substrate contact angle θ , which reflects the balance of interfacial energies via Young's equation.

Finally, we note that lithium redistribution could, in principle, occur along the electrode surface; however, this pathway is unlikely to be significant beyond the initial nucleation stage. Although a few reports have considered such on-surface migration [48], its efficiency is expected to be low: for surface migration, the effective cross-sectional area of the transport channel scales as $2\pi rh$, where h is on the order of the Van-der-Waals diameter of a lithium atom (≈ 2.24 Å), whereas the surface area of a nucleus scales as $\sim \pi r^2$. Unless the lithium diffusion coefficient along the electrode surface is several orders of magnitude greater than through the SEI—which seems improbable given that the surface is typically fully passivated before nucleation [49]—this redistribution channel is unlikely to play a dominant role beyond the earliest stages.

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- [1] J. Zheng, M. S. Kim, Z. Tu, S. Choudhury, T. Tang, and L. A. Archer, *Regulating electrodeposition morphology of lithium: Towards commercially relevant secondary Li metal batteries*, *Chem. Soc. Rev.* **49**, 2701 (2020).
 [2] A. Jetybayeva, D. S. Aaron, I. Belharouak, and M. M. Mench, *Critical review on recently developed lithium*

- and non-lithium anode-based solid-state lithium-ion batteries*, *J. Power Sources* **566**, 232914 (2023).
 [3] C. Monroe and J. Newman, *Dendrite growth in lithium/polymer systems: A propagation model for liquid electrolytes under galvanostatic conditions*, *J. Electrochem. Soc.* **150**, A1377 (2003).
 [4] N. M. Schneider, J. H. Park, J. M. Grogan, D. A. Steingart, H. H. Bau, and F. M. Ross, *Nanoscale evolution of interface morphology during electrodeposition*, *Nat. Commun.* **8**, 2174 (2017).
 [5] J. Barton and J. Bockris, *The electrolytic growth of dendrites from ionic solutions*, *Proc. R. Soc. London, Ser. A* **268**, 485 (1962).
 [6] P. Bai, J. Li, F. R. Brushett, and M. Z. Bazant, *Transition of lithium growth mechanisms in liquid electrolytes*, *Energy Environ. Sci.* **9**, 3221 (2016).
 [7] J. K. Stark, Y. Ding, and P. A. Kohl, *Nucleation of electrodeposited lithium metal: Dendritic growth and the effect of co-deposited sodium*, *J. Electrochem. Soc.* **160**, D337 (2013).
 [8] G. Feng, Y. Shi, H. Jia, S. Risal, X. Yang, P. Ruchhoeft, W.-C. Shih, Z. Fan, W. Xu, and X. Shan, *Progressive and instantaneous nature of lithium nucleation discovered by dynamic and operando imaging*, *Sci. Adv.* **9**, eadg6813 (2023).
 [9] K. C. Russell, *Grain boundary nucleation kinetics*, *Acta Metall.* **17**, 1123 (1969).
 [10] D. R. Ely and R. E. García, *Heterogeneous nucleation and growth of lithium electrodeposits on negative electrodes*, *J. Electrochem. Soc.* **160**, A662 (2013).
 [11] I. M. Lifshitz and V. V. Slyozov, *The kinetics of precipitation from supersaturated solid solutions*, *J. Phys. Chem. Solids* **19**, 35 (1961).
 [12] C. Wagner, *Theorie der alterung von niederschlägen durch umlösen (ostwald-reifung)*, *Z. Elektrochem. Berichte Bunsengesellschaft Phys. Chem.* **65**, 581 (1961).
 [13] A. Pei, G. Zheng, F. Shi, Y. Li, and Y. Cui, *Nanoscale nucleation and growth of electrodeposited lithium metal*, *Nano Lett.* **17**, 1132 (2017).
 [14] K. Yan, J. Wang, S. Zhao, D. Zhou, B. Sun, Y. Cui, and G. Wang, *Temperature-dependent nucleation and growth of dendrite-free lithium metal anodes*, *Angew. Chem.* **131**, 11486 (2019).
 [15] P. L. Redmond, A. J. Hallock, and L. E. Brus, *Electrochemical Ostwald ripening of colloidal Ag particles on conductive substrates*, *Nano Lett.* **5**, 131 (2005).
 [16] L. Geng, Q. Liu, J. Chen, P. Jia, H. Ye, J. Yan, L. Zhang, Y. Tang, and J. Huang, *In situ observation of electrochemical Ostwald ripening during sodium deposition*, *Nano Res.* **15**, 2650 (2022).
 [17] H. Hwang, H. Oh, and H. Song, *Shaping copper oxide layers on gold nanoparticle ensembles by controlled electrodeposition with single particle scatterometry*, *Small* **19**, 2301241 (2023).
 [18] L. Ye, C. Zhang, Y. Zhou, B. Ülgüt, Y. Zhao, and J. Qian, *Guided lithium nucleation and growth on lithiophilic tin-decorated copper substrate*, *J. Energy. Chem.* **74**, 412 (2022).
 [19] R. Zhang, X.-R. Chen, X. Chen, X.-B. Cheng, X.-Q. Zhang, C. Yan, and Q. Zhang, *Lithiophilic sites in doped graphene guide uniform lithium nucleation for dendrite-free lithium*

- metal anodes, *Angew. Chem., Int. Ed.* **56**, 7764 (2017). [10.1002/anie.201702099](https://doi.org/10.1002/anie.201702099)
- [20] K. V. Kravchyk, H. Zhang, and M. V. Kovalenko, *On the interfacial phenomena at the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)/Li interface*, *Commun. Chem.* **7**, 257 (2024).
- [21] J. Wang, W. Huang, A. Pei, Y. Li, F. Shi, X. Yu, and Y. Cui, *Improving cyclability of Li metal batteries at elevated temperatures and its origin revealed by cryo-electron microscopy*, *Nat. Energy* **4**, 664 (2019).
- [22] L. Que and W. Chen, *Analysis of the lithium electrodeposition behavior in the charge process of lithium metal battery associated with overpotential*, *J. Power Sources* **557**, 232536 (2023).
- [23] G. M. Hobold, J. Lopez, R. Guo, N. Minafra, A. Banerjee, Y. S. Meng, Y. Shao-Horn, and B. M. Gallant, *Moving beyond 99.9% coulombic efficiency for lithium anodes in liquid electrolytes*, *Nat. Energy* **6**, 951 (2021).
- [24] R. M. Kasse, N. R. Geise, J. S. Ko, J. Nelson Weker, H.-G. Steinrück, and M. F. Toney, *Understanding additive controlled lithium morphology in lithium metal batteries*, *J. Mater. Chem. A* **8**, 16960 (2020).
- [25] N. Boaretto, I. Garbayo, S. Valiyaveetil-SobhanRaj, A. Quintela, C. Li, M. Casas-Cabanas, and F. Aguesse, *Lithium solid-state batteries: State-of-the-art and challenges for materials, interfaces and processing*, *J. Power Sources* **502**, 229919 (2021).
- [26] A. Schröder, J. Fleig, D. Gryaznov, J. Maier, and W. Sitte, *Quantitative model of electrochemical Ostwald ripening and its application to the time-dependent electrode potential of nanocrystalline metals*, *J. Phys. Chem. B* **110**, 12274 (2006).
- [27] M. Hess, *Non-linearity of the solid-electrolyte-interphase overpotential*, *Electrochim. Acta* **244**, 69 (2017).
- [28] G. M. Hobold, K.-H. Kim, and B. M. Gallant, *Beneficial vs inhibiting passivation by the native lithium solid electrolyte interphase revealed by electrochemical Li^+ exchange*, *Energy Environ. Sci.* **16**, 2247 (2023).
- [29] S. Solchenbach, X. Huang, D. Pritzl, J. Landesfeind, and H. A. Gasteiger, *Monitoring SEI formation on graphite electrodes in lithium-ion cells by impedance spectroscopy*, *J. Electrochem. Soc.* **168**, 110503 (2021).
- [30] R. Amin and I. Belharouak, *Part I: Electronic and ionic transport properties of the ordered and disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel cathode*, *J. Power Sources* **348**, 311 (2017).
- [31] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/xqcq-f8q1> for Notes 1–3, which includes Refs. [3, 11, 12, 21, 32].
- [32] K. Kroenlein, C. Muzny, A. Kazakov, V. Diky, R. Chirico, J. Magee, I. Abdulagatov, and M. Frenkel, *NIST/TRC web thermo tables (WTT) NIST standard reference subscription database 3 - professional edition version 2* (2011).
- [33] J. Bartels, U. Lembke, R. Pascova, J. Schmelzer, and I. Gutzow, *Evolution of cluster size distribution in nucleation and growth processes*, *J. Non-Cryst. Solids* **136**, 181 (1991).
- [34] B. Scharifker and G. Hills, *Theoretical and experimental studies of multiple nucleation*, *Electrochim. Acta* **28**, 879 (1983).
- [35] J. L. Fransaer and R. M. Penner, *Brownian dynamics simulation of the growth of metal nanocrystal ensembles on electrode surfaces from solution. i. instantaneous nucleation and diffusion-controlled growth*, *J. Phys. Chem. B* **103**, 7643 (1999).
- [36] Y.-H. Xu, W.-Z. Fang, K.-B. An, Z.-H. Xuan, D.-K. Hu, Y. Zhu, and W.-Q. Tao, *Rapid predictions of platinum degradation in cathode catalyst layers based on Ostwald ripening theory and numerical insights*, *Chem. Eng. J.* **529**, 172952 (2026).
- [37] J. Wang, H. Wang, J. Xie, A. Yang, A. Pei, C.-L. Wu, F. Shi, Y. Liu, D. Lin, Y. Gong, and Y. Cui, *Fundamental study on the wetting property of liquid lithium*, *Energy Storage Mater.* **14**, 345 (2018).
- [38] L. Shi *et al.*, *Monolayer amorphous carbon: Unlocking disorder-induced lithiophilicity*, *Adv. Sci.* **13**, e16490 (2026).
- [39] C. Park, M. Kanduč, R. Chudoba, A. Ronneburg, S. Risse, M. Ballauff, and J. Dzubiella, *Molecular simulations of electrolyte structure and dynamics in lithium–sulfur battery solvents*, *J. Power Sources* **373**, 70 (2018).
- [40] S. Zhang, Y. Li, L. J. Bannenberg, M. Liu, S. Ganapathy, and M. Wagemaker, *The lasting impact of formation cycling on the Li-ion kinetics between SEI and the Li-metal anode and its correlation with efficiency*, *Sci. Adv.* **10**, 8889 (2024).
- [41] L. Liu and M. Zhu, *Modeling of SEI layer growth and electrochemical impedance spectroscopy response using a thermal-electrochemical model of Li-ion batteries*, *ECS Trans.* **61**, 43 (2014).
- [42] This value likely underestimates ohmic R_{SEI} due to the omission of small nuclei in the original size histograms. While this discrepancy has a negligible effect on the $\langle r \rangle$, it can lead to an overestimation of $\langle r^3 \rangle$, and thus an underestimation of N by up to a factor of five.
- [43] A. V. Teran, A. Bill, and R. B. Bergmann, *Time-evolution of grain size distributions in random nucleation and growth crystallization processes*, *Phys. Rev. B* **81**, 075319 (2010).
- [44] A. R. Despic, J. Diggle, and J. O.'M. Bockris, *Mechanism of the formation of zinc dendrites*, *J. Electrochem. Soc.* **115**, 507 (1968).
- [45] C.-J. Ko, C.-H. Chen, and K.-C. Chen, *Influence of inhomogeneity of lithium-ion transport within the anode/electrolyte interface on mossy lithium formation*, *J. Power Sources* **563**, 232779 (2023).
- [46] P. Du, J. Wan, J. Qu, H. Xie, D. Wang, and H. Yin, *Passivation and corrosion of Al current collectors in lithium-ion batteries*, *npj Mater. Degrad.* **8**, 43 (2024).
- [47] Q. Fu, Y. Xue, and Z. Cui, *Size- and shape-dependent surface thermodynamic properties of nanocrystals*, *J. Phys. Chem. Solids* **116**, 79 (2018).
- [48] Z. Wu, C. Wang, Z. Hui, H. Liu, S. Wang, S. Yu, X. Xing, J. Holoubek, Q. Miao, H. L. Xin, and P. Liu, *Growing single-crystalline seeds on lithiophobic substrates to enable fast-charging lithium-metal batteries*, *Nat. Energy* **8**, 340 (2023).
- [49] K. Xu, *Electrolytes, Interfaces and Interphases* (The Royal Society of Chemistry, 2023), [10.1039/9781837671311](https://doi.org/10.1039/9781837671311).