

Article

State-of-Charge-Dependent Anisotropic Lithium Diffusion and Stress Development in Ni-Rich NMC Cathodes: A Multiscale Simulation Study

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Abstract

Understanding the relationship between state-of-charge (SOC) and anisotropic lithium diffusion is essential for improving the durability of Ni-rich layered oxide cathodes. However, quantitative insights into directional lithium diffusivity and its influence on mechanical degradation remain limited. In this study, molecular dynamics (MD) simulations were performed for $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) compositions with varying nickel content and SOC levels to reveal composition- and direction-dependent lithium transport behavior. The numerical indices in NMC compositions (e.g., NMC111, NMC532, NMC811) indicate the relative molar ratios of Ni, Mn, and Co, respectively, in $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$. The results show that lithium diffusion is enhanced at low SOC, owing to the abundance of vacant sites, while diffusion along the out-of-plane (c-axis) direction is strongly constrained, particularly in Ni-rich systems. To bridge the atomistic and continuum scales, the SOC-dependent anisotropic diffusivities obtained from MD simulations were incorporated into a chemo-mechanical finite-element model of an NMC811 particle. The coupled analysis demonstrates that anisotropic and SOC-dependent diffusion accelerates lithium depletion and stress localization, elucidating the origin of particle cracking in Ni-rich cathodes. This multiscale framework provides quantitative parameters and mechanistic understanding critical for designing durable next-generation lithium-ion batteries.

Keywords: Ni-rich NMC cathodes; molecular dynamics simulations; anisotropic lithium diffusivity; state of charge dependence; multiscale simulation



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1. Introduction

Lithium-ion batteries (LIBs) are central to modern energy storage solutions, particularly for electric vehicles and renewable energy systems, owing to their high energy density, superior electrochemical performance, and long cycle life [1]. The performance of LIBs significantly depends on the cathode materials used, influencing energy capacity, structural stability, and long-term durability [2]. Among various cathode options, lithium nickel manganese cobalt oxides (NMC) have attracted considerable attention due to their balanced characteristics of high energy density, improved thermal stability, and enhanced electronic conductivity, surpassing conventional single-metal oxides such as LiCoO_2 , LiMn_2O_4 [3], and LiNiO_2 [4,5].

However, despite these advantages, Ni-rich NMC cathodes such as NMC811 exhibit critical drawbacks, primarily rapid capacity fade due to mechanical degradation [6]. Particle

cracking is identified as one of the primary mechanisms behind this degradation. Repeated intercalation and deintercalation cycles generate mechanical stress due to anisotropic lattice expansion and contraction, which eventually leads to microcracks within and between primary and secondary particles. These cracks significantly hinder lithium-ion diffusion, increasing internal resistance and ultimately accelerating capacity fade and performance deterioration [7,8].

Understanding the underlying chemo-mechanical coupling between lithium diffusion and stress development is therefore crucial for improving the structural integrity of Ni-rich layered oxides. To gain fundamental insights into the mechanisms driving particle cracking and to address these mechanical issues, theoretical studies have been extensively conducted [9–13]. In these theoretical studies, diffusivity emerges as a critical parameter. Recently, Iqbal et al. demonstrated that anisotropic diffusion significantly influences stress generation in single-crystal NMC particles [14]. Nevertheless, directional diffusivity data for NMC materials remain scarce in the literature, and the lack of quantitative, direction-dependent diffusivity information limits accurate prediction of stress evolution and fracture behavior.

Despite extensive experimental efforts, gaining atomic-scale insights into lithium-ion diffusion remains challenging because of limitations in spatial and temporal resolution. This motivates the use of atomistic simulations to obtain SOC-dependent and anisotropic diffusion coefficients that are difficult to measure experimentally. To address these limitations, computational modeling, particularly molecular dynamics (MD) simulations, has become a crucial tool [15]. Molecular dynamics simulations provide precise insights into lithium-ion pathways, diffusion behavior, and structural transformations under diverse conditions, as demonstrated in related material studies [16]. MD simulation is particularly useful for examining dynamic behavior and identifying dynamic properties of materials [17,18].

Using MD simulations, prior studies have elucidated diffusion characteristics in various cathode materials. For example, Huang et al. revealed three-dimensional Li^+ diffusion mechanisms in Li_2MnO_3 involving tetrahedral-site-driven delithiation and partial Mn migration toward spinel-like structures [19]. Fallahzadeh and Farhadian demonstrated the dependency of Li^+ diffusion in LiCoO_2 on voltage and vacancy concentrations, emphasizing directional differences parallel to the layered structures [20,21]. Similarly, MD analyses on LiFePO_4 indicated significant impacts of anti-site defects on Li^+ diffusivity, transitioning from hindered one-dimensional diffusion to enhanced isotropic diffusion at elevated temperatures and defect densities [22]. Lee et al. showed using MD with a 2NNMEAM+Qeq potential that vacancy concentration minimally affects activation energy but greatly boosts Li diffusion in $\text{Li}_x\text{Mn}_2\text{O}_4$ [23].

Only a few studies have investigated the diffusion behavior in NMC materials using MD simulations. Ji and Lee demonstrated that moderated Li/Ni intermixing boosts Li diffusion and stability in Ni-rich NMC, while excessive intermixing increases stress [24]. Classical MD simulations on $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ identified favorable Li-Ni antisite defects, size-dependent dopant solubility, and anisotropic, temperature-enhanced Li diffusivity [25]. Zhu et al. reported MD simulations on Ni-rich NMC, indicating Li diffusion peaks at moderate Ni^{2+} content due to a balance between TM-layer enhancement and anti-site hindrance [26]. Despite these studies, detailed insights into state-of-charge (SOC)-dependent directional diffusivity in NMC cathodes, particularly regarding the anisotropic nature of diffusion processes, remain sparse in the literature. Therefore, a systematic analysis that connects SOC-dependent diffusion anisotropy with stress generation is still lacking and is essential for understanding degradation in Ni-rich cathodes.

In this study, we systematically investigate the influence of nickel content on directional lithium-ion diffusion coefficients in NMC cathodes, employing MD simulations

with empirical interatomic potentials. We aim to quantify the anisotropic diffusion behaviors and elucidate their relationship to compositional variations. The SOC-dependent directional diffusivities derived from MD are further integrated into a continuum-scale chemo-mechanical model to directly link atomic-scale transport to stress evolution in NMC811. By highlighting the directional dependence of lithium-ion diffusion, particularly in relation to nickel concentration and SOC levels, this work contributes valuable insights into the atomic-scale mechanisms underlying mechanical degradation. This integrated multiscale approach provides a physically consistent framework to explain how diffusion anisotropy governs stress localization and cracking, offering guidance for designing durable Ni-rich NMC cathodes.

2. Methods

First, we calculated SOC-dependent diffusivities with different Ni content in NMC materials using molecular dynamics simulations. Next, we applied the calculated diffusivities in the continuum model to test the effect of SOC dependent diffusivity on stress development. We describe each simulation method in the following sections.

2.1. Molecular Dynamics Simulations

The total energy of the NMC material is composed of short-range pairwise and long-range electrostatic interactions. For the pairwise interactions, the Morse potential was employed [27]. The Morse potential is a standard method for modeling covalent bond interactions:

$$E = D_e \left[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right] \quad (1)$$

where D_e is the potential well depth, α is the width parameter, r is the distance between ions, and r_0 is equilibrium interatomic distance where potential energy is minimized. Interatomic Morse parameters were taken from Ref. [28].

The electrostatic interaction part of the total energy is calculated by

$$E = \frac{Cq_iq_j}{\epsilon r} \quad (2)$$

where C is the energy conversion constant, q_i and q_j represent the charges of two atoms, and ϵ is the dielectric constant. These interactions are critical, as the intercalation and deintercalation of lithium ions during battery cycling induce significant electrostatic forces between the lithium ions and the surrounding lattice. The interatomic Morse potential parameters and atomic charge values used in the MD simulations are summarized in Table 1.

Table 1. Interatomic Morse potential parameters and atomic charges used in MD simulations.

Interaction Pair	D_0 (eV)	r_0 (Å)	α (Å ⁻¹)
Li ⁺ –O ²⁻	0.001114	2.681360	3.429506
Ni ²⁺ –O ²⁻	0.029356	2.500754	2.679137
Ni ³⁺ –O ²⁻	0.029356	2.500754	2.679137
Mn ⁴⁺ –O ²⁻	0.029658	2.440000	3.012000
Co ³⁺ –O ²⁻	0.010958	2.400628	3.461272
O ²⁻ –O ²⁻	0.042395	3.358701	1.659316

Atomic charges: Li⁺ = +0.6 e, Ni²⁺ = +1.2 e, Ni³⁺ = +1.8 e, Mn⁴⁺ = +2.4 e, Co³⁺ = +1.8 e, O²⁻ = −1.2 e.

The NMC structure adopts a layered hexagonal structure with space group R-3m [29]. In this study, we constructed a simulation cell containing 360 ions (90 lithium ions, 180 oxygen ions, and 90 transition metals of nickel, manganese, and cobalt), which was subsequently replicated ($4 \times 2 \times 2$) along the x, y, and z directions to form a 5760-atom

supercell suitable for diffusion analysis. Figure 1 shows the atomic unit structure used for MD simulations. To reduce potential biases from specific atomic arrangements, transition metals are randomly placed. By changing the ratio of the transition metals, five composition ratios of NMC111, NMC532, NMC622, NMC721, and NMC811 are considered. A detailed breakdown of transition metal composition ratios is shown in Table 2. For nickel, both Ni^{2+} and Ni^{3+} are considered. As the ratio of nickel increases, Ni^{3+} content is increased to maintain the system neutrality.

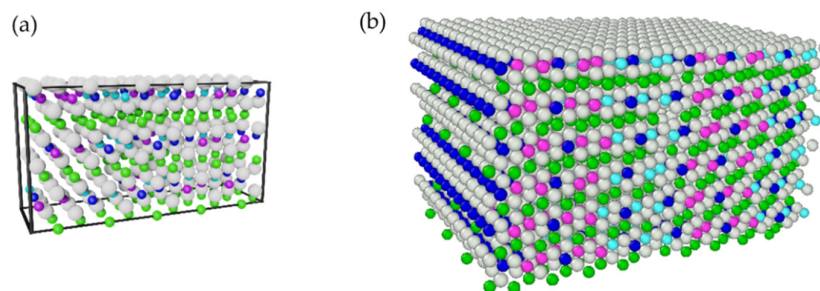


Figure 1. Atomic structure of (a) unit cell and (b) supercell of NMC111 (green: Li, cyan: Ni, blue: Co, purple: Mn, gray: O).

Table 2. Composition ratios of transition metals in $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC, where the numerical indices in NMCxyz indicate the relative molar ratios of Ni, Mn, and Co).

Composition (NMCxyz)	Ni^{2+}	Ni^{3+}	Mn^{4+}	Co^{3+}
NMC111	0.33	0.00	0.33	0.33
NMC532	0.30	0.20	0.30	0.20
NMC622	0.20	0.40	0.20	0.20
NMC721	0.20	0.50	0.20	0.10
NMC811	0.10	0.70	0.10	0.10

Due to the typically stronger nature of long-range Coulombic forces compared to short-range interactions, it is necessary to appropriately scale atomic charges to achieve a balanced interaction profile. To determine suitable charge scaling, we computed the elastic constant of NMC111 for different atomic charge values and compared these results against previously reported data in the literature. The computed stiffness values obtained using 60% of the formal charges demonstrated excellent consistency with existing data. Consequently, this study adopted a scaling of 60% formal charges, specifically assigning atomic charges as $\text{Li}^{0.6+}$, $\text{Ni}^{1.2+}$, $\text{Ni}^{1.8+}$, $\text{Mn}^{2.4+}$, $\text{Co}^{1.8+}$, and $\text{O}^{1.2-}$.

In this study, we performed MD simulations using the open-source simulation tool LAMMPS package (version 22 December 2022) [30]. Each structural configuration was equilibrated for 50 ps under NPT ensemble at 300 K and 1 atm. Following equilibration, the mean square displacement (MSD) was calculated with NPT ensemble for 150 ps with a 1 fs timestep. A cutoff radius of 10 Å and Ewald summation were used for long-range Coulombic interactions. All MD simulations were performed under thermal activation at 300 K without applying any external electric field; lithium-ion motion occurred purely due to thermal energy.

The MSD of lithium ions is calculated to study their diffusion behavior using Einstein's equation [31].

$$\text{MSD} = \langle |\mathbf{r}(t) - \mathbf{r}_0|^2 \rangle \quad (3)$$

where $\mathbf{r}(t)$ represents the position of a particle at time t , and $\mathbf{r}_0$ is its initial position, and $\langle \cdot \rangle$ indicates an ensemble average. The MSD represents how the position of the lithium ions

changes over time; its slope provides information about the rate of diffusion. The diffusion coefficient D is calculated by

$$D = \frac{1}{2n} \frac{d(\text{MSD})}{dt} \quad (4)$$

where n is the dimensionality. The slope was obtained over the 100–150 ps interval of the production run, after equilibration, where the MSD exhibited a stable linear trend. The initial non-linear regime corresponding to vibrational motion was excluded from the fitting process. The adequacy of the equilibration and production run times was confirmed by an additional 1 ns test simulation for the representative NMC111 system, which showed consistent diffusivity results.

2.2. Continuum Simulations

Figure 2 shows the 3D model of single-crystalline NMC particle used in this study. The x and y axes correspond to the in-plane crystallographic directions, while the z axis represents the normal direction. A coupled chemo-mechanical model was implemented to investigate the interactions between lithium diffusion and stress development within the particle [32].

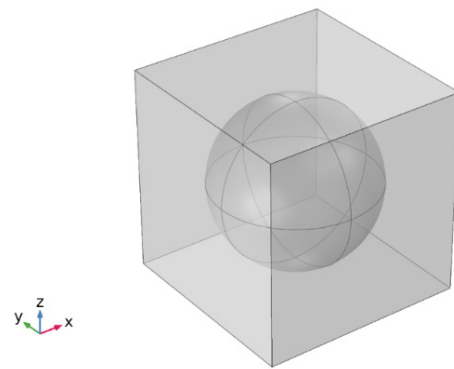


Figure 2. Three-dimensional NMC particle continuum model.

Lithium diffusion is governed by following equation:

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[D \nabla c - \frac{c}{RT} (1 - X) D \nabla (\Omega \sigma_w) \right] \quad (5)$$

where c is the lithium concentration, t is time, D is the diffusion coefficient, R is the gas constant, and T is the temperature. X is the molar fraction, defined as $X = c/c_{\max}$, where $c_{\max}$ is the maximum lithium concentration. Ω represents the partial molar volume, and σ_w is the weighted stress, contributing stress-driven diffusion.

The total strain is decomposed into elastic strain and diffusion-induced strain:

$$\varepsilon_t = \varepsilon_e + \varepsilon_d \quad (6)$$

The elastic strain follows Hook's law:

$$\varepsilon_e = K^{-1} \sigma \quad (7)$$

where K is the stiffness matrix. The diffusion-induced stress is calculated analogously to thermal stress as

$$\varepsilon_d = \eta \Delta X \quad (8)$$

where η is the partial molar strain, which acts as an effective thermal expansion coefficient in response to changes in lithium concentration.

The coupled equations were numerically solved using COMSOL Multiphysics 6.3. The simulation begins with a fully lithiated particle, and delithiation is simulated by imposing an outward lithium flux on the particle surface at a rate equivalent to 1 C. The spherical particle has a radius of 5 μm . Continuum simulations were carried out at 300 K and ambient pressure. No external electric field was applied in the continuum simulations; lithium transport was driven solely by chemical potential gradients generated by the imposed lithium flux. The materials parameters used in the simulation are summarized in Table 3.

Table 3. Parameters in continuum simulations [32].

Parameters	Symbol	Units	Values
Universal gas constant	R	$\text{Jmol}^{-1}\text{K}^{-1}$	8.3145
Absolute temperature	T	K	300
Partial molar strain in x direction	η_1	-	0.019029
Partial molar strain in y direction	η_2	-	0.019029
Partial molar strain in z direction	η_3	-	0.045407
Young's modulus	E	GPa	194.4
Maximum lithium concentration	c_{max}	molm^{-3}	37,825
Poisson's ratio	ν	-	0.25
Density	ρ	kgm^{-3}	4750

The diffusivity values obtained from molecular dynamics simulations were fitted as a function of the SOC for each crystallographic direction. The fitted functions $D_x(\text{SOC})$, $D_y(\text{SOC})$, and $D_z(\text{SOC})$ were implemented into the diffusion equation using a user-defined function. During simulation, the local diffusivity was dynamically updated according to the instantaneous lithium concentration, enabling the continuum model to reflect SOC-dependent transport behavior derived from MD. This procedure establishes a direct multiscale coupling between atomistic diffusion characteristics and the microscale chemo-mechanical response.

The present continuum model describes the chemo-mechanical behavior at the microscale, where material properties and field variables can be treated as spatially continuous. Atomistic effects such as surface reconstruction or discrete hopping, which become significant at the nanoscale, are not explicitly captured but are implicitly reflected through material parameters obtained from molecular dynamics simulations.

3. Results

3.1. MD Calculations

To validate the accuracy of our analysis, we computed the lattice constants for five different NMC compositions by averaging the system size over the equilibration period. Table 4 presents a comparison of the calculated lattice constants with reference values from the literature. Although there is a slight deviation of 3–4%, the computed values align well with the reference data.

Accurate treatment of lithium transport requires the presence of vacant sites to enable Li-ion migration, thereby mimicking realistic electrochemical conditions. For each composition, we introduced a lithium vacancy concentration commensurate with the target SOC, ensuring that the simulated structures exhibit vacancy-mediated Li^+ transport. Our analysis focuses on lithium-ion diffusion at specific SOC levels of 0.25, 0.5, and 0.75, which correspond to low, medium, and high battery charge levels. Here, SOC represents the ratio of lithium ions remaining in the material to the maximum lithium that can be stored. For instance, $\text{SOC} = 1.0$ indicates a fully lithiated state, while $\text{SOC} = 0$ corresponds to a completely delithiated state. Thus, SOC levels of 0.25, 0.5, and 0.75 reflect 25%, 50%, and

75% of the total lithium content, enabling us to capture diffusion behavior across different stages of battery operation.

Table 4. Comparison of lattice constants.

Composition (NMCxyz)	Simulation Result (Å)		Reference Result (Å)		[Ref]
	x-Axis	z-Axis	x-Axis	z-Axis	
NMC111	2.955	14.703	2.862	14.238	[33]
			2.865	14.249	[34]
			2.865	14.250	[35]
			2.868	14.213	[25]
			2.813	14.420	[36]
NMC532	2.951	14.685	2.925	14.420	[36]
NMC622	2.936	14.610	2.910	14.390	[36]
NMC721	2.942	14.638	2.857	14.158	[37]
NMC811	2.932	14.590	2.830	14.300	[38]

Figure 3 shows the calculated MSD for lithium ions at 300 K for each composition at different SOC levels. The diffusion coefficients are calculated from the slopes of the MSD curves over time. At high SOC levels, some MSD curves become nearly horizontal, indicating that Li ions are confined to local potential wells and primarily exhibit localized vibrational motion due to the limited number of vacant sites available for long-range diffusion.

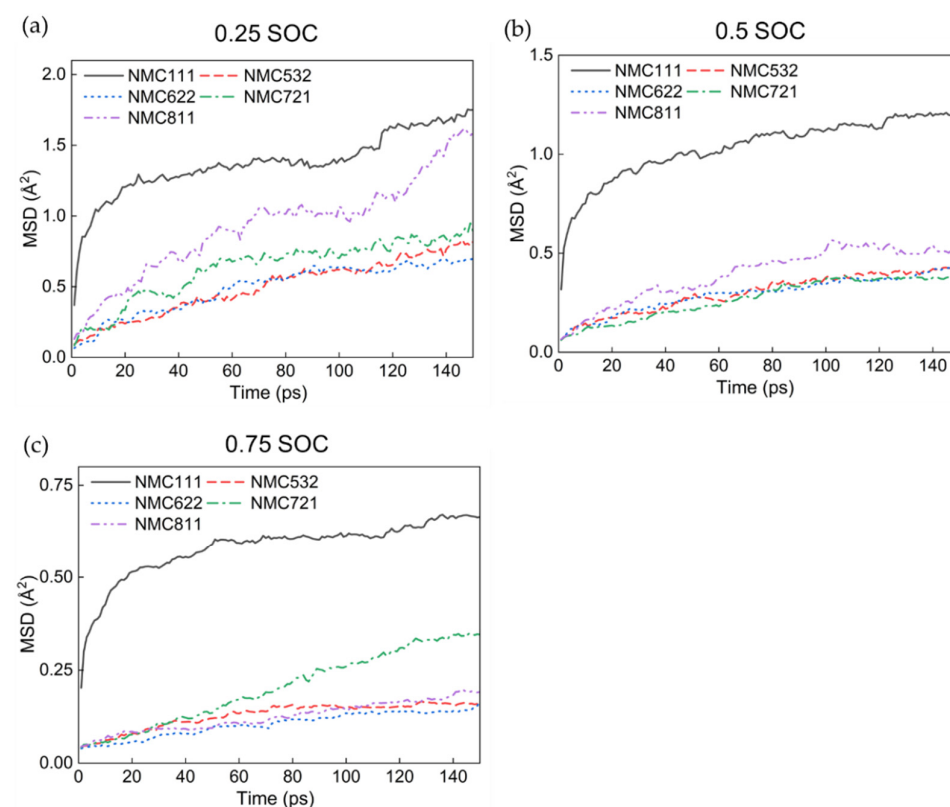


Figure 3. MSD curves for five NMC compositions at (a) 0.25 SOC, (b) 0.5 SOC, and (c) 0.75 SOC.

Figure 4 and Table 5 provide the computed diffusion coefficients for each composition across the three directional axes. Table 5 reports the calculated lithium-ion diffusion coefficients, while Figure 4 presents their corresponding graphical trends for better visualization. Our results show a trend where, as the SOC decreases, the diffusion coefficient increases, meaning ions move more readily at lower states of charge where the structure with many

vacant sites provides more accessible migration paths for lithium. As SOC decreases, the number of vacant Li sites increases and the electrostatic interactions between Li ions are weakened, resulting in lower migration barriers and enhanced diffusion coefficients.

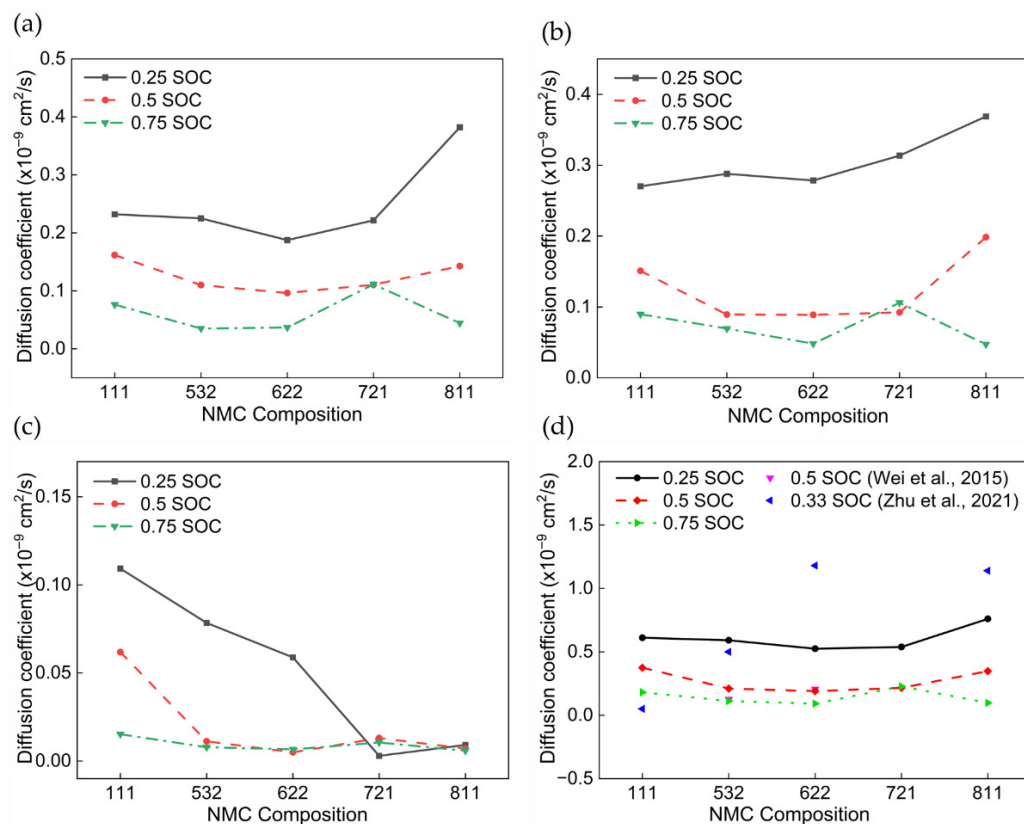


Figure 4. Diffusion coefficients of NMC compositions (NMC111, NMC532, NMC622, NMC721, and NMC811) at three SOC levels: (a) x-axis, (b) y-axis, (c) z-axis, and (d) total diffusion coefficient with reference data [26,39].

Table 5. Diffusion coefficient values ($\times 10^{-9} \text{ cm}^2/\text{s}$) along the x, y, and z axes at different SOC and composition.

Axis	Composition (NMCxyz)	SOC		
		0.25	0.5	0.75
x	NMC111	0.23193	0.16178	0.07625
	NMC532	0.22500	0.11000	0.03500
	NMC622	0.18750	0.09638	0.03664
	NMC721	0.22154	0.11052	0.11126
	NMC811	0.38202	0.14268	0.04433
y	NMC111	0.27028	0.15097	0.08978
	NMC532	0.28785	0.08932	0.06946
	NMC622	0.27841	0.08889	0.04816
	NMC721	0.31358	0.09236	0.10592
	NMC811	0.36881	0.19839	0.04718
z	NMC111	0.10928	0.06187	0.01524
	NMC532	0.07844	0.01121	0.00782
	NMC622	0.05887	0.00497	0.00665
	NMC721	0.00295	0.01306	0.01054
	NMC811	0.00914	0.00706	0.00585

When examining individual SOC levels, we observe distinct diffusion behaviors along the x, y, and z-axes. In Figure 4a, the diffusion coefficients in the x-axis remain relatively stable across compositions, with a slight increase for high-nickel compositions specifically at a 0.25 SOC. Similarly, diffusion coefficients along the y-axis show minimal change across compositions, except for a notable rise at 0.25 SOC. Although the x- and y-directions are crystallographically equivalent in the layered NMC structure, slight variations occasionally appear in the calculated diffusivities. These discrepancies stem from the random distribution of transition metals within the simulation cell and finite supercell effects, rather than from any intrinsic structural anisotropy.

The z-axis results, however, differ markedly, with a clear trend of decreasing diffusion coefficient values as the nickel content in the compositions increases. This finding suggests that the z-axis diffusion becomes increasingly constrained with higher nickel concentrations, which may be due to the impact of nickel on lattice structure or site availability. These findings are consistent with previous studies, as cited in reference [40], supporting the notion that compositional differences significantly affect lithium-ion diffusion characteristics. Figure 4d presents the total diffusion coefficient along with previously reported values for the same compositions, showing a consistent trend of increasing diffusion coefficient with higher nickel content.

Although total diffusivity increases with Ni, out-of-plane (c-axis) diffusion decreases, reflecting layered-structure anisotropy rather than a contradiction with mobility. The term “enhanced mobility” refers to in-plane lithium migration facilitated by Ni-rich transition-metal layers, whereas stronger Li–Ni interactions and cation mixing suppress cross-plane motion. Thus, the Einstein relation between diffusivity and mobility remains valid within each direction, but the apparent inconsistency arises from directional anisotropy rather than a physical inconsistency.

Increasing the Ni concentration enhances Li-ion diffusivity within the basal planes (x–y directions) but suppresses diffusion along the c-axis (z direction). This anisotropic behavior arises because higher Ni content promotes percolation of Li-vacancy pathways within the transition-metal slabs, facilitating in-plane migration. In contrast, Ni^{2+} ions, having an ionic radius similar to Li^+ , tend to occupy Li layers through cation mixing, which partially blocks the interlayer pathways and increases Li–Ni interactions. As a result, Li-ion motion becomes more confined within the planes. This finding suggests that Ni-rich NMC cathodes could benefit from electrode architectures or coatings that maintain open interlayer diffusion channels while leveraging enhanced in-plane transport for improved rate capability.

To rationalize these diffusion trends, we examined radial distribution functions (RDFs) to probe the local environments and the availability of migration pathways. Figure 5 shows Li^+ – Ni^{2+} RDF curves for 0.5 SOC, where the first peak appears at approximately 2.8 Å and its intensity increases from 2.5 to 3.75 with higher Ni content, indicating stronger local ordering and more pronounced Li^+ – Ni^{2+} interactions. Because Ni^{2+} has an ionic radius comparable to Li^+ , it can more readily undergo cation mixing into lithium layers as reported in other cathode materials [41]. Partial occupation of Li sites by Ni^{2+} obstructs diffusion channels, while the narrowing of RDF minima indicates that lithium ions experience stronger spatial confinement and fewer accessible migration pathways within the local structure. The RDF analysis further suggests that these stronger Li^+ – Ni^{2+} interactions not only reduce the available diffusion channels but also generate heterogeneous Li-ion fluxes. Such locally confined diffusion can intensify concentration gradients and induce stress localization within the lattice. These effects directly link the RDF features to the observed reduction in diffusivity and may further act as precursors for crack initiation in Ni-rich NMC cathodes.

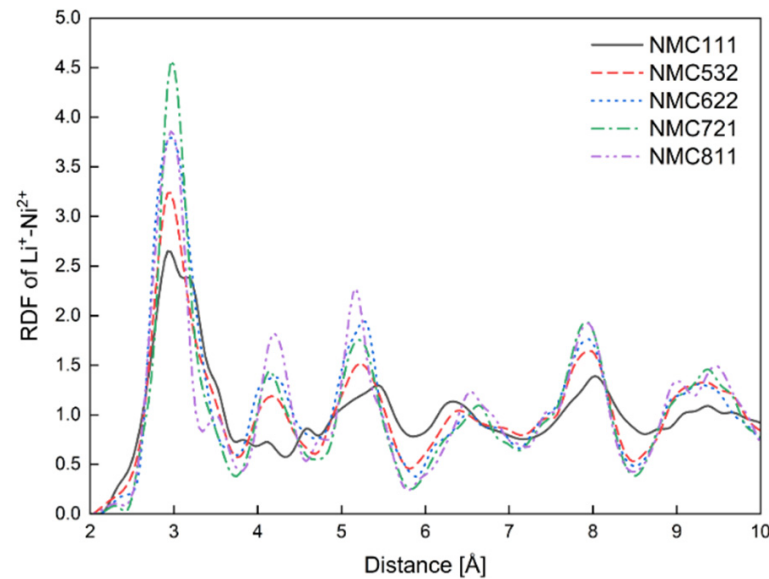


Figure 5. RDF curves of $\text{Li}^+ - \text{Ni}^{2+}$ pairs for NMC compositions at 0.5 SOC.

In contrast, Figure 6 shows the $\text{Li}^+ - \text{Ni}^{3+}$ RDFs, where the first peak remains near 2.9 Å and the height varies only slightly (from 3.9 to 4.4) across compositions, suggesting that Ni^{3+} perturbs the immediate Li coordination less strongly than Ni^{2+} . Nevertheless, a gradual narrowing of the RDF minima with increasing Ni content still points to subtle constraints that can moderately impede diffusion. Unlike Ni^{2+} , Ni^{3+} is more stable within the transition-metal layers and is less prone to cation mixing, leading to a less direct blockage of Li pathways. However, even these modest constraints reflected in the RDF can contribute to anisotropic transport, producing uneven lithium migration across crystallographic directions. Such anisotropic diffusivity may in turn drive nonuniform stress development, highlighting that both Ni^{2+} and Ni^{3+} environments play interconnected roles in diffusion limitation and the potential onset of mechanical degradation. Additionally, the partial RDFs for Li–Mn and Li–Co pairs were also analyzed but showed no significant systematic variations with composition or SOC. This behavior is consistent with the stable oxidation states and limited mobility of Mn^{4+} and Co^{3+} within the transition-metal layers during delithiation.

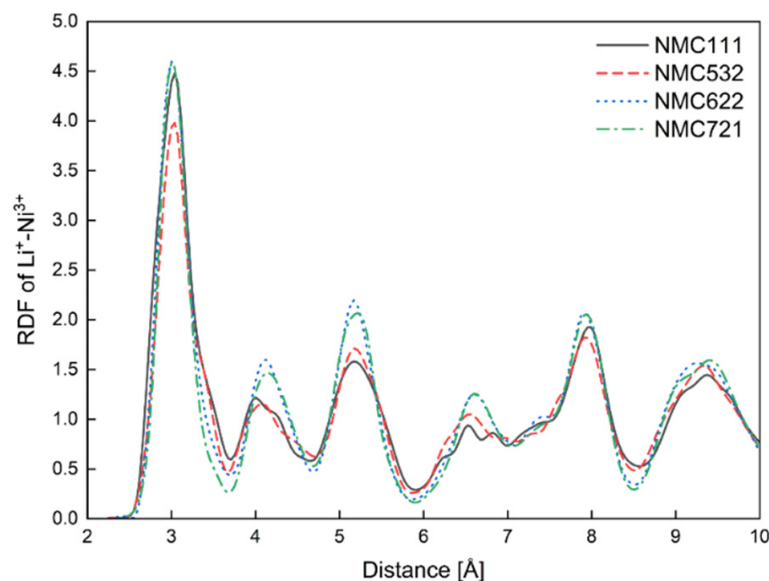


Figure 6. RDF curves of $\text{Li}^+ - \text{Ni}^{3+}$ pairs for NMC compositions at 0.5 SOC.

Notably, the 811 composition exhibits a slight recovery in diffusion relative to other high-Ni systems. The RDF analysis indicates a reduced $\text{Li}^+ - \text{Ni}^{2+}$ peak intensity and broader minima, consistent with weaker $\text{Li}^+ - \text{Ni}^{2+}$ interactions and a more open local environment. A lower fraction of mobile Ni^{2+} together with a relatively higher proportion of Ni^{3+} that is less inclined to mix into Li layers mitigates channel blocking and helps restore Li-ion transport in 811 despite its overall high Ni content.

3.2. Stress Development from SOC-Dependent Anisotropic Diffusion

As a representative application of MD calculations, SOC-dependent diffusivity was applied to single-crystal NMC811 particles. The SOC-dependent diffusivity was obtained by fitting a quadratic equation to the calculated diffusivity values at 0.25, 0.5, and 0.75 SOC, and the fitted curve is presented in Figure 7. To investigate the effects of anisotropy and SOC-dependent diffusivity, three cases were compared: constant diffusivity in all three directions, constant but anisotropic diffusivity in x, y, and z directions, and SOC-dependent anisotropic diffusivity. For the case with constant diffusivity in all three directions, nine values from the combination of three SOC and three directions were averaged and used. For the case with constant but anisotropic diffusivity, the diffusivity values averaged over SOC were applied separately for each direction.

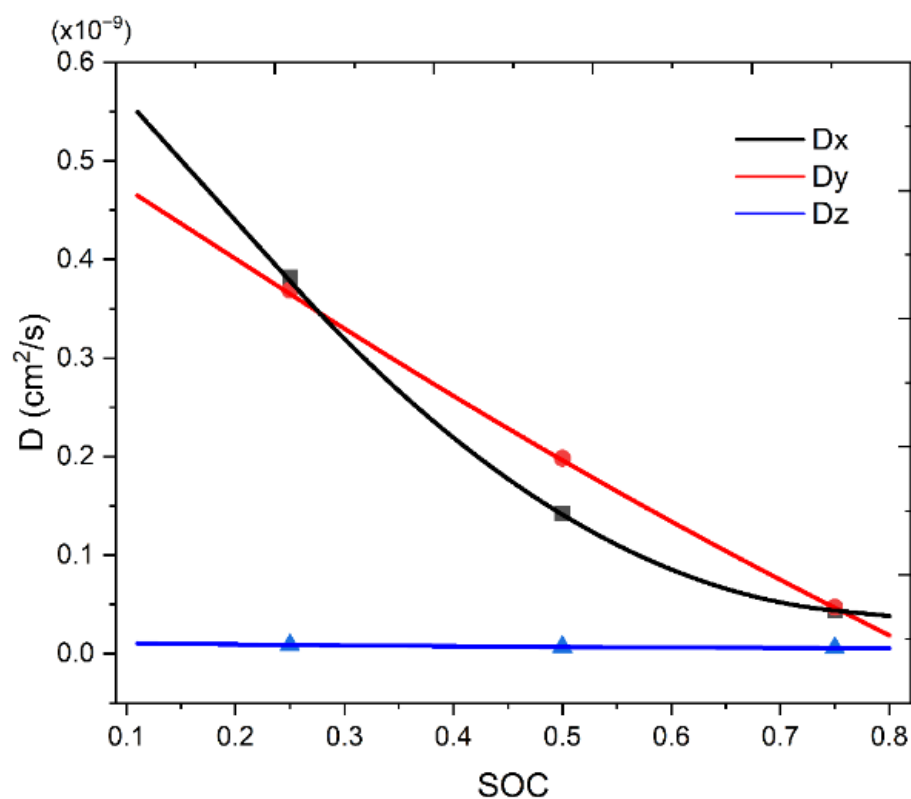


Figure 7. SOC-dependent diffusivity in x, y, and z directions.

Figures 8 and 9 show the lithium concentration and stress distributions, respectively, at the end of delithiation. Because NMC has a layered crystal structure, the z-axis represents the layer-normal direction while the x and y axes are in-plane. Consequently, the contour plots are isotropic in the xy plane but anisotropic in the yz plane. The xz plane distributions are similar to those in the yz plane and are therefore not presented here.

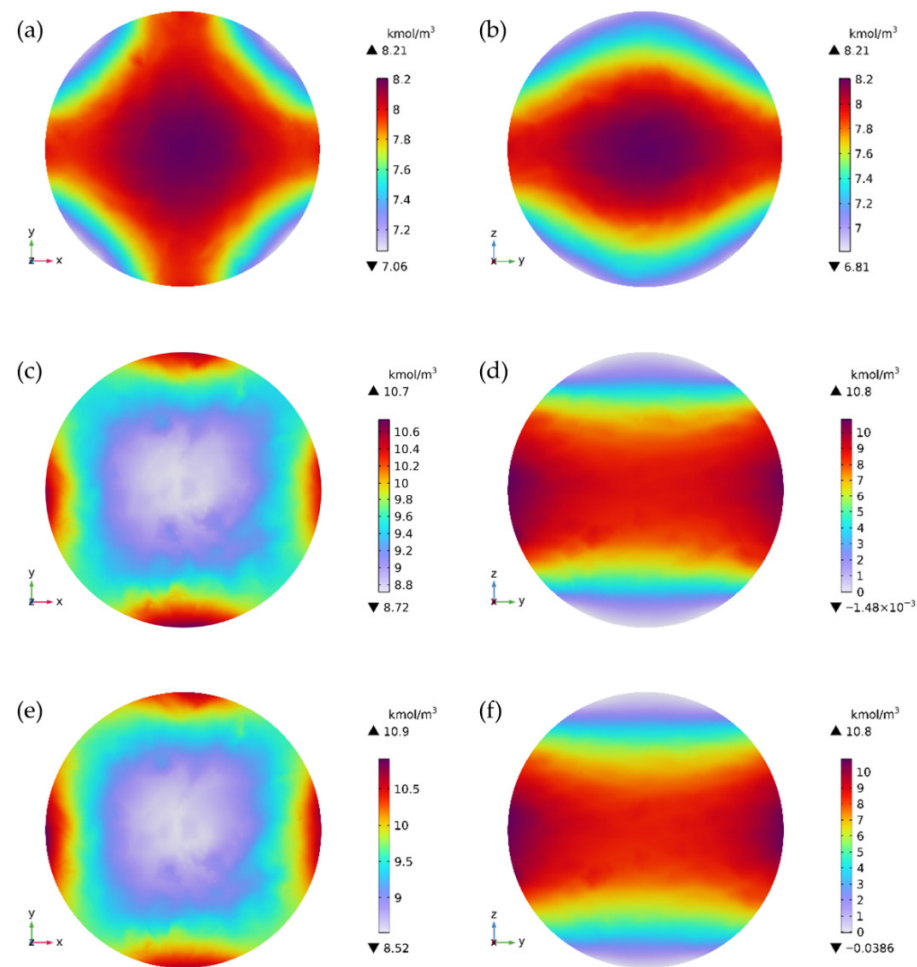


Figure 8. Lithium concentration distribution at the end of delithiation for NMC811 single-crystal particle with (a,b) constant diffusivity, (c,d) anisotropic diffusivity, and (e,f) SOC-dependent anisotropic diffusivity. Panels (a,c,e) show the xy-plane, while panels (b,d,f) show the yz-plane distributions.

In Figure 8a,b, even though a constant diffusivity is used in all three directions, directional lithium concentration distributions emerge due to anisotropic mechanical strains. When anisotropic diffusivity is applied (Figure 8c,d), the directional distribution becomes more pronounced. In the xy plane, where diffusivity is higher, lithium concentration becomes lower at the particle center due to faster transport. In contrast, in the yz plane, where diffusivity is lower in the z direction, lithium concentration remains lower along z. As lithium is extracted from the particle surface, lithium from the center preferentially moves along the x and y directions rather than the z direction, leaving regions along z less replenished.

When SOC-dependent diffusivity is applied in the x, y, and z directions (Figure 8e,f), the center region shows even lower concentrations. This occurs because diffusivity increases as SOC decreases, which accelerates lithium depletion in the center as delithiation proceeds. As a result, the coupling between anisotropy and SOC-dependent diffusivity promotes faster lithium transport from the center, intensifying concentration gradients and the associated stress development.

Figure 9 shows that overall larger stresses develop near the particle surface, as stresses are generated by lithium concentration gradients. Lithium is extracted from the surface, producing steep concentration gradients, whereas the gradients in the central region remain relatively gentle. When a constant diffusivity is applied in all directions, the maximum stresses appear around the particle equator. However, when anisotropic diffusivity is

introduced, the maximum stresses shift to approximately 45° direction from the equator. Furthermore, when SOC-dependent diffusivity is applied, stresses at top and bottom regions increase. This occurs because higher diffusivity at low SOC accelerates lithium diffusion, creating steeper concentration gradients and larger stresses in those regions.

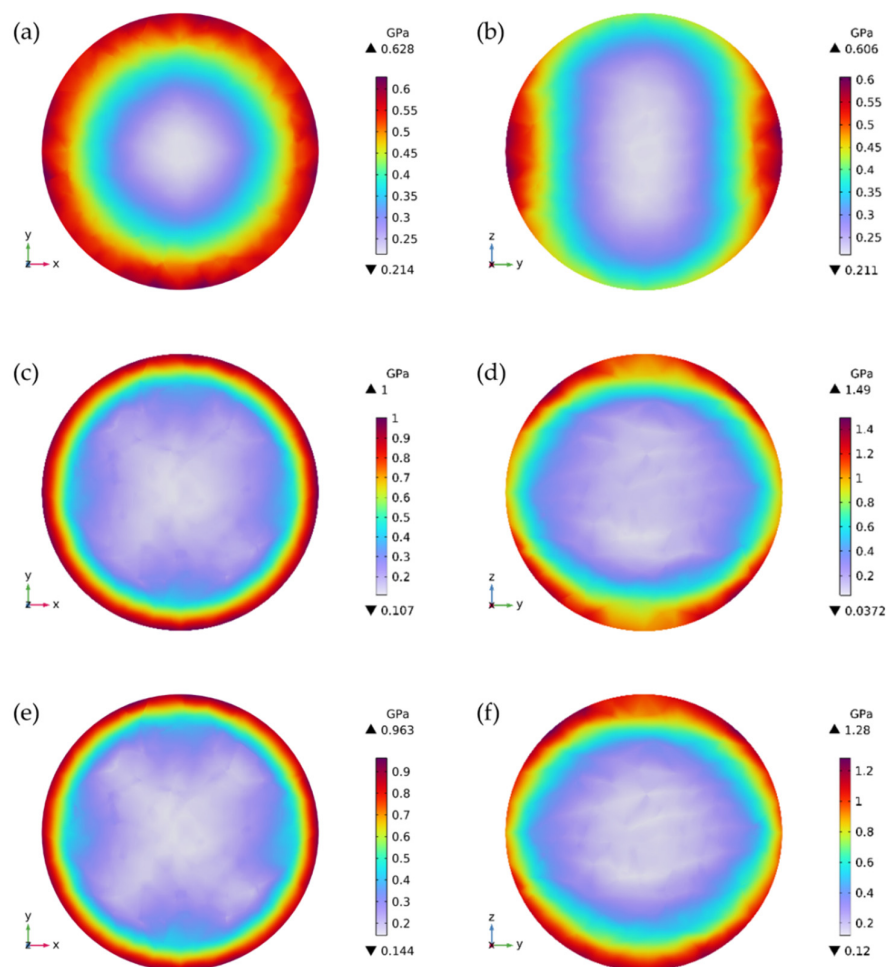


Figure 9. First principal stress distribution at the end of delithiation for NMC811 single-crystal particle with (a,b) constant diffusivity, (c,d) anisotropic diffusivity, and (e,f) SOC-dependent anisotropic diffusivity. Panels (a,c,e) show the xy-plane, while panels (b,d,f) show the yz-plane distributions.

The pronounced stress localization observed near the surface along the z-axis originates from anisotropic lithium diffusion and the elastic constraint of the layered structure. As delithiation proceeds, lithium depletion occurs faster in the in-plane directions, while slower diffusion along the layer-normal direction produces non-uniform volume contraction. This mismatch generates tensile stresses at the particle surface, particularly near the poles, which can act as preferred sites for crack initiation. Such diffusion-induced stresses are known to drive micro-crack formation in Ni-rich NMC materials, thereby accelerating mechanical degradation during cycling.

A representative secondary particle size of $5\ \mu\text{m}$ was adopted in this study to demonstrate the multiscale modeling approach. A detailed investigation of particle-size-dependent stress evolution will be carried out in future work.

4. Conclusions

In this study, we conducted an in-depth analysis of the dynamic properties of $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ materials using molecular dynamics simulations. Our focus was

on understanding how different NMC compositions influence the diffusion coefficient, a parameter that plays a crucial role in material performance. We calculated the diffusion coefficients for five different NMC compositions across four distinct SOC levels. Among the compositions, NMC811, characterized by the highest nickel content, demonstrated enhanced Li-ion diffusivity at low SOC, showing significantly higher diffusion coefficient compared to other SOC states for all compositions. However, we observed that the diffusion coefficient along the z-axis showed a decreasing trend as the nickel content in the NMC compositions increased. This behavior suggests that although higher nickel concentrations can enhance certain dynamic properties, they simultaneously constrain directional diffusion.

Furthermore, the results indicate that while higher Ni content enhances the theoretical capacity, it simultaneously increases diffusion anisotropy and stress concentration. This suggests that an intermediate Ni composition (e.g., NMC622 or NMC721) may provide a more favorable balance between electrochemical performance and mechanical integrity. Identifying this optimal Ni content trade-off through combined computational and experimental studies will be an important direction for future work.

Overall, the diffusivity values obtained in this work should not be regarded merely as atomic-scale descriptors but rather as essential parameters that bridge molecular dynamics with continuum-level modeling. By incorporating the SOC- and direction-dependent diffusivities into a continuum model of an NMC811 cathode particle, we demonstrated how anisotropic and SOC-dependent diffusion accelerates lithium depletion in the particle core, intensifies concentration gradients, and amplifies stress localization during delithiation. This multiscale framework illustrates how atomic-scale transport properties directly affect mesoscale mechanical responses. By providing SOC- and composition-dependent diffusivities, this study offers reliable inputs for electro-chemo-mechanical models that simulate stress evolution and fracture behavior in Ni-rich NMC cathodes. Such multiscale integration is critical for understanding the origin of particle cracking and guiding the design of mitigation strategies. Ultimately, the insights gained here can guide the optimization of particle size, composition, and cycling protocols to improve the structural stability and extend the lifetime of next-generation lithium-ion battery cathodes.

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