

Morphology-Property Interplay in Chemo-Mechanics of Ion-Intercalation Active Particles

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Abstract

Morphology, material property, and mechanical constraint jointly govern the chemo-mechanical behavior of ion-intercalation particles, yet their coupled effects remain insufficiently understood. Here we establish a thermodynamically consistent single-particle framework and combine analytical solutions with multiphysics simulations to determine how these factors regulate lithiation and stress generation. We study hollow spherical, cylindrical, and ellipsoidal particles with isotropic or transversely isotropic material properties under fully constrained, inner-free, or unconstrained boundary conditions. We show that the transient lithiation pathway and the associated stress and strain fields are governed not by morphology, property, or constraint alone, but by their coupled interaction: isotropic particles are sensitive to the mechanical constraint, whereas transversely isotropic particles exhibit persistent heterogeneous lithiation dominated by anisotropic diffusivity. Flux decomposition analysis reveals that the mechanical contribution to Li flux is negligible in spheres but dominant in ellipsoids. Correlation analysis further shows that Li concentration and volumetric strain exhibit strong anti-correlation in unconstrained particles but weak correlation under full constraints. Bayesian optimization of hollow ellipsoids identifies Pareto-optimal morphologies that balance lithiation capacity against peak tensile stress. These results provide a unified framework for the morphology-property interplay in intercalation particles and offer morphology design principles for chemo-mechanical stability.

Keywords: chemo-mechanical coupling, ion-intercalation particles, anisotropic diffusivity, mechanical constraints, morphology optimization

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1. Introduction

Lithium-ion batteries (LIBs) have become the dominant electrochemical energy storage technology. As their applications expand from consumer electronics to more demanding use cases such as electric vehicles and grid-scale storage, the mechanics of electrodes has emerged as a critical determinant of the battery lifetime and performance. During a battery charge-discharge cycle, intercalation (lithiation) and deintercalation (delithiation) of Li ions induce considerable swelling and contraction of electrodes (Ipers et al., 2024; Oh et al., 2016; Höschle et al., 2023). Associated with this volumetric deformation is the complex evolution of the electrode microstructure (Song et al., 2025; Xu et al., 2021; Lu et al., 2021), manifested by changes in characteristic features such as particle size, porosity, and tortuosity. Such microstructural evolution and deformation in electrodes can ultimately result in fracture and degradation of battery performance over repeated cycling (Edge et al., 2021; Han et al., 2019; Jiao et al., 2026).

Across the multiple length scales of electrodes, chemo-mechanical processes at the particle level are particularly critical as degradation mechanisms are predominantly controlled by interactions at interfaces and within solid domains (Han et al., 2019; Shearing, 2016; de Vasconcelos et al., 2022). During lithiation and delithiation, inhomogeneous Li concentration and local deformation generate a nonuniform strain field (Beaulieu et al., 2001; Schiele et al., 2018) and internal stress (Zhao et al., 2010; Xu et al., 2019a; Pharr et al., 2012; Zhao et al., 2011, 2012), which can also be associated with phase separation (Bai et al., 2011; Cogswell and Bazant, 2012). Theories of chemo-mechanical coupling in solids have been developed over decades to understand these phenomena. Early work by Prussin (1961) quantified the stress field in Si wafers arising from the concentration gradient of dopant, drawing an analogy to thermal stress. This effort was later extended to a thermodynamically consistent framework by Larché and Cahn (1973, 1978) for solids undergoing simultaneous diffusion and deformation, in which chemical potentials explicitly account for elastic energy contributions. Recent progress in chemo-mechanical modeling of electrodes has been comprehensively reviewed by de Vasconcelos et al. (2022) and Zhao et al. (2019). These studies build on the general framework proposed by Larché and Cahn, which decomposes the total deformation into elastic and chemical contributions while incorporating reaction kinetics into boundary conditions.

Another key feature of electrode particles in both research and industrial applications is their diverse morphologies that depend strongly on the manufacturing process. Natural graphite particles are typically thin, plate-like flakes with high aspect ratios, while synthetic graphite particles are mostly spherical owing to production via spheroidization. In practice, graphite anode particles are often obtained by crushing or milling, yielding irregular shapes that are frequently highly porous (Zhu et al., 2018a,b). Cathode particles, such as lithium nickel manganese cobalt oxide $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$ (NMC) and lithium iron phosphate LiFePO_4 (LFP), generally appear as spherical or plate-like structures. A single secondary cathode particle typically consists of dozens of smaller primary particles bonded together by van der Waals forces (Han et al., 2025). The morphology and crystallographic orientation of these primary particles are often engineered during manufacturing and sintering to achieve radial alignment. Moreover, secondary particles are commonly hollow, a feature that helps preserve structural integrity (Mao et al., 2019; Singh et al., 2024; Han et al., 2025; Wang et al., 2023). Beyond commercial products, electrode particles can also be synthesized in rod-like (Zhang et al., 2013; Xie et al., 2024) or other nonstandard geometries in the laboratory for research purposes, particularly to investigate directional Li diffusion and mechanical stabilization (Cai et al., 2016).

The morphology of an electrode particle is intimately coupled to its material properties, including the elastic modulus, Li diffusivity, and lithiation/delithiation-induced spontaneous deformation, each of which may be isotropic or anisotropic. These couplings affect both the chemistry (e.g., Li intercalation) and the mechanics (e.g., internal stress and strain) of the electrode, with direct consequences for battery performance and stability during cycling. The couplings further raise a fundamental question: when a single particle incorporating a given amount of ions deforms, which particle morphology best promotes chemo-mechanical stability? Christensen and Newman (2006) introduced a stress-generation model for Li intercalation in single-phase spherical particles to study the influence of particle size and charge rate on fracture. Subsequent studies have found that layered cathode materials synthesized as near-equiaxed secondary particles can effectively reduce the initiation of microcracks by more uniformly distributing internal strain during cycling (Meng et al., 2023). Structural changes driven by anisotropic expansion of primary grains have also been observed, which can be suppressed by designing aligned nanoplate architectures (Lee et al., 2014; Jiao et al., 2022). However, these existing ef-

forts have each focused on specific morphologies (e.g., spherical or layered) and material properties (e.g., isotropy or anisotropy in modulus, diffusivity, and/or spontaneous deformation), leaving a systematic investigation of the morphology-property interplay in electrode chemo-mechanics largely unexplored.

A second knowledge gap concerns the lack of quantitative understanding of how mechanical constraints affect the chemo-mechanics of individual particles. In a real porous electrode containing millions of particles, each particle simultaneously deforms and interacts with neighboring particles, conductive and binder material (CBM), liquid electrolyte, and occasionally gas generated from side reactions during charge-discharge cycling. These complex interactions make it nearly impossible to identify the specific mechanical constraints acting on individual particles. Simulations based on reconstructed microstructures have revealed that the magnitude and distribution of stress fields are highly sensitive to particle arrangement, microstructural features, and spatial distribution of CBM (Xu et al., 2019a, 2021; Lu et al., 2021, 2020; Song et al., 2025; Hofmann et al., 2020). However, existing modeling approaches remain limited in their ability to reliably resolve particle-level mechanical constraints. To address this limitation, single-particle testing has emerged as a powerful electrochemical technique (Tsai et al., 2018; Fang et al., 2022; Fang and Li, 2021; Song et al., 2023; Lee et al., 2023), in which an individual particle is isolated from a porous electrode, fabricated into a microelectrode, and cycled against a counter electrode. Nevertheless, the mechanical constraints present in such isolated testing differ significantly from those in real porous electrodes. Furthermore, recent experiments have shown that externally applied mechanical constraints can effectively extend battery lifetime by suppressing gas generation and delamination between component layers (Ihuenyi et al., 2025a). Collectively, these observations underscore the critical role of mechanical constraints in determining electrode chemo-mechanics, yet their intrinsic coupling with particle morphology and material properties remains poorly understood.

In this work, we develop a coupled chemo-mechanical single-particle framework and apply it across three particle geometries, two classes of material symmetry, and three representative types of mechanical constraints. Section 2 presents the formulation of the thermodynamically consistent theory. Section 3 applies the theory to spherical particles as a baseline, then to cylindrical particles where axial confinement and crystal orientation

introduce additional coupling, and finally to ellipsoidal particles where the loss of high symmetry activates the full interplay among geometry, material anisotropy, and external constraint. Section 4 introduces two cross-field diagnostics, a flux decomposition that separates chemical from mechanical contributions to lithiation, and a Pearson correlation metric that quantifies the spatial correlation between the Li concentration and deformation fields. Section 5 formulates a multi-objective optimization of geometric parameters and crystal orientation in hollow ellipsoidal particles to navigate the trade-off between electrochemical capacity and mechanical integrity.

2. General Chemo-Mechanical Framework

We start by developing a general chemo-mechanical framework based on a single secondary particle, a fundamental building block of a porous electrode. While the framework applies to both anode and cathode materials, this study will focus on ceramic-type cathode particles as a model system. During the discharge process, the cathode particle undergoes Li-ion intercalation driven by the gradient of electrochemical potential. The intercalation-induced strain generates a stress field under certain mechanical constraints, which alters the total free energy of the system and thereby the diffusion kinetics.

To investigate the morphology-property interplay in the electrode under different mechanical constraints, we formulate our framework based on the following mechanical and electrochemical assumptions.

First, from mechanics, we model the particle as a linear elastic material throughout Li intercalation. This assumption is justified because most transition-metal-layered oxides undergo small deformation (i.e., up to 5% (Zhao et al., 2019)) during intercalation, and intergranular fracture usually occurs before the onset of plastic deformation in a secondary agglomerate (Yan et al., 2017). While slip may still take place prior to fracture in single-crystal particles (Qian et al., 2020; Shu et al., 2025), the current study focuses on particles made of oxide active materials that are mostly polycrystalline.

Second, from electrochemistry, we model the particle as an ideal solution of Li ions and vacancies. The ideal solution model inherently assumes no phase separation or short-range ordering in the particle during intercalation, where all Li ions experience the same binding energy to the host lattice, independent of their local environment. For example, in a transition metal oxide (TMO_2), both the interlayer (sliding of O-TM-O slabs) and

intralayer (hexagonal-monoclinic transformation) phase separations can be alleviated by operation at moderate charging/discharging rates (Liu et al., 2023) and proper doping and coating, respectively (Cho et al., 2001; Shim et al., 2015; Mikami et al., 2024). In the ideal solution model, Li ions and vacancies are assumed to be randomly mixed without correlated hopping, such that the enthalpy of mixing is neglected and only the entropy of mixing contributes to the free energy (Zhao et al., 2022). Furthermore, this model assumes an isopotential state within the particle, such that the electric potential is disregarded in the governing equation. The dielectric relaxation time of the particle is estimated as $\tau_e = \varepsilon_e / \sigma_e$, and the diffusion time of Li ions in the particle is estimated as $\tau_{\text{Li}} = r^2 / D$. Taking the permittivity $\varepsilon_e \approx 10\varepsilon_0$ (Yasuhara et al., 2019), the electronic conductivity $\sigma_e = 10^{-4}$ S/m (Tukamoto and West, 1997; Kang et al., 2019), the characteristic length of particle $r = 10 \mu\text{m}$, and the diffusivity of Li ions $D = 10^{-14}$ m²/s (Wiedemann et al., 2013), we obtain $\tau_e \approx 10^{-6}$ s $\ll$ $\tau_{\text{Li}} \approx 10^4$ s. In other words, the system is limited by the diffusion of Li ions, while the electron transport reaches equilibrium in a much shorter time scale and can be regarded as isopotential.

The present formulation is intended for single-phase intercalation in small-strain elastic particles, with ideal Li-vacancy mixing and quasi-static mechanical equilibrium. Therefore, it isolates the coupling among transport, transformation strain, crystallographic anisotropy, and external constraint within a reduced but thermodynamically consistent setting. In addition, the formulation neglects the effect of grain boundaries when considering a polycrystalline secondary particle, such that a simplified thermodynamic framework with analytical or semi-analytical solutions can help highlight and quantify the morphology-property interplay under different mechanical constraints. Other effects not considered here, including phase separation, concentration-dependent material properties, plasticity, fracture, grain-boundary incompatibility, and explicit electrolyte/electronic overpotential fields, may alter quantitative predictions and, in some cases, qualitative behavior.

2.1. Continuum framework

Fig. 1 illustrates our continuum framework using a representative electrode particle of volume V subjected to a mechanical load $\mathbf{P}$ and connected to a reservoir of Li ions with a prescribed chemical potential μ . During Li intercalation, the mechanical load and lithiation generates a stress field $\boldsymbol{\sigma}(\mathbf{x}, t)$, a strain field $\boldsymbol{\varepsilon}(\mathbf{x}, t)$, and a Li concentration

field $c(\mathbf{x}, t)$ in the material, where $\mathbf{x}$ is the 3D spatial coordinate and t denotes the time elapsed since the onset of lithium intercalation.

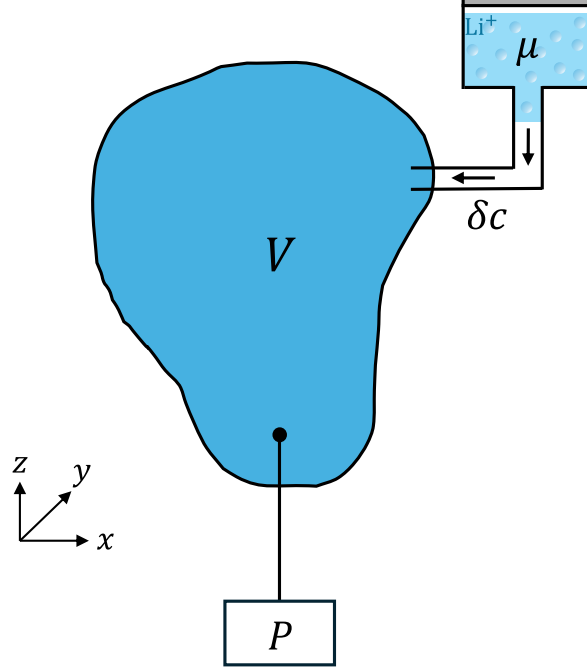


Figure 1: Schematic illustration of a representative electrode particle subjected to a mechanical load $\mathbf{P}$ and connected to a reservoir of Li ions with a prescribed chemical potential μ .

Under local equilibrium, associated with small variations $\delta\varepsilon_{ij}$ and δc , the Helmholtz free energy density changes by

$$\delta w = \sigma_{ij} \delta\varepsilon_{ij} + \mu \delta c. \quad (1)$$

Assuming $w = w(\boldsymbol{\varepsilon}, c)$, we obtain the variation of free energy as

$$\delta w = \frac{\partial w(\boldsymbol{\varepsilon}, c)}{\partial \varepsilon_{ij}} \delta\varepsilon_{ij} + \frac{\partial w(\boldsymbol{\varepsilon}, c)}{\partial c} \delta c. \quad (2)$$

Combining Eq. 1 and Eq. 2, we have

$$\sigma_{ij} = \frac{\partial w(\boldsymbol{\varepsilon}, c)}{\partial \varepsilon_{ij}}, \quad (3)$$

and

$$\mu = \frac{\partial w(\boldsymbol{\varepsilon}, c)}{\partial c}. \quad (4)$$

2.2. Equilibrium and kinetics

The electrode particle, the external mechanical load, and the reservoir together form a thermodynamically closed system. In this system, the rate of change of the total free

energy, dW/dt , is expressed as

$$\frac{dW}{dt} = \int_V \frac{\partial w}{\partial t} dV - \int_A T_i \frac{\partial u_i}{\partial t} dA + \int_A \mu J_i n_i dA, \quad (5)$$

where T_i is the traction on the material boundary A , u_i is the displacement field that satisfies $\varepsilon_{ij} = (u_{i,j} + u_{j,i})/2$, J_i is the flux of the Li ions, and n_i is the normal vector of the boundary. The three terms on the right hand side of Eq. 5 represent changes in the bulk free energy of the particle, the potential energy of the external mechanical load, and the free energy of the reservoir, respectively. In addition, the conservation of Li ions in the particle follows

$$\frac{\partial c}{\partial t} = -\frac{\partial J_i}{\partial x_i}. \quad (6)$$

Substituting Eq. 3, Eq. 4, and Eq. 6 into Eq. 5 and applying the divergence theorem, we obtain

$$\frac{dW}{dt} = \int_A (\sigma_{ij} n_j - T_i) \frac{\partial u_i}{\partial t} dA - \int_V \frac{\partial \sigma_{ij}}{\partial x_j} \frac{\partial u_i}{\partial t} dV + \int_V \frac{\partial \mu}{\partial x_i} J_i dV. \quad (7)$$

The second law of thermodynamics dictates that $dW/dt \leq 0$ for any arbitrary $\partial u_i/\partial t$ and $\partial c/\partial t$. To satisfy this condition, we assume mechanical equilibrium in the system, since the characteristic time of elastic deformation (governed by the speed of elastic wave) is much shorter than that of Li diffusion. As a result, the first two integrands in Eq. 7 vanish, leading to

$$\sigma_{ij} n_j - T_i = 0, \quad (8)$$

as the traction boundary condition and

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0, \quad (9)$$

as the balance of force in the bulk. Furthermore, we assume that the flux $\mathbf{J}$ is linearly proportional to the gradient of chemical potential $\partial \mu/\partial x_j$, following

$$J_i = -M_{ij} c \frac{\partial \mu}{\partial x_j}, \quad (10)$$

where $\mathbf{M} = M_{ij}$ is a second-rank mobility tensor, related to the diffusivity tensor by the Nernst-Einstein relation $M_{ij} = D_{ij}/(RT)$, and RT is the thermal energy per mole of particles in unit of J/mol. So long as $\mathbf{M}$ (and $\mathbf{D}$) is positive-definite, we have $dW/dt \leq 0$, satisfying the second law of thermodynamics.

2.3. Free energies

We assume that the free energy $w(\boldsymbol{\varepsilon}, c)$ can be additively decomposed into the elastic energy $w_{\text{elastic}}(\boldsymbol{\varepsilon}, c)$ and the chemical energy $w_{\text{chem}}(c)$:

$$w(\boldsymbol{\varepsilon}, c) = w_{\text{elastic}}(\boldsymbol{\varepsilon}, c) + w_{\text{chem}}(c). \quad (11)$$

Assuming linear elasticity, we express the elastic energy as (Bai et al., 2021a,b)

$$w_{\text{elastic}}(\boldsymbol{\varepsilon}, c) = \frac{1}{2} C_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^{\text{chem}}(c)) (\varepsilon_{kl} - \varepsilon_{kl}^{\text{chem}}(c)), \quad (12)$$

where C_{ijkl} is the fourth-rank stiffness tensor and $\boldsymbol{\varepsilon}^{\text{chem}}(c)$ is the transformation strain depending on the Li concentration c . We assume the transformation strain $\boldsymbol{\varepsilon}^{\text{chem}}(c)$ as a linear function of c :

$$\varepsilon_{ij}^{\text{chem}}(c) = \beta_{ij}(c - c_0) = \beta_{ij}\tilde{c}, \quad (13)$$

where $\boldsymbol{\beta} = \beta_{ij}$ is the constant second-rank Vegard tensor, c_0 is the initial Li concentration in the particle, and $\tilde{c} = c - c_0$ is the amount of Li inserted. As a result, $\boldsymbol{\varepsilon}^{\text{chem}}(c)$ is generalized beyond the common volumetric expansion or compression due to lithiation (Zhang et al., 2007). In particular, this generalized form of $\boldsymbol{\varepsilon}^{\text{chem}}(c)$ captures the possible anisotropic deformation induced by lithiation, due to different electronic structures, binding energies, and crystal lattices (Moon et al., 2019; Zhou et al., 2019; Reimers and Dahn, 1992). The linear form of $\varepsilon_{ij}^{\text{chem}}(c)$ represents the equal contribution of the lithiation fraction to changes of all lattice parameters of the crystal (Malavé et al., 2014).

We express the chemical energy by assuming ideal mixing of Li ions and vacancies (Li et al., 2021; Shishvan et al., 2020; Fang et al., 2024)

$$w_{\text{chem}}(c) = c\mu_{\text{Li}}^0 + (c_{\text{max}} - c)\mu_V + c_{\text{max}}RT(x_{\text{Li}} \ln x_{\text{Li}} + (1 - x_{\text{Li}}) \ln(1 - x_{\text{Li}})), \quad (14)$$

where $\mu_{\text{Li}}^0 = -nFE_{\text{Li}}^0$ is a constant that represents the chemical potential of Li in the stress-free reference state, $n = 1$ is the number of electrons transferred per Li atom, F is the Faraday constant, and E_{Li}^0 is the standard electrode potential of Li with respect to the reference electrode. μ_V is the molar enthalpy of vacancy formation. c_{max} is a constant in unit of mol/m^3 representing the total number of intrinsic sites, such that $(c_{\text{max}} - c)$ is the concentration of vacancies and $x_{\text{Li}} = c/c_{\text{max}}$ represents the normalized Li composition.

2.4. Material models

Combining Eq. 13, Eq. 14, Eq. 11, and Eq. 3, the stress is expressed as

$$\sigma_{ij} = C_{ijkl} (\varepsilon_{kl} - \varepsilon_{kl}^{\text{chem}}) = C_{ijkl} (\varepsilon_{kl} - \beta_{kl} \tilde{c}). \quad (15)$$

Furthermore, combining Eq. 13, Eq. 12, Eq. 11, and Eq. 4, the chemical potential is expressed as

$$\mu = \mu_0 + RT \ln \frac{c}{c_{\text{max}} - c} - C_{ijkl} \beta_{kl} \varepsilon_{ij} + C_{ijkl} \beta_{ij} \beta_{kl} \tilde{c}, \quad (16)$$

where $\mu_0 = \mu_{\text{Li}}^0 - \mu_V$ is a constant. Substituting this into Eq. 10, the resultant flux is expressed as

$$J_i = -\frac{D_{ij}}{RT} \left(RT \frac{c_{\text{max}}}{c_{\text{max}} - c} \frac{\partial c}{\partial x_j} - C_{klmn} \beta_{mn} c \frac{\partial \varepsilon_{kl}}{\partial x_j} + C_{klmn} \beta_{kl} \beta_{mn} c \frac{\partial c}{\partial x_j} \right). \quad (17)$$

2.5. Material isotropy

Atomic force microscopy (AFM) experiments have shown that particles made of amorphous active materials experience volumetric deformation with lithiation (Beaulieu et al., 2003; Timmons and Dahn, 2007). In this case, assuming material isotropy in all relevant properties of the particle, we can express the transformation strain, stiffness tensor, and diffusivity tensor as

$$\varepsilon_{ij}^{\text{chem}}(c) = \beta c \delta_{ij}, \quad (18)$$

$$C_{ijkl} = \lambda \delta_{ij} \delta_{kl} + G(\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}), \quad (19)$$

and

$$D_{ij} = D \delta_{ij}, \quad (20)$$

where $\beta_{ij} = \beta \delta_{ij}$, δ_{ij} is the identity tensor, and $3\beta = \Omega$ is the partial molar volume of Li. λ and G are the Lamé parameters related to the Young's modulus E and the Poisson's ratio ν as

$$\lambda = \frac{E\nu}{(1+\nu)(1-2\nu)}, \quad (21)$$

$$G = \frac{E}{2(1+\nu)}, \quad (22)$$

and D is the isotropic diffusivity of Li in the material. With these, the stress tensor, chemical potential, and flux are simplified as

$$\sigma_{ij} = \frac{E}{1+\nu} [(\varepsilon_{ij} - \beta c \delta_{ij}) + \frac{\nu}{1-2\nu} (\varepsilon_{kk} - 3\beta c) \delta_{ij}], \quad (23)$$

$$\mu = \mu_0 + RT \ln \frac{c}{c_{\max} - c} - \Omega \sigma_h + (3\lambda + 2G)\beta^2 \tilde{c}, \quad (24)$$

and

$$J_i = -\frac{D}{RT} \left[\left(RT \frac{c_{\max}}{c_{\max} - c} + (9\lambda + 6G)\beta^2 c \right) \frac{\partial c}{\partial x_i} - c\Omega \frac{\partial \sigma_h}{\partial x_i} \right], \quad (25)$$

where $\sigma_h = (\lambda + 2G/3)(\varepsilon_{kk} - 3\beta c)$ is the hydrostatic stress.

2.6. Model Parameters

In this work, we take Li_xCoO_2 (LCO) as a model electrode particle that is widely used in portable devices because of its high volumetric energy density. We conduct simulations for three cases of different material properties: (1) isotropic with randomly oriented LCO crystals in spherical, cylindrical, and ellipsoidal particles, (2) anisotropic with LCO crystals aligned in the axial direction of a cylindrical particle, and (3) anisotropic with LCO crystals aligned in the radial direction of an ellipsoidal particle.

In our simulations, we adopt material parameters extracted from experimental data. For anisotropic material parameters, results from X-ray diffraction of single crystal shows significant anisotropic strains in the hexagonal lattice, such that at 50% lithiation, the lattice parameter of the a and b axes has a small increase by 0.23%, while the c axis exhibits a strong contraction by -2.39% due to the layered atomic structure and the pronounced electrostatic repulsion of oxygen in adjacent layers. These result in a volume change of around -1.91% (Wang et al., 2005; Reimers and Dahn, 1992). Therefore, we take the crystallographically anisotropic Vegard coefficients in our model as $\beta_a = \beta_b = 1.65 \times 10^{-6} \text{ m}^3/\text{mol}$, and $\beta_c = -1.72 \times 10^{-5} \text{ m}^3/\text{mol}$. In addition, we implement an anisotropic diffusivity tensor to simulate the Li flux between TMO_2 layers. All modeling parameters are summarized in Table 1.

3. Morphology-Property Interplay under Various Mechanical Constraints

Building on the theoretical framework, we next explore the interplay among particle morphology, material anisotropy, and mechanical constraint in chemo-mechanical lithiation. We study hollow particles of spherical, cylindrical, and ellipsoidal shapes that are commonly used in research and applications, under various representative mechanical constraints. We also study the effects of different material properties including isotropic and transversely isotropic stiffness, diffusivity, and transformation strain.

Table 1: Model parameters

Parameter	Symbol	Value
Young’s modulus (Mücke et al., 2021)	E	123.6 GPa
Poisson’s ratio (Mücke et al., 2021)	ν	0.288
Elastic stiffness (transverse isotropy) (Yamakawa et al., 2018; Wu and Zhang, 2015)	C_{11}	303.86 GPa
	C_{12}	101.71 GPa
	C_{13}	32.58 GPa
	C_{33}	98.93 GPa
	C_{44}	18.02 GPa
Diffusivity (Wiedemann et al., 2013)	D	$5.387 \times 10^{-15} \text{ m}^2/\text{s}$
Saturation Li concentration (Wiedemann et al., 2013)	c_{max}	$22.37 \times 10^3 \text{ mol}/\text{m}^3$
Initial Li concentration (Wiedemann et al., 2013)	c_0	$10.56 \times 10^3 \text{ mol}/\text{m}^3$
Isotropic Vegard coefficient	β	$-4.6 \times 10^{-6} \text{ m}^3/\text{mol}$
Anisotropic Vegard coefficient (Reimers and Dahn, 1992; Malavé et al., 2014)	β_a	$1.65 \times 10^{-6} \text{ m}^3/\text{mol}$
	β_c	$-1.72 \times 10^{-5} \text{ m}^3/\text{mol}$
Partial molar volume	Ω	$-1.37 \times 10^{-5} \text{ m}^3/\text{mol}$
Anisotropic diffusivity (Uxa et al., 2023)	D_a	$1.7 \times 10^{-15} \text{ m}^2/\text{s}$
	D_c	$6 \times 10^{-18} \text{ m}^2/\text{s}$
Temperature	T	298 K
Discharging rate		1C

We describe each kind of mechanical constraint using an idealized set of boundary conditions. A particle with fully traction-free boundaries at both the outer and inner surfaces (herein called *unconstrained*) represents an isolated or weakly constrained particle. A particle with a fixed-displacement outer surface and a traction-free inner surface (herein called *fully constrained*) represents strong confinement by surrounding media, coating, or neighboring solids. A particle with a constrained outer surface but a traction-free inner surface (herein called *inner-free*) represents a hollow particle only confined by surrounding media.

For chemical boundary conditions, we apply concentration-dependent insertion fluxes at the outer and inner surfaces of a hollow particle. The boundary conditions ensure a comparable charging across different particle geometries while preserving the leading site-availability dependence near the dilute and saturated limits. Specifically, we assume a steady-state Li flux at the outer surface as $-J|_R = j/F$ and a zero flux at the inner surface. Here, $j = j_0 g(\bar{c})$ with $g(\bar{c}) = 2\sqrt{\bar{c}(1-\bar{c})}$ and $\bar{c} = c/c_{\text{max}}$, following (Allen et al., 2021).

This choice retains the leading site-availability dependence of the Butler-Volmer exchange current in porous electrode theory (Doyle et al., 1993), for which $i_0 \propto \sqrt{c(c_{\max} - c)}$ in the symmetric case. Accordingly, the flux vanishes in both the dilute and near-saturated limits and reaches its maximum in the range between. Factor 2 in $g(\bar{c})$ normalizes its value to the range of $[0, 1]$, such that j_0 remains the nominal galvanostatic flux scale at 1C rate while $g(\bar{c})$ acts as a physically motivated throttling factor. Therefore, the boundary conditions are regarded as a reduced particle-level surrogate for the concentration dependence of intercalation kinetics, rather than a full Butler-Volmer law (Allen et al., 2021). This interpretation is also consistent with the coupled ion-electron theory (CIET), in which site occupancy and vacancy availability increasingly hinder insertion near full lithiation (Fraggedakis et al., 2021).

3.1. Spherical particles

Previous studies show that polycrystalline spherical particles with radially aligned single-crystal primary grains exposing 010 facets enhance diffusion and cycling performance (Xu et al., 2019b), whereas random grain orientations produce macroscopic isotropy (Hu and Zhao, 2025). We first study a hollow particle with isotropic material properties and spherical symmetry. We fix the ratio of inner and outer radii as $r_0/R_0 = 0.6$ (Fig. 2a left).

The conservation of Li in Eq. 6 under spherical symmetry is

$$\frac{\partial c}{\partial t} + \frac{1}{r^2} \frac{\partial(r^2 J)}{\partial r} = 0, \quad (26)$$

where the radial flux is

$$J = -D_{\text{eff}} \frac{\partial c}{\partial r} + \frac{Dc}{RT} (3\lambda + 2G) \beta \frac{\partial}{\partial r} \left(\frac{\partial u_r}{\partial r} + 2 \frac{u_r}{r} \right), \quad (27)$$

with the effective diffusivity

$$D_{\text{eff}} = D \frac{c_{\max}}{c_{\max} - c} + \frac{Dc}{RT} (9\lambda + 6G) \beta^2, \quad (28)$$

and the radial displacement u_r .

The balance of force in Eq. 9 is simplified as

$$\frac{\partial \sigma_r}{\partial r} + \frac{2}{r} (\sigma_r - \sigma_\theta) = 0, \quad (29)$$

where the radial and hoop stresses are obtained from Eq. 15 as

$$\sigma_r = 2G \left(\frac{\partial u_r}{\partial r} - \varepsilon_r^{\text{chem}} \right) + \lambda \left[\left(\frac{\partial u_r}{\partial r} + 2 \frac{u_r}{r} \right) - (\varepsilon_r^{\text{chem}} + 2\varepsilon_\theta^{\text{chem}}) \right], \quad (30)$$

$$\sigma_\theta = 2G \left(\frac{u_r}{r} - \varepsilon_\theta^{\text{chem}} \right) + \lambda \left[\left(\frac{\partial u_r}{\partial r} + 2 \frac{u_r}{r} \right) - (\varepsilon_r^{\text{chem}} + 2\varepsilon_\theta^{\text{chem}}) \right]. \quad (31)$$

Here, $\varepsilon_r = \partial u_r / \partial r$ and $\varepsilon_\theta = u_r / r$ are the radial and hoop strains. $\varepsilon_r^{\text{chem}} = \varepsilon_\theta^{\text{chem}} = (\Omega/3)c$ are the isotropic transformation strains. Combining the above equations and solving the ODE analytically, we obtain

$$u_r(r) = \frac{1+\nu}{1-\nu} \frac{\Omega}{3} \frac{1}{r^3} \int_{r_0}^r \tilde{c} r^2 dr + Ar + \frac{B}{r^2}, \quad (32)$$

$$\sigma_r(r) = E \left[-\frac{2}{1-\nu} \frac{\Omega}{9} \frac{3}{r^3} \int_{r_0}^r \tilde{c} r^2 dr + \frac{A}{1-2\nu} - \frac{2B}{r^3(1+\nu)} \right], \quad (33)$$

$$\sigma_\theta(r) = E \left[\frac{1}{1-\nu} \frac{\Omega}{9} \frac{3}{r^3} \int_{r_0}^r \tilde{c} r^2 dr - \frac{1}{1-\nu} \frac{\Omega}{3} \tilde{c} + \frac{A}{1-2\nu} + \frac{B}{r^3(1+\nu)} \right]. \quad (34)$$

The constants A and B are determined from specific boundary conditions: fully constrained ($u_r|_{r=r_0, R_0} = 0$), inner-free ($\sigma_r|_{r=r_0} = 0$ and $u_r|_{r=R_0} = 0$), and unconstrained ($\sigma_r|_{r=r_0} = 0$ and $\sigma_r|_{r=R_0} = 0$).

Using material parameters from Table 1, we model the discharge of the hollow spherical particle until full lithiation ($t = 3600$ s). We plot the total elastic energy as a function of the normalized Li concentration averaged over the entire particle, $\langle c \rangle / c_{\text{max}}$, for particles under different mechanical constraints: fully constrained, inner-free, and unconstrained (Fig. 2a right). During discharge, the elastic energy increases monotonically in fully constrained and inner-free particles, the former more dramatically than the latter. By contrast, the elastic energy maintains nearly zero in unconstrained particles, indicating negligible lithiation-induced elasticity. These trends in elastic energy under different mechanical constraints have been widely reported in literature, showing the direct consequence of lithiation-induced transformation strain, $(\Omega/3)c$ (Christensen and Newman, 2006; de Vasconcelos et al., 2022).

We further compare the calculated results (Fig. 2a right) to those from uncoupled chemical and mechanical governing equations. To do so, we solve the classical Fick's law by neglecting the contribution from mechanical fields, and subsequently calculate the stress and strain fields using Eqs. 32-34. In all cases of mechanical constraints, the results remain nearly indistinguishable with or without the full chemo-mechanical coupling (see

Fig. A.10 in Appendix A). Indeed, assuming material isotropy and spherical symmetry, the contribution of mechanics to the flux J is expressed as $J_{\text{mech}} = -(Dc/RT)(3\lambda + 2G)\beta[\Omega\partial c/\partial r - 3\partial\varepsilon/\partial r]$, where $3\partial\varepsilon/\partial r \approx \Omega\partial c/\partial r$ since the strain field is volumetric. As a result, in isotropic spherical particles, lithiation is predominantly governed by the reaction-diffusion process but negligibly by mechanics, as previously suggested by Clerici et al. (2020).

3.2. Cylindrical particles

Next, we investigate cylindrical morphology as another common form of electrode particles (Fig. 2b&c). Compared to spherical particles, cylindrical particles can exhibit additional failure mechanisms, such as significant increase in length during lithiation (Chan et al., 2008) and buckling under large axial constraints by a stiff coating material (Chakraborty et al., 2015; Zang and Zhao, 2012). The chemo-mechanics of a cylindrical particle may further depend on its possible anisotropy, for example, crystals can align along the axial direction of the cylinder, leading to transversely isotropic properties.

We model a hollow cylindrical particle with the same ratio of inner and outer radii as $r_0/R_0 = 0.6$. We assume the length of cylinder is much larger than its radius R_0 . Under cylindrical symmetry, all stress, strain, and concentration fields depend only on the radial coordinate r . The conservation of Li and the balance of force are simplified as

$$\frac{\partial c}{\partial t} + \frac{1}{r} \frac{\partial(rJ_r)}{\partial r} = 0, \quad (35)$$

and

$$\frac{\partial\sigma_{rr}}{\partial r} + \frac{\sigma_{rr} - \sigma_{\theta\theta}}{r} = 0, \quad (36)$$

respectively, where J_r is the flux in the radial direction, and σ_{rr} and $\sigma_{\theta\theta}$ are the radial and hoop stresses. In the axial direction, we assume that the particle is either fully constrained in displacement (axial strain $\varepsilon_{zz} = 0$, Fig. 2b left) or unconstrained (total axial force $\int_{r_0}^{R_0} \sigma_{zz} r dr = 0$, Fig. 2c left). See further detailed analytical expressions in Appendix B.

We compare two types of material properties that are commonly observed in cylindrical particles. An isotropic particle follows the same description of diffusivity, transformation strain, and elastic constants as discussed in Section 2.5. A transversely isotropic particle has the symmetry axis c of the crystal lattice aligned with the cylindrical axial

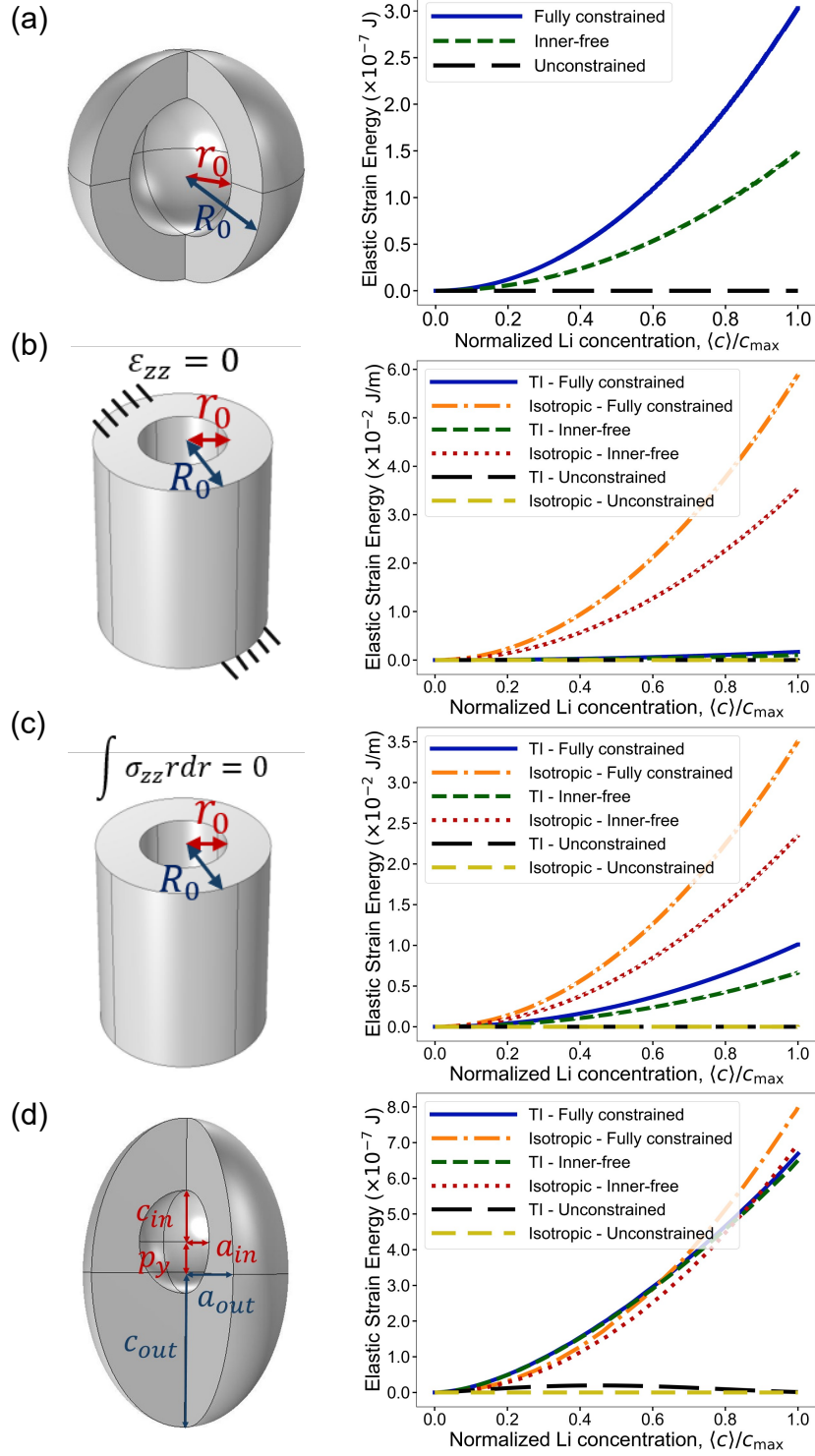


Figure 2: Evolution of elastic energy as a function of normalized volume-averaged Li concentration, $\langle c \rangle / c_{\max}$, for particles with different isotropic or transversely isotropic (TI) properties, morphologies, and mechanical constraints: fully constrained, inner-free, and unconstrained. (a) Spherical particle with isotropic properties. (b) Cylindrical particle with constrained axial displacement. (c) Cylindrical particle with unconstrained axial displacement (zero total axial force). (d) Ellipsoidal particle. In (a) and (d), the total elastic energy is plotted in unit of J. In (b) and (c), the elastic energy per unit axial length is plotted in unit of J/m.

axis z , such that the diffusivity tensor is expressed as $\mathbf{D} = \text{diag}(D_a, D_a, D_c)$, the Vegard tensor $\boldsymbol{\beta} = \text{diag}(\beta_a, \beta_a, \beta_c)$, and the stiffness tensor $\mathbf{C}$ composed of five independent constants $C_{11}, C_{12}, C_{13}, C_{33}, C_{44}$, with $C_{66} = (C_{11} - C_{12})/2$.

Figs. 2b&c show the evolution of elastic energy per unit axial length in isotropic or transversely isotropic cylindrical particles during discharge, under various mechanical constraints. Similar to the case of spherical particle, lithiation-induced increase in elastic energy depends strongly on mechanical constraints: the most significant increase in fully constrained particles, less so in inner-free particles, and negligible in unconstrained particles. The axial constraint further amplifies this effect (i.e., comparing Figs. 2b and c).

Table 2 summarizes the axial stress and strain in isotropic and transversely isotropic particles under different mechanical constraints. When being axially unconstrained (Table 2 bottom row), both particles experience lithiation-induced contraction in the axial direction due to their negative Vegard coefficients ($\beta = -4.6 \times 10^{-6} \text{ m}^3/\text{mol}$ and $\beta_c = -1.72 \times 10^{-5} \text{ m}^3/\text{mol}$, respectively). However, in the radial and hoop directions, while the isotropic particle undergoes the same contraction, the transversely isotropic particle expands due to the positive Vegard coefficient $\beta_a = 1.65 \times 10^{-6} \text{ m}^3/\text{mol} > 0$. The opposite signs of transformation strains effectively ameliorate the elastic energy induced by lithiation in the transversely isotropic particle. Consequently, under the same constraints, less elastic energy builds up compared to that in the isotropic particle (comparing curves in Figs. 2b&c). When the particles are axially constrained, the negative Vegard coefficients lead to tensile axial stresses (Table 2 top row). The stress levels are similar between two particles and decrease with fewer mechanical constraints (i.e., from fully constrained, inner-free, to unconstrained).

3.3. Ellipsoidal particles

We further study a hollow ellipsoidal particle that represents a more generalized case of irregular, spherical-like morphology. As illustrated in Fig. 2d left, the ellipsoid contains a spherical inner cavity, with its position described by geometric parameters, $a_{\text{in}} = c_{\text{in}} = 2 \mu\text{m}$ and $p_y = 0$. The aspect ratio of the ellipsoid is set as $a_{\text{out}}/c_{\text{out}} = 0.5$. We use cylindrical coordinates (r, θ, z) and assume rotational symmetry about the long axis z , such that all fields are independent of θ . Later in Section 5, we will take this configuration as a baseline case and treat all geometric parameters as design variables for an optimization

Table 2: Axial stress and strain under different boundary conditions

		Fully strained	con-	Inner-free	Unconstrained
Axial stress [MPa] (axially constrained)	Isotropic	15.7		9.89	6.67
	TI	15.9		9.39	5.93
Axial strain (axially unconstrained)	Isotropic	-0.098		-0.075	-0.053
	TI	-0.190		-0.182	-0.177

study.

With these simplifications, the conservation of Li is expressed as

$$\frac{\partial c}{\partial t} + \frac{1}{r} \frac{\partial(rJ_r)}{\partial r} + \frac{\partial J_z}{\partial z} = 0. \quad (37)$$

The balance of force is governed by

$$\begin{aligned} \frac{\partial \sigma_{rr}}{\partial r} + \frac{\sigma_{rr} - \sigma_{\theta\theta}}{r} + \frac{\partial \sigma_{rz}}{\partial z} &= 0, \\ \frac{\partial \sigma_{rz}}{\partial r} + \frac{\sigma_{rz}}{r} + \frac{\partial \sigma_{zz}}{\partial z} &= 0. \end{aligned} \quad (38)$$

For the ellipsoidal morphology, we consider an isotropic particle using the same description as discussed in Section 2.5, and further consider a transversely isotropic particle with the crystal c -axis aligned along the radial direction r and the crystal a - b plane coinciding with the θ - z plane. Consequently, the diffusivity tensor is $\mathbf{D} = \text{diag}(D_c, D_a, D_a)$, the Vegard tensor is $\boldsymbol{\beta} = \text{diag}(\beta_c, \beta_a, \beta_a)$, and the stiffness tensor $\mathbf{C}$ is composed of five independent constants $C_{11}, C_{12}, C_{13}, C_{33}, C_{44}$. In each case of different material properties and mechanical constraints, we calculate the flux analytically, as detailed in Appendix C, and then solve the differential equations for stress, strain, and displacement fields numerically using COMSOL Multiphysics (Solid Mechanics Module). Later in Section 5, we will also take this radially aligned crystal configuration as a baseline case and treat the crystal alignment as a design parameter.

We first examine the evolution of total elastic energy during lithiation (Fig. 2d). Similar to the spherical and cylindrical cases, elastic energy in ellipsoidal particles increases monotonically with lithiation under fully constrained and inner-free conditions but remains near-zero when unconstrained. However, there is no significant difference between

the former two mechanical constraints or between the isotropic and transversely isotropic particles. These observations indicate that the ellipsoidal morphology itself plays a dominant role in determining the total lithiation-induced elastic energy.

To further examine the effects of mechanical constraints and material properties, we calculate the full field of Li concentration, $x_{\text{Li}} = c/c_{\text{max}}$, in the ellipsoidal particle at both an intermediate stage ($t = 2000$ s) and the end of discharge ($t = 3600$ s) under 1C. In an isotropic particle at $t = 2000$ s, the concentration field depends strongly on the mechanical constraint. Fully constrained boundaries lead to a near-homogeneous lithiation of $x_{\text{Li}} \approx 0.88$ (Fig. 3a). Unconstrained boundaries introduce slight heterogeneity and anisotropy (Fig. 3c). In contrast, inner-free boundaries produce the most pronounced heterogeneous and anisotropic lithiation (Fig. 3b), despite the isotropy of the material itself: lithiation proceeds fastest along the short axis and slowest along the long axis, with markedly different Li concentrations of $x_{\text{Li}} \approx 0.9$ and $x_{\text{Li}} \approx 0.84$, respectively. Furthermore, a diffusion-reaction process that neglects elasticity (i.e., $w_{\text{elastic}}(\boldsymbol{\epsilon}, c)$ in Eq. 12) yields heterogeneous but nearly isotropic lithiation (Fig. 3d). At the end of discharge ($t = 3600$ s, Figs. 3e-h), particles under most constraints are nearly fully lithiated, except for the inner-free case.

These results indicate the *constraint-sensitivity* of isotropic particles: the ellipsoidal morphology alone induces only mild spatial heterogeneity in lithiation (i.e., Fig. 3d), but varying mechanical constraints greatly alters the lithiation pathway. Among the various constraints, the inner-free condition most strongly amplifies heterogeneous and anisotropic lithiation.

Compared to isotropic particles, transversely isotropic particles show much less constraint-sensitivity throughout lithiation (Fig. 4). At $t = 2000$ s (Fig. 4a-c), particles under all three different constraints exhibit similar heterogeneous and anisotropic lithiations, with $x_{\text{Li}} \approx 1$ near the outer surface along the short axis and $x_{\text{Li}} \approx 0.3$ along the long axis. Similar heterogeneous and anisotropic patterns further persist at the end of discharge ($t = 3600$ s, Fig. 4d-f), where varying the mechanical constraints only alters the overall magnitude of x_{Li} but minimally affects the spatial distribution. In other words, unlike in isotropic particles where mechanical constraints exert a strong influence, lithiation in transversely isotropic particles is predominantly governed by the interplay between the ellipsoidal morphology and the transversely isotropic material properties.

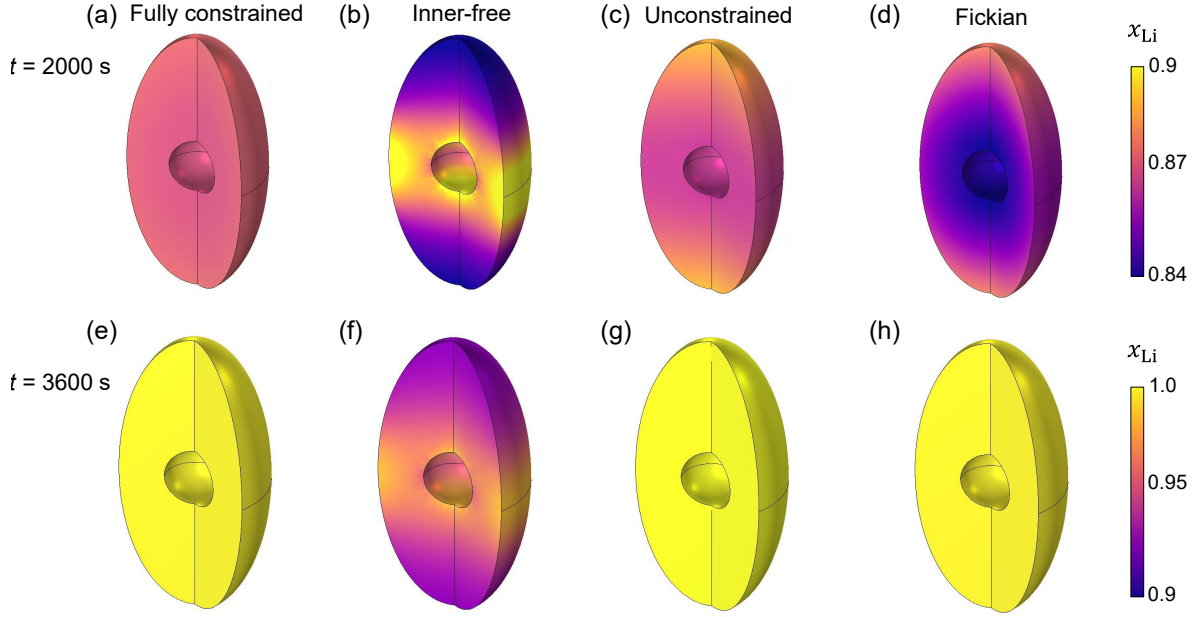


Figure 3: Full fields of normalized Li concentration $x_{\text{Li}} = c/c_{\text{max}}$ in an isotropic ellipsoidal particle at $t = 2000$ s (first row) and $t = 3600$ s (second row) under different mechanical constraints: (a)&(e) fully constrained, (b)&(f) inner-free, (c)&(g) unconstrained, and (d,h) Fickian-like process neglecting elasticity.

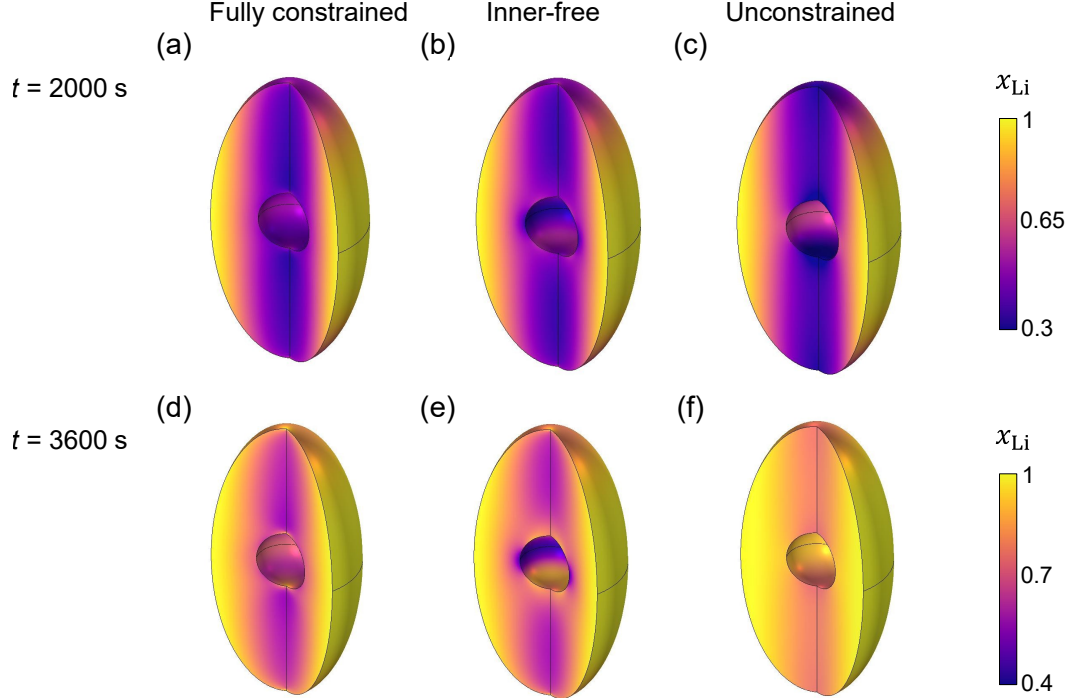


Figure 4: Full fields of normalized Li concentration $x_{\text{Li}} = c/c_{\text{max}}$ in a transversely isotropic ellipsoid at $t = 2000$ s (first row) and $t = 3600$ s (second row) under different mechanical constraints: (a)&(d) fully constrained, (b)&(e) inner-free, and (c)&(f) unconstrained.

4. Cross-Field Analysis of Chemo-Mechanical Coupling

To further quantify the contribution of each mechanism (i.e., chemistry and mechanics) as well as their correlations during lithiation, we next conduct cross-field analysis of chemo-mechanical coupling in these particles using flux decomposition and a correlation metric.

4.1. Flux decomposition

To first quantify the contribution of each mechanism to lithiation, we decompose the total Li flux into:

$$\mathbf{J}_{\text{tot}} = \mathbf{J}_{\text{c}} + \mathbf{J}_{\text{m}}, \quad (39)$$

where

$$J_{\text{c},i} = -D_{ij} \frac{c_{\text{max}}}{(c_{\text{max}} - c)} \frac{\partial c}{\partial x_j}, \quad (40)$$

represents the chemical contribution from the classical Fickian diffusion-reaction, and

$$J_{\text{m},i} = \frac{D_{ij}c}{RT} C_{klmn} \beta_{mn} \frac{\partial}{\partial x_j} (\varepsilon_{kl} - \beta_{kl}c), \quad (41)$$

represents the mechanical contribution from the lithiation-induced transformation strain.

We then define the *global flux ratio* to quantify the signed contribution of each component to the total flux:

$$C_{\alpha}(t) = \frac{\int_V \mathbf{J}_{\alpha}(\mathbf{x}, t) \cdot \mathbf{J}_{\text{tot}}(\mathbf{x}, t) dV}{\int_V \|\mathbf{J}_{\text{tot}}(\mathbf{x}, t)\|^2 dV}, \quad \alpha \in \{\text{c}, \text{m}\}. \quad (42)$$

Positive and negative values of C_{α} indicate global reinforcement and reduction of the total flux, respectively, by the corresponding flux component. Because $C_{\text{c}} + C_{\text{m}} = 1$, values greater than unity or negative indicate that individual components are partially canceled by other components.

Fig. 5 plots the evolution of C_{c} and C_{m} in ellipsoidal particles with different material properties and mechanical constraints. In all cases, the mechanical contribution (from lithiation-induced transformation strain) dominates over the chemical contribution (from Fickian diffusion-reaction). This dominance reverses near the end of lithiation $\langle c \rangle / c_{\text{max}} = 1$ in some cases (Figs. 5a, c, and d, corresponding to fully constrained and unconstrained isotropic particles and a fully constrained transversely isotropic particle), but the total flux itself is small by that point. The observation, that the mechanical contribution

dominates across all constraints and material properties, suggests that this behavior is an intrinsic characteristic of the ellipsoidal morphology. In contrast, lithiation in isotropic spherical particles is governed by Fickian diffusion-reaction, with a negligible mechanical contribution (Section 3.1, Fig. A.10).

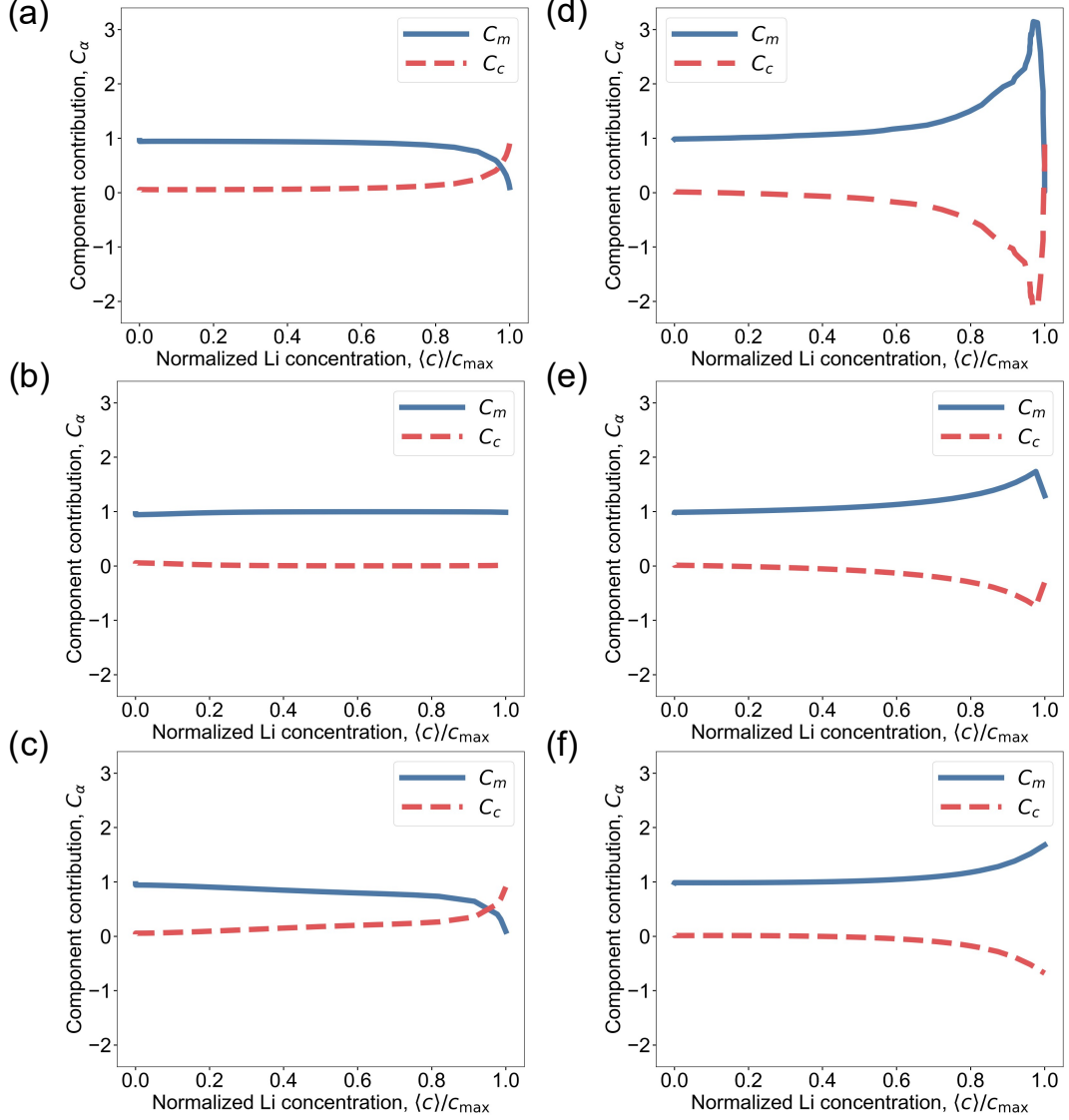


Figure 5: Evolution of global flux ratio C_α as a function of normalized volume-averaged Li concentration, $\langle c \rangle / c_{\max}$, in (a) fully constrained, (b) inner-free, and (c) unconstrained isotropic ellipsoidal particles, as well as (d) fully constrained, (e) inner-free, and (f) unconstrained transversely isotropic ellipsoidal particles.

4.2. Correlation between concentration and deformation

We next investigate the correlation between the chemical (Li concentration) and mechanical (strain) fields throughout lithiation. This is motivated by recent evidence that

underscores the need for cross-field learning, i.e., whether one can learn the knowledge of a field (e.g., lithiation) from the measurement of another field (e.g., lithiation-induced deformation). For example, using in-situ coupled optical diagnostics, Yang et al. (2019) report that Li concentration and deformation in a graphite-Li cell are positively correlated and vary nonlinearly along the diffusion direction. Other data-driven and multi-field quantification efforts such as (Ihuaenyi et al., 2025c) further motivate moving beyond isolated metrics toward unified descriptors of cross-field coupling.

To do so, we introduce the Pearson correlation metric to quantify spatial co-variation between the volumetric strain field $\varepsilon_v(\mathbf{x}, t) = \varepsilon_{rr} + \varepsilon_{\theta\theta} + \varepsilon_{zz}$ and the Li concentration field $c(\mathbf{x}, t)$ (Lee Rodgers and Nicewander, 1988):

$$\rho_{\varepsilon c}(t) = \frac{\int_V (\varepsilon_v(\mathbf{x}, t) - \bar{\varepsilon}_v(t))(c(\mathbf{x}, t) - \bar{c}(t)) dV}{\sqrt{\int_V (\varepsilon_v(\mathbf{x}, t) - \bar{\varepsilon}_v(t))^2 dV \int_V (c(\mathbf{x}, t) - \bar{c}(t))^2 dV}}, \quad (43)$$

where the overbar denotes the spatial average over the particle volume.

We compute $\rho_{\varepsilon c}(t)$ for isotropic and transversely isotropic ellipsoidal particles (Figs 6a&b, respectively) under different mechanical constraints. Overall, $\rho_{\varepsilon c}(t)$ is strongest in the unconstrained case, intermediate in the inner-free case, and weakest in the fully constrained case. Indeed, in unconstrained particles, $\varepsilon_v(\mathbf{x}, t)$ is dominated by the *local* lithiation-induced transformation strain, leading to near-fully anti-correlated two fields with $\rho_{\varepsilon c} \approx -1$ throughout lithiation, consistent with (Ihuaenyi et al., 2025c). This anti-correlation reflects the negative Vegard response: higher Li concentration produces more negative volumetric strain (see values of β in Table 1), corresponding to greater volumetric shrinkage. In fully constrained particles, by contrast, $\varepsilon_v(\mathbf{x}, t)$ is governed by the *nonlocal* elastic response to the transformation-strain field under the stronger constraints. Material anisotropy further modulates the correlation, as the anisotropic stiffness, Vegard, and diffusivity tensors introduce additional degrees of freedom that reshape both the concentration field and the elastic response.

These physical pictures are confirmed by the corresponding strain and concentration fields during lithiation (left and right of Figs. 7a-f). Fully constrained transversely isotropic particles exhibit no clear visual correlation between the two fields throughout lithiation (Figs. 7a-c): the concentration field (right) develops an overall horizontal gradient, whereas the strain field (left) is more multi-axially distributed owing to the nonlocal

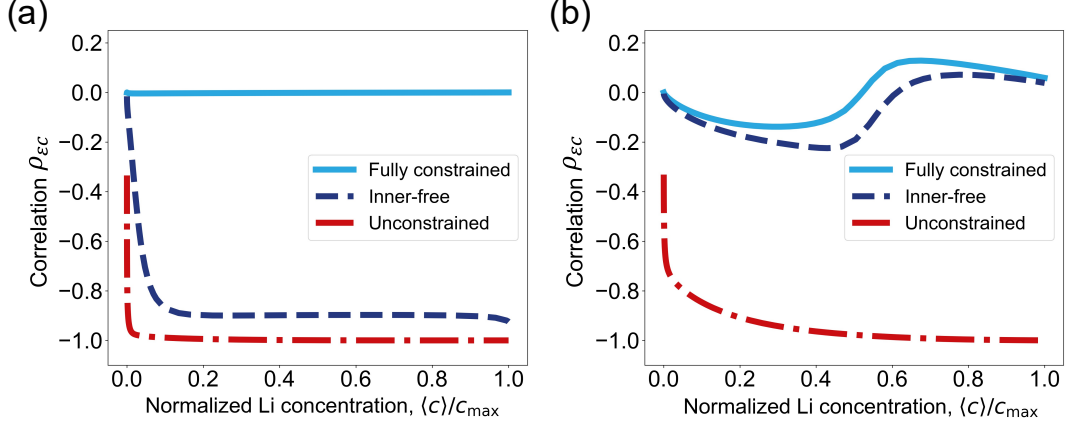


Figure 6: Pearson correlation metric to quantify spatial co-variation between the volumetric strain field $\varepsilon_v(\mathbf{x}, t) = \varepsilon_{rr} + \varepsilon_{\theta\theta} + \varepsilon_{zz}$ and the Li concentration field $c(\mathbf{x}, t)$, for (a) isotropic and (b) transversely isotropic ellipsoidal particles under different mechanical constraints.

elastic response. As a result, regions of high concentration do not coincide with regions of high strain. Unconstrained particles, by contrast, show a clear visual correlation (Figs. 7d-f): the strain field closely tracks the concentration field throughout lithiation, with higher concentrations yielding more negative strains.

5. Morphology Optimization

The preceding sections show that particle morphologies, material properties, and mechanical constraints affect chemo-mechanical behavior through distinct but coupled mechanisms. The analysis suggests that the chemo-mechanical performance of a particle cannot be optimized against a single objective or by tuning a single material or geometric parameter. Therefore, we formulate a multi-objective optimization problem with a set of design variables that describe the particle morphology including its geometry and crystal orientation. As a demonstration, we take the inner-free transversely isotropic ellipsoidal particle under half-cycle lithiation ($t = 3600$ s) and apply the proposed framework. The optimization seeks to maximize lithiation capacity while suppressing the lithiation-induced peak tensile stress.

5.1. Formulation of the optimization problem

We start with defining a vector of optimization parameters, $\boldsymbol{\theta} = [a_{\text{in}}, c_{\text{in}}, p_y, \alpha]^T$, where a_{in} and c_{in} are the semi-axes of the internal ellipsoidal void of the hollow ellipsoidal particle, p_y describes the centroid position of the void along the z -axis (Figure 2d left),

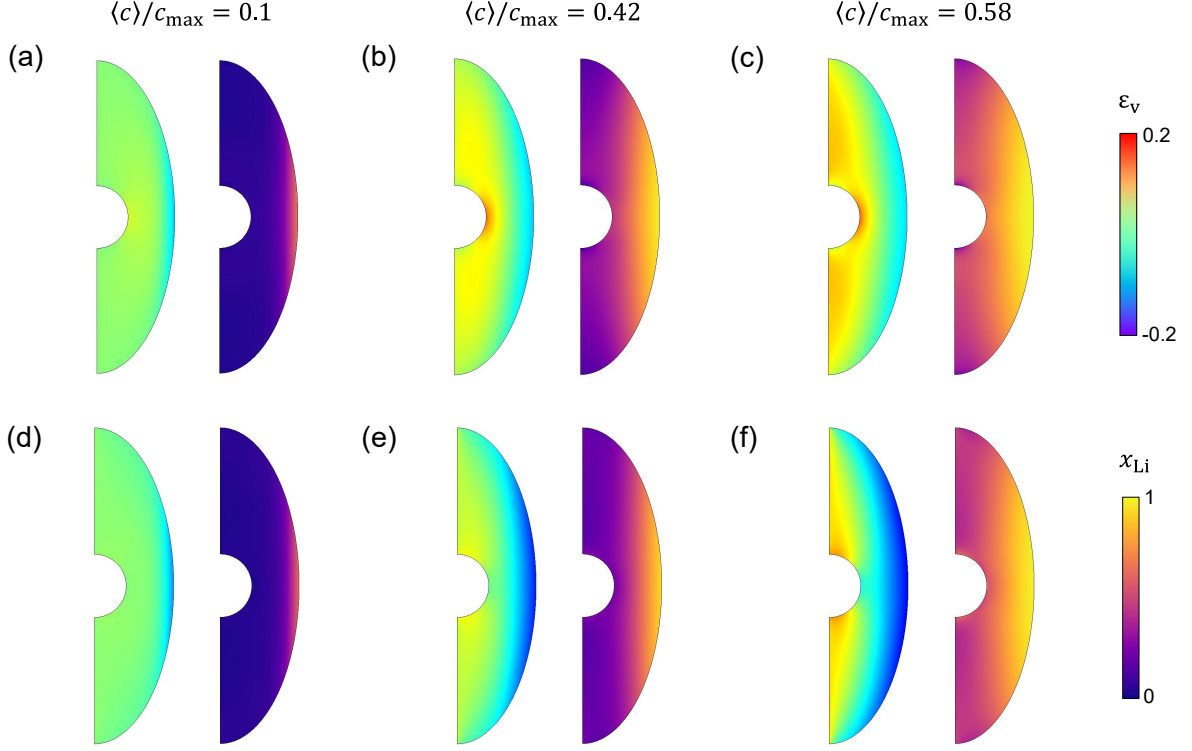


Figure 7: Representative fields of volumetric strain $\varepsilon_v(\mathbf{x}, t)$ (left) and normalized Li concentration $x_{\text{Li}} = c/c_{\max}$ (right) during lithiation, $\langle c \rangle / c_{\max} = 0.10$, 0.42 , and 0.58 , in transversely isotropic ellipsoidal particles. (a-c) show fully constrained particles. (d-f) show unconstrained particles.

and α represents the angle between the crystallographic c -axis and the short axis of the ellipsoid. Throughout the optimization, we restrict α within the first quadrant $0 \leq \alpha \leq \pi/2$ due to symmetry, and fix the outer semi-axes of the ellipsoid as $a_{\text{out}} = 5 \mu\text{m}$ and $c_{\text{out}} = 10 \mu\text{m}$.

We take the radially aligned crystal configuration in the transversely isotropic ellipsoidal particle as the baseline (Section. 3.3). For an arbitrarily prescribed α , the diffusivity, Vegard, and stiffness tensors are expressed as

$$\mathbf{D} = \mathbf{R}(\alpha) \mathbf{D}^{(\text{base})} \mathbf{R}^T(\alpha), \quad (44)$$

$$\boldsymbol{\beta} = \mathbf{R}(\alpha) \boldsymbol{\beta}^{(\text{base})} \mathbf{R}^T(\alpha), \quad (45)$$

and

$$\mathbf{C} = \mathbf{T}(\alpha) \mathbf{C}^{(\text{base})} \mathbf{T}^T(\alpha), \quad (46)$$

where $\mathbf{D}^{(\text{base})}$, $\boldsymbol{\beta}^{(\text{base})}$, and $\mathbf{C}^{(\text{base})}$ are the corresponding quantities in the baseline particle,

and the rotation matrices are

$$\mathbf{R}(\alpha) = \begin{bmatrix} \cos \alpha & 0 & \sin \alpha \\ 0 & 1 & 0 \\ -\sin \alpha & 0 & \cos \alpha \end{bmatrix}, \quad (47)$$

and

$$\mathbf{T}(\alpha) = \begin{bmatrix} \cos^2 \alpha & \sin^2 \alpha & 2 \cos \alpha \sin \alpha \\ \sin^2 \alpha & \cos^2 \alpha & -2 \cos \alpha \sin \alpha \\ -\cos \alpha \sin \alpha & \cos \alpha \sin \alpha & \cos^2 \alpha - \sin^2 \alpha \end{bmatrix}.$$

The flux in a particle with a prescribed α is given by Eq. C.4 in Appendix Appendix C.

The morphology optimization is formulated as a constrained multi-objective problem that seeks the optimal parameter vector $\boldsymbol{\theta}^*$ following:

$$\boldsymbol{\theta}^* = \arg \min_{\boldsymbol{\theta} \in \mathcal{D}} \{-\bar{c}_{\text{ave}}(\boldsymbol{\theta}), \sigma_{1,\text{max}}(\boldsymbol{\theta})\}, \quad (48)$$

subject to geometric admissibility that ensures ellipsoidal morphology:

$$a_{\text{in}} > 0, \quad c_{\text{in}} > 0, \quad (49)$$

$$p_x^2/a_{\text{out}}^2 + p_y^2/c_{\text{out}}^2 < 1, \quad (50)$$

$$|p_x| + a_{\text{in}} \leq a_{\text{out}} - t_{\text{min}}, \quad |p_y| + c_{\text{in}} \leq c_{\text{out}} - t_{\text{min}}, \quad (51)$$

$$\frac{(p_x + a_{\text{in}} \cos \theta)^2}{a_{\text{out}}^2} + \frac{(p_y + c_{\text{in}} \sin \theta)^2}{c_{\text{out}}^2} < 1 - \frac{t_{\text{min}}}{L_c} \quad \forall \theta \in [0, 2\pi], \quad (52)$$

$$0.01\% V_{\text{out}} \leq V_{\text{in}} \leq 95\% V_{\text{out}}, \quad (53)$$

where $\bar{c}_{\text{ave}} = \langle c \rangle / c_{\text{max}}$ is the normalized average lithium concentration after half-cycle lithiation and $\sigma_{1,\text{max}}$ is the corresponding maximum principal stress in the particle, normalized by the elastic modulus $E = 123.6$ GPa. $\mathcal{D} = [\lambda_{\text{min}}, \lambda_{\text{max}}]^N$ denotes the admissible design space with component-wise lower (λ_{min}) and upper bounds (λ_{max}) on each of the $N = 4$ design variables. Eq. 49 requires strictly positive void semi-axes, preventing degenerate zero-volume voids. Eq. 50 ensures that the void is inside the particle, where $p_x = 0$ represents an axisymmetric void about the z -axis. Eq. 51 enforces a minimum wall thickness t_{min} of the hollow particle along each principal axis, which is a necessary but not sufficient condition for full enclosure. Eq. 52 requires that every point on the parametric void boundary satisfies the outer ellipsoid inequality with a margin t_{min}/L_c , where $L_c = \sqrt{a_{\text{out}}^2 + c_{\text{out}}^2}$ is the characteristic length of the outer ellipsoid and $t_{\text{min}} = 0.1 \mu\text{m}$.

This inequality ensures a minimum clearance between the void surface and the outer boundary of the ellipsoid. Eq. 53 bounds the volume ratio of the void with respect to the outer ellipsoid, $V_{\text{in}}/V_{\text{out}} = a_{\text{in}}^2 c_{\text{in}}/a_{\text{out}}^2 c_{\text{out}}$, between 0.01% and 95%.

The multi-objective functional in Eq. 48 aims to maximize $\bar{c}_{\text{ave}}$ while minimizing $\sigma_{1,\text{max}}$. The former represents the electrochemical capacity and state of charge, and the latter indicates susceptibility to tensile failure. The optimization thus promotes lithium uptake while preserving structural integrity. As identified in the preceding sections, we expect a design trade-off between the two objectives: greater Li uptake increases the lithiation-induced transformation strain and hence the resulting stress and strain fields. As a result, the optimization yields multiple possible results that form a Pareto front.

5.2. Computational implementation

We solve the optimization problem using sequential model-based optimization (SMBO) (Hutter et al., 2011), wherein a probabilistic surrogate iteratively approximates the multi-objective functional Eq. 48 to direct sampling toward regions of high potential. This approach also reduces computational cost by minimizing the number of expensive function evaluations required for convergence.

We employ the Tree-structured Parzen Estimator (TPE) (Bergstra et al., 2011) as a surrogate within the SMBO framework. TPE reformulates the conventional expected improvement (EI) acquisition function via Bayes' rule. Rather than modeling the objective function directly, TPE partitions the observed data at a threshold into superior and inferior configurations. Separate probability density functions are fitted to each partition using adaptive Parzen window estimators. This recasts the EI criterion as a likelihood-based sampling problem, biasing new candidates toward regions with higher probability of improvement relative to current best evaluations. Mathematical details of TPE are provided in (Bergstra et al., 2011), with extensions to information-driven mechanical specimen design described in (Ihuaenyi et al., 2024, 2025b; Ihuaenyi and Zhu, 2026). Implementation proceeds via the Optuna framework (Akiba et al., 2019), which provides an efficient realization of TPE, including multivariate kernel density estimation and robust acquisition optimization. The study employs a computational budget of 400 trials. In each trial, a candidate parameter vector $\boldsymbol{\theta}$ is sampled from uniform priors, used to generate the particle geometry, executed in the finite element solver, and evaluated for the relevant degradation metrics. The algorithm maintains a complete record

of evaluated configurations and objective values, enabling post-optimization analysis and identification of the optimal morphology.

5.3. Optimization results

Fig. 8 shows the sequential trial histories produced by the Bayesian optimization procedure over 300 evaluations, each maximizing $\bar{c}_{\text{ave}}$ or minimizing $\sigma_{1,\text{max}}$. Each exploration point corresponds to a distinct candidate morphology sampled from the admissible design space $\mathcal{D}$. The dashed lines denote the best-so-far value for each objective and visualize convergence trends. The optimal $\bar{c}_{\text{ave}} = 0.76$ is reached relatively early and remains close to the upper envelope of the sampled designs, indicating that high-lithiation morphologies are accessible within $\mathcal{D}$. In contrast, $\sigma_{1,\text{max}}$ continues to improve over a broader range of trials before reaching its minimum $\sigma_{1,\text{max}} = 0.0248$, suggesting that stress mitigation is more sensitive to the specific combination of optimization parameters.

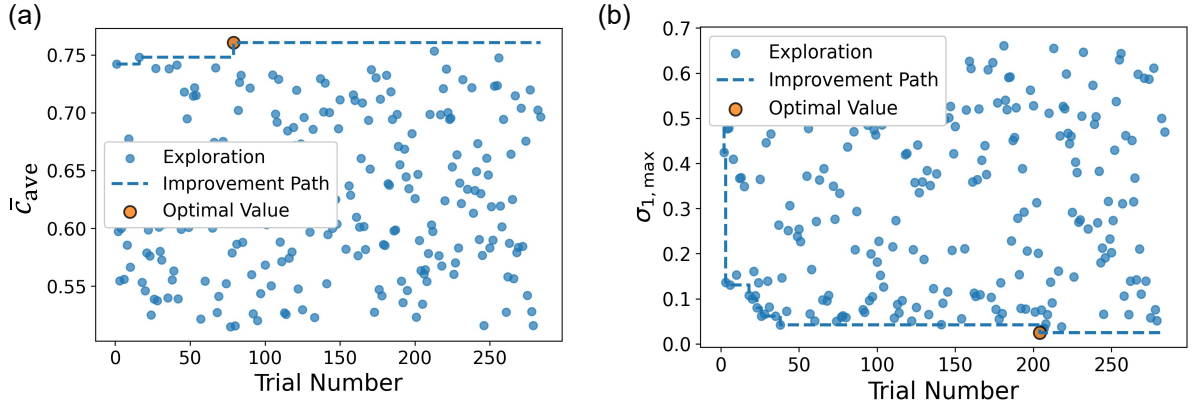


Figure 8: Sequential trial histories of morphology optimization of the inner-free transversely isotropic ellipsoidal particle under half-cycle lithiation ($t = 3600$ s). (a) Maximizing the normalized average lithium concentration $\bar{c}_{\text{ave}}$. (b) Minimizing the normalized maximum principal stress $\sigma_{1,\text{max}}$. Blue dots denote explored designs, dashed lines represent improvement paths, and yellow dots denote selected optimal values. Each optimization procedure includes 300 evaluations.

Table 3: Parameters of optimized solutions

Optimized solution	p_y	a_{in}	c_{in}	α
Best compromise	-3.67	4.35	0.422	23.93°
Highest $\bar{c}_{\text{ave}}$	-3.79	4.47	0.400	15.38°
Lowest $\sigma_{1,\text{max}}$	-2.29	4.41	0.412	89.30°

While the sequential search converges to morphologies that individually maximize $\bar{c}_{\text{ave}}$ or minimize $\sigma_{1,\text{max}}$, the two optima conflict and cannot coexist in a single morphology. As shown in Fig. 9a, larger $\bar{c}_{\text{ave}}$ generally accompanies larger $\sigma_{1,\text{max}}$, establishing an intrinsic trade-off. Such a trade-off is a defining characteristic of multi-objective optimization problems, in which no single design simultaneously optimizes all objectives, requiring a generalized solution concept.

One appropriate framework that addresses this conflict is Pareto optimality (Deb, 2001; Deb et al., 2002), where a design $\boldsymbol{\theta}^*$ is Pareto optimal if no alternative feasible design improves at least one objective without degrading another. The set of all such non-dominated solutions constitutes a Pareto front, which characterizes the complete envelope of achievable trade-offs in the objective space. Non-dominated solutions are identified via exhaustive pairwise dominance checking. A candidate $\boldsymbol{\theta}_i$ is eliminated if any $\boldsymbol{\theta}_j$ satisfies:

$$f_k(\boldsymbol{\theta}_j) \leq f_k(\boldsymbol{\theta}_i) \quad \forall k, \quad \text{and} \quad f_k(\boldsymbol{\theta}_j) < f_k(\boldsymbol{\theta}_i) \quad \text{for at least one } k, \quad (54)$$

where f_k represents the k -th objective (here $k = 1$ or 2) and maximization objectives are converted to equivalent minimization form by sign negation. Among the resulting Pareto-optimal set, a best-compromise design is selected by maximizing a balanced utility score $\mathcal{U}$, computed as the arithmetic mean of per-objective normalized sub-scores (Deb, 2001):

$$\mathcal{U}(\boldsymbol{\theta}_i) = \frac{1}{K} \sum_{k=1}^K s_k(\boldsymbol{\theta}_i), \quad s_k(\boldsymbol{\theta}_i) = \frac{f_k(\boldsymbol{\theta}_i) - f_k^{\text{worst}}}{f_k^{\text{best}} - f_k^{\text{worst}}}, \quad (55)$$

where $K = 2$ is the number of objectives in the current problem, f_k^{best} and f_k^{worst} denote the best and worst observed values of objective k across all trials, respectively, and s_k is oriented so that higher values are preferred for all objectives.

Following Eqs. 54&55, we perform Pareto analysis to identify the family of non-dominated morphologies (blue dots in Fig. 9a) and extract the best-compromise morphology from them (Fig. 9a black star). The best-compromise morphology achieves $\bar{c}_{\text{ave}} = 0.65$ and $\sigma_{1,\text{max}} = 0.21$, neither of which is individually optimal. For comparison, the morphologies with the highest $\bar{c}_{\text{ave}} = 0.76$ (with $\sigma_{1,\text{max}} = 0.65$) and the lowest $\sigma_{1,\text{max}} = 0.025$ (with $\bar{c}_{\text{ave}} = 0.56$) are also highlighted (red and orange stars in Fig. 9a, respectively). The design parameters of these three optimized solutions are listed in Table 3.

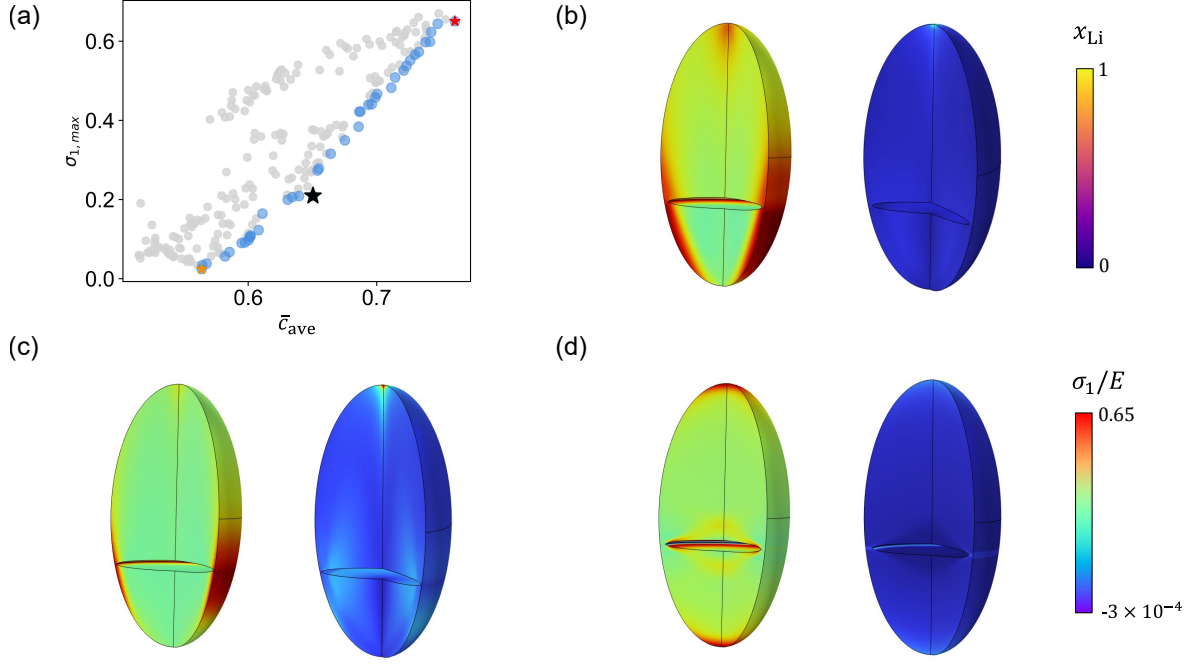


Figure 9: Multi-objective optimization results from Pareto analysis and the corresponding morphologies with field distributions. (a) Trade-off between the average lithium concentration $\bar{c}_{ave}$ and the maximum principal stress $\sigma_{1,max}$. Gray dots denote all explored designs. Blue dots represent the family of non-dominated morphologies from Pareto analysis. The black, red, and orange stars represent (b) the best-compromise morphology, (c) the morphology with the highest $\bar{c}_{ave}$, and (d) the morphology with the lowest $\sigma_{1,max}$, respectively. (b)-(d) plot their corresponding fields of normalized Li concentration $x_{Li} = c/c_{max}$ (left) and normalized maximum principal stress σ_1 (right).

We also plot the fields of normalized Li concentration $x_{Li} = c/c_{max}$ (left) and normalized maximum principal stress σ_1 (right) for the optimized morphologies corresponding to the best-compromise design (Fig. 9b), the highest $\bar{c}_{ave}$ (Fig. 9c), and the lowest $\sigma_{1,max}$ (Fig. 9d). These fields are consistent with the optimized $\bar{c}_{ave}$ and $\sigma_{1,max}$ values in each case. The results further illustrate the non-intuitive nature of the optimal particle morphology, which is governed jointly by geometric parameters and crystal orientation.

6. Conclusion

We have shown that the chemo-mechanical response of an ion-intercalation active particle during lithiation is governed not by particle geometry, material property, or mechanical constraint alone, but by their coupled interaction. In spherical particles with isotropic properties, the concentration-gradient-driven and strain-gradient-driven flux contributions nearly cancel, leaving lithiation effectively governed by diffusion-reaction alone.

In cylindrical particles, axial constraint substantially raises the induced elastic energy, while the opposing signs of the basal-plane and c-axis Vegard coefficients in transversely isotropic materials effectively ameliorate the elastic energy by partially accommodating the lithiation-induced deformation. In ellipsoidal particles, isotropic materials are constraint-sensitive: varying the level of mechanical constraints produces markedly different Li concentration distributions. Transversely isotropic ellipsoidal particles, by contrast, exhibit persistent heterogeneous lithiation governed by anisotropic diffusivity, with the mechanical constraints modifying the magnitude but not the spatial pattern of Li distribution. Cross-field analysis reinforces these observations: flux decomposition shows that the mechanical contribution to Li transport is negligible in spherical particles but dominant in ellipsoidal particles, and the Pearson correlation between Li concentration and volumetric strain transitions from strong anti-correlation in unconstrained particles to weak correlation under full constraints. Bayesian optimization of hollow ellipsoidal particles further demonstrates how these mechanistic insights translate into morphology design. The optimization identifies a Pareto front of non-dominated morphologies that trade off average Li concentration against maximum principal stress, from which a best-compromise design can be extracted by simultaneously tuning void geometry and crystal orientation.

These conclusions are subject to the assumptions of single-phase intercalation, ideal Li-vacancy mixing, small-strain elasticity, concentration-independent material properties, and idealized boundary conditions. Within this scope, the present study clarifies under what combinations of particle geometry, material symmetry, and mechanical constraint the mechanical contribution to transport can be safely neglected or must be retained. The results also provide quantitative guidance for tailoring particle morphology to manage the capacity-stress trade-off in active electrode materials.

CRedit authorship contribution statement

Rongyue Lin: Writing – original draft, Writing – review & editing, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation. **Royal C. Ihuaenyi:** Writing – original draft, Writing – review & editing, Visualization, Software, Methodology. **Juner Zhu:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptual-

ization. **Ruobing Bai:** Writing – original draft, Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare no conflict of interest.

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Appendix A. Fickian solution without elasticity in spherical particles

We solve the classical Fick's law in spherical particles by neglecting the contribution from mechanical fields, based on the governing equation

$$J = -D \frac{c_{\max}}{c_{\max} - c} \frac{\partial c}{\partial r}. \quad (\text{A.1})$$

Fig. A.10 compares the Fickian solution to the calculated results in Fig. 2a right.

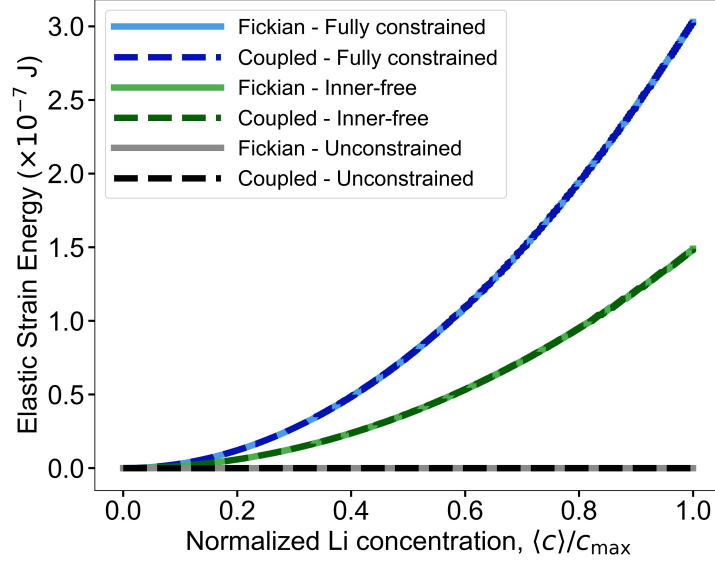


Figure A.10: Evolution of elastic energy as a function of normalized volume-averaged Li concentration, $\langle c \rangle / c_{\max}$ for spherical isotropic particles under different mechanical constraints. Dashed lines represent Fickian solutions from Eq. A.1. Solid lines represent solutions from the fully coupled model as shown in Fig. 2a right.

Appendix B. Analytical expressions in cylindrical particles

Under cylindrical symmetry, the radial flux in a transversely isotropic cylindrical particle is expressed as

$$J_r = -D_a \frac{c_{\max}}{c_{\max} - c} \frac{\partial c}{\partial r} + \frac{D_a c}{RT} \left[((C_{11} + C_{12})\beta_a + C_{13}\beta_c) \frac{\partial}{\partial r} \left(\frac{\partial u_r}{\partial r} + \frac{u_r}{r} \right) + (2C_{13}\beta_a + C_{33}\beta_c) \frac{\partial \varepsilon_{zz}}{\partial r} \right] - \frac{D_a c}{RT} \frac{\partial c}{\partial r} [2(C_{11} + C_{12})\beta_a^2 + 4C_{13}\beta_a\beta_c + C_{33}\beta_c^2]. \quad (\text{B.1})$$

In the axial direction, we assume that the particle is either fully constrained in displacement (axial strain $\varepsilon_{zz} = 0$, Fig. 2b left) or unconstrained (total axial force

$\int_{r_0}^{R_0} \sigma_{zz} r dr = 0$, Fig. 2c left). The former leads to an axial stress of

$$\sigma_{zz} = C_{13} \left(\frac{\partial u_r}{\partial r} + \frac{u_r}{r} \right) - (2C_{13}\beta_a + C_{33}\beta_c) \tilde{c}, \quad (\text{B.2})$$

while the latter leads to an axial strain of

$$\varepsilon_{zz} = -\frac{2C_{13}}{C_{33}} \frac{R_0 u_r(R_0) - r_0 u_r(r_0)}{R_0^2 - r_0^2} + \frac{2(2C_{13}\beta_a + C_{33}\beta_c)}{(R_0^2 - r_0^2)C_{33}} \int_{r_0}^{R_0} \tilde{c} r dr. \quad (\text{B.3})$$

For isotropic cylindrical particles, Eqs. B.1-B.3 further reduce to

$$J_r = -D \frac{c_{\max}}{c_{\max} - c} \frac{\partial c}{\partial r} + \frac{Dc}{RT} (3\lambda + 2G) \beta \frac{\partial}{\partial r} \left(\frac{\partial u_r}{\partial r} + \frac{u_r}{r} \right) - \frac{Dc}{RT} (9\lambda + 6G) \beta^2 \frac{\partial c}{\partial r}, \quad (\text{B.4})$$

$$\sigma_{zz} = \lambda \left(\frac{\partial u_r}{\partial r} + \frac{u_r}{r} \right) - (3\lambda + 2G) \beta \tilde{c}, \quad (\text{B.5})$$

and

$$\varepsilon_z = -\frac{2\lambda}{(\lambda + 2G)(R_0^2 - r_0^2)} (R_0 u_r(R_0) - r_0 u_r(r_0)) + \frac{2(3\lambda + 2G)\beta}{(\lambda + 2G)(R_0^2 - r_0^2)} \int_{r_0}^{R_0} \tilde{c} r dr. \quad (\text{B.6})$$

Appendix C. Analytical expressions in ellipsoidal particles

Under cylindrical symmetry, the flux components along the r and z axes in a transversely isotropic ellipsoidal particle are expressed as

$$\begin{aligned} J_r = & -D_c \frac{c_{\max}}{c_{\max} - c} \frac{\partial c}{\partial r} \\ & + \frac{D_c c}{RT} \left[(C_{33}\beta_c + 2C_{13}\beta_a) \frac{\partial \varepsilon_{rr}}{\partial r} + (C_{13}\beta_c + (C_{11} + C_{12})\beta_a) \frac{\partial \varepsilon_{\theta\theta}}{\partial r} + (C_{13}\beta_c + (C_{11} + C_{12})\beta_a) \frac{\partial \varepsilon_{zz}}{\partial r} \right] \\ & - \frac{D_c c}{RT} \frac{\partial c}{\partial r} [C_{33}\beta_c^2 + 4C_{13}\beta_c\beta_a + 2(C_{11} + C_{12})\beta_a^2], \end{aligned} \quad (\text{C.1})$$

and

$$\begin{aligned} J_z = & -D_a \frac{c_{\max}}{c_{\max} - c} \frac{\partial c}{\partial z} \\ & + \frac{D_a c}{RT} \left[(C_{33}\beta_c + 2C_{13}\beta_a) \frac{\partial \varepsilon_{rr}}{\partial z} + (C_{13}\beta_c + (C_{11} + C_{12})\beta_a) \frac{\partial \varepsilon_{\theta\theta}}{\partial z} + (C_{13}\beta_c + (C_{11} + C_{12})\beta_a) \frac{\partial \varepsilon_{zz}}{\partial z} \right] \\ & - \frac{D_a c}{RT} \frac{\partial c}{\partial z} [C_{33}\beta_c^2 + 4C_{13}\beta_c\beta_a + 2(C_{11} + C_{12})\beta_a^2]. \end{aligned} \quad (\text{C.2})$$

In the isotropic particle, the flux reduces to

$$\mathbf{J} = - \left[D \frac{c_{\max}}{c_{\max} - c} + \frac{Dc}{RT} (9\lambda + 6G) \beta^2 \right] \nabla c + \frac{Dc}{RT} (3\lambda + 2G) \beta \nabla \text{tr}(\boldsymbol{\varepsilon}). \quad (\text{C.3})$$

When considering a transversely isotropic ellipsoidal particle with an arbitrary crystal orientation of angle α in Section 5, the axisymmetric flux is expressed as

$$\mathbf{J} = -\frac{1}{RT} \mathbf{D}(\alpha) \left[\frac{RT c_{\max}}{c_{\max} - c} \nabla c - c \nabla(\mathbf{B}(\alpha) : \boldsymbol{\varepsilon}) + c(\mathbf{B}(\alpha) : \boldsymbol{\beta}(\alpha)) \nabla c \right] \quad (\text{C.4})$$

where $\mathbf{J} = [J_r, J_z]^T$, $\nabla c = [\partial_r c, \partial_z c]^T$, $\boldsymbol{\varepsilon}$ is the strain tensor, and $\mathbf{D}(\alpha)$ is the orientation-dependent diffusivity tensor projected onto the (r, z) plane. The second-rank tensor $\mathbf{B}(\alpha)$ is defined as

$$B_{ij}(\alpha) = C_{ijkl}(\alpha) \beta_{kl}(\alpha) \quad (\text{C.5})$$

such that $\mathbf{B}(\alpha) : \boldsymbol{\varepsilon} = B_{ij}(\alpha) \varepsilon_{ij}$ and $\mathbf{B}(\alpha) : \boldsymbol{\beta}(\alpha) = C_{ijkl}(\alpha) \beta_{ij}(\alpha) \beta_{kl}(\alpha)$ are orientation-dependent scalars.

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