



#### 공학박사학위논문

# 차세대 소듐 이온 전지 고체 양극 활물질의 화학역학적 성능 열화에 대한 다차원 해석

Multiscale analysis of chemomechanical degradation in solid-state cathode materials for advanced sodium-ion secondary batteries

2023년 8월

서울대학교 대학원 기계공학부 김 형 준

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이 논문을 공학박사 학위논문으로 제출함

2023년 4월

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### Abstract

Over the last few decades, notable advancements have been made in the electrochemical performance of lithium-ion secondary batteries through numerous efforts. However, there is an emphasis on the need for more affordable secondary batteries owing to the growing demand for energy storage systems. Various next-generation secondary batteries, such as sodium-ion batteries using relatively abundant sodium oxides, have been proposed to address these issues. However, these next-generation secondary batteries cannot fully utilize their electrochemical performance owing to the intrinsic limitations of electrode materials, and there needs to be more understanding of the fundamental causes. Notably, a precise knowledge of the complex electrochemical and mechanical phenomena occurring in next-generation secondary batteries that store electrochemical energy through the transport of ionic charge carriers (e.g., Li<sup>+</sup> or Na<sup>+</sup>) within solid electrode materials is necessary. For this purpose, multiscale analysis techniques capable of interpreting the physical behavior of secondary battery materials across multiple scales are essential.

In this study, we establish a first-principles calculation-based multiscale analysis technique to examine the electrochemical performance degradation in solidstate materials of secondary batteries. Specifically, we integrate various simulation techniques, such as density functional theory, thermodynamic analysis, electrochemical analysis, and kinetic analysis at the electronic and atomic scale, electro-chemo-mechanical phase field models at the single particle scale, and finite element analysis at the microstructure scale, to reflect phenomena at the microscale and analyze the behavior of secondary battery materials at the macroscale. Through this approach, we identify the causes of various challenges in enhancing energy density, extending the lifetime, and improving the safety of next-generation secondary batteries.

This dissertation focused our research on sodium-ion secondary battery cathode materials. First, sodium cathode materials store energy through redox reactions involving the transport of relatively larger sodium ions within solid oxide than lithium ions. Due to the role of the relatively larger sodium ions as charge carriers, there are inherent limitations in sodium cathode materials. This methodology analyzed the thermodynamic phase stability and phase transition phenomena of manganese-based layered oxides to overcome intrinsic limitations and identify the physicochemical factors for stably maintaining high energy density for long cyclability. As a result of analyzing the uniform free energy calculated by this methodology, the manganese-nickel layered oxide shows a faster phase transition than the manganese layered oxide in the cation redox reaction region, showing a relatively reduced charge and discharge cyclability. However, a higher energy density in the anion redox reaction region can be stable owing to the small number of sodium-ions present only in the manganese-nickel layered oxide. In addition, it was found that the voltage hysteresis in the anion redox reaction region was reduced in the manganese-nickel layered oxide due to the sodium-ion poor phase. Through this, (i) increases the solubility of sodium-ions and vacancy in the manganese-nickel layered oxide in the cation redox reaction region and (ii) mitigates the phase transition of the manganese-nickel layered oxide in the anion redox reaction region. It was suggested that a high energy density could be stable for a long cycle if the phase with a minimal amount of sodium-ion was well utilized.

Additionally, by applying our methodology, we observed that the primary particles of nickel-manganese layered oxides experience anisotropic structural deformation during charge and discharge, resulting in the accumulation of elastic stress within the randomly oriented secondary particles, causing partial destruction and leading to the degradation of the cyclability of the secondary battery. In contrast, for radially oriented secondary particles, even when anisotropic structural deformation of primary particles occurs, the concentration of elastic stress is alleviated, suppressing secondary particle destruction and improving the cyclability of the secondary battery.

By applying the established first-principles-based multiscale analysis method to various next-generation solid-state cathode materials for secondary batteries, this study successfully elucidates the fundamental causes of electrochemical performance degradation through theoretical calculations and provides remedies to address these challenges. This demonstrates the usefulness of the suggested multiscale approach and is expected to offer a reliable direction for improving electrochemical performance based on theory, in addition to the conventional approach of developing next-generation electrode materials through experience. Furthermore, the proposed multiscale analysis method is expected to apply to various electrode systems that involve complex electrochemical reactions and mechanical behaviors, even in cases where experimental parameters are unavailable.

**Keyword :** Secondary batteries, Sodium-ion batteries, Solid-state cathode materials, Electrochemical performance degradation, First-principles calculation, Multiscale analysis **Student Number :** 2017-26678

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### Chapter 1 Introduction

#### **1.1 Sodium-ion Batteries**

In 1990, the global production of secondary batteries amounted to 200,000 MWh, almost entirely of lead-acid batteries. By 2019, this figure had grown to 650,000 MWh (including 450,000 MWh of lead-acid batteries). The additional growth of 200,000 MWh from 1990 to 2019 can be attributed to the rapid growth of lithium-ion battery (LIB) manufacturing, which increased by 25% per year during 2010-2019. LIBs have experienced significant advancements in the last few decades, resulting in improved performance and reduced costs.[1] Present-day LIBs have evolved from the 1991 Sony LIB, which featured a graphite anode, organic liquid electrolytes, and a LiCoO<sub>2</sub> layered oxide cathode. Over the past three decades, the LiCoO<sub>2</sub> cathode has progressed to high-capacity cathodes with increasing Ni content replacing Co, starting from Li(Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>)O<sub>2</sub> or NCM111 and advancing to commercialized NCM811 cathodes. At the same time, the rising demand for energy storage in the electric vehicles market and large-scale energy storage solutions like energy storage systems (ESSs) necessitates the development of more efficient, affordable, and safer battery technologies.[2,3]

Despite the decrease in production cost thanks to mass production, the cost of cathodes still needs to be lowered for their use in ESSs. Hence, sodium-ion batteries (SIBs) have emerged as an attractive alternative, given the abundant supply of sodium sources and the potential for cost benefits that are well-suited for large-scale applications. Furthermore, the similarities in the operational mechanisms of SIBs and LIBs have facilitated the development of SIB cathodes based on existing LIB designs.[4,5]

As illustrated in Figure 1.1, secondary batteries function electrochemically, with charge carriers (Li<sup>+</sup> for LIBs and Na<sup>+</sup> for SIBs) migrating through the electrolyte placed between the negative (anode) and positive (cathode) electrodes.[6] Based on this mechanism, high capacity refers to the ability to store a large number of ionic charge carriers in both the cathode and anode. On the other hand, high voltage indicates a high electrochemical potential when an ionic charge carrier is theoretically inserted and extracted from the cathode and anode. Combining high capacity and voltage leads to high energy density. Moreover, the phase and structural stability of the anode and cathode during electrochemical reactions influence cyclic performance and voltage drop. Additionally, power characteristics depend on the ionic charge carrier migration rate, primarily determined by ionic and electronic conductivity. Lastly, among the numerous essential electrochemical properties, an appropriate electrolyte must meet the minimum conditions to conduct ions effectively, maintain stability, separate electrodes to avoid short circuits and remain compatible with electrode materials to minimize resistance. Consequently, the electrochemical performance of secondary batteries is judged by a composite of all these factors.



Figure 1.1 Schematic of a LIB with LiTMO<sub>2</sub> layered cathode and graphite anode (Li<sup>+</sup> for LIBs and Na<sup>+</sup> for SIBs), reproduced from J. B. Goodenough[6]

#### **1.2 Issues and Challenges**

There are essential issues and challenges to enhancing and designing electrodes for next-generation electrochemical energy storage systems, especially for SIBs. These mainly include factors such as the capacity for accommodating ionic charge carriers, the potential for insertion and extraction, structural stability, and cyclability. The intrinsic disadvantages of Na<sup>+</sup> frequently hamper the performance of cathode materials in SIBs. For one, the operating voltage of sodium is roughly 0.3 V less than that of lithium, which leads to a diminished energy density in SIBs. Additionally, the considerable size of Na<sup>+</sup> ions (1.02 Å) results in a more pronounced volumetric change in the crystal lattice during the (de)intercalation process compared to LIBs. The substantial ion size of Na<sup>+</sup> presents numerous challenges in solid-state cathode active materials. Firstly, irreversible phase transitions occur during the discharge and charge processes involving Na<sup>+</sup> transport within the materials, which ultimately lead to voltage hysteresis and reduced cycle performance of the solid-state cathode active materials. Furthermore, the large ion intercalation and deintercalation processes induce considerable structural deformation in the solid-state cathode active material. These characteristics not only affect the primary particles but also have a more pronounced impact on secondary particles, such as mechanical integrity and longterm stability of the electrode structure. Consequently, addressing these challenges is crucial for developing high-performance SIBs.[7]

An innovative strategy involving the anionic redox reactions of O2-/On- species have been proposed to surmount inherent restrictions. This strategy is designed to alleviate the theoretical limitations imposed by the lower standard redox potential of Na/Na<sup>+</sup> in contrast to Li/Li<sup>+</sup>.[8] The superior energy density of SIB cathode materials relative to LIB counterparts is primarily due to the electrochemical redox potential conferred by pure lattice oxygen in layered oxides. Both computational and experimental data corroborate the presence of a high-voltage plateau, approximately at 4.2 V versus Na/Na<sup>+</sup>.[9–11] This conceptual framework, anchored in a comprehensive comprehension of the redox mechanism in Li<sub>2</sub>MnO<sub>3</sub> for LIBs through the crystal field theory (CFT), has been computationally and experimentally validated across a diverse range of intercalation compounds.[12]

Initially, a thoughtfully engineered Na[Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> layered oxide, which operates through the O 2*p*-electron and features a Na–O–Li linear configuration, was proposed as a revolutionary advancement in the design of cathode materials for SIBs.[13] This material demonstrates a high degree of anion-induced redox potential of 4.2 V vs. Na/Na<sup>+</sup>, providing a substantial theoretical capacity of 285 mAh/g. Mnbased layered compounds exhibited reversible redox plateaus with minimal polarization, while a typical anion-based electrochemical voltage curve was observed at around 4.2 V, accompanied by notable voltage hysteresis during the initial charge-discharge cycle. This was achieved by managing the Li to Mn ratio in the transition metal (TM) layer, which partially preserved the outstanding oxygen redox characteristics following the initial charging process. Further, the Mn-based TM vacancy layered compound,  $Na_{4/7,x}[\Box_{1/7}Mn_{6/7}]O_2$ , demonstrates a high voltage (4.1 V vs. Na/Na<sup>+</sup>) stemming from the oxygen redox reaction prompted by the nonbonding O 2*p*-electron adjacent to Mn vacancies.[14] Furthermore, Yabuuchi et al. extended the use of divalent Mg<sup>2+</sup> species, surpassing the monovalent elements of Na<sup>+</sup> and Li<sup>+</sup> in the TM layer, and presented a high-capacity Na<sub>2/3</sub>[Mg<sub>0.28</sub>Mn<sub>0.72</sub>]O<sub>2</sub> positive electrode offering 150 mAh/g upon charging and 220 mAh/g upon discharging.[15] This suggests that the surplus capacity is due to oxygen redox reactions. Moreover, diverse layered oxides incorporating 3*d*, 4*d*, and 5*d* transition metals have been widely investigated to advance anionic redox reactions.[16–19]

Recently, Mn-based sodium layered oxides that are neither rich in alkali metals nor characterized by TM vacancy layered structures have been reported to exhibit anionic redox reactions involving  $O^{2-}/O^{n-}$  as well.  $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$  has been theoretically and experimentally shown to undergo reversible anionic redox reactions with excellent cycling stability.[20,21] Furthermore, Kim et al. discovered anionic redox reactions of  $O^{2-}/O^{n-}$  taking place in the high voltage region of around 4.2 V vs. Na/Na<sup>+</sup>, following the cumulative cationic Ni<sup>2+</sup>/Ni<sup>4+</sup> redox in 2.5  $\leq x \leq$ 3.7 in Mn-based Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>.[22] Despite these studies indicating the potential for anion-based redox processes to play a role in achieving high-energy-density cathode materials, a deeper understanding of the behavior of anion-activated compounds in maintaining the initial energy density throughout charge/discharge cycles remains elusive.

While the enhanced properties of anion-redox typically result in structural instability and several electrochemical issues, such as irreversible charge-discharge capacities and significant voltage fade during cycling, researchers have sought to counteract these shortcomings by introducing various metal ions into cathode materials.[23–27] This approach has led to considerable improvements in electrochemical performance. Nevertheless, for the more comprehensive development of the involvement of oxygen redox reactions (ORR), it is imperative to understand thermodynamic phase-stability in tandem with anionic redox reactions.[27–31] The urgency of this understanding arises from the observation that harsh phase changes during discharge-charge operations are a principal factor in the formation of Na-based layered cathode compounds. Furthermore, transitioning into Na-poor and Na-rich phases from a phase kinetics viewpoint is crucial for enhancing lifespan and mitigating rapid capacity decline.

Following this line of investigation, one standard method for addressing these issues comes from the preparation technique for cathode particles, particularly in LIBs and SIBs, known as coprecipitation.[32–34] This method combines nano-sized primary particles into micron-sized secondary ones. While spherical secondary polycrystalline cathode particles produced by this method exhibit superior electrochemical performance, they are also influenced by significant intergranular micro-cracking, a primary cause of capacity fading in LIBs.[35,36] This phenomenon is particularly noticeable in the Li-poor phase of Li-based layered oxides, which is attributable to the anisotropic mechanical strain.[37–41] Considering Na-based layered oxides, stress-induced mechanical fatigue becomes

even more significant given the bigger size of Na<sup>+</sup> (1.02 A) in comparison to Li<sup>+</sup> (0.76 A). Further complicating the matter is the observed relationship between Ni ions' two-step change in ionic radius, Jahn-Teller distortion (JTD) by Ni<sup>3+</sup>, and the c lattice constant, with ORR playing a pivotal role. This intricate interplay suggests that a reduction in Ni ionic radii and increased JTD could intensify mechanical anisotropy in Ni-Mn binary-layered oxides during discharge and charge processes. These findings underscore the need for more extensive studies considering phase transformation, kinetics perspectives, and standard interventions like doping coating and particle size control.

This degradation of electrochemical performances caused within solid-state materials can be computed by employing electronic and atomic-scale simulation and first-principles calculations. Phase field simulations are necessary to predict phase behaviors at the primary particle level. These simulations rely on a bridged homogeneous bulk free energy derived from atomic scale physics to construct the fundamental equation that governs the phase field model. The impact of ion transport on secondary particle behavior can also be analyzed using the finite element method, providing another perspective on these complex phenomena. This approach facilitates a comprehensive understanding of material properties and behaviors across different scales.

## **1.3 First-Principles Calculations Based Multiscale** Analysis

The first-principles calculation-based multiscale analysis for secondary battery materials is paramount in the field of battery research and development. It is a

powerful tool that allows researchers to investigate material properties at various lengths scales and timeframes, from the atomic and electronic structure of materials to their macroscopic behavior. This comprehensive approach enables an understanding of the fundamental electrochemical performance degradation mechanism of battery materials, providing insights into their performance and stability, which are crucial for developing higher energy density, more efficient, safer, and cost-effective secondary batteries.[42]

One of the critical advantages of first-principles calculation-based multiscale analysis is its ability to predict the essential characteristics of secondary battery materials, like the thermodynamic and kinetic stability, electronic structure, and ion transport characteristics. By utilizing density functional theory (DFT), researchers can explore the complex interplay between the atomic and electronic structures of materials, which govern their electrochemical performance. This enables the identification of potential bottlenecks in secondary battery performance and proposes new strategies to overcome these limitations.

Additionally, multiscale analysis allows for integrating first-principles calculations with more macroscopic models, such as phase field models and finite element analysis. This integration facilitates investigating complex processes in secondary batteries, such as phase transformations, stress generation, and mechanical degradation. By bridging the gap between the atomic and macroscopic scales, the multiscale analysis provides a comprehensive understanding of the factors influencing battery performance, enabling the design of advanced materials and battery architectures to overcome existing challenges.

Therefore, first-principles calculation-based multiscale analysis of secondary battery materials is an indispensable tool in battery research, providing critical insights into atomic scale phenomena during charge/discharge, ultimately leading to advancements in the field. It provides deep insights into the fundamental properties of materials and the complex processes governing battery performance, enabling the identification and enhancement of novel materials and technologies. By employing multiscale analysis, researchers can address the pressing challenges facing the battery industry, like enhancing energy density, prolonging the lifespan of cycles, and improving safety, ultimately contributing to developing more efficient and sustainable energy storage solutions for various applications.

#### **1.4 Objectives and Contributions**

In this dissertation, we introduce a first-principles calculations-based multiscale analysis for the solid-state cathode materials of SIBs to elucidate the electro-chemomechanical performance degradation. We employ DFT, thermodynamic analysis, electrochemical analysis, kinetic analysis, defect chemistry, and CFT for electronic and atomic levels scrutiny. Furthermore, we use the electro-chemo-mechanical phase field model for primary particle level investigations and finite element analysis (FEA) for studying secondary particle level examinations.

In Chapter 2, utilizing first-principles calculations, the multiscale methodology is comprehensively outlined, detailing the characteristics examined at each scale and the physical values exchanged between higher scales. From the electronic and atomistic aspects of this methodology, we can predict intrinsic phase and structural thermodynamic stability, surface and interface characteristics, mechanical and electrochemical properties, kinetic features, and qualitative and quantitative electronic attributes. Based on these electronic and atomistic properties, we can define the total free energy functional and governing equations, which enable the evaluation of chemical potential, macroscopic kinetic performance, and phase transformation kinetics that induce mechanical deformation of the primary particle of solid-state cathode active materials during electrochemical reactions. By integrating these fundamental electro-chemo-mechanical properties, we can investigate phase transition-induced stress evolution at the secondary particle level of solid-state cathode active materials, which is challenging to be measured using experimental methods.

In Chapter 3, we thoroughly investigate the thermodynamic phase-transition kinetics and phase-stability in Mn-based binary layered oxides to attain high-energy-density and consistent cyclic performance using the multiscale analysis. We focused on Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>, which exhibits double cationic and subsequent anionic redox reactions. Using first-principle calculations and phase field simulations, we discovered that a more rapid phase-transition occurs for Mn-Ni binary oxide than pure Mn oxide. Moreover, Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> maintains a higher voltage-hysteresis and more minor energy density loss during the initial charge-discharge process than typical anion-activated layered cathodes. Based on these findings, we propose design principles to optimally utilize anion and cation species for redox reactions in Mn-based binary oxides.

In Chapter 4, we explore the anisotropic character of structural deformation during charge and discharge processes by utilizing first-principles calculations. Additionally, we analyzed the impact of these anisotropic structural deformations on the cyclability of the secondary battery using the finite element method.[43,44] By employing multiscale analysis, we illuminate that the secondary particle morphology can significantly affect the electrochemical performance of the cathode active material.

In Chapter 5, we extend the application of the first-principles calculation-based multiscale analysis to the all-solid-state batteries (ASSBs) to demonstrate the applicability of the proposed methodology. Indeed, we conduct an in-depth examination of the performance deterioration of solid electrolytes through multiscale analysis. Using first-principles calculations, we examine the mechanism behind lithium phase formation within metal the perovskite-type oxide  $(Li_{3x}La_{(2/3)-x}\square_{(1/3)-2x}TiO_3)$ .[45,46] Understanding this mechanism is crucial for addressing the electrochemical performance degradation in solid electrolytes. Moreover, by integrating first-principles calculations and kMC simulations, we identified the fundamental principles governing carboxymethyl cellulose (CMC) that enhance interfacial ion conduction properties in ASSBs, in conjunction with experimental investigations. [47,48] By employing multiscale analysis, we illuminate the deterioration of electrochemical performance in solid electrolytes for secondary batteries.

In conclusion, the observed phenomena, the thermodynamics phase-stability, phase-transition kinetics, and chemo-mechanical behavior of solid-state cathode active materials exhibit unique behaviors that non-multiscale theories and experiments cannot explore. The current approaches can be implemented for diverse electrode systems involving intricate electrochemical reactions and mechanical failures, even without experimental model parameters. These techniques offer broad applicability across a wide spectrum of established simulation methodologies.

## Chapter 2 First-Principles Calculations-Based Multiscale Analysis

#### 2.1 Electronic and Atomic Scale

#### 2.1.1 Density Functional Theory

The first step in conducting multiscale analysis involves utilizing firstprinciples calculations, also known as ab initio calculations, which rely solely on fundamental data such as nuclear charge and the quantity of electrons rather than empirical calculations that use fitting parameters. By employing the density functional theory (DFT) and solving the time-independent Schrödinger equation with an exchange-correlation potential  $\hat{V}_{XC}$ , the entire information of the system in question is computed in the form of a wave function  $\Psi$  as follows:[49,50]

$$\widehat{H}\Psi = [\widehat{T} + \widehat{V} + \widehat{U} + \widehat{V}_{XC}]\Psi = E\Psi$$
(2.1),

where  $\hat{H}$ ,  $\hat{T}$ ,  $\hat{V}$ ,  $\hat{U}$ , and *E* represent the Hamiltonian operator, kinetic energy operator, potential energy operator from the external field, electron-electron interaction energy operator, and total energy, respectively. The wave function contains all the relevant electronic and structural features of the system, like the electron density, energy levels, and chemical reactivity. Therefore, DFT is a potent tool for simulating the electronic structure and properties of materials. Owing to its capability to accurately predict the features of materials, DFT has become an essential computational tool in various research fields, including secondary batteries' solid-state materials. One major advantage of DFT is its ability to describe the electronic configuration of materials, making it well-suited for simulating redox reactions in secondary batteries' solid-state materials. Additionally, DFT is known for its ability to accurately capture the chemical bonding and electronic interactions in complex materials, which is essential for understanding the kinetic and thermodynamic properties of secondary batteries' solid-state materials. Therefore, DFT has become a prominent tool for investigating the properties of secondary batteries' solid-state materials with improved electrochemical performance.

This study utilized a spin-polarized generalized gradient approximation (GGA) with a Perdew-Burke-Ernzerhof (PBE)[51] parameterized exchangecorrelation functional, implemented in the Vienna Ab Initio Simulation Package (VASP) using a projector-augmented wave (PAW) and a plane-wave basis set.[52-55] The cut-off energy of the plane-wave basis and k-point meshes were determined through a convergence test of total energies within 10 meV per atom. The strong correlation effect among *d*-orbital electrons of transition metals was resolved using the Hubbard U correction, with U values taken from previous works.[43–45,56–58] For Chapter 5.2, the DFT-D3 van der Waals-corrected scheme is applied. [59] In all but specific instances, both ions and cells underwent complete relaxation. A hybrid functional called Heyd-Scuseria-Ernzerhof (HSE06) was implemented to accurately evaluate electronic structures to correct self-interaction errors in transition metals and oxygen exchange-correlation energy.[51] For the grain boundary (GB) calculations, the GB cell's lattice vector was held constant while all the positions of atoms were adjusted until the electronic convergence criterion was satisfied. For surface calculations, a Gibbs dividing surface model was carefully developed for the surface model.[45] The volume of the surface's cell remained constant, and the ions

underwent internal relaxations using Hellman-Feynman forces.

#### 2.1.2 Thermodynamic Approach

Investigating the thermodynamic stabilities and kinetic feasibilities of diverse atomic configurations is crucial for comprehending the effects of various electrode modifications, such as lithium extraction, oxygen defect formation and evolution, elemental doping, dissolution processes, etc. Therefore, we have introduced an array of thermodynamic parameters for the generalized case of AM<sub>x</sub>TM<sub>y</sub>O<sub>z</sub> compounds; AM serves as the ionic charge carrier, TM corresponds to transition metals, and O denotes the oxygen anion.

To assess the phase stability, taking into account all potential AM/vacancy atomic arrangements, the formation energy associated with mixing enthalpy is ascertained as follows:[60]

$$\Delta H_{mix}^{DFT} = E_{AM_x TM_y O_z} - x_{AM} E_{AMTM_y O_z} - (1 - x_{AM}) E_{TM_y O_z}$$
(2.2),

where  $x_{AM}$  represents the normalized AM content ( $0.0 \le x_{AM} \le 1.0$ ), and *E* denotes the total system energy derived from DFT calculations.

The GB formation energy is a fundamental quantity that provides insights into the stability and behavior of grain boundaries in polycrystalline materials. Specifically, a lower GB formation energy indicates a greater propensity for GB formation, while a higher GB formation energy suggests more excellent stability against forming GBs. The energy needed to form a grain boundary from the bulk materials is commonly known as GB formation energy, denoted as  $\gamma_{GB}$ . This quantity can be calculated using a well-established method as follows:

$$\gamma_{GB} = \frac{E_{GB} - nE_{bulk}}{2A} \tag{2.3},$$

where  $E_{GB}$  indicates the energy of the GB,  $E_{bulk}$  is the energy of bulk, *n* denotes the number of the bulk units contained in the GB, and *A* represents the area of the GB plane.

The surface energy, denoted as  $\gamma_{surf}$ , can be defined as the excess energy per unit area required to create a new surface in a material. The calculation of the surface energy is particularly relevant in the context of slab structures of materials. The examination of the surface energy concerning slab structures of material is performed using the following method:

$$\gamma_{surf} = \frac{E_{slab} - nE_{bulk} - \sum n_i \mu_i}{2A}$$
(2.4),

where  $E_{slab}$  is the energy of the slab,  $n_i$  indicates the deviation in the number of atoms of type *i* from the stoichiometric amount, and  $\mu_i$  is the thermodynamic potential of the *i* species, which is a measure of its free energy in a system and referred to as the chemical potential of the species *i*. Specifically, the parameter  $n_i$ takes negative values to indicate the removal of atoms and positive values to indicate the addition of atoms.

For computing the elastic properties of the thermodynamic ground states, the universal linear-independent coupling strains (ULICS) approach is utilized with an increased plane-wave energy cutoff (600 eV) and a finer *k*-points grid applied.[44,61]

#### 2.1.3 Electrochemical Approach

The equilibrium potential is closely linked to the different chemical potentials between the anode and the cathode. Although it is challenging to compute the chemical potential of the charge carrier ion in cathode materials to the ionic charge carrier content, the average equilibrium potential,  $\overline{V}$ , can be readily derived by comparing the total system energy values obtained through the use of DFT calculation as follows:[62]

$$\bar{V} = -\frac{\Delta G_r}{(AM_{x_2} - AM_{x_1})F}$$
(2.5),

where  $\Delta G_r$ ,  $(AM_{x_2} - AM_{x_1})$ , and F the Gibbs free energy, two charge carrier ions limit, and the Faraday constant, respectively.

The difference of the Gibbs free energy  $(\Delta G_r = \Delta E_r + P \Delta V_r - T \Delta S_r)$ , a critical thermodynamic property, can be judiciously approximated by considering the perturbations in the internal energy of a system. This approximation holds primarily because the effect of pressure on the free energy becomes virtually negligible under circumstances where the system's volume undergoes an exceedingly diminutive alteration ( $\Delta V_r \approx 0$ ). It is also essential to consider the impact of the thermal energy term on the overall free energy, which, for the most part, can be regarded as inconsequential. Specifically, within the context of DFT computations, the entropic component of the system exhibits only a slight variation in correspondence to the absolute temperature at 0 K. As a consequence, the influence of the entropy on the free energy is substantially minimized, rendering the thermal energy term's contribution to the total free energy predominantly insignificant. Therefore, this relationship permits the simplification of the Gibbs free energy calculation by primarily emphasizing the fluctuations in the internal energy, thus providing a practical approach for comprehending and dissecting how the system behaves in question. Consequently, the average equilibrium potential derived from DFT calculations can be simplified as:[62]

$$\bar{V} = -\frac{E_{AM_{x_2}TM_yO_z} - E_{AM_{x_1}TM_yO_z} - (x_2 - x_1)\mu_{AM}}{(AM_{x_2} - AM_{x_1})F}$$
(2.6).

#### 2.1.4 Kinetic Approach

In computational chemistry and materials science, the migration of ionic charge carriers along specific pathways is of fundamental importance for understanding numerous physical and chemical processes. To accurately compute the migration barrier associated with the diffusion of ionic charge carriers along a designated pathway, the climbing-image nudged elastic band (CI-NEB) method is utilized.[63,64] utilizes This approach the limited-memory Broyden-Fletcher-Goldfarb-Shanno optimizer (LBFGS) to minimize the residual forces along the pathway until convergence is achieved, typically when the residual forces are less than 0.05 eV/Å.[65] Moreover, for the CI-NEB calculations, employing an appropriate number of images that can capture the intricate details of the underlying potential energy surface is crucial. In this regard, the imagedependent pair potential method has proven reliable and computationally efficient in obtaining the necessary images.[66] In our study, we utilized seven images from this method to perform the CI-NEB calculations.

Computing the diffusion behavior of ionic charge carriers is paramount for understanding the chemical and physical properties of materials. To this end, one widely used approach is the Ab initio molecular dynamics (AIMD) simulation method, which accurately estimates the dynamics and energetics of atoms and molecules based on first principles calculations. In the present study, AIMD simulations are employed to investigate the diffusion behavior of ionic charge carriers under non-spin-polarized calculation conditions. To optimize computational efficiency, we lowered the energy cutoff to 300 eV. Moreover, for Chapter 5.2, to facilitate the diffusion of Li<sup>+</sup>, an important ionic species, we performed AIMD
simulations at a fixed temperature of 500 K, below the melting temperature of CMC. The NVT ensemble using a Nosé–Hoover thermostat was utilized to control the temperature for a duration of 60 ps, which allowed for the collection of sufficient statistical data for subsequent analysis.[67] For the study of the AIMD simulation data, we employed the Python Materials Genomics package (pymatgen) to perform probability density analysis.[68,69] Probability density is a fundamental quantity that characterizes the likelihood of finding an atom or molecule at a given location in space. Specifically, we visualized the probability density as a yellow isosurface with a value of 0.001, which allowed for the visualization of the paths followed by the ionic charge carriers during diffusion..

### 2.1.5 Defect Formation Energy

The main parameter of interest is the defect formation energy,  $E_f[X^q]$ , representing the energy required to generate an isolated defect, X, within a host material. In the dilute limit, the formation energy of an individual defect is dependent on the defect's charge state, q. This can be determined through DFT supercells using:[70]

$$E_f[X^q] = E_{defect}[X^q] - E_{perfect} - \sum_i n_i \mu_i + q(E_F + E_V + \Delta V_0) + E_{corr}$$
(2.7),

where  $E_{defect}[X^q]$  and  $E_{perfect}$  represent the defected and pristine structure's energy, respectively.  $n_i$  and  $\mu_i$  are the number of atoms of type *i* that have been added (positive) or removed (negative) and the chemical potential of species *i*, respectively. q,  $E_F$ ,  $E_V$ ,  $\Delta V_0$ , and  $E_{corr}$  represent the defect's charge state, the Fermi level, the maximum valence band of the defect-free structure, a term for aligning the electrostatic potentials of the pristine and defective structures, and a corrective term for non-zero charges in a periodic system, respectively. The Makov-Payne approach has been adopted for the correction term among various computational schemes.[71] In Chapter 5.1, the reference energy for an individual Li atom is derived from bulk body-centered cubic Li metal.

### 2.1.6 Crystal Field Theory

The investigation of cathode materials in transition metal coordination complexes necessitates the utilization of CFT, which was first introduced by H. Bethe and later advanced into the ligand field theory by J.H. Van Vleck. The CFT postulate fundamentally asserts that the interactions between transition metal ions and their corresponding ligands are predominantly dictated by electrostatic forces, wherein the ligands are conveniently represented as point charges to facilitate the modeling and analysis of such interactions.[72,73]

The central focus of this dissertation is the application of CFT in the octahedral field, which is particularly relevant for investigating cathode materials in LIBs and SIBs. In these materials, metal ions are surrounded by six oxygen ions in octahedral sites. As depicted in Figure 2.1, the energy levels are divided into two sets of orbitals, commonly referred to as  $e_g$  and  $t_{2g}$  bands, which are split by the crystal field. Stabilizing coordination geometries' crystal fields holds a vital role in the redox mechanism of transition metals and oxygen. Electronic structure analysis is performed to determine the occupied and unoccupied electrons, using projected partial density of states (PDOSs) profiles calculated by DFT.



Figure 2.1 Energy levels of *d*-orbitals in spherical and octahedral fields: The five initially degenerate *d*-orbitals separate into two groups, known as the  $e_g$  and  $t_{2g}$  bands, due to crystal field splitting

## 2.2 Single Particle Scale

### 2.2.1 Electro-Chemomechanical Phase Field Model

The electro-chemomechanical phase field model, which incorporates firstprinciples calculations, examines the kinetics of phase separation, chemical potentials, and mechanical properties. All mixing enthalpies are calculated by considering the various A/vacancy configurations as Equation (2.2) to facilitate the transmission of first-principles calculations results to the electro-chemomechanical phase field model.

To investigate the electro-chemomechanical behavior using theoretically calculated thermodynamic data, a double-well polynomial function is employed to fit the mixing enthalpies of both the ground-state and pseudo-ground state within the solid-solution region ranging from  $x_i$  to  $x_f$  as follows:[41,74,75]

$$\Delta \mathcal{H}_{mix}^{CP} = \Omega (x - x_i)^2 (x - x_f)^2$$
(2.8),

where  $\Omega$  is the enthalpy coefficient. By utilizing the mixing enthalpies obtained through the fitting process using the double-well polynomial function, the homogeneous free energy,  $\mathcal{F}_{homo}$ , and chemical potential,  $\mu_{homo}$ , are determined. This is achieved by considering the configurational entropy as follows:[41]

$$\mathcal{F}_{homo} = \Delta \mathcal{H}_{mix}^{CP} + 2k_B T \{ x \ln x + (1-x) \ln(1-x) \}$$
(2.9),

$$\mu_{homo} = -\frac{\partial \mathcal{F}_{homo}}{\partial x} \tag{2.10},$$

where  $k_B$  and T represent the Boltzmann constant and absolute temperature, respectively.

In addition, to investigate the mechanical behavior during phase separation, the elastic energy,  $\mathcal{F}_{el}$ , is computed based on first-principles calculations of the constitutive tensor,  $C_{ijkl}$ , and the eigen-strain,  $\varepsilon_{ij}^{0}(x)$ , as follows:

$$\mathcal{F}_{el} = \frac{1}{2} \mathcal{C}_{ijkl} \varepsilon_{ij}^{el} \varepsilon_{kl}^{el} \tag{2.11},$$

$$\varepsilon_{ij}^{el} = \frac{1}{2} \left( u_{i,j} - u_{j,i} \right) - \varepsilon_{ij}^{0}(x)$$
(2.12),

where the elastic strain,  $\varepsilon_{ij}^{el}$ , is the total strain,  $\frac{1}{2}(u_{i,j} - u_{j,i})$ , subtracted by the eigenstrain,  $\varepsilon_{ij}^0(x)$ .

To obtain a solution for the electro-chemomechanical phase field model, the total free-energy functional,  $E_{free}$ , is defined as follows:

$$E_{free} = \int_{V} \left\{ \rho_n \left( \mathcal{F}_{homo} + \frac{\kappa}{2} |\nabla x|^2 \right) + \mathcal{F}_{el} \right\} dV$$
(2.13),

where  $\rho_n$  represents the density of the charge carrier ions' sites, and the parameter  $\kappa$  denotes the gradient energy coefficient.[76] To determine the ionic charge carrier concentration equilibrium phase transition and stress equilibrium, the Cahn-Hilliard and the mechanical equilibrium equations are solved based on the total free-energy

functional, respectively. These calculations are performed under periodic boundary conditions and can be expressed as follows:

$$\frac{\partial x}{\partial t} = \nabla \cdot \left( M \nabla \frac{\delta E_{free}}{\rho_n \delta x} \right) \tag{2.14},$$

$$\sigma_{ij,j} = 0 \tag{2.15},$$

where *M* denotes the mobility of the ionic charge carrier, while the symbol  $\sigma_{ij}$  represents the elastic stress that arises from lattice mismatch during the phase transition process. Neglecting the elastic energy, the total free-energy functional is defined as follows:

$$E_{free} = \int_{V} \left\{ \rho_n \left( \mathcal{F}_{homo} + \frac{\kappa}{2} |\nabla x|^2 \right) \right\} dV$$
(2.16),

by neglecting the elastic energy, Equation (2.10) is solved to identify the ionic charge carrier's equilibrium phase transition. The semi-implicit Fourier-spectral method was utilized to solve the Cahn-Hilliard equation,[77] while the finite element method was employed to solve the mechanics equilibrium equation. Moreover, the physical quantities of time, length, and energy were non-dimensionalized using  $D/\lambda$ ,  $\lambda$ , and  $k_BT$ , where D represents the diffusion coefficient and  $\lambda$  is the characteristic length.

### 2.2.2 Kinetic Monte Carlo

The kMC is a computational method employed for modeling the dynamic evolution of intricate systems with many interacting entities, such as molecules or particles. It is beneficial for studying the dynamics of materials at the atomic or molecular scale. The kMC algorithm typically defines a set of reaction rules and corresponding rate constants for the system. These rules can be based on experimental data or theoretical calculations and may be refined as the simulation progresses. The simulation is carried out over many time steps, allowing the system to reach a steady state or equilibrium.

Compared to DFT, the kMC approach offers a computationally efficient alternative for simulating systems characterized by many interacting entities. This heightened efficiency enables exploring larger-scale systems, which may be prohibitively complex or computationally demanding for DFT-based methods. Moreover, the kMC method facilitates the elucidation of the fundamental mechanisms governing the behavior of intricate systems, thus empowering researchers to understand how alterations in reaction rules and rate constants impact the overall system dynamics. Therefore, the kMC method is adopted for computing Li<sup>+</sup> diffusion features in complex structures in Chapter 5.2.[67,78] For Chapter 5.2, the overall diffusion characteristics of Na-CMC at a macroscopic level were investigated using the kMC method. To accomplish this, the predicted Li<sup>+</sup> diffusion path in Na-CMC and LSM-CMC was taken into account, and a kMC model was constructed, allowing for nearest neighbor diffusion and periodic boundary conditions. A detailed compilation of potential Li<sup>+</sup> diffusion events and their respective frequency of occurrence was determined using DFT calculations. The microscopic rate constants for each individual diffusion processes i were then calculated by considering the DFT diffusion barriers,  $\Delta E_a$ , as follows:

$$k_i = k_0 exp(-\Delta E_a/k_B T) \tag{2.17},$$

where  $k_0$  is the attempt frequency and  $\Delta E_a$  represents the energy barrier associated with the process *i*.

To initiate the kMC simulation, a single interstitial Li atom was randomly placed within the periodic cell, as interstitial diffusion of Li<sup>+</sup> was the primary diffusion mechanism under consideration. The cumulative probability of all conceivable Li<sup>+</sup> diffusion scenarios in the system was then assessed by summing up all individual diffusion rates, represented as  $R_{tot} = \sum_i k_i$ . A specific diffusion event, *p*, was then selected based on its probability, which was determined using a formula as follows:

$$\sum_{i=0}^{p-1} k_i < rR_{tot} < \sum_{i=0}^{p} k_i$$
(2.18),

where *r* is a random number uniformly distributed between 0 and 1. The physical time evolution was then computed based on this selected diffusion event as follows:  $\Delta t = -\ln(r') / R_{tot}$ (2.19),

where r is another uniform random number between 0 and 1.

To calculate the macroscopic diffusion constant of the Li atom, the mean square displacement of the atom was utilized as follows:

$$D = \lim_{t \to \infty} \frac{\langle [r(t) - r(0)]^2 \rangle}{2dt}$$
(2.20),

where d is the system dimension, t indicates the total physical time, and r(t) represents and the location of the Li atom at a given time t. To determine the mean square displacement of the Li atom, 1000 samples were calculated for each case using the ensemble average. The macroscopic diffusion constant obtained from the kMC simulations was then used to fit the Arrhenius expression, allowing for the acquisition of the associated macroscopic diffusion activation energy,  $E_a$ .

$$D = D_0 \exp\left(-E_a/k_B T\right) \tag{2.21}$$

## 2.3 Microstructure Scale

FEA is a powerful numerical technique employed for solving complex problems in engineering and physics by discretizing continuous domains into a finite number of more minor, interconnected elements. Utilizing mathematical models and equations that describe the underlying physical behavior of the system, FEA provides an approximation for solving the partial differential equations that govern the problem. By subdividing the domain into a mesh composed of elements and nodes and employing interpolation functions to match the unknown variables within each element, the method effectively transforms the continuous problem into a discrete system of algebraic equations. FEA is widely applied in various fields, including structural analysis, heat transfer, fluid dynamics, and electrochemistry, allowing researchers and engineers to predict and optimize the performance, stability, and reliability of designs and materials under various conditions.[79]

To model the alterations in the number of ionic charge carriers and the consequent mechanical response in cathode host materials throughout the charging or discharging of charge carrier ions, FEA utilizes the COMSOL Multiphysics software, which incorporates the MUMPS time-dependent solver, are employed.[44] To facilitate the simulation of a secondary particle with a spherical shape for Chapter 4.3, a 2D circular model consisting of multiple primary particles possessing random shapes and orientations is constructed through the Voronoi tessellation method (Figure 2.2),[80] which allowed for a more feasible approach. The specific model parameters implemented in FEA are provided in Table 2.1.



**Figure 2.2 Illustration of primary and secondary particles** 

Parameter		Value
Particle radius		5 µm
Maximum Na concentration		58418 mol/m <sup>3</sup>
Na diffusivity along the <i>ab</i> -plane		$7x10^{-15} \text{ m}^2/\text{s}$
Na diffusivity along the <i>c</i> -lattice direction		$7x10^{-16} \text{ m}^2/\text{s}$
Elastic constants	C <sub>11</sub>	222 GPa
	C <sub>12</sub>	77 GPa
	C <sub>13</sub>	36 GPa
	C <sub>33</sub>	245 GPa
	C <sub>44</sub>	26 GPa
	C <sub>66</sub>	72.5 GPa

#### Table 2.1 Parameters used in the finite element analysis

The dynamics of charge carrier ions diffusion are ascertained through the application of Fick's law, a fundamental principle governing the kinetics of mass transport phenomena, as follows:

$$\frac{\partial c}{\partial t} = \left[ D_{ij} c_{,j} \right]_{,i} \tag{2.22},$$

where *c* and  $D_{ij}$  indicate the ionic charge carrier concentration and diffusivity, respectively. To accurately represent the anisotropic diffusion kinetics of sodium ions within the Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> (NMNO) material, it is crucial to consider the varying diffusivity in different crystallographic planes. Specifically, the diffusivity in the *ab* plane was found to be an order of magnitude greater (i.e., ten times higher) than that along the *c* direction. The initial concentration of charge carrier ions was established based on the maximum concentration derived from the first-principles atomic model, which provides a theoretically informed starting point for the simulation. Furthermore, to ensure a realistic simulation of the system, a concentration boundary condition that remains constant for charge carrier ions, equal to 20% of the maximum concentration (0.2  $c_{max}$ ), was applied to the surface of the secondary particle. This

boundary condition is depicted in Figure 2.3. By accounting for the anisotropic nature of charge carrier ion diffusion and imposing appropriate boundary conditions, the simulation is better equipped to capture the complex behavior of the system and provide valuable insights into the underlying mechanisms that control ion transport in NMNO materials.



Figure 2.3 Concentration of Na ions for (a) the randomly oriented and (b) the radially oriented shape secondary particles at  $c/c_{max} \approx 1.0$ 

To investigate the mechanical behavior resulting from alterations in the anisotropic lattice structure during the charging process, it is imperative to compute the lattice strain,  $\varepsilon_{ij}^0(c)$ , for each lattice direction. Subsequently, the associated elastic strain,  $\varepsilon_{ij}^{el}$ , is ascertained under the following methodology:

$$\varepsilon_{ij}^0(c) = \frac{l(c) - l_0}{l_0} \tag{2.23},$$

$$\varepsilon_{ij}^{el} = \frac{1}{2} \left( u_{i,j} - u_{j,i} \right) - \varepsilon_{ij}^0(c)$$
(2.24),

where l is the lattice parameter during the deintercalation of charge carrier ions and  $l_0$  denotes the initial lattice parameter. The governing equation employed to delineate the relationship between stress and strain within the material system is formally specified as follows:

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \tag{2.25},$$

where  $\sigma_{ij}$  is the elastic stress that arises because of the anisotropic lattice deformation occurring throughout the charging process, and  $C_{ijkl}$  is the elastic property of the NMNO material, determined through the utilization of first-principles computational techniques. The mechanical characteristics of the secondary particle is governed by the equation of momentum equilibrium, Equation (2.15). Regarding the boundary conditions for momentum equilibrium, the surface of the secondary particle was subject to a traction-free condition. At the central area of the secondary particle, a zero-displacement constraint was applied.

# Chapter 3 Phase-transition Kinetics and Thermodynamics

# 3.1 Thermodynamic Phase Stability of Na<sub>1-x</sub>MnO<sub>2</sub> and Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>

To effectively utilize anion-based redox reactions in binary layered oxides for sodium-ion batteries, two strategies have been proposed: (i) stabilizing the electronic structures of redoxable transition metals and (ii) optimizing the involvement range of the oxygen redox reaction. These strategies aim to enhance and improve the electrochemical performance of cathode materials. A comprehensive understanding of phase-separation kinetics and thermodynamic phase stability is crucial to devise a viable redox mechanism that counterbalances the charge imbalance resulting from Na-extraction. The ability of cathode materials to retain capacity is significantly influenced by their thermodynamic phase stability during the removal of Na<sup>+</sup> ions. It is important to note that these thermodynamic phenomena manifest more prominently during (de)intercalation processes in SIBs compared to LIBs, due to the larger dimensions of Na<sup>+</sup> ions .



Figure 3.1 Energies of formation considering the enthalpy of mixing for Na ions and their vacancies dependent on the inverse Na content (x) in (a) Na<sub>1-x</sub>MnO<sub>2</sub> and (b) Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> oxides, partitioned into four regions (1<sup>st</sup>  $0 \le x \le 0.25$ , 2<sup>nd</sup>  $0.25 \le x \le 0.5$ , 3<sup>rd</sup>  $0.5 \le x \le 0.75$ , and 4<sup>th</sup>  $0.75 \le x \le 1.0$ ). Combined profiles of partial density of states (PDOSs) of Mn and Ni 3*d*-electron and O 2*p*-electron at x = 0.0 and 1.0 in (c-d) Na<sub>1-x</sub>MnO<sub>2</sub> and (e-f) Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> oxides. The previous paper provided data on the mixing enthalpy values and PDOS for the Mn-Ni binary compound[22]



Figure 3.2 The energy disparities between the antiferromagnetic and ferromagnetic configurations of the ground states (x = 0.0, 0.25, 0.5, 0.75, and 1.0) for Na<sub>1-x</sub>MnO<sub>2</sub>



Figure 3.3 The ground states configurations of  $Na_{1-x}MnO_2$  (upper) and  $Na_{1-x}[Mn_{1/2}Ni_{1/2}]O_2$  (lower) following the desodiation process



Figure 3.4 Calculated desodiation potentials of  $Na[Mn_{1/2}Ni_{1/2}]O_2$  and the experimentally recorded charge profile replicated from Ref.[81,82]

Reexamining the thermodynamic phase stability of NaMnO<sub>2</sub> (NMO) and Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> (NMNO) during the Na-extraction process was carried out derived from a phase diagram of a binary mixture that accounts for fully (de)sodiated phases. Figures 3.1a and b depict the formation energy of mixing enthalpy ( $\Delta Hmix$ ) as a function of vacancy (x) concentration in  $Na_{1-x}MnO_2$  and  $Na_{1-x}[Mn_{1/2}Ni_{1/2}]O_2$ , covering the entire range of  $0 \le x \le 1$ . The ground state structure for NMNO was determined using a supercell of binary mixtures with a 2 x 2 x 1 configuration consisting of eight formula units of P2-layered NaNiO<sub>2</sub> and NaMnO<sub>2</sub>. In this specific configuration of atoms, the transition metal layer comprises octahedral  $MnO_6$  or NiO<sub>6</sub>, while the interlayer consists of prismatic NaO<sub>6</sub> structures. In the thermodynamic calculations, various atomic structures were considered for Na[Mn<sub>1</sub>.  $v_{\rm Ni}$  [O<sub>2</sub> by varying the Ni content (v). This approach allowed for considering every potential arrangement of Mn and Ni octahedral sites in the transition metal layer, as per the given scale.[22] To determine the structures of the two Mn-based compounds in their ground state during the desodiation process, the mixing enthalpy values were computed by incorporating every conceivable combination of Na ions and their vacancies in the respective oxides. It is worth noting that for  $Na_{1-x}MnO_2$ , magnetic spin ordering was taken into account, as the energetically favorable spin ordering depends on the Na content (Figure 3.2).[83] To account for thermodynamics, the atomic configurations with the lowest energy were identified as the ground states (represented by red-filled circles) and pseudoground states (represented by grayfilled circles) for each vacancy content in the two Mn-based compounds. The configurations of the ground states in Na<sub>1-x</sub>MnO<sub>2</sub> and Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> can be found in Figure 3.3. While the convex-hulls in the results represent 0 K conditions, the voltage profile obtained from the mixing enthalpy formation energy shows good

agreement with experimental findings. This suggests that the convex-hulls efficiently capture the phase-transition trends (Figure 3.4). Using a phase diagram of the binary mixture, the energy diagrams were classified into four regions (1<sup>st</sup>:  $0 \leq$  $x \le 0.25, 2^{\text{nd}}: 0.25 \le x \le 0.5, 3^{\text{rd}}: 0.5 \le x \le 0.75, \text{ and } 4^{\text{th}}: 0.75 \le x \le 1.0)$ to systematically compare NMO and NMNO. The ground states located on the tie line between x = 0.0 and 0.25 in Na<sub>1-x</sub>MnO<sub>2</sub> indicate the initiation of the initial twophase reaction induced by the initial Na-extraction. A comparable phase response was noted for  $Na_{1-x}[Mn_{1/2}Ni_{1/2}]O_2$  within the same range. In the second section, spanning from x = 0.25 to 0.5, both NMO and NMNO cathodes undergo two-phase reactions. Further extraction of Na results in a third two-phase reaction, progressing until 0.75 Na is depleted from the structures of NMO and NMNO. Notably, distinct phase stability was observed in the third region, characterized by two ground states situated on the tie line between x = 0.5 and x = 0.75 in terms of thermodynamics. The solubility of vacancies in Na<sub>1-x</sub>MnO<sub>2</sub> increases until x = 0.5 but decreases beyond the inflection point (x = 0.5). This implies that the Na<sub>1-x</sub>MnO<sub>2</sub> exhibits an increase in relative phase stability as the vacancy content varies from 0 to 0.5, and the phase stability diminishes with subsequent Na-extraction for x > 0.5. Similarly, in Na<sub>1</sub>.  $_{x}$ [Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>, the mixing enthalpy value indicates that the solubility of vacancies steadily rises with amount of vacancies until x = 0.5, similar to NMO. However, the solubility continues to increase even when 0.25 Na is further extracted from the cathode (0.5  $\leq x \leq$  0.75). Consequently, it is expected that thermodynamic phase instability arises following the inflection point (x = 0.5) in Na<sub>1-x</sub>MnO<sub>2</sub>, whereas it occurs when the vacancy content surpasses (x = 0.75) in Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>. In the x = 0.75 to 1.0 range, NMO exhibits a subsequent fourth two-phase reaction,

transitioning into the Na-non phase (at x = 1.0) and Na-poor phase (at x = 0.75) exhibiting diminished phase stability. This phase response differs from its Ni-mixed binary counterpart, Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>, where the existence of a ground state at x =0.875 indicates the emergence of a new phase. This extension enables a more logical utilization of Na content during charge/discharge processes. It is worth noting that the extended charge plateaus that stem from the anionic redox reaction involving lattice oxygen at high voltages during the initial charge process do not persist throughout subsequent discharge processes. [23,84,85] Consequently, a significant voltage hysteresis accompanied by distinctive variations in the electrochemical charge curve were noted. However, it is expected that the prominent Na-poor phase at x = 0.875 acts a crucial function in facilitating an anionic redox reaction involving lattice oxygen and a charge-discharge plateau that exhibits reversible behavior and minimal voltage hysteresis. This behavior resembles that of Li-doped Mn-layered oxides. While Na and vacancy orderings primarily influence the phase transition, changes in the arrangement of layers in the interlayer stack have minimal impact on the presence of the Na-poor phase at x = 0.875 in Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>. This is because Na and vacancy orderings exert greater control the phase-transition kinetics than changes in the sequence of interlayer stacking (Figures 3.5a and b). Furthermore, it is noteworthy that the Na-poor phase, with its essential role, remains consistent, and the phase-transition kinetics of both NMO and NMNO exhibit coherence, even when considering the transition between stacking sequences of P2- and O2-layers (Figure 3.5). Examining the unique convex-hull properties of the two Mn-based compounds, it can be observed that the thermodynamic phase stability in highly desodiated phases is more resilient in NMNO compared to NMO. However, for a better understanding of the electrochemical stability and performance of the binary oxide

over repeated cycles, a more comprehensive assessment of thermodynamic phase stability, including the pseudoground states, is required, aiming to enhance the rational utilization of the single-phase at x = 0.875 in Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> compared to traditional Mn layered cathodes.



Figure 3.5 Formation energies involving both Na/ $\Box$  orderings and interlayer stacking modifications (P2- or O2-stacking) dependent on the inverse Na content (x) for (a) Na<sub>1-x</sub>MnO<sub>2</sub> and (b) Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> oxides in the anion-redox-related regions (3<sup>rd</sup> 0.5  $\le$  x  $\le$  0.75, and 4<sup>th</sup> 0.75  $\le$  x  $\le$  1.0). Atomic structure of P2- or O2-stacking for (c) Na<sub>1-x</sub>MnO<sub>2</sub> and (d) Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> at x = 0.75

Furthermore, gaining insights into the thermodynamic stability of phases during the charging process necessitates a thorough investigation of the redox process in the two compounds. Figures 3.1c-f illustrates the collective profiles of the PDOSs for Mn and Ni 3*d*-electrons and O 2*p*-electrons derived from fully sodiated and desodiated Na<sub>1-x</sub>MnO<sub>2</sub> and Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> at x = 0.0 and 1.0, respectively. The PDOSs of Na<sub>1-x</sub>MnO<sub>2</sub> spanning from x = 0.0 to 1.0 indicate that a single cationic redox reaction involving  $Mn^{3+}/Mn^{4+}$  occurs across the entire range of  $0 \le x \le 1$ based on the energetics derived from crystal field theory (Figure 3.1c and d). Conversely, Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> exhibits a cationic redox process with two steps involving Ni<sup>2+</sup>/Ni<sup>4+</sup> from x = 0.0 to 0.75, as well as anionic redox reactions emerge from the lattice oxygen (O<sup>2</sup>/O<sup>-</sup>) above x = 0.75 to compensate for the charge associated with Na-extraction. These redox reactions were extensively investigated in a previous study.[22] The thermodynamic energy diagrams show two well-defined inflection points, occurring at x = 0.75 for Na<sub>1-x</sub>MnO<sub>2</sub> and at x = 0.75 for Na<sub>1-x</sub>  $_{x}[Mn_{1/2}Ni_{1/2}]O_{2}$ , indicating the occurrence of single and cumulative redox reactions during the charging process. In the case of the NMO cathode, it is anticipated that the symmetry of the thermodynamic convex-hull in Na<sub>1-x</sub>MnO<sub>2</sub> is primarily dictated by the free energy of mixing, which encompasses the effect of temperature and the alteration in configurational entropy for an ideal solution when  $\Delta Hmix = 0$ . However, for the NMNO compound, an asymmetrical feature is observed in the thermodynamic convex hull, characterized by the inflection point at x = 0.75 deviates from the theoretical free diagram.[86] We hypothesize the presence of this asymmetrical feature arises from the occurrence of the cationic double redox reaction involving Ni<sup>2+</sup>/Ni<sup>4+</sup> and the existence of the Na-poor phase, which pushes the characteristic point of inflection (x = 0.5) observed in AMO<sub>2</sub> compounds to a higher desodiated phase (x = 0.75) in the binary oxide containing Ni and Mn.

# 3.2 Phase-transition and -kinetics of Na<sub>1-x</sub>MnO<sub>2</sub> and Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>

From a thermodynamic perspective, the transition barrier in the consistent free energy profile denotes the extent of phase instability and the impetus of the phase shift, which is a consequence of the variances in enthalpy during the mixing of pseudoground and actual ground states. Consequently, utilizing the mixing enthalpy during formation quantities at minimal-energy arrangements (Figure 3.1), we performed computations on the unvarying mass free energy ( $\mathcal{F}_{homo}$ ) to provide a qualitative thermodynamical analysis of the phase stability and its respective kinetics for both NMO and NMNO throughout the charging procedure. Figures 3.6a and b present the homogeneous free energy categorized into four regions as per the content (x) in Na<sub>1-x</sub>MnO<sub>2</sub> and Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>, across the complete spectrum (0.0  $\leq x$  $\leq$  1.0) at 300 K, correspondingly. The energy representations display comparable phase actions to the convex hull forecasts of the duo cathodes, demonstrated in Figure 3.1. To facilitate a more detailed contrast, the homogeneous free energies are portrayed individually in the four unique sectors (Figures 3.6c-f). Each characteristic region is further divided into the spinodal decomposition area as per the spinodal instability definition,  $\frac{\partial^2 \mathcal{F}_{homo}}{\partial x^2} < 0$  (Na<sub>1-x</sub>MnO<sub>2</sub>: light blue and Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>: light magenta). From the 1<sup>st</sup> to 3<sup>rd</sup> region, the extent of each spinodal decomposition area for NMNO resembles that of NMO. This suggests that both cathode materials share similarities regarding the range of thermodynamic phase-instability. However, a distinct threshold characteristic is apparent in the free energies between Na<sub>1-x</sub>MnO<sub>2</sub> and Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>. Figures 3.7a and b depict meticulously adjusted formation

enthalpies derived from first-principle computations using a quadratic double-well function. In the 1<sup>st</sup> region, a noticeably elevated phase-transition enthalpy barrier value was discerned for Na<sub>1-x</sub>MnO<sub>2</sub> (0.0  $\leq x \leq$  0.25) in comparison to Na<sub>1-x</sub>  $x[Mn_{1/2}Ni_{1/2}]O_2$  (0.0  $\leq x \leq 0.25$ ). This implies that the intermediary phase in Na<sub>1-</sub> <sub>x</sub>MnO<sub>2</sub> exhibits less stability than in Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>. Given these findings, it can be predicted that pure Mn oxide undergoes a faster phase-transition activity than Mn-Ni oxide, primarily because the magnitude of the phase-transition barrier significantly influences the phase-transition kinetics.[87] Nonetheless, the converse trend was observed in the 2<sup>nd</sup> and 3<sup>rd</sup> regions, with their respective enthalpy barriers depicted in the corresponding figures. Considering the characteristics of the enthalpy barriers in the two oxides, the free energy values at 300 K suggest that a swifter phase-transition is likely to occur for NMNO as compared to NMO over a larger region (0.25  $\leq x \leq$  0.75) during the (dis)charging process. Even though the degree of thermodynamic phase instability is akin for both compounds, NMNO is relatively more susceptible to faster phase-transition over a larger region (0.25  $\leq x$  $\leq$  0.75), leading to more rapid and substantial capacity degradation during cycling.

In the 4<sup>th</sup> region, however, NMO and NMNO display divergent behaviors regarding phase instability and phase-transition (Figure 3.6f). NMO exhibits the spinodal decomposition area concurrent with the phase-transition barrier, leading to the phase separation reaction showcasing the Na-depleted phase (x = 1.0) evolution resulting from the Na-deficient (x = 0.75) phase in the oxide. Conversely, a Nadepleted phase at x = 1.0 does not evolve for NMNO, attributable to the thermodynamically stable HN-deficient phase at x = 0.875. Given the anionic redox reaction for NMNO in the sodium-deficient area, the thermodynamically stable HN- poor phase is likely to facilitate the reversible anion-triggered redox reaction with minimal voltage hysteresis observed during the initial charging and subsequent discharging stages. This is due to the rapid escalation of voltage hysteresis as the vacancy content in cathode materials increases. This HN-poor phase is considered a crucial part for the segregation reaction transitioning from P2 to O2, which stems from the anionic redox reaction caused by lattice oxygen in the Mn–Ni compound. This observation aligns with experimental findings and suggests the potential for reversibly applying redox processes with anions by strategically employing the HN-poor phase.



Figure 3.6 Homogeneous bulk free energy,  $\mathcal{F}_{homo}$ , of (a) NaMnO<sub>2</sub> and (b) Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> at room temperature varies with the inverse Na content *x*, exhibiting four distinct characteristic regions. The comparison of NaMnO<sub>2</sub> (upper graph) and Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> (lower graph) in different regions is depicted in (c-f), with the colored areas (light blue: NaMnO<sub>2</sub>, light magenta: Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>) indicating the regions of spinodal decomposition



Figure 3.7 The combined-phase mixing enthalpy, obtained by fitting the ground/pseudo-ground states from first-principles formation energies of mixing enthalpy, is shown for (a) NaMnO<sub>2</sub> and (b) Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> in Figures 3.1a-b using the quadratic double-well function

The kinetic aspects of the phase-transition were investigated using phase-field simulations to extrapolate the outcomes of atomistic computations to the nano-scale. Figure 3.8 illustrates the color contours representing the phase changes in both cathode materials, depicted in the upper (NMO) and lower (NMNO) row of graphs, respectively, corresponding to each region  $(1^{st}: (a) \text{ and } (e), 2^{nd}: (b) \text{ and } (f), 3^{rd}: (c)$ and (g), 4<sup>th</sup>: (d) and (h)). The simulations for phase transitions were assessed at the midpoint concentration of each region, and all observable properties were rendered dimensionless using characteristic values for precise comparisons. As per the homogeneous bulk free energy findings, NMNO demonstrates a conspicuous phasetransition relative to NMO in the same non-dimensional time in each region. To further clarify, snapshots taken at each part during the non-dimensional time for both cathodes are depicted in Figures 3.9–12, thereby highlighting a more rapid phasetransition for  $Na_{1-x}[Mn_{1/2}Ni_{1/2}]O_2$  compared to  $Na_{1-x}MnO_2$  in the region where 0.25  $\leq x \leq 0.75$ , and the inverse behavior is evident in the range  $0.0 \leq x \leq 0.25$ . In the 4<sup>th</sup> region, nevertheless, NMNO does not demonstrate a transition to the Nadepleted phase (at x = 1.0) during the charging process, which corroborates the solid presence of the HN-deficient phase. This HN-deficient phase for NMNO becomes thermodynamically stable without undergoing any additional phase changes, suggesting a considerable degree of reversibility of the redox reaction involving anions.



Figure 3.8 Contours illustrating the kinetics of phase transitions for (a-d) NaMnO<sub>2</sub> and (e-h) Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> in four distinct characteristic regions at various representative non-dimensional times  $\hat{t}$  (1<sup>st</sup> region:  $\hat{t} = 0.20$ , 2<sup>nd</sup> region:  $\hat{t} = 0.40$ , 3<sup>rd</sup> region:  $\hat{t} = 0.60$ , 4<sup>th</sup> region:  $\hat{t} = 0.80$ )



Figure 3.9 Contours illustrating the kinetics of phase transitions for (a-e) NaMnO<sub>2</sub> and (f-j) Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> in 1<sup>st</sup> region at various representative nondimensional times  $\hat{t}$  ( $\hat{t} = 0.00, 0.20, 0.40, 0.60, \text{ and } 0.80$ )



Figure 3.10 Contours illustrating the kinetics of phase transitions for (a-e) NaMnO<sub>2</sub> and (f-j) Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> in the 2<sup>nd</sup> region at various representative non-dimensional times  $\hat{t}$  ( $\hat{t} = 0.00, 0.20, 0.40, 0.60, \text{ and } 0.80$ )



Figure 3.11 Contours illustrating the kinetics of phase transitions for (a-e) NaMnO<sub>2</sub> and (f-j) Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> in the 3<sup>rd</sup> region at various representative non-dimensional times  $\hat{t}$  ( $\hat{t} = 0.00, 0.20, 0.40, 0.60, \text{ and } 0.80$ )



Figure 3.12 Contours illustrating the kinetics of phase transitions for (a-e) NaMnO<sub>2</sub> and (f-j) Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> in the 4<sup>th</sup> region at various representative non-dimensional times  $\hat{t}$  ( $\hat{t} = 0.00, 0.20, 0.40, 0.60, \text{ and } 0.80$ )

# 3.3 Voltage Hysteresis of Na<sub>1-x</sub>MnO<sub>2</sub> and Na<sub>1-x</sub> x[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>

At equilibrium, all active particles within a given electrode should exhibit identical chemical potential. Consequently, the chemical potential of multiple active particle systems adheres to the local crests/troughs of the chemical potential of individual particles during the charging and discharging process. Considering  $U = \frac{-\mu}{e} + U_0$ , where U represents the cell voltage, and  $U_0$  signifies the fundamental cell voltage, the difference in the chemical potential hysteresis provides a qualitative measure of the degree of polarization in the electrochemical process. This critical aspect allowed us to compute the chemical potential ( $\mu_{homo}/e$ ) to gain a qualitative

comprehension of the relationship between phase-transition and voltage hysteresis. Consequently, using the homogeneous bulk free energy, we computed the chemical potential at a temperature of 300 K. Figures 3.13a and b depict the variation of chemical potential with respect to the content (x) in Na<sub>1-x</sub>MnO<sub>2</sub> and Na<sub>1</sub>.  $x[Mn_{1/2}Ni_{1/2}]O_2$  across the full range ( $0.0 \le x \le 1.0$ ) at 300 K, respectively. In general, NMNO demonstrates a chemical potential landscape that exhibits more fluctuations than NMO in the broader regions where the transition between phases happens ( $0.25 \le x \le 0.75$ ). This suggests that the binary oxide containing Mn and Ni experiences an escalating voltage hysteresis, decreasing the efficiency of electrochemical energy as the cycle progresses. For a comprehensive assessment, the chemical potential is individually represented in the four regions of transition, as shown in Figures 3.13c–f. The colored areas indicate the disparity between the crest and trough values of the chemical potential. In the 1<sup>st</sup> region, NMO displays a marginally more significant chemical potential hysteresis than NMNO. However, in the  $2^{nd}$  to  $3^{rd}$  regions, hysteresis in the chemical potential greater than approximately 0.1 V is observed for NMNO. This implies that NMNO might exhibit relatively lower electrochemical efficiency in areas where phase transitions occur more quickly. In contrast, for the 4<sup>th</sup> region, NMNO displays absence of hysteresis in the thermodynamic chemical potential due to the presence of the HN-poor phase at x =0.875, indicating the potential to maintain its voltage with reduced polarization during the anionic redox reaction region. Ordinarily, cathode materials based on layered structures leveraging redox processes with anions exhibit substantial voltage discrepancy, resulting in poor electrochemical efficiency. Though, recent research indicates the potential to diminish polarization by managing the structural composition or phase state of sodium-layered oxides.[88,89] The phase separation, which manifests as a narrowing of the area where spinodal decomposition occurs, has been experimentally shown to have a considerable effect in mitigating voltage hysteresis in  $Na_r[Li_{0.2}Mn_{0.8}]O_2$  and aligns with the comparison of chemical potential for NMNO in qualitative terms .[89] In conclusion, the distinctive HN-poor phase in NMNO allows for a greater capacity attributed to anionic redox processes, with reduced phase instability in ongoing charging/discharging cycles. Thus, by judiciously controlling the HN-poor phase in NMNO, where minimal polarization occurs, the reversible utilization of the anionic redox reaction enables us to achieve high energy density and electrochemical efficiency.

In light of our findings, we propose two rules for designing materials to effectively leverage the joint redox reaction of cationic and anionic species in Mnbased binary layered cathode materials. Firstly, from the viewpoint of phasetransition kinetics, enhancing the solubility of vacancies within the materials undergoing the redox reaction centered around cations could retard the reaction involved in the phase change towards Na-rich and Na-poor phases through cycling, leading to improved cycle performance. Secondly, thoughtful application of the HNpoor phase during the anion-centered redox reaction could increase the range of Na content that can be used at an elevated electrical potential, thereby yielding high capacity and reducing the markedly considerable voltage discrepancy typically noted in layered oxides activated by anions. This concept fosters the preservation of the charging curve triggered by the lattice O in the subsequent discharge profile, thus ensuring enhanced electrochemical energy efficiency as the cycle advances.



Figure 3.13 Chemical potential,  $\mu_{homo}/e$ , of (a) NaMnO<sub>2</sub> and (b) Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> at room temperature regarding the inverse Na content *x*, with four distinct regions of interest. The comparison between NaMnO<sub>2</sub> (left graph) and Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> (right graph) in different regions are shown in (c-f), and the colored regions (green: NaMnO<sub>2</sub>, orange: Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>) indicate the gap of hysteresis,  $\Delta\mu_{homo}/e$ 

## 3.4 Conclusion

In our quest to effectively employ cathode materials in SIBs to achieve high energy density and reliable cyclability, we investigated thermodynamic phase stability and phase-transition kinetics, both crucial elements for capacity retention in Mn-based layered cathode oxides (NMO and NMNO). Our calculations of homogeneous free energies, which were derived from the formation energies of mixing enthalpy, show a more rapid phase change for  $Na_{1-x}[Mn_{1/2}Ni_{1/2}]O_2$  compared to Na<sub>1-x</sub>MnO<sub>2</sub>. This can be attributed to the significant phase-transition barrier at the  $2^{nd}$  to  $3^{rd}$  regions (0.25  $\leq x \leq 0.75$ ), where most capacity arises from the cation redox reaction. In the 4<sup>th</sup> region (0.75  $\leq x \leq 1.0$ ), Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> does not exhibit the Na-non phase transition (x = 1.0) during the charging process due to the existence of a thermodynamically stable HN-poor phase at x = 0.875. On the other hand, Na<sub>1-x</sub>MnO<sub>2</sub> continues to show an unmixing phase reaction, resulting in the Nanon phase's evolution at x = 1.0. This suggests that the anionic redox reaction in Na<sub>1</sub>. <sub>x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> exhibits a high level of reversibility. Moreover, phase-transition kinetics are discerned in the nano-domain phase-transition depiction via phase field simulation. Furthermore, the results of chemical potential demonstrate a roughly 0.1 V greater voltage hysteresis for Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> than for Na<sub>1-x</sub>MnO<sub>2</sub> for a significant part of the cation redox reaction (0.25  $\leq x \leq$  0.75). Nevertheless, the HN-poor phase in Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> (x = 0.875) keeps lower polarization in its voltage in the region of the redox reaction with involvement of anionic species (by lattice O), which is not common for usual layered cathodes that utilize anions and exhibit a large voltage hysteresis during the first charge-discharge process. To attain both high energy density and reliable cyclability for cathode materials in SIBs, we

propose two tactics: (i) enhancing the solubility of vacancy/Na for the Ni–Mn binary oxide in the process of the cation-driven redox reaction and (ii) strategically harnessing the HN-poor phase during the redox reaction with involvement of anionic species.

## Chapter 4 Mechanical Degradation and Mitigating Structure Deformation

# 4.1 Anisotropic Deformation of Na<sub>1-x</sub>MnO<sub>2</sub> and Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>

The atomic arrangements pertaining to each of them were built to examine the structural behavior of NMO and NMNO with P2-type structures, depicted in Figure 4.1a. This illustration reveals that MnO<sub>6</sub> and MnO<sub>6</sub>/NiO<sub>6</sub> octahedra form the TM layers within NMNO and NMO, respectively, while the prismatic NaO<sub>6</sub> positions are filled with Na ions between these TM layers. The arrangement of cations involving Mn and Ni ions within the TM layers for NMNO was obtained through the thermodynamic energy of formation from a prior investigation.[22] Figure 4.1b displays lattice strain a ( $\varepsilon_a$ ) dependent on the content (x) in Na<sub>1</sub> $x[Mn_{1/2}Ni_{1/2}]O_2$  and Na<sub>1-x</sub>MnO<sub>2</sub>-layered oxides across the vacancy range (0.25  $\leq x \leq$ 1.0), and their values were computed based on Equation (2.23). To account for the O2–P2 phase transition at x = 0.75, [43] the lattice sizes of O2-Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> were utilized when computing the lattice strain for x = 0.875 and 1.0. Compressive *a* lattice strain ( $\varepsilon_a < 0$ ) is consistently noticed across the vacancy range ( $0.25 \le x \le 10^{-3}$ ) 1.0) for the oxide models, showing a reduction in lattice parameters as desodiation occurs. It was noted that the *a* lattice strain steadily decreased with x in both Na<sub>1-</sub>  $x[Mn_{1/2}Ni_{1/2}]O_2$  and  $Na_{1-x}MnO_2$  for values below x = 0.75, whereas the degree of  $\varepsilon_a$ in Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> was distinctly more considerable at x = 0.75. These findings

suggest that the continuous reduction in Na<sub>1-x</sub>MnO<sub>2</sub> results from the single cationbased redox reaction by Mn<sup>3+</sup>/Mn<sup>4+</sup>. In contrast, the reduction in ionic size caused by the double cationic redox from Ni<sup>2+</sup> to Ni<sup>4+</sup> is a primary element leading to substantial structural modifications. Considering the patterns exhibited by the alattice strain, we examined the *c*-lattice strains during the charging process in the models of the two-layered oxide. Figure 4.1c displays the *c*-lattice strain ( $\varepsilon_c$ ) depending on the vacancy content (x) in Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> and Na<sub>1-x</sub>MnO<sub>2</sub> over the vacancy range  $0.25 \le x \le 1.0$ , obtained through the same calculation method as that used for calculating  $\varepsilon_a$ . Unlike the *a*-lattice strain behaviors, tensile  $\varepsilon_c$  ( $\varepsilon_c > 0$ ) occurs upon Na-extraction for  $0.25 \le x \le 0.75$ , and compressive ones ( $\varepsilon_c < 0$ ) appear for values above x = 0.75 in Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> and Na<sub>1-x</sub>MnO<sub>2</sub>. Similar anisotropic lattice behaviors have been observed in various layered oxides employed in SIBs and LIBs, and they are the main factor responsible for the formation of intergranular microcracks among their primary particles. Furthermore, the anisotropic-induced interfacial stresses in the layered cathodes cause mechanical failure, leading to a decline in reversible capacity and voltage fading. Consequently, although NMNO and NMO display a comparable trait in the c-lattice strain, the degree of  $\varepsilon_c$  in the binary-layered compound composed of Ni and Mn is relatively more extensive than that in the Mn oxide over the range of vacancies  $0.25 \le x \le 0.75$ . Specifically, the discrepancy in  $\varepsilon_c$  between NMNO and NMO consistently elevated before attaining the value at x = 0.75. For a direct comparison of the anisotropy extent in both compounds during the desodiation process, the c/a ratios were determined by altering x in  $Na_{1-x}[Mn_{1/2}Ni_{1/2}]O_2$  and  $Na_{1-x}MnO_2$  (Figure 4.1d). The figure demonstrates that the value of c/a for Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> is further prominent in the unstrained state (x = 0.25) compared to Na<sub>1-x</sub>MnO<sub>2</sub> in the vacancy range ( $0.25 \le x \le$  0.75), and this pattern intensifies further until reaching the inflection point (x = 0.75). This suggests the two-component oxide may experience a further pronounced asymmetric lattice alteration during charging.



Figure 4.1 (a) Diagram depicting the P2-type layered Na<sub>1-x</sub>[TM]O<sub>2</sub> structure. Calculated (b) *a*-lattice strains ( $\varepsilon_a$ ), (c) *c*-lattice strains ( $\varepsilon_c$ ), and (d) *c/a* ratios are presented depending on the vacancy content (x) in Na<sub>1-x</sub>MnO<sub>2</sub> (purple) and Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> (gray) across the complete range (0.25  $\le x \le 1.0$ ) with the experimentally measured lattice strain reproduced from Ref.[82,90]

To conduct a comprehensive examination, we classified the two types of interlayer spaces in NMO and NMNO involving the oxygen planes contributing to the rise in *c*-lattice strains: (i) interslab space ( $d_{slab}$ ) and (ii) interlayer space of TM layers ( $d_{TM}$ ). Here,  $d_{slab}$  and  $d_{TM}$  represent the perpendicular distance separating the two oxygen sheets across the NaO<sub>2</sub> layers and the normal space between the two oxygen layers that run parallel to each other in the TM layers, respectively (Figure 4.2a). The interslab space generally expands due to electrostatic repulsion between the oxygen layers when Na or Li ions are extracted from the host-layered oxides in Na- or Li-based cathodes. As shown in Figure 4.2b, we calculated the interslab

strains ( $\varepsilon_{slab}$ ) depending on the vacancy content (x) in Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> and Na<sub>1-</sub> <sub>*x*</sub>MnO<sub>2</sub> across the range of different vacancy concentrations of  $0.25 \le x \le 1.0$ , which were determined using the original state (x = 0.25). The figure demonstrates that both tensile  $\varepsilon_{slab}$  values are noted from x = 0.25 to x = 0.75 in NMNO and NMO, while compressive values grow for values above x = 0.75. While these changes in geometry align with the trend of the c-lattice strain, they are not enough to explain the difference in c-lattice strain between NMNO and NMO. Consequently, as depicted in Figure 4.2c, the latter distance was calculated based on the vacancy content (x) in  $Na_{1-x}[Mn_{1/2}Ni_{1/2}]O_2$  and  $Na_{1-x}MnO_2$ , and their values were converted to TM interlayer strains ( $\varepsilon_{TM}$ ). To gain a deeper insight,  $\varepsilon_{TM}$  values were meticulously approximated using a first-order linear regression (see the dashed lines in Figure 4.2c), suggesting the presence of compressive strains across the entire range ( $0.25 \le x \le 1.0$ ) in NMNO and NMO. While  $\varepsilon_{slab}$  exhibits a consistent alteration tendency during charging in the layered oxides, a fascinating difference was noticed in the TM interlayer strain. The extent of compressive  $\varepsilon_{TM}$  is more significant in NMO than in NMNO during charge procedure. Moreover, the  $\varepsilon_{TM}$  difference between NMNO and NMO becomes more pronounced with desodiation, following a similar trend as observed in  $\varepsilon_c$  across the same vacancy range, as depicted in Figure 4.2c. Thus, the substantial variance in the *c*-lattice strain within the two compounds is attributed to the comparatively low  $\varepsilon_{TM}$ values in NMNO.


Figure 4.2 (a) Illustration of P2-Na<sub>1-x</sub>[TM]O<sub>2</sub> along the *a*-axis.  $d_{slab}$  and  $d_{TM}$  represent the interslab and TM interlayer distances in the layered oxides. Computed (b) interslab strains ( $\varepsilon_{slab}$ ) and (c) TM interlayer strains ( $\varepsilon_{TM}$ ) are presented based on the vacancy content (x) in Na<sub>1-x</sub>MnO<sub>2</sub> (purple) and Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> (gray) throughout the whole vacancy range (0.25  $\le x \le 1.0$ )

Generally, the reduction of the *a*-lattice value matches to the diminish in the ionic radius of redox-active TM species, compensating for the charge inequality resulting from the removal of AM ions, where AM represents Li or Na ions. Conversely, the enlargement of the *c*-lattice value results from the electrostatic repulsive force between the lower and upper oxygen layers based on the AM ions upon charge procedure. Furthermore, many theoretical and experimental investigations have identified major oxygen-based redox reactions combined with fractional Ni<sup>3+</sup>/Ni<sup>4+</sup> redox reactions through the anti-bonding band of Ni–O (Ni–O<sup>\*</sup>) at approximately 4.2 V versus Na<sup>+</sup>/Na.[21,22,91] This occurs with a non-polarized voltage profile during the initial discharge and charge for Mn-Ni oxides with a layered structure comprising two elements in SIBs. Hence, the heightened lattice behavior with anisotropy observed in the Mn-Ni oxides with a layered structure comprising two elements for  $0.25 \le x \le 0.75$  can be tied to the double redox by cation couple of  $Ni^{2+}/Ni^{4+}$ , which can be ungrouped into two driving forces: (i) lattice contraction induced by changes in ionic radius, and (ii) TM interlayer compression repression owing to Jahn-Teller effect. The Mn-Ni binary-layered oxides exhibiting oxygen redox reactions are particularly interesting when compared to Na-layered

oxides based on Mn, which display oxygen redox activities[10,92,93] due to their nonhysteretic voltage and high reversibility during discharge and charge.[43,91] Nevertheless, the fundamental relationship between the Ni redox mechanism and anisotropic lattice change, coupled with oxygen-based redox, remains vague. Thus, gaining a deeper comprehension is crucial for harnessing their entire potential and is a critical part in achieving extended reversible high energy density upon cycling in NMNO.

## 4.2 Origin of Anisotropy in Ni–Mn Binary Layered Oxide

To clarify the role of the Ni<sup>2+</sup>/Ni<sup>4+</sup> double redox couple as a critical factor in the hastened anisotropic lattice change  $(0.25 \le x \le 0.75)$ , we examined the electronic configurations at x = 0.25, 0.5, and 0.75 in Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>. Figure 4.3a presents combined graphs of PDOSs for Mn and Ni 3d-electrons and O 2p-electrons at every level of vacancy content in the Mn–Ni binary oxide. The PDOSs at x = 0.25 display the hybridized band of Ni(3d)–O(2p) in the valence band (-1.0  $\leq$  E-E<sub>f</sub>  $\leq$  0.0), while the Mn(3d)–O(2p) band is not discernible in the same energy range. As reported in numerous prior studies, the electronic configuration of Mn is Mn<sup>4+</sup>, which remains redox-inert during (de)intercalation. As the process continues further desodiation beyond x = 0.25, the intensity of 3*d*-electron in Ni PDOSs steadily rises in the conduction band ( $0.0 \le \text{E-E}_{\text{f}} \le 1.0$ ) up to x = 0.75, suggesting that the cationd  $\mathrm{Ni}^{2+}/\mathrm{Ni}^{4+}$  redox reaction plays a role in compensating for the charge during desodiation. To conduct a more thorough investigation, we calculated spatial electron densities at x = 0.25, 0.5, and 0.75 in Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> based on the wave functions between -1.0 and 0.0 eV, as depicted in Figure 4.3b. The yellow isosurfaces, representing electron densities at x = 0.25, can be explained as Ni ions surrounded by either  $d_{z^2}$  and  $d_{x^2-y^2}$  electrons (light gray atoms) or single  $d_{z^2}$ electrons (black atoms), corresponding to Ni<sup>2+</sup>  $(t_{2g}^{\ 6}e_g^{\ 2})$  and Ni<sup>3+</sup>  $(t_{2g}^{\ 6}e_g^{\ 1})$  ions, respectively. The electron densities at x = 0.75 suggest that electrons do not coordinate Ni<sup>4+</sup>  $(t_{2g}^{\ \ 6}e_{g}^{\ \ 0})$  ions (orange atoms) in the  $e_{g}$  band. These findings demonstrate that the considerable *a*-lattice contraction (refer to Figure 4.1a) is intimately associated with the two- stage reduction in the ionic radius of Ni (Ni<sup>2+</sup>: 83 pm, Ni<sup>3+</sup>: 70 pm, Ni<sup>4+</sup>: 62 pm). Generally, the anisotropic electron structure of Ni<sup>3+</sup> ions in layered oxide cathodes results in JTD, causing constriction and extension of Ni<sup>3+</sup>–O bonds along xy in-plane and the z-axis directions, respectively, taking into account the coordinates of the octahedral complex. Considering the Ni redox mechanism in NMNO, the JT-distorted Ni<sup>3+</sup>O<sub>6</sub> population in the TM layer rises for values above x = 0.25, and its expansion could inhibit the considerable compression in the TM interlayer. Considering that the hastened  $\varepsilon_c$  originates from the inhibition of shrinkage in the TM interlayer, the evolution of JTD in NMNO plays a critical role in accelerating the anisotropic lattice change upon charging below x = 0.75. As depicted in Figure 4.3c, we examined the Ni–O bonds' populations at x = 0.25, 0.5, 0.5and 0.75 in  $Na_{1-x}[Mn_{1/2}Ni_{1/2}]O_2$  and derived them based on the Ni ions' valence state: (i) Ni<sup>2+</sup>-O (light gray), Ni<sup>3+</sup>-O (black), and Ni<sup>4+</sup>-O (orange). The populations of Ni<sup>3+</sup>cO bonds can be divided into two distinct groups: elongated and compressed Ni<sup>3+</sup>–O bonds, which offers compelling evidence of JTD at every vacancy content within the oxide (Figure 4.4). Compared to the Ni<sup>3+</sup>–O bond populations at x = 0.25, they increase at x = 0.5. This demonstrates the emergence of distorted Ni<sup>3+</sup>O<sub>6</sub> and arises from the oxidation of remaining Ni<sup>2+</sup> to Ni<sup>3+</sup>, which agrees with the earlier qualitative evaluations of the electronic configurations. At x = 0.75 in NMNO, the lengthened Ni<sup>3+</sup>–O bond populations diminish, while those of Ni<sup>4+</sup>–O (1.9 Å) grow considerably. This bond variation, varying according to the valence states of the Ni ions from x = 0.5 to x = 0.75, suggests that JTD is unleashed. These observations in the Ni–O bond population strongly agree with the  $\varepsilon_c$  NMNO's response across the range of vacancies of  $0.25 \le x \le 0.75$ .



Figure 4.3 (a) Combined graphs of PDOSs of 3*d*-electrons for Ni (gray) and Mn (purple) and 2*p*-electrons for O (red) and (b) the computed spatial electron densities (yellow iso-surface) for Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> (x = 0.25, 0.5, and 0.75) within the range of  $-1.0 \le E \cdot E_f \le 0.0$ . Orange, black, and light gray atoms represent Ni<sup>4+</sup>, Ni<sup>3+</sup>, and Ni<sup>2+</sup> ions, respectively. The red dashed box indicates bonding for Ni<sup>3+</sup>–O extended along the z-direction. (c) Ni–O bonds' populations at x = 0.25, 0.5, and 0.75 in Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>



Figure 4.4 Ni<sup>3+</sup>O<sub>6</sub> representing Ni<sup>3+</sup>O<sub>6</sub> octahedra in Na<sub>0.5</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>. The electron densities surrounding the Ni<sup>3+</sup> atom are represented in yellow. The spatial electron densities around oxygen atoms are neglected. The direction of O–Ni<sup>3+</sup>–O configurations consisting of Ni<sup>3+</sup>O<sub>6</sub> is indicated in blue dashed lines indicate. The short ones (right) does the compression of Ni<sup>3+</sup>–O bonds in the *xy* in-plane direction (right), whereas the long O–Ni<sup>3+</sup>–O bond (left) shows the elongation of Ni<sup>3+</sup>–O bonds along the *z*-direction

## 4.3 Anisotropic Mechanical Behavior in Secondary Particles

Based on a thorough comprehension of the correlation between the Ni redox process and the NiO<sub>6</sub> octahedral complex's changes upon charging, the advanced lattice's anisotropic transformation stems from two critical elements: (i) two-stage reduction in ionic radius and (ii) JT-prompted inhibition of the contraction of TM interlayer. This suggests that employing the cation-based Ni<sup>3+</sup>/Ni<sup>4+</sup> redox process can be a detrimental factor causing microscopic cracks between the grains in Nicontaining layered oxides during charge and discharge cycles. To comprehend the influence of the rapid lattice's anisotropic alteration at the particle scale, we utilized finite element analysis to gauge the distribution of Na ions in an NMNO particle during charging and the following accumulated elastic strain energy density. The Na ion distribution within an NMNO particle was ascertained based on diffusion kinetics, and the subsequent mechanical response was dictated by momentum equilibrium. The secondary NMNO particle forms a collection of primary particles of random orientations and sizes, achieved through Voronoi tessellation (Figure 3.29a).[80] This occurs since secondary particles, created through the coprecipitation technique, display a spherical shape and are composed of primary particles that aggregate randomly.[33,34] In general, Na ions non-uniformly enter the particle due to the uneven overpotential or electrochemical reaction on the surface, which hastens the deterioration observed at the secondary particle level. To examine the impact of the anisotropic lattice change on the secondary particle, we did not take into account the non-uniform distribution of Na ions resulting from local charge irregularities on

the particle surface. We considered a fixed concentration boundary condition on the secondary particle surface to simulate the even removal of Na ions. Consequently, the distribution of charge and the consequent mechanical response of Na ions, attributable to the inherent anisotropic characteristic, were determined in the secondary particle of NMNO. As shown in Figure 4.5, the multiscale analysis technique proposed in this dissertation, which reflects the anisotropic deformation characteristics of the primary particle derived through first-principle calculation, is more accurate than previous studies that assumed that the change of primary particles was linear deformation.[94] In Figure 4.6a, the upper graph illustrates the spatial distribution of Na ions, while the lower graph shows the accumulated elastic strain energy density. These results are obtained at a remaining Na ions ratio  $(c/c_{max})$ , which corresponds to the inverse of the state of charge (SoC), equal to 0.3 in a secondary particle. This demonstrates that Na ions are gradually and uniformly extracted from the secondary particle's surface. Nevertheless, the distribution of elastic strain energy density resulting from the anisotropic lattice change in the primary particles is not uniform, with prominent concentration near the grain boundaries. This uneven distribution points to potential sites for structural damage within the primary particles. A localized region of the secondary particle is depicted in Figure 4.6b to provide more clarity. The figure illustrates that neighboring primary particles have different orientations within a typical secondary particle and form grain boundaries with directionally mismatched planes. The particles exhibit different orientations, with one having a (100) plane facing the boundary, and the other showing a (002) plane orientation towards the same boundary. In this arrangement, during the extraction of Na ions, both primary particles experience compression along the alattice direction and expansion along the c-lattice direction. Nevertheless, their expansions take place in perpendicular directions since they are bound and oriented at right angles to each other. Consequently, the strain in opposing directions results in the accumulation of elastic strain energy at the grain boundaries within the secondary particle, especially in regions formed by randomly aggregated primary particles. The uneven distribution of elastic strain energy density suggests notable damage development at the grain boundaries. This aligns with multiple prior experiments that observed cracks occurring between the grains in secondary particles containing layered-type cathode oxides.[36–39,95] This damage along the grain boundaries enables liquid electrolytes to infiltrate the core of particle, hence accelerating the expansion of the degraded region and resulting in capacity degradation or even voltage reduction.



Figure 4.5 NMNO Secondary particle analysis reflecting the anisotropic characteristics of primary particles derived through first-principles calculations shows the aspects seen in experiments better than when the primary particle deformation is assumed to be linear[94]

The non-uniform deformation of primary particles plays a role in the structural degradation of secondary particles (e.g., intergranular cracks). While the anisotropic lattice change is a typical inherent feature of many layered-type cathode materials, removing or minimizing the structural changes at the primary particle

level is challenging. Nevertheless, creating secondary particles that leverage the anisotropic properties of primary particles may present a viable alternative solution. Hence, An et al. endeavored to alleviate the mechanical breakdown resulting from the non-uniform volume change in crystalline silicon over Li-ion intercalation through anisometric morphology engineering.[96] Furthermore, by comprehending the specific structural deformation characteristics of NMNO and other layered-type cathode materials, it opens up possibilities for designing a secondary particle morphology that can improve cyclability. As discussed earlier, NMNO undergoes an anisotropic lattice transformation during the deintercalation of Na ions, with shrinkage in the *ab*-plane and expansion in the *c*-lattice direction. For clusters of primary particles, having each primary particle deform in a consistent direction could minimize uneven stress at their interfaces. Thus, arranging the primary particles in a uniform direction would be advantageous. Additionally, since majority of secondary particles created via coprecipitation exhibit a spherical form, the *ab*-plane or *c*-lattice should be oriented towards the sphere's core. Given that the primary diffusion pathway for Na ions in NMNO occurs along the ab-plane, it would be more beneficial to have the *ab*-plane facing the secondary particle's surface. As illustrated in Figure 4.6c, the secondary particle shape with radial orientation, where the clattice is directed tangentially, would effectively handle the anisotropic lattice change. To provide a more straightforward comparison with the secondary particle containing randomly aggregated primary particles, the Na ion distribution (upper graph) and the corresponding elastic strain energy density (lower graph) were computed at  $c/c_{max} = 0.3$  for the secondary particles comprising primary particles arranged in a radial orientation (Figure 4.6c). Similar to the randomly aggregated case, Na ions were progressively and uniformly removed from the outermost layer

of the secondary particle. However, in contrast to the randomly aggregated primary particles, the secondary particle with radially oriented primary particles exhibits a relatively low and uniformly dispersed accumulated elastic strain energy density along its perimeter, indicating more uniform mechanical behavior. To comprehend the underlying reasons for this occurrence, the atomic configuration at the local level within the primary particles is depicted in Figure 4.6d. The diagram illustrates how adjacent primary particles form a grain boundary along the *c*-axis direction, and the *ab*-plane of each grain is oriented towards the surface. Under these conditions, when Na ions are extracted, all primary particles uniformly expand in the tangential direction, resulting in a consistent buildup of elastic strain energy in a ring-like pattern. Given the ordered deformation of the aggregated primary particles, the total stored mechanical energy is reduced compared to the randomly aggregated case. This result may impede the infiltration of the electrolyte into the core of the secondary particle due to reduced grain boundary gaps as the primary particles expand in a coordinated tangential direction. Consequently, this phenomenon could potentially slow down the degradation of the secondary particle. Additionally, the orientation of the *ab*-lattice plane of primary particles, acting as the diffusion path for Na ions, toward the surface of the secondary particle could facilitate faster extraction and insertion of Na ions, thereby enabling rapid charging in both SIBs and LIBs (Figures 4.7 and 8). Incidentally, as shown in Figure 4.9, it shows more elastic strain energy is accumulated in the secondary particle structure of NMNO than that of NMO at the same time. This indicates that NMO with less anisotropic primary particle deformation accumulates less elastic strain energy even at the level of individual secondary particles. Suppressing the deformation of the primary particles could also enhance the cyclability of secondary batteries.



Figure 4.6 Arrangement of Na ions and the corresponding elastic strain energy density for (a) randomly oriented and (c) radially oriented secondary particle configurations at  $c/c_{max} = 0.3$ . The atomic structure arrangement in primary particles corresponding to the (b) randomly oriented and (d) radially oriented secondary particle shapes



Figure 4.7 The change in Na ion concentration over time during desodiation for the randomly oriented (blue) and the radially oriented (red) secondary particles



Figure 4.8 Degree of Na ion percolation for each of A and B at 1000 s



Figure 4.9 The displacement field inside the secondary particle showing that the structural deformation of NMO with less anisotropic deformation of primary particles is relatively less than that of NMNO for the same time

### 4.4 Conclusion

We determined the anisotropic lattice change during (de)intercalation. This is crucial for SIBs due to the comparatively large size of Na ions and its fundamental relationship with the Ni redox figure in conjunction with oxygen-based redox reactions. During desodiation, the *a*-lattice undergoes consistent contraction across the entire vacancy range. Simultaneously, the *c*-lattice expands within the  $0.25 \le x \le$ 0.75 range and contracts within the  $0.75 \le x \le 1.0$  range, resulting in alterations to the anisotropic structure. The mechanical anisotropy is further enhanced in the Ni-Mn binary-layered oxide as a result of the reduction in Ni ionic radii (Ni<sup>2+</sup>/Ni<sup>3+</sup>/Ni<sup>4+</sup>) and the distortion of the TM layer caused by the Jahn-Teller effect, even during high-voltage charging when oxygen evolution takes place. By thoroughly understanding the structural deformation with anisotropic characteristics, we verified that the manipulation of secondary particle morphology, specifically the secondary particle with radial orientation, can efficiently alleviate structural breakdown, resulting in improved recyclability. In a similar vein, Kim *et al.* lately demonstrated that by partially doping Ni-rich-layered LIB cathodes, primary particle shapes could be manipulated (with varying aspect ratios), and the secondary particle shape can be altered consequently (from random to radial orientation), potentially impacting long-term cycling performance.[97] Consequently, adjusting the secondary particles' morphology emerges as an apt approach to manage the anisotropic characteristics of primary particles, which may facilitate improved cycle performanceand rapid charging for both SIBs and LIBs.

## **Chapter 5** Extension of Multiscale Analysis to All-Solid-State-Battery

### 5.1 Internal Degradation of Solid Electrolyte

#### 5.1.1 Introduction

Despite high expectations for solid electrolytes, it has been observed that solid electrolytes do not effectively prevent infiltration of lithium metal into the Li electrode interface, and dendrites form along the interfaces between adjacent grains of solid electrolytes.[98-101] Specifically, Cheng et al. noticed lithium metal nucleation through intergranular spaces in polycrystalline Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) during the cycling of a symmetric Li|LLZO|Li cell,[99] while Ren et al. documented lithium metal growth between grains in Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.75</sub>Ta<sub>0.25</sub>O<sub>12</sub> pellets.[98] Additionally, Porz et al. identified the presence of lithium metal regions within the intergranular spaces of polycrystalline  $\beta$ -Li<sub>3</sub>PS<sub>4</sub>, indicating that the solid electrolyte crystalline grains' interface is a significant route for lithium metal dendrite formation.[100] Numerous current investigations have uncovered the underlying factors responsible for the intrusion of lithium metal dendrites into solid electrolytes from the anode interface. Different advanced surface treatments have been suggested as potential methods to minimize the formation of lithium dendrites within solid electrolytes.[102–104] While efforts to tackle the problem at the anode interface have primarily focused on preventing the growth of lithium dendrites from the Li anode into the inter-grain spaces of solid electrolytes, there is a possibility that metallic Li phases might initiate at a grain boundary (GB) within the solid electrolyte, arising due to the amalgamation of Li ions and electrons that have permeated through the GB, thereby giving rise to the creation of lithium metallic phases. Assuming that lithium metal phases have the potential to form within the intergranular spaces of solid electrolytes. In that case, there remains a risk of short-circuiting as metallic domains that have nucleated uniformly connect to form a continuous dendrite complex. While indication exists that lithium metal phases form within the intergranular spaces of solid electrolytes, the precise mechanisms responsible for the formation of lithium metal phases in solid electrolytes remain incompletely understood.[105,106] Considering the present production methods for solid-state batteries is crucial. Solid electrolyte membranes are fabricated through a sintering process that involves applying high pressure and temperature to solid electrolyte powders. Despite this, the sintering temperature is lower than the usual ceramic sintering temperatures, where the powders experience surface melting, resulting in densely sintered ceramics with infinitesimal porosity (i.e., greater than 99% of the bulk material density). Conversely, sintering temperatures for solid electrolyte powders are not permitted to achieve the surface melting temperature. This would impair the ion-conducting properties of the sintered solid electrolyte membranes, leading to a higher anticipated porosity. As a result, various inter-grain structures can be anticipated in the solid electrolyte membrane, and these structures have a habit of exhibit distinct interactions with Li ions and leaked electrons. A comprehensive modeling investigation has the potential to offer a comprehensive atomistic understanding of lithium metal phase formation mechanisms within the interfaces of solid electrolyte crystalline grains, which is crucial for proposing effective mitigation strategies.

To investigate the effects of intergranular microstructure for solid electrolytes,

the perovskite  $Li_{3x}La_{(2/3)-x}\square(1/3)-2xTiO_3$  (0 < x < 0.167) lithium lanthanum titanium oxide (LLTO) system, characterized by an ABO<sub>3</sub> structure with A representing La, Li, or vacancies and B denoting Ti, was selected as a representative model to investigate the nucleation of the Li metallic phase within the grain boundary or solid electrolyte crystalline grain interface. Owing to its notable room temperature bulk ionic conductivity (~10<sup>-3</sup> S/cm), LLTO has been examined as a promising candidate for solid electrolytes.[107,108] In fact, the structural properties of LLTO can be altered by factors such as lithium concentration, heat treatment cooling rate, and heating temperature, impacting its Li<sup>+</sup> conductivity characteristics.[109] Despite its potential, LLTO has been found to exhibit significant stability issues when it comes into direct touch with metallic lithium. It is anticipated that LLTO will decompose into Li2O, La2O3, and Ti6O because of chemical interactions with lithium metal.[107,110] This issue could hinder the real-world utilization of LLTO as a solid electrolyte in contact with an anode. Lately, it has been noted that introducing a buffer layer, such as polyethylene oxide, between lithium metal and LLTO can facilitate the use of LLTO in lithium metal-based full cells by managing the disintegration of LLTO.[111] In this section, DFT explores the potential mechanisms underlying Li metallic phase germination within the grain boundary areas or solid electrolyte crystalline grain interfaces, using LLTO as a model system. To encompass a variety of interface between crystalline grains configurations, three intergranular structures that have been experimentally observed are taken into account as the representative for the modeling study: (i) stoichiometric GB, (ii) A-site deficient GB, and (iii) intergranular pore space.

# 5.1.2 Interaction of Li with a stoichiometric grain boundary

In constructing the LLTO GB models, the arrangement of A-site cations in the bulk LLTO (x = 0.1167 in Li<sub>3x</sub>La<sub>(2/3)-x</sub> $\Box_{(1/3)-2x}$ TiO<sub>3</sub>) atomic structure was precisely followed, where Li-rich and La-rich layers are known to exist together (Figure 5.1).[107,112,113] The selection of grain orientations for the LLTO symmetric tilt GBs was based on common grain boundary orientations observed in different perovskite materials.[114–116] Out of the symmetric tilt GBs, the  $\Sigma$ 3(111) GB exhibits a comparatively low formation energy for grain boundary ( $\gamma_{GB} = 0.584$  J/m<sup>2</sup>) compared to other orientations, and it also demonstrates lower formation energy when compared to grain boundaries found in other perovskite materials (Table 5.1).[117–121] This suggests that  $\Sigma$ 3(111) GB is likely more prevalent in LLTO solid electrolytes. Consequently,  $\Sigma$ 3(111) GB is primarily chosen for detailed Li-ion conduction analysis and electronic structure calculations.



Figure 5.1 The atomic arrangement of LLTO consists of alternating La-rich and Li-rich layers

Grain boundary types	Grain boundary formation energy (J/m <sup>2</sup> )		
∑ <b>3</b> (111)	0.584		
∑5(210)	1.613		
∑5(001)	1.364		

Table 5.1 Formation energy of grain boundary for LLTO (x = 0.1167) with various grain boundary orientations

To determine the energetically stable relative atomic configurations for  $\Sigma$ 3(111) GBs, a rigid-body displacement of grains at the grain boundary was performed. To explore the potential energy landscape, a lateral rigid-body displacement restricted to the interfacial plane was taken into account for Lisaturated LLTO (x = 0.1667; Li<sub>0.5</sub>La<sub>0.5</sub>TiO<sub>3</sub>), Li-rich LLTO (x = 0.1167), and Li-poor LLTO (x = 0.0417), as shown in Figure 5.3a.[122] Figure 5.3b demonstrates that the  $\Sigma$ 3(111) GB without lateral displacement, as depicted in Figure 5.2, has the lowest energy state. The optimized GB structure, similar to bulk LLTO, exhibits a periodic arrangement of Li-rich and La-rich layers. To comprehend the characteristics of the GB, a detailed examination of the atomic arrangement in the immediate vicinity of the GB core was conducted. As depicted in the magnified representation of the optimized GB core's atomic structure, Ti preserves a coordination number of 6 in the form of TiO<sub>6</sub> octahedra, which is identical to that in bulk LLTO, but forms facesharing octahedra, which is unlike bulk LLTO (Figure 5.4a). When displacement is applied to the GBs, however, uncoordinated Ti-O bonds are present in the GB core (Figure 5.4b). This implies that uncoordinated bonds at the GB core are energetically unfavorable. Indeed, numerous theoretical and experimental findings validate the plausibility of intergranular configurations featuring face-sharing TiO<sub>6</sub> octahedra.[115,123]



Figure 5.2 The atomic arrangement and formation energy of a stoichiometric GB in LLTO are depicted. The core region of the GB is emphasized with a blue-shaded area. The La, Li, Ti, and O atoms are represented by green, yellow, blue, and red spheres, respectively



Figure 5.3 (a) Diagram illustrating the rigid-body translation between two distinct grains. LLTO  $\sum 3(111)$  GB's potential energy surfaces at (b) x = 0.1167, (c) 0.0417, and (d) 0.1667. Blue regions indicate regions of energetically stability



Figure 5.4 (a) Variation of Ti coordination number at x = 0.1167 for  $\sum 3(111)$  boundary depending on the normalized coordination perpendicular to the GB plane. (b) The uncoordinated Ti–O bonds in the GB core of  $\sum 3(111)$  boundary at x = 0.1167

Considering the optimized  $\Sigma 3(111)$  GB structure, the interaction of metallic phase germination at the GB and Li ions was explored. Firstly, to assess the potential for electron conduction within the GBs, the optimized  $\Sigma 3(111)$  GB configuration's electronic structures were scrutinized. Figure 5.5a displays the local regiondecomposed PDOS for Ti 3*d*-electron, La 5*d*-electron, and O 2*p*-electron in each GB core (middle) and bulk-like (upper and lower) region. The bulk-like area's PDOS resembles that of bulk LLTO, as it has a comparably wide band gap (~1.9 eV), signifying a characteristic of electron insulation (Figure 5.6). It is essential to mention that the PDOS of the GB core region shows a similar profile to the bulklike PDOS, with a band gap of ~1.6 eV, demonstrating minimal deviation from bulk LLTO. Although the DFT with GGA tends to underestimate the band gap, the predicted sufficiently large gap confirms that the LLTO GB core offers limited viable electron conduction pathways. As a result, this emphasizes that the stoichiometric GB core has a minimal impact on electronic conductivity.



Figure 5.5 (a) Combined graphs displaying the regionally-decomposed partial density of states for Ti 3*d*-electron (blue), La 5*d*-electron (green), and O 2*p*-electron (red) in GB core (middle) regions and bulk-like (upper and lower); the areas corresponding to the stoichiometric GB structure are depicted within the red dashed rectangle in the right panel. (b) Formation energy for Li interstitial defect, considering the Li metal chemical potential in two distinct charge states (+1: green and neutral: black), for bulk-like (left) and GB core (right) regions in the LLTO GB structure



Figure 5.6 Integrated graphs of the PDOSs for Ti 3*d*-electron (blue), La 5*d*-electron (green), and O 2*p*-electron (red) for bulk LLTO

Additionally, to examine the interaction of Li-ions with the LLTO GB core, the formation energy of Li interstitial defects is computed for the LLTO  $\Sigma 3(111)$  GB structure, examining the notable sites for defect (Figures 5.7a and b). Figure 5.5b displays the formation energy of Li interstitial defects with respect to the lithium metal chemical potential in two distinct charge states (+1 (green) and neutral (black)) for both the GB core (right) and bulk-like (left) regions, respectively. As illustrated in Figure 5.5b, within the bulk-like area, the formation of Li-ion interstitial defects in the +1 charge state (-3.93 eV) is energetically more favorable compared to the neutral state (-1.56 eV), as anticipated for bulk LLTO solid electrolytes. Moreover, a comparable pattern is observed in the GB core region (-3.5 eV formation energy of Li-ion interstitial defects). In addition, the charge transition level (+1/0) for both GB core and bulk-like regions is situated deep within the conduction band (Figure 5.7c). This suggests that Li atoms are more likely to get in LLTO in the +1 charge state, as opposed to Li<sup>0</sup> or lithium metal, in both the GB core and bulk-like regions of LLTO. Moreover, to account for the changing characteristics of the chemical potential of Li in the solid electrolyte (i.e., at cathode and anode interfaces), the formation energy of Li interstitial defect is also calculated while considering a Li chemical potential that is ~4.2 eV lower (at the cathode interface). The reason for this is that the chemical potential of Li in the solid electrolyte falls between that of the cathode active materials and lithium metal. Specifically, it is ~4.2 eV lower than that of lithium metal, which is a result of the Li binding energy to cathode oxides (Table 5.2). Similarly, in this scenario, the Li atom remaining in the +1 charge state at both GB core and bulk-like regions is thermodynamically more stable. It is important to mention that the energy needed for Li<sup>+</sup> to move from the bulk-like region to the GB

core region only differs by ~0.4 eV. This indicates that  $Li^+$  can readily enter the GB core region of LLTO, and the stoichiometric GB does not show any significant microstructural effects on the extent of Li-ion insertion. Combined with the electronic insulating nature, it is deduced that the Li metallic phase is unlikely to form in the LLTO's stoichiometric GB.



Figure 5.7 Li interstitial defect in (a) bulk-like and (b) GB core regions of stoichiometric GB. (c) The charge transition levels for the Li interstitial defect in bulk-like (left) and GB core regions (right) of stoichiometric GB are illustrated. The shaded areas represent the valence band (VB) and conduction band (CB) edges

	Near anode ( $\mu_{Li} = -1.91 \text{ eV}$ )		Near cathode ( $\mu_{Li} = -6.11 \text{ eV}$ )	
	neutral	+1	neutral	+1
Bulk	-1.56	-3.93	2.64	0.27
GB	-1.58	-3.50	2.62	0.70

Table 5.2 The formation energy for Li interstitial defect in two different charge states (+1 and neutral) for GB core and bulk-like regions in LLTO's stoichiometric GB structure. The defect formation energy calculated based on the near cathode and anode Li chemical potential corresponds to the lower and upper limit, respectively, of formation energy for defect

As mentioned previously, LLTO is recognized for its stability across a broad

spectrum of A-site La, Li, and vacancy ( $\Box$ ) compositions (0 < x < 0.167), and these alterable composition features enable the forming of a high Li ion conductivity complex. Considering the impact of A-site composition on the ionic conductivity of LLTO, we explore the potential influence of these compositional variations on conductivity of electron. To examine the effect of A-site D/Li concentrations on conductivity of electron,  $\Sigma$ 3(111) grain boundary structures with two distinct A-site  $\Box$ /Li ratios are built and relaxed: (i) Li-poor LLTO (x = 0.0417) and (ii) Li-saturated LLTO (x = 0.1667). The relaxed  $\Sigma 3(111)$  grain boundary structures at x = 0.0417 and 0.1667 are shown in Figures 5.8a and b, respectively. Both  $\Sigma 3(111)$  GBs at x = 0.0417and 0.1667 exhibit comparatively low grain boundary formation energies ( $\gamma_{GB}$  = 0.880 J/m<sup>2</sup> and 0.743 J/m<sup>2</sup>, respectively), comparable to the GB at x = 0.1167 for Lirich LLTO. This suggests that the  $\Sigma 3(111)$  GB is likely to be present in a high proportion across a range of  $\Box/Li$  concentrations. Analogous to the  $\Sigma 3(111)$  GB structure at x = 0.1167, both GBs at x = 0.1667 and 0.0417 display an alternating arrangement of Li-rich and La-rich layers and a comparable atomic configuration for GB core, with face-sharing TiO<sub>6</sub>. The sole distinction is the presence of more Li or vacancies in the GB core region for x = 0.1667 and 0.0417, respectively.

The relaxed  $\Sigma 3(111)$  GB structures' electronic structures at x = 0.1667 and 0.0417 were investigated to determine if electron conduction happens in the GB core region. As illustrated in Figure 5.8a, the GB core and bulk-like regions in  $\Sigma 3(111)$  GB structures at x = 0.0417 exhibit a broad band gap of approximately 1.75 eV and 1.80 eV, respectively. Similarly, the bulk-like and GB core regions in  $\Sigma 3(111)$  GB structures at x = 0.1667 exhibit a considerable band gap of ~1.84 eV and 1.96 eV, respectively, as shown in Figure 5.8b. Regardless of varying A-site  $\Box/\text{Li}$  concentrations, the band gap of GB core and bulk-like regions closely resembles that

of bulk LLTO, suggesting that the electronic configuration remains stable even when A-site  $\Box$ /Li concentration changes. Consequently, this indicates that alterations in the A-site ratio do not impact the electronic conductivity of stoichiometric LLTO, preventing the accumulation of Li metallic phase in the space between the grains.



Figure 5.8 Combined graphs of the regional-decomposed PDOSs of Ti 3*d*-electron (blue), La 5*d*-electron (green), and O 2*p*-electron (red) in the GB core (middle) region and each bulk-like (upper and lower) for (a) x = 0.0417 and (b) 0.1667 of LLTO; the areas corresponding to the stoichiometric GB structure are depicted within the red dashed rectangle in the right panel

# 5.1.3 Interaction of Li with A-site deficient grain boundary

Various GB configurations may exist in actual systems, not just stoichiometric GB cores. Experimental observations reveal numerous GB configurations with deficiencies in La and Li ions, which can be attributed to factors like the partial reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup>.[124] Consequently, the study considers the GB with A-site deficient to account for the diverse configurations of GB structures (Figure 5.9a).[125] The GB with A-site deficient exhibits a marginally higher GB formation energy ( $\gamma_{GB} = 0.882 \text{ J/m}^2$ ) than the  $\Sigma3(111)$  GB. Nevertheless, it remains relatively low in comparison to other perovskite materials, suggesting that the GB with A-site deficient will probably occur in real LLTO systems. To compare with stoichiometric GBs, the atomic structure at the core of the grain boundary was extensively investigated. Contrary to the stoichiometric  $\Sigma 3(111)$  GB structure, Ti displays diverse oxygen coordination numbers (4-7; as illustrated in Figure 5.9b), but uncoordinated bonds are scarcely observed at the GB core.



Figure 5.9 (a) The atomic configuration and formation energy of grain boundary for the GB with A-site deficient for LLTO are depicted. The GB core region is emphasized with a blue-shaded area. The La, Li, Ti, and O atoms are represented by green, yellow, blue, and red spheres, respectively. (b) Ti coordination number for GB in-complex with respect to the normalized coordination perpendicular to the GB plane

Similarly to the  $\Sigma 3(111)$  GB configurations, the electronic configuration of the GB with A-site deficient structure was investigated. Figure 5.10a presents combined graphs of the layer-decomposed PDOS for Ti 3*d*-electron, La 5*d*-electron, and O 2*p*-electron in GB core (middle) and each bulk-like (upper and lower) region. As demonstrated in the PDOS, the bulk-like area exhibits a wide band gap of ~2.0 eV, similar to bulk LLTO (Figure 5.10a). This suggests that the bulk-like region exhibits electron-insulating properties. However, the Fermi level shifts slightly within the oxygen valence band in the GB core region, demonstrating p-type conductive characteristics. This suggests that holes can be caught in the GB with Asite deficient region, indicating a great likelihood of conductivity of electron.

While the GB with A-site deficient region appears to be electrically conductive, it is of paramount importance to ascertain the energetic favorability of Li ions entering this GB region, initiating Li dendrite formation in the intergranular gap. To investigate the thermodynamic predilection of Li ions moving into the GB with A-site deficient, the formation energy of Li interstitial defect is computed, considering the designated sites for defect (Figures 5.11a and b). Figure 5.10b presents the formation energy of Li interstitial defect, considering the chemical potential of lithium metal, in two distinct charge states (+1 (green) and neutral (black)) for both GB core (right) and bulk-like (left) regions. In Figure 5.10b, it can be observed that in the bulk-like area, the Li-ion interstitial defects in the +1 charge state (-4.56 eV) have a lower formation energy compared to the neutral state (-4.43 eV). Likewise, in the GB core region, the Li atom is more energetically favorable to reside in the +1 charge state than in the neutral state (-3.44 eV formation energy of Li<sup>+</sup> interstitial defect). It is crucial to emphasize that the computed charge transition level (+1/0) for the GB core region is relatively closer to the valence band edge compared to the bulk-like area (Figure 5.11c). This suggests that Li atoms are more likely to reside in the +1 charge state than as  $Li^0$  in the GB core and bulk regions of LLTO. Even though the formation energy of Li interstitial defect in the bulk-like area differs from that observed in the stoichiometric GB configurations, it remains consistent that the energetically more favorable state for Li is in the +1 charge state within the bulk-like region as opposed to the GB core region. Furthermore, to evaluate the influence of the external environment on the chemical potential of Li in the solid electrolyte, the formation energy of Li interstitial defect considering a

roughly 4.2 eV lower Li chemical potential is also computed (Table 5.3). In this scenario, the Li atom is more thermodynamically stable in the +1 charge state within the bulk, and entering the GB core region involves an endothermic reaction ( $\Delta E = 1.12 \text{ eV}$ ), indicating that Li<sup>+</sup> movement into the GB core region is challenging. The considerable energy gap suggests that Li<sup>+</sup> tends to remain in the bulk region due to the higher energetic preference. The results suggest that the transfer of Li<sup>+</sup> from the LLTO's bulk region to the intergranular space of the GB with A-site deficient is hindered by a substantial energy barrier, making it a challenging process. The thermodynamic outcome is attributed to the positive repulsion force of densely clustered oxidized O atoms present in the intergranular gap. This outcome also aligns with another experimental observation of the GB with A-site deficient exhibits electron conductive properties, the presence of a Li metallic phase in the intergranular gap is improbable because of the challenging energy barrier for Li ions to transfer from the bulk region to the GB core.



Figure 5.10 (a) Combined graphs display layer-decomposed PDOSs for Ti 3*d*-electron (blue), La 5*d*-electron (green), and O 2*p*-electron (red) in GB core (middle) ad each bulk-like (upper and lower) region; a red dashed line in the right panel indicates the corresponding layers in the GB with A-site deficient structure. (b) Formation energy of Li interstitial defect, considering the chemical potential of Li metal in two different charge states (+1: green and neutral: black), is shown for GB core (right) and bulk-like (left) regions in the LLTO grain boundary configuration



Figure 5.11 Li interstitial defect in (a) bulk-like and (b) GB core regions of the GB with A-site deficient. (c) The charge transition levels for the Li interstitial defect are shown in both the bulk-like region (left) and the GB core region (right) of the GB with A-site deficient. The shaded regions illustrate the valence band (VB) and conduction band (CB) edges

	Near anode ( $\mu_{Li} = -1.91 \text{ eV}$ )		Near cathode ( $\mu_{Li} = -6.11 \text{ eV}$ )	
	neutral	+1	neutral	+1
Bulk	-4.43	-4.56	-0.23	-0.36
GB	-3.40	-3.44	0.80	0.76

Table 5.3 The formation energy of Li interstitial defect in two different charge states (+1 and neutral) for GB core and bulk-like regions in the GB with A-site deficient structure of LLTO. The defect formation energy computed based on the near cathode and anode chemical potential of Li corresponds to the lower and upper limit, respectively

#### 5.1.4 Interaction of Li with the intergranular pore space

In solid electrolytes fabricated through powder sintering in ceramics, the presence of small pores is unavoidable. Pores typically comprise about 2 to 5% of the volume of the material in most dense ceramics.[127] Pores in solid electrolytes

have been correlated with low performance or problems in many studies.[128] In the process of powder sintering to fabricate ceramic-based solid electrolytes, there will inevitably be some presence of pores, albeit in minimal quantities.[127] To explore the effect of pores at the grain boundary between solid electrolyte grains on the formation of the Li metallic phase, a model structure of LLTO with incorporated pores is designed (Figure 5.12). A surface structure with (111) pores aligned in the same plane direction as the stoichiometric grain boundary is created to investigate the specific impact of the pores while removing other structural influences. The atomic arrangement in the pore region exhibits a similar configuration to the stoichiometric grain boundary, with the Ti atom maintaining six oxygen coordination numbers and exposing an octahedral face towards the pore space (Figure 5.12). For an accurate calculation of the energy in the (111) pore-containing structure of LLTO with nonstoichiometric composition, defining the chemical potential for each element becomes necessary. Since the symmetric oxygen termination results in a nonstoichiometric surface, thermodynamic arguments are used to establish definite chemical potentials  $(\mu_i)$  for the elements La, Li, Ti, and O through a suitable combination of three compounds in equilibrium with LLTO. This section focuses on defining the chemical potential for each component to precisely compute the energy of the nonstoichiometric (111) pore-containing surface of LLTO. The composition of LLTO, La<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O, and O<sub>2</sub> was considered to simulate the experimental synthesis and oxidizing conditions of LLTO (Table 5.4).[129] Based on the computed chemical potentials, the (111) surface with pore exhibited a surface energy of  $1.326 \text{ J/m}^2$ , which is greater than the formation energy for  $\Sigma 3(111)$  GB. This suggests that the formation of the GB is thermodynamically more favorable than maintaining the structure with pore in the same plane direction. Thus, the GB formation ratio inside

the solid electrolyte in polycrystalline is likely to be greater. However, the surface energy of the (111) plane direction exhibits similarities with that of other oxides, as reported in previous studies.[114,120] This suggests that the prevalence of GBs is expected to be higher in the (111) plane direction compared to surfaces with pores in the intergranular regions of powder-sintered solid electrolytes. Thus, we studied the (111) surface with pore structure to investigate the mechanisms behind lithium metal germination from surface electrons and Li ions.

Elements	Li	La	Ti	0
$\mu_i (\mathrm{eV})$	-4.949	-14.405	-18.658	-4.364

Table 5.4 In an oxidizing condition, the chemical potentials of La, Li, Ti, and O were determined



Figure 5.12 (a) Combined graphs illustrate the layer-decomposed PDOSs for O 2*p*-electron (red) and Ti 3*d*-electron (blue) in intergranular pore (upper and lower) and each bulk-like (middle) region; the relevant layers in the LLTO surface structure are indicated by a red dashed rectangle in the right pane. (b) Formation energy of Li interstitial defect, taking into account the chemical potential of Li metal in two different charge states (+1 charged and neutral), is presented for the LLTO surface's pore regions configuration

To investigate the electron conductivity at the interface of solid electrolyte grains with pores, the electron configurations of the internal surface within the LLTO's pore space were examined. The study analyzed the combined graphs of the layer-decomposed PDOS of the O 2*p*-electron and Ti 3*d*-electron in pore (upper and lower) and each bulk-like (middle) region. The findings indicated that the bulk-like region in the surface structure, similar to other GB models, exhibits electronic insulation with a significant band gap of approximately 2.0 eV (Figure 5.12a). In contrast, the Fermi level moved inside the valence band in the pore surface region, resembling the GB core region of the GB with A-site deficient, indicating p-type conductivity. The study also found that the uncoordinated oxygen at the surface was the main contributor to electronic conductivity. Therefore, the study suggests that the presence of holes in the intergranular pore area suggests a high likelihood of electronic conductivity in this region.

By investigating the electronic conduction pathway facilitated by oxygen atoms in the intergranular pore space, we also explore the possibility of Li ions accumulating as lithium metal in this area . To assess the likelihood of formation of Li metallic phase within the intergranular pore space, we compute the formation of Li interstitial defect, considering the chemical potential of lithium metal, in two distinct charge states (+1 and neutral) at the pore region (Figure 5.12b). As shown in Figure 5.12b, a Li atom is energetically more favorable to form as Li<sup>0</sup> (-4.24 eV) than as Li<sup>+</sup> (-4.15 eV) within the pore zone. Despite the ~4.2 eV decrease in chemical potential of Li resulting from external potential effects, Li atoms are inclined to form as Li<sup>0</sup>. Given the electronic conductivity of the pore region, this finding implies that LLTO's internal pore surface is conducive to facilitate Li ion reduction, leading to the formation of a metallic phase on the surface. In other words, the presence of defects in the atomic bonding at the intergranular pore surface leads to a shift in the Fermi level, which offers pathways or trapping sites for inherent carriers (electrons/holes), enabling Li ions to reach the pore area for a reaction with the captured electron. This results in generating a Li metallic phase within the intergranular pore zone. Hence, in contrast to other interfaces between crystalline grains, the formation of the Li metallic phase initiates within the intergranular pore space of the solid electrolyte.

#### 5.1.5 Conclusion

We comprehensively understand the source of Li metallic phase germination at the interfaces of solid electrolyte crystalline grains. As depicted in Figure 5.13, the intergranular pore area is vital. By integrating the findings from Asite deficient and stoichiometric GBs, we confirm the difficulty of Li ions aggregation into the Li metallic phase within tightly connected intergranular or GBs areas. Conversely, the intergranular pore space or GB exhibits a p-type conductive characteristic. Li-ions preferentially aggregate in the pore area with a charge state in neutral, leading to the Li metallic phase germination in intergranular area. Essentially, the pores within solid electrolytes represent critical sites where Li metallic phase germination initiates. Due to the reactivity of LLTO with the lithium metal phase, any lithium metal nuclei present within LLTO would probably react with the LLTO rather than continuing to grow, leading to decomposition starting from the interior of LLTO. Additionally, while it is recognized that LLTO reacts with the lithium metal phase, causing  $Ti^{4+/3+}$  reduction, the findings suggest that the lithium metal phase can form within LLTO even in the absence triggering Ti<sup>4+/3+</sup> reduction. This study offers valuable insights into designing and controlling Li metal phase-free solid electrolytes, particularly emphasizing the importance of tailoring solid electrolyte grain condensation. Importantly, this applies to both solid electrolytes that are reactive with lithium metal at the interface (e.g., LiPON and Li<sub>3</sub>PS<sub>4</sub>) and those that are not (e.g., Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>),[101] the pore spaces within solid electrolytes are likely to serve as electron trapping regions, leading to the creation of either a lithium metal phase in the solid electrolyte or solid electrolyte interphase. Consequently, creating a densified intergranular microstructure and eliminating the pore space in solid electrolytes represents a general approach for all solid electrolyte materials to minimize undesired phase creation within solid electrolytes. Indeed, a recent investigation validates the superior performance of compacted solid electrolytes in comparison to traditionally produced solid electrolytes.[130]



Figure 5.13 Depiction of the influence of the intergranular region (compacted grain boundary and grain boundary containing a pore) on the initiation of lithium metal phase growth
# 5.2 Mitigating Interfacial Impedance for All-Solid-State-Battery

#### 5.2.1 Introduction

ASSBs represent a promising energy storage technology wherein the conventional liquid electrolyte is substituted by solid electrolytes, necessitating the establishment of an efficient ion transport pathway in the electrode.[131,132] To construct ASSBs, the layer for solid electrolyte is positioned between the anode and cathode while also incorporated within each electrode to facilitate effective Li<sup>+</sup> transport, emulating the electrode configuration found in liquid electrolyte-infused LIBs. Furthermore, it is crucial to appropriately match the composite electrode with a suitable solvent and binder for the solid electrolyte, as commonly utilized sulfide solid electrolytes exhibit considerable sensitivity to polar solvents, restricting the available binder-solvent pair options.[133] Notably, substantial capacity degradation is frequently seen in composite electrodes, primarily owing to the comprehensive decomposition reactions between the active materials, solid electrolyte, and carbon additives.[134] Lately, studies have demonstrated that Li<sup>+</sup> transport in ASSBs is achievable through interparticle diffusion between active materials via their closely connected interfaces.[135] Moreover, active materials such as graphite, possessing adequate electron conductivity, no longer require carbon additives. Consequently, streamlined ASSBs electrodes, composed exclusively of binders and active materials, can fully leverage ion-conductive binders and distinctly assess their impact on Li<sup>+</sup> transport within the electrodes (Figure 5.14). This is attributed to binders being chiefly accountable for area-specific resistances, as they are between active materials.[136] Furthermore, the absence of a significant polarity mismatch between

electrode components allows for utilizing and assessing various traditional polar binders known for their strong binding capabilities.[136] Herein, we conducted multiscale modeling simulations to confirm that the conductive lithium-substitutionmodulated (LSM)-CMC facilitated additional Li<sup>+</sup> transport routes, significantly reducing internal resistance by enhancing interfacial conduction.



Figure 5.14 Comparative schematic of a conventional cell with a liquid electrolyte-impregnated electrode versus an all-solid-state cell with an electrolyte-free electrode, reproduced from D. O. Shin[47]

#### 5.2.2 Performance Enhancement with Li Introduction

To elucidate the connection between interfacial  $Li^+$  conduction in the electrode and the Na/Li mixing ratio ( $DS_{Li}$ ), the CMC binders' Li<sup>+</sup> diffusion kinetics were investigated using first-principles calculations. Initially, Na/Li vacancy and Li interstitial formation energies were computed utilizing a logically arranged atomic model to determine the Li<sup>+</sup> diffusion mechanism within the LSM-CMC binders (Figure 5.15). Table 5.5 shows that the formation energy of Li<sup>+</sup> interstitials is lower compared to the formation energy of Li/Na vacancies, suggesting that the dominant

diffusion mechanism for LSM-CMC binders is the migration of Li<sup>+</sup> interstitials. Subsequently, AIMD simulations were conducted to explore the Li<sup>+</sup> transport characteristics in two extreme cases, Li-CMC ( $DS_{Li} = 0$ ) and Na-CMC ( $DS_{Li} = \infty$ ) binders containing an additional Li<sup>+</sup>. As displayed in Figures 5.16a and b, both cases exhibit a 2D-like Li<sup>+</sup> diffusion network along the CMC, represented by the yellow isosurface. Nonetheless, Li-CMC demonstrates an extra coordinated exchange movement of existing Li<sup>+</sup> ions and interstitial Li<sup>+</sup> ions is observed, facilitating a 3Dlike pathway for Li<sup>+</sup> diffusion. At the same time, Na-CMC scarcely exhibits coordinated exchange migration of interstitial Li<sup>+</sup> and pre-existing Na<sup>+</sup>.



Figure 5.15 Atomic models of (a) Na-CMC and (b) Li-CMC binder, where onethird of the functional groups are exchanged to CH<sub>2</sub>COONa and CH<sub>2</sub>COOLi, respectively. (c) LSM-CMC structure composed of three CMC sheets where the position of each CMC sheet is optimized (O: red, C: brown, H: light pink, Li: orange, and Na: blue spheres)

Materials	Avg. vacancy form	Avg. Li interstitial	
	Na	Li	formation energy (eV)
Na-CMC	4.55	-	0.65
DS <sub>Li</sub> 2-CMC	4.22	4.89	0.16
DS <sub>Li</sub> 0.5-CMC	4.18	4.75	0.21
Li-CMC	-	4.71	1.02

Table 5.5 Average Li/Na vacancy and Li interstitial defect formation energy for LSM-CMC



Figure 5.16 The probability density of Li<sup>+</sup> spatial distribution throughout AIMD at 500 K for (a) Na-CMC and (b) Li-CMC binder (O: red, C: brown, H: light pink, Li: orange, and Na: blue spheres). Migration energy barriers in Li-CMC and Na-CMC for (c) in-plane Li<sup>+</sup> hopping and (d) out-of-plane coordinated migration of Li<sup>+</sup>/Na<sup>+</sup> and Li<sup>+</sup> along the migration pathway (displayed adjacent to the graph)

To qualitatively assess the Li<sup>+</sup> migration barrier in two extreme cases, Na-CMC ( $DS_{Li} = \infty$ ) and Li-CMC ( $DS_{Li} = 0$ ), NEB calculations were performed for Li<sup>+</sup> interstitial hopping in two situations: out-of-plane and in-plane Li<sup>+</sup> hopping. In the in-plane direction, referring to the pathway along the CMC gap, Na-CMC exhibited a marginally lower migration barrier (0.89 eV) compared to Li-CMC (1.05 eV) (Figure 5.16c). Considering external factors or various Na-CMC or Li-CMC morphologies, the variance cannot distinguish outstanding in-plane Li<sup>+</sup> diffusion between Na-CMC and Li-CMC.[67,137] Regarding the out-of-plane direction, which pertains to the pathway traversing the CMC via a coordinated movement with pre-existing Na<sup>+</sup> or Li<sup>+</sup>, Li-CMC demonstrated a significantly lower migration barrier (0.79 eV) compared to Na-CMC (1.34 eV) (Figure 5.16d). This notable variance suggests the presence of an extra rapid Li<sup>+</sup> diffusion pathway in Li-CMC. Furthermore, the migration barrier for Na-CMC displayed a consistently increasing trend, signifying that replacing Na<sup>+</sup> with Li<sup>+</sup> is not energetically advantageous. In other words, Na-CMC and Li-CMC exhibit comparable Li<sup>+</sup> migration barriers along the CMC gap. Still, the coordinated migration of interstitial Li<sup>+</sup> and pre-existing Na<sup>+</sup> or Li<sup>+</sup> is enhanced explicitly in Li-CMC. These results are consistent with earlier research, which reported that the impact of marginally increased diffusivity on capacity utilization becomes notably significant under high C-rates or elevated loading levels.[138] As a result, the 3D-like Li<sup>+</sup> diffusion network in Li-CMC would enhance the Li<sup>+</sup> transport performance, especially pronounced in the electrolyte-free electrode.

### 5.2.3 Performance Enhancement Based on Substitution Ratio

To comprehend how performance varies based on the lithium substitution rate, we assessed LSM-CMC binders in various Na/Li mixing ratios ( $DS_{Li} = \infty$ , 2, and 0.5). Firstly, to anticipate potential Li<sup>+</sup> diffusion pathways for LSM-CMC binders ( $DS_{Li} > 0$ ), Li atoms were organized within the CMC interlayer gaps at onefifth intervals, accompanied by structural optimization (Figures 5.17a and b). Examining the calculated outcomes suggests a reasonable hypothesis that Li<sup>+</sup> diffusion might transpire along the CMC gap by hopping over pre-existing Li<sup>+</sup> or Na<sup>+</sup>, as illustrated in Figure 5.17c. We performed NEB calculations to evaluate the Li<sup>+</sup> diffusion activation barrier in LSM-CMC binders with  $DS_{Li}$  greater than 0, considering three potential diffusion scenarios: Li<sup>+</sup> diffusion (i) through Na<sup>+</sup>, (ii) through Li<sup>+</sup>, and (iii) along the CMC gap. For Li<sup>+</sup> diffusion through Na<sup>+</sup>, referring to the path traversing over Na<sup>+</sup> to another CMC gap, all LSM-CMC binders exhibited a energy barrier for diffusion of approximately 0.16-0.19 eV (Figure 5.18a). Li<sup>+</sup> diffusion through Li<sup>+</sup> exists only when  $DS_{Li} < \infty$ , the energy barrier for diffusion was roughly 0.11-0.12 eV (Figure 5.18b). For Li<sup>+</sup> diffusion along the CMC gap, all three CMC binders exhibit a energy barrier for diffusion of approximately 0.09-0.10 eV (Figure 5.18c). Each path presents a similar energy barrier for diffusion irrespective of the CMC, implying that directly comparing diffusion behavior at the microscopic level is inadequate. Given the extremely stochastic nature of the diffusion procedure, influenced by the three suggested pathways, it becomes essential to assess the macroscopic diffusion characteristics based on the Na/Li mixing ratio ( $DS_{Li}$ ) in CMC.



Figure 5.17 (a) Systematic Li<sup>+</sup> insertion at the CMC gap (b) with 1/5 interval of the CMC gap plane to find possible Li<sup>+</sup> diffusion path. (c) Schematic illustration for possible Li<sup>+</sup> diffusion pathway based on the interstitial formation energy



Figure 5.18 Three distinct representative Li<sup>+</sup> diffusion pathways for Na-CMC (blue),  $DS_{Li}2$ -CMC (green), and  $DS_{Li}0.5$ -CMC (orange): Li<sup>+</sup> diffusion (a) via Na<sup>+</sup>, (b) via Li<sup>+</sup>, and (c) along the CMC gap. The energy landscape for Li<sup>+</sup> diffusion obtained through calculations (displayed on the right panel of each graph). (d) The relative diffusion constant of  $DS_{Li}0.5$ -CMC and  $DS_{Li}2$ -CMC compared to Na-CMC varying with the reciprocal of temperature

Based on our DFT findings on nanoscale Li<sup>+</sup> diffusion, we created a simplified kMC model to compare the microscopic Li<sup>+</sup> diffusion properties of each CMC binder. Figure 5.18d presents the relative microscopic Li<sup>+</sup> diffusion coefficients of DS<sub>Li</sub>2-CMC and DS<sub>Li</sub>0.5-CMC compared to Na-CMC, computed at temperatures lower than the melting point of the CMC binders (300-600 K). The microscopic Li<sup>+</sup> diffusion coefficients showing positive values confirm that DS<sub>Li</sub>2-CMC and DS<sub>Li</sub>0.5-CMC exhibit enhanced microscopic Li<sup>+</sup> diffusion properties compared to Na-CMC at various operating temperatures. Moreover, the distinction in kinetic performance was particularly noticeable at lower temperatures. To qualitatively compare the microscopic diffusion activation energies (*E<sub>a</sub>*), the relative microscopic Li<sup>+</sup> diffusion constants were adjusted using the Arrhenius equation based on the computations, as detailed in Equation (2.21). Both LSM-CMC binders exhibit a reduced activation

energy for diffusion compared to Na-CMC. Furthermore, the CMC binder with a lower DS<sub>Li</sub> demonstrated a lower microscopic diffusion barrier, enhancing Li<sup>+</sup> diffusion characteristics. As depicted in Figure 5.19, Li<sup>+</sup> must traverse the diffusion route via Na<sup>+</sup> in all potential Li diffusion pathways, suggesting that the diffusion via Na<sup>+</sup> constitutes the rate-determining step for DS<sub>Li</sub>2-CMC. Nevertheless, DS<sub>Li</sub>0.5-CMC possesses a distinct diffusion pathway comprised solely of low energy barriers for diffusion (diffusion along the CMC gap and via pre-existing Li<sup>+</sup> and), resulting in improved Li<sup>+</sup> diffusion properties compared to DS<sub>Li</sub>2-CMC. For example,  $DS_{Li}0.5$ -CMC can establish a Li<sup>+</sup> percolation path without traversing a route with a high energy barriers for diffusion (diffusion via Na<sup>+</sup>), demonstrating superior kinetic features. Hence, we can infer that a lower LSM would enhance the continuous lowenergy-diffusion-barrier percolation complex for Li<sup>+</sup> transport performance, particularly accentuated in the electrolyte-free graphite-electrode structure. These observations align with previous studies where even a modest increase in diffusivity could positively impact capacity utilization, specifically under rapid cycling conditions.[138]



Figure 5.19 Schematic illustration for Li<sup>+</sup> diffusion pathway considered for the kMC simulation for each LSM-CMC binder. The Li<sup>+</sup> diffusion via Na<sup>+</sup> determines the Li<sup>+</sup> diffusion rate of DS<sub>Li</sub>2-CMC, while DS<sub>Li</sub>0.5-CMC has a relatively fast percolation pathway containing the low energy barriers for diffusion (pathways along the CMC gap and via pre-located Li<sup>+</sup>)

#### 5.2.4 Conclusion

We examined the association between interfacial  $Li^+$  conduction in electrodes and the Na/Li substitution ratio ( $DS_{Li}$ ) in CMC binders through firstprinciples calculations and AIMD simulations. Our study revealed that  $Li^+$  interstitial migration is the predominant diffusion mechanism for LSM-CMC binders. A thorough evaluation of various Na/Li mixing ratios demonstrated that CMC binders with lower  $DS_{Li}$  values exhibit lower microscopic diffusion barriers, resulting in enhanced  $Li^+$  diffusion properties. This observation suggests that increasing the substitution ratio contributes to forming a continuous low-energy-diffusion-barrier percolation complex, essential for optimal  $Li^+$  transport characteristic. Particularly, the Li-CMC binder presents a remarkable 3D-like diffusion pathway, improving  $Li^+$ transport efficiency. This improvement in  $Li^+$  diffusion is vital for capacity utilization, particularly under fast cycling conditions, and is especially pronounced in electrolyte-free graphite-electrode configurations. The capacity to adjust the Na/Li mixing ratio in CMC binders to optimize Li<sup>+</sup> diffusion characteristics offers considerable potential for developing high-performance Li-ion secondary batteries, especially ASSBs. These findings deepen our understanding of the underlying diffusion mechanisms and lay the groundwork for creating novel binder materials that can further augment the performance of Li-ion secondary batteries, especially ASSBs, across various applications.

### **Chapter 6** Conclusion

In this dissertation, we propose a robust multiscale analysis based on firstprinciples calculations to elucidate the underlying electrochemical performance degradation mechanism of solid-state materials for next-generation secondary batteries, such as SIBs. Utilizing a multiscale approach that combines first-principles calculations, phase field models, statistical thermodynamics and kinetics, and continuum theory, this proposed integrated methodology addresses atomic physics and chemistry, encompassing electronic structures, nano- and microscale thermodynamics and kinetics, primary particle-level phase transitions, stress generation, and secondary particle-level mechanical deformation through the application of multiscale computational approaches. This suggested methodology offers significant advantages for examining solid-state electrodes in electrochemical energy storage systems. Their performance is closely linked to physical and chemical properties at the atomic scale, electrochemical phase transition at the nanoscale, and mechanical deformation and failure at the microscale.

Based on this multiscale modeling framework, as the initial stage in developing high-energy density cathodes with consistent cycling performance for SIBs, we examined the thermodynamic stability of phase and the kinetics of phase transitions. These elements are integral to maintaining the capacity of manganese-based layered cathode oxides (specifically Na[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> and NaMnO<sub>2</sub>) and within the context of their application in rechargeable batteries. We explored that the compound Na<sub>1</sub>. x[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub> avoids the transition to a Na-non phase during charging due to the existence of a thermodynamically stable HN-poor phase at x = 0.875, contrasting with Na<sub>1-x</sub>MnO<sub>2</sub> which exhibits a phase separation reaction leading to the formation of a Na-non phase at x = 1.0, thereby suggesting higher reversible nature of the anionic redox reaction for Na<sub>1-x</sub>[Mn<sub>1/2</sub>Ni<sub>1/2</sub>]O<sub>2</sub>. Considering these results, we propose two requirements for high-energy-density and consistent cycling performance for solid-state cathode active materials for SIBs: (i) improving the solubility of vacancy/Na for the Ni–Mn binary oxide during the redox reaction involving cations and (ii) effectively exploiting the HN-poor phase during the redox reaction involving anions.

Furthermore, using this proposed multiscale methodology, we identified the fundamental cause for the mechanical deterioration of Ni-rich layered oxides  $(Na[Mn_{1/2}Ni_{1/2}]O_2)$ . We found that the comparatively large size of Na ions maximizes anisotropic deformation during the (dis)charging process in the material. This anisotropic lattice deformation substantially impacts the secondary particle deformation, leading to capacity fading. However, we propose that such performance degradation at the secondary particle scale can be mitigated through morphological engineering.

Indeed, since the proposed multiscale modeling approach in this dissertation is the versatile methodology to investigate electro-chemo-mechanical phenomena in secondary batteries as well as complex electrochemical systems, such as supercapacitors, solar cells, and catalysts, this framework could serve as a valuable foundation for studying and developing various energy storage materials. In future work, multiscale modeling will illuminate the critical issues in all-solid-state batteries. It will be further expanded to address the design of hydrogen energy conversion systems and next-generation energy storage systems like lithium metalfree ASSBs and Li-S batteries.

### Appendix

# Appendix. A Inferior Electrochemical Properties of Sodium-ion Battery Cathode Materials

Cathode materials for SIBs exhibit suboptimal electrochemical performance due to inherent limitations associated with Na<sup>+</sup>. Firstly, sodium-ion's approximately 0.3 V lower working voltage than lithium-ion results in reduced energy density for SIBs. Several studies have proposed Ni-doped Mn-based P2-type layered oxides to tackle this issue, which display a higher average potential of approximately ~3.25 V versus Na/Na<sup>+</sup>.[9,11] Furthermore, numerous investigations have demonstrated that additional metal substitutions (e.g., Li,[139-141] Ti,[142,143] Co,[144-146] and Fe[147]) in Ni-doped oxides enhance electrochemical performance. Secondly, the substantial size of Na<sup>+</sup> (1.02 Å) leads to increased volumetric enlargement in the crystal structure during (de)intercalation compared to LIBs. To address this handicap, Wang et al. presented Al-doped Na<sub>0.67</sub>Mn<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>2</sub>, which exhibits improved cycle performance by reducing volumetric strain.[148] In addition, Kim et al. synthesized  $Na_4Mn_3(PO_4)_2(P_2O_7)$  with an open framework owing to mixed polyanions  $(P_2O_7)^{4-1}$ and (PO<sub>4</sub>)<sup>3-</sup>.[149] This compound also demonstrates Na<sup>+</sup> diffusion channel enlargement, facilitated by the extraordinary Jahn-Teller distortion provoked by manganese redox reactions, enhancing cycle stability. Even though these conventional tactics have effectively ameliorated cyclability and voltage issues related to sodium cathode materials, comprehensive study on the specific

requirements for the rational design of inherent electronic structures and atomic of sodium cathode materials is lacking. Moreover, the heterogeneous Na<sup>+</sup> spread in cathode materials is essential since phase separation during (de)sodiation exacerbates chemical potential non-uniformity, resulting to increased polarization during the cycle. This uneven Na<sup>+</sup> distribution also results in localized stress accumulation in active materials, causing significant structural deterioration in electrodes. Nevertheless, there is a scarcity of systematic studies from this viewpoint, and conventional methods involving doping or stoichiometric adjustments have been frequently used. Thus, a thorough understanding of structural evolution, thermodynamic stability, and electronic structures from cyclability and energy density viewpoints is essential to surmount the inherent constraints on the electrochemical performance of cathode materials in SIBs.

Generally, LNMO is a lithium cathode material known for its high energy density, which is attributed to a high working potential of ~4.7 V versus Li/Li<sup>+</sup>.[150–152] This favorable high working potential feature primarily arises from the Ni<sup>2+</sup>/Ni<sup>4+</sup> redox couple, while Mn<sup>4+</sup> keeps its oxidation state throughout the discharge/charge procedure.[150–152] Given the narrower voltage window (~0.3 V) for SIBs compared to LIBs, it is believed that a theoretically well-designed NNMO would serve as a promising high-energy-density cathode for SIBs, as the cationic redox reaction is expected to occur at a high potential of ~4.4 V versus Na/Na<sup>+</sup>.

We computed the mixing enthalpy's formation energies to validate the high voltage prediction. We considered all potential vacant Na/Li sites during the deintercalation of LNMO and NNMO (Figures A.1a and b). Based on the mixing enthalpy's formation energies, both materials possess thermodynamically stable ground states at fully intercalated (x = 0) and fully deintercalated (x = 1) states

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(Figures A.1c and d). Considering these ground states, we computed the equilibrium potential varying with the reciprocal of the alkali metal (AM; orange: Na, green: Li) content (*x*) in AM<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>. Figure A.1e reveals that LNMO exhibits a high potential (4.7 V vs Li/Li<sup>+</sup>), consistent with experimental findings.[151,152] Additionally, NNMO exhibits a relatively elevated equilibrium voltage (3.8 V vs. Na/Na<sup>+</sup>), resulting in a significantly higher energy density compared to other cathodes for sodium-ion batteries, indicating potential high energy density cathode candidates for SIBs. Contrary to our expectations (i.e., the lower redox potential of Na versus that of Li), NNMO experiences an ~0.6 V voltage drop compared to LNMO. To better comprehend this extra voltage loss, we analyzed the electronic structures of the transition metals in LNMO and NNMO, as electrochemical potential is generally intimately associated with the redox characteristics of transition metals.



Figure A.1 Formation energies per formula unit of mixing enthalpy at 0 K, calculated using first-principles considering all possible (a) Li/vacancy configuration in Li<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, and (b) Na/vacancy configuration in Na<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> both for  $0 \le x \le 1$ . (c) Atomic models of lithiated (x = 0) and delithiated (x = 1) Li<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, and (d) sodiated (x = 0) and desodiated (x = 1) Na<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, both depicted in the (100) direction. (e) Computed potentials for delithiation or desodiation as functions of the inverse alkali metal (AM; orange for Na, green for Li) content (x) in AM<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>

To explore the redox process in NNMO during desodiation, we conducted an in-depth examination of the electronic configuration of NNMO. Based on CFT, PDOS in totally sodiated (x = 0.0) NNMO reveals the electronic structure of Mn with a charge state of  $4+(t_{2g}{}^{3}e_{g}{}^{0})$  and Ni with a charge state of  $2+(t_{2g}{}^{6}e_{g}{}^{2})$ . In contrast, the PDOS in totally desodiated (x = 1.0) NNMO shows a charge state of Ni in  $4+(t_{2g}{}^{6}e_{g}{}^{0})$  (Figures A.2a and b). Examining the oxidation states of transition metals in fully sodiated and desodiated NNMO, we observed that only the 3*d*-electrons of Ni in the valence band undergo oxidation into the conduction band to compensate for the charge during desodiation. Likewise, in LNMO, Ni serves as a redox center

(Ni<sup>2+</sup>/Ni<sup>4+</sup>), as we consider the electronic configuration change of transition metals during delithiation (Figures A.2c and d). To perform a quantitative analysis of the redox mechanism, we employed Bader analysis to calculate the net charges of Ni and Mn in NNMO at different Na inverse content levels (Figures A.2e and f).[153] Throughout the desodiation process, the net charges of Mn remain unchanged, while the net charges of Ni steadily increase to maintain charge balance in NNMO, ultimately reaching the same net charges of Mn and Ni observed in LNMO (Figures A.2g and h). These charge trends correspond with the calculated PDOS of Ni and Mn during Na extraction, providing confirmation that the redox mechanism in NNMO is mainly analogous to that of LNMO. Both utilize a dual redox couple of Ni<sup>2+</sup>/Ni4<sup>+</sup> to facilitate the high voltage characteristics of the material.[150–152] Nevertheless, these findings do not account for the additional voltage loss in NNMO, indicating the need for further investigation and comprehension.



Figure A.2 Variations in Mn and Ni 3*d*-electrons during the sodiation (lithiation) process of Na<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (Li<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>). PDOS graphs for Mn (purple) and Ni (gray) 3*d* orbitals, ranging from x = 1.0 to x = 0.0, in (a-b) Na<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (unfilled) and (c-d) Li<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (filled), respectively. Bader charge analysis-based calculated net charges for (e) Ni and (f) Mn in Na<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, and for (g) Ni and (h) Mn in Li<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, as functions of inverse Li or Na content (x)

To clarify the unwanted potential loss, we closely analyzed the polyhedral structures of Mn–O and Ni–O in NNMO and LNMO, as the transition metals' 3delectrons are chemically engaged in the redox potential and physically influence bonding with the nearest oxygen (Figures A.3a and b).[154] In tetrahedra containing charge carrier ions, both volume and bond length are expanded in NNMO due to the comparatively bigger ionic radius of Na<sup>+</sup> compared to Li<sup>+</sup> (by  $\sim 0.26$  Å) (Table A.1). Despite the MnO<sub>6</sub> octahedra in NNMO being nearly indistinguishable from those in LNMO, the bond length and volume of NiO<sub>6</sub>, which serves as the redox center, significantly expand. From a bonding perspective, the nature of transition metal bonding is dictated by the local site energy of the transition metal.[154] The lengthened Ni-O bond suggests a reduction in Ni-O local bonding strength, increasing Ni local site energy. The higher local site energy facilitates electron extraction with lower potential, leading to a decrease in the equilibrium voltage of NNMO. Such occurrences have been observed in various cathode types through experimental investigations.[154] Additionally, the reduced local bonding strength can be inferred from the softer elastic properties (B<sub>H</sub> and E<sub>H</sub>) of fully sodiated NNMO compared to fully lithiated LNMO (Table A.2).

Compound	Guest ions concentration	Average structure parameter						
		Volume (Å <sup>3</sup> )			Bond length (Å)			
		AMO <sub>4</sub>	MnO <sub>6</sub>	NiO <sub>6</sub>	АМ-О	Mn–O	Ni-O	
LNMO	x = 0	4.04	9.65	11.52	1.99	1.94	2.08	
	x = 1	-	9.64	8.79	-	1.95	1.88	
NNMO	x = 0	5.18	9.73	11.90	2.17	1.96	2.13	
	x = 1	-	9.63	8.79	-	1.95	1.88	

Table A.1 Table showing computed polyhedral structural parameters (e.g., bond length and tetrahedral or octahedral volume) for MnO<sub>6</sub>, NiO<sub>6</sub>, and Li/NaO<sub>4</sub>, for Li<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and Na<sub>1-x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> compounds.

Material	Guest ions content	c <sub>11</sub> [GPa]	c <sub>12</sub> [GPa]	c <sub>44</sub> [GPa]	B <sub>H</sub> [GPa]	G <sub>H</sub> [GPa]	E <sub>H</sub> [GPa]	$\nu_{_{ m H}}$
LNMO -	<i>x</i> = 0	178.1	82.7	78.2	114.5	64.1	162.1	0.26
	<i>x</i> = 1	135.2	54.3	66.1	81.3	54.3	133.2	0.23
NNMO-	<i>x</i> = 0	143.0	95.1	59.0	111.1	41.1	109.8	0.34
	<i>x</i> = 1	135.2	54.3	66.1	81.3	54.3	133.2	0.23

Table A.2 Elements of the constitutive tensor and the elastic characteristics of polycrystals, calculated using the Voigt-Reuss-Hill approximation for  $Na_{1-x}Ni_{0.5}Mn_{1.5}O_4$  and  $Li_{1-x}Ni_{0.5}Mn_{1.5}O_4$ 



Figure A.3 (a-b) NiO<sub>6</sub>, MnO<sub>6</sub>, and AMO<sub>4</sub> (Li for LNMO and Na for NNMO) octahedra in LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and NaNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, respectively. Spatial charge density within the occupied band from -2–0 eV (Fermi level) for oxygen bonded to Ni and (c) Li or (d) Na

To delve deeper into the electron density distribution related to bonding, we computed the partial charge distribution of the valence band in the  $-2 \sim 0$  eV range (Figures A.3c and d). Figure A.3c illustrates that the charge density of the delocalized 2p-orbitals of O<sup>2-</sup> aligns parallel to the Ni–O bond direction in LNMO. However, for NNMO, the charge distribution of the delocalized 2p-orbitals of O<sup>2-</sup> exhibits a

slight rotation toward Na<sup>+</sup> (Figure A.3d), verifying the weakened Ni–O local bonding. The distorted and expanded bonds between the oxygen and redox center atoms indicate the elevated local site energy of Ni, promoting the extraction of *3d*electrons from the redox center. This leads to an unforeseen voltage loss in NNMO. While the computed equilibrium potential of NNMO (3.8 V vs. Na/Na<sup>+</sup>) is enough for consideration as a high-energy-density cathode in SIBs, further improvements in energy density require addressing the octahedral bonding environment.

Although LNMO possesses a high energy density resulting from its high working potential, capacity declining remains an issue, leading to reduced cyclability.[150] Past experiments have demonstrated that phase separation phenomena and internal stresses due to lattice mismatch between phases contribute to crack generation, which may cause LNMO's capacity fading.[155,156] To comprehend the cyclability of NNMO, we examined phase stability by considering structural evolution and thermodynamic factors aspects that influence the cathode materials' cyclability.[13,41,157]

Considering the material stability of NNMO and LNMO, we computed the mixing enthalpy's formation energies for all potential Li/vacancy and Na/vacancy combination in LNMO and NNMO, respectively (Figures A.1a and b), to investigate NNMO's thermodynamic phase stability in comparison to LNMO. The mixing enthalpy of pseudo-ground states in NNMO (orange-filled circles in Figure A.1b) displays a significant deviation from the ground states (red-filled circles in Figure A.1b) as opposed to the pseudo-ground states (green-filled circles in Figure A.1a) in LNMO. From a phase stability standpoint, the difference in mixing enthalpy between ground and pseudo-ground states is dictated by the extent of thermodynamic metastability of the pseudo-ground states, signifying the likelihood of phase

separation during a two-phase reaction. Moreover, a higher enthalpy barrier for phase transition corresponds to a more rapid phase transition caused by metastability.[74,157] More precisely, the phase transition barrier height is directly associated with the steepness of the chemical potential, a negative derivative of free energy; sharper chemical potential slope results in rapid phase а transformation.[74,157] Considering this characteristic, the pseudo-ground/ground states' mixing enthalpy, computed from first-principles formation energies, was regressed using a quadratic double-well function for clear comparison (Figures A.4a and b). NNMO exhibited a significantly higher phase transition enthalpy barrier value  $(H_b)$  of ~0.128 eV, which represents the energy difference between the most unstable and ground states according to the fitted quadratic double-well function. In contrast, LNMO showed a lower value of ~0.066 eV. This finding indicates that intermediate phases in NNMO are less stable than those in LNMO, suggesting a thermodynamically more favorable phase transition for NNMO. Moreover, the elevated barrier in NNMO compared to LNMO suggests a quicker phase transition, implying lower cyclability compared to LNMO.



Figure A.4 Combined-phase mixing enthalpy derived from the pseudoground/ground states obtained through first-principles calculations of mixing enthalpy for (a)  $Na_{1-x}Ni_{0.5}Mn_{1.5}O_4$  and (b)  $Li_{1-x}Ni_{0.5}Mn_{1.5}O_4$  using a quadratic double-well function

Additionally, to account for the impact of structural deformation on phase stability during (de)intercalation, the structural parameters are derived based on the atomic models of LNMO and NNMO. Figure A.5 displays the computed structural parameters (average lattice constant (filled circle) and unit cell volume (open circle)) as functions of the inverse Li and Na content in LNMO and NNMO, respectively. For LNMO, ~5% volumetric strain ( $\Delta V$ ) and ~2% lattice change ( $\Delta l$ ) occur during delithiation (Figure A.5b), which aligns well with previous experimental findings.[152] Conversely, the unit cell volume contracts ( $\Delta V \approx 17\%$ ), and the average lattice constant decreases ( $\Delta l \approx 5\%$ ) for NNMO (Figure A.5a) during desodiation. After deintercalation, NNMO accommodates nearly three times more strains compared to LNMO, primarily due to the difference in size between the Na<sup>+</sup> radius (1.02 Å) and the Li<sup>+</sup> radius (0.76 Å). While LNMO and NNMO possess the same crystal structure (Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>) as a host, the Na<sup>+</sup> radius is almost 34% larger than Li<sup>+</sup>, leading to a substantial volume change in NNMO.



Figure A.5 Computed changes in unit cell lattice constants and volume for (a)  $Na_{1-x}Ni_{0.5}Mn_{1.5}O_4$  and (b)  $Li_{1-x}Ni_{0.5}Mn_{1.5}O_4$ , both in the range of  $0 \le x \le 1$ 



Figure A.6 (a, c) Free energies and (b, d) chemical potentials at 300 K with respect to inverse AM (green: Li, orange: Na) content (x) in  $AM_{1-x}Ni_{0.5}Mn_{1.5}O_4$ , considering elastic energy (dashed line) and homogeneous free energy (solid line)

To examine the mixed influences of thermodynamics and strain on phase stability, we computed the free energies that account for the elastic strain energy of all potential Li/vacancy and Na/vacancy configurations in LNMO and NNMO, respectively, using nanomechanics (Figures A.6a and c). To facilitate a direct comparison, we determined the homogeneous free energy (solid line in Figures A.6a and c) as well as the free energy considering elastic energy (dashed line in Figures A.6a and c) for NNMO/LNMO at 300 K. Upon comparison with the homogeneous free energy, the inclusion of elastic strain effects leads to an elevated phase transition barrier for both materials. Nevertheless, the elastic strain in NNMO significantly increases the phase transition barrier compared to LNMO, potentially indicating accelerated phase separation for NNMO. Considering the previously mentioned phase stability principle, such rapid phase separation could result in a lower cyclability and loss of high potential than LNMO. Moreover, Figures A.6b and d display the chemical potential, obtained from the homogeneous free energy and accounting for the elastic strain energy in NNMO/LNMO at 300 K, is plotted against the inverse AM (orange: Na, green: Li) content in  $AM_{1-x}Ni_{0.5}Mn_{1.5}O_4$ . This analysis indicates the presence of a voltage hysteresis gap between discharge and charge cycles.[148] According to the chemical potential computed using only the homogeneous free energy, NNMO exhibits a more considerable disparity in minimum and maximum values (~0.6 eV/f.u.) than LNMO (~0.4 eV/f.u.) (orange (AM: Na) and green (AM: Li) solid lines in Figures A.6b and d), which signifies the degree of voltage hysteresis. Nevertheless, when considering the elastic strain effects, a considerably more significant hysteresis gap (~1.2 eV/f.u.) is anticipated for NNMO, resulting in a progressively decreasing voltage per cycle (orange (AM: Na) and green (AM: Li) dashed line in Figures A.6b and d).[148]



Figure A.7 Contours of phase separation after  $\hat{t} = 0.08$  in the ab-plane for [a(1)] NNMO and [b(1)] LNMO. Stress fields on the *ab*-plane, resulting from phase separation, comprising  $\sigma_{xx}$ ,  $\sigma_{yy}$ , and  $\sigma_{xy}$  for [a(2-4)] NNMO and [b(2-4)] LNMO, respectively



Figure A.8 Contours of phase separation in the *ab*-plane for LNMO at (a1)  $\hat{t} = 0.02$ , (a2)  $\hat{t} = 0.04$ , (a3)  $\hat{t} = 0.06$ , and (a4)  $\hat{t} = 0.08$ . Similarly, contours for NNMO at (b1)  $\hat{t} = 0.02$ , (b2)  $\hat{t} = 0.04$ , (b3)  $\hat{t} = 0.06$ , and (b4)  $\hat{t} = 0.08$ 

Expanding upon the principles of nanomechanics, we examined the electrochemomechanical stress exerted on LNMO/NNMO during the half-charged state under non-operating circumstances (Figure A.7). To ensure a fair comparison, all physical values were made dimensionless using characteristic values. Due to the cubic nature of the spinel materials, only results on the ab-plane are presented. For the identical non-dimensional time duration ( $\hat{t}$ ) within the equivalent nondimensional cathode material domain, NNMO (Figure A.7b) exhibits a faster phase separation into Na-poor/-rich regions (red and blue regions, respectively) compared to LNMO's separation into Li-rich/-poor regions (Figure A.7a), which aligns with expectations based on free-energy analyses. At non-dimensional time  $\hat{t} = 0.08$ , the interphase between Li-poor/-rich regions for LNMO is difficult to ascertain (Figure A.8). In contrast, distinct interphases are discovered for NNMO (Figure A.8). Furthermore, to explore nanoscale mechanical behaviors within the phase-separating domain, we computed the electro-chemo-mechanical stresses provoked by eigenstrain due to lattice constant changes, utilizing the constitutive tensor derived from ground states (Table A.2). Based on the computed elastic properties (G<sub>H</sub>, B<sub>H</sub>, and E<sub>H</sub> in Table A.2), LNMO exhibits greater stiffness compared to NNMO, implying that LNMO would experience higher mechanical pressure. However, when accounting for eigenstrain during (de)intercalation, the stress fields calculated at the same non-dimensional time  $\hat{t} = 0.08$  reveal more significant tensile or compressive stress in NNMO (~-4 to 4 GPa) (Figures A.7b2-4) compared to LNMO (~-0.5 to 0.5 GPa) (Figures A.7a2-4). Throughout the process toward equilibrium, Figure A.9 demonstrates that more significant stress occurs in NNMO compared to LNMO (Figure A.10). In summary, these findings suggest that the positive electrode containing NNMO could encounter higher interior pressure compared to the one containing LNMO under the same charge state, despite NNMO exhibits a lower stiffness than LNMO. Consequently, considering the electro-chemomechanical and thermodynamic outcomes, strategies to alleviate phase separation are necessary to enhance NNMO's cycle performance.



Figure A.9 Stress fields in the *ab*-plane, arising from phase separation at  $\hat{t} = 0.02$  to  $\hat{t} = 0.08$ , for NNMO, comprising (a1-4)  $\sigma_{xx}$ , (b1-4)  $\sigma_{yy}$ , and (c1-4)  $\sigma_{xy}$ 



Figure A.10 Stress fields in the *ab*-plane, resulting from phase separation at  $\hat{t} = 0.02$  to  $\hat{t} = 0.08$ , for LNMO, comprising (a1-4)  $\sigma_{xx}$ , (b1-4)  $\sigma_{yy}$ , and (c1-4)  $\sigma_{xy}$ 

Investigations into the prerequisites for achieving high-performance Mn-

based sodium spinel cathode materials, specifically NNMO, were conducted from cyclability and energy density standpoints. The persistent low working potential characteristic of SIBs is enhanced to function at a higher voltage (3.8 V vs. Na/Na<sup>+</sup>) for NNMO, attributable to the Ni<sup>2+</sup>/Ni<sup>4+</sup> double redox mechanism. Nonetheless, the inherently considerable size of the sodium ion attenuates the Ni–O bond and facilitates electron removal from the redox center, leading to unwanted voltage loss and diminished energy density in NNMO. Additionally, based on homogeneous free-energy outcomes, NNMO is predicted to experience phase separation into totally (de)intercalated phases, generating lattice mismatches at the interfaces between the phases. The larger sodium ion and elevated phase transition barrier for NNMO result in accelerated phase separation, causing increased polarization occurring in each cycle and a significant stress field for NNMO. Considering the outcomes of the phase separation analysis, it is expected that NNMO would exhibit less favorable cyclability in comparison to LNMO.

Hence, by meticulously examining the relationship between thermodynamic stability, electronic structure, and structural evolution with the electrochemical performance of Mn-based sodium spinel cathodes, three conditions for high electrochemical performance are proposed: (i) regulating the local site energy of the redox center by reinforcing Ni–O bonding to avoid unwanted voltage loss, (ii) augmenting the Na/vacancy solubility during the redox reaction to enhance reversibility and reduce voltage polarization, and (iii) mitigating volume or lattice changes during (de)sodiation to avert mechanical failure (e.g., intra- or inter-granular cracks). Taking these essential aspects into account, it is expected that M-pillared Na<sub>1-x</sub>M<sub>x</sub>Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (divalent or monovalent species M), wherein M serves to fortify the redox center for increased energy density and to restrain radical structural

alterations and voltage hysteresis for improved cyclability, will exhibit enhanced electrochemical performance (Figure A.11). Moreover, these vital considerations offer guidance for developing sophisticated strategies to refine such cathodes.[57]



Figure A.11 M-pillared in NNMO enhancing cyclability and electrochemical performance

# Appendix. B Origin of Hysteretic Oxygen Capacity

The concept of oxygen redox was initially introduced and comprehended by studying a Li-excess non-stoichiometric Mn layered oxide, Li<sub>2</sub>MnO<sub>3</sub>, which exhibited an abnormal charge capacity with a sustained plateau at ~4.5 V versus Li<sup>+</sup>/Li.[158–162] To ascertain the root of this interesting oxygen redox phenomenon in Li<sub>2</sub>MnO<sub>3</sub>, combined theoretical calculations and experimental analyses were performed. The findings revealed that the redox-inactive Mn<sup>4+</sup> species, within the context of CFT, prompted the involvement of O(2p)-electrons in redox reactions at higher energy levels, as opposed to the Mn(3d)-electron, which formed the stabilized  $t_{2g}$  band with three electrons at a lower energy level. [163,164] Numerous investigators have expanded the range of cathode oxides to include Li<sub>2</sub>[TM]O<sub>3</sub> (Li/TM = 2) compounds, incorporating 5*d*- and 4*d*-based oxides such as Li<sub>2</sub>IrO<sub>3</sub> and Li<sub>2</sub>RuO<sub>3</sub>. The aim was to explore the practical application of oxygen redox during battery operation and to understand the function of the monovalent Li<sup>+</sup> species in the TM layer.[17,165] The theoretical substantiation of oxygen redox chemistry in Nabased layered oxides was achieved through the application of an Mn<sup>4+</sup>-containing  $Na[Li_{1/3}Mn_{2/3}]O_2$  (NLMO) oxide cathode. The cathode was theoretically designed through first-principles calculations and experimentally certified via synthesizing the O3-type structure in the C2/m space group.[13] Analogous to the underlying redox mechanism observed in Li<sub>2</sub>MnO<sub>3</sub>, NLMO demonstrated oxygen redox activity through a Li–O–Na configuration during charging. Nevertheless, the ensuing discharge curve exhibited significant voltage hysteresis. The thermodynamic

formation energy suggested the presence of a substantial two-phase reaction occurring for values above  $x \approx 0.67$  in Na<sub>1-x</sub>[Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub>, which was identified through synchrotron ex-situ X-ray powder diffraction.[13] The experimental investigation revealed that Li<sup>+</sup> migration from the TM layer to the Na layer progressively occurred during charging, primarily polarizing the oxygen redox capacity and bringing on an irreversible capacity following the first charge process.[13] In recent studies, incorporating boron or copper has explored the potential for employing lattice oxygen redox reversibility with minimal voltage hysteresis in SIB cathodes.[166–168] Stemming from the monovalent Li<sup>+</sup>, Yabuuchi et al. stated a divalent Mg<sup>2+</sup>-substituted Mn layered oxide, Na<sub>2/3</sub>[Mg<sub>0.28</sub>Mn<sub>0.72</sub>]O<sub>2</sub>, which exhibited a substantial reversible capacity surpassing the standard  $Mn^{3+}/Mn^{4+}$ cation redox.[15] Maitra et al. investigated the ambiguous reaction mechanism in the Mg<sup>2+</sup>-doped Mn oxide, where the extra capacity was attributed to charge compensation via reactions involving oxygen redox.[10] Unlike NLMO, Mg<sup>2+</sup> ions in the doped compound did not migrate to the Na layers at the end of charging. This was conclusively verified through annular dark-field and bright-field scanning transmission electron microscopy.[10] Moreover, no direct O2 gas release was observed during charging in the Mg-doped material, suggesting that Mg<sup>2+</sup> contributed to stabilizing reversible reactions involving oxygen redox. However, hysteretic voltage origination persisted as a functional reactions involving oxygen redox involving divalent species.[10] The inherent mechanism behind the immobility of Mg<sup>2+</sup> ions during the reaction involving oxygen redox remains unclear and is a subject of ongoing debate.

Figure B.1a presents the comparative site energies of  $Li^+$  and  $Mg^{2+}$  concerning the crystallographic sites, such as 2c, 2b, and 4h, based on the Wyckoff positions in

Na<sub>2</sub>MnO<sub>3</sub> (denoted as Na[Na<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub>). Both Li<sup>+</sup> and Mg<sup>2+</sup> exhibit more excellent stability at the 2b site than other sites, suggesting that these substitutions are mainly concentrated the Mn-containing layer rather than the NaO<sub>2</sub> layer. The accompanying atomic configurations for the Mg<sup>2+</sup> sites are depicted as insets for improved comprehension. Furthermore, the relative energy in Mg<sup>2+</sup> escalates as the divalent species sites change (2b  $\rightarrow$  4h  $\rightarrow$  2c), implying an increase in the extent of site instability. Similarly, upon substituting the monovalent species into the alkali metal layer, the energy values of Li<sup>+</sup> experience an increase (4h and 2c sites); though, the energy values of Li<sup>+</sup> at the 4h and 2c sites show remarkable similarity. These results can be illustrated through the electrostatic interaction between Li<sup>+</sup> or Mg<sup>2+</sup> and Na<sup>+</sup> in conjunction with the geometric characteristics of the three site types. Figure B.1b displays the atomic configurations considering Li<sup>+</sup>–Na<sup>+</sup> and Mg<sup>2+</sup>–Na<sup>+</sup> bonds within the cutoff distance (< 3.2 Å) at the 2c, 4h, and 2b sites in the  $Li^+$  and  $Mg^{2+}$ incorporated Mn-based layered oxides. Due to the higher coulombic repulsion between Na<sup>+</sup> and Mg<sup>2+</sup> compared to that between Na<sup>+</sup> and Li<sup>+</sup> and the presence of (non)overlapping 2p-electrons between (Li-1s) Mg-2p and Na-2p, the Mg ions at the 2b, 4h, and 2c sites have 0, 6, and 8 coordination numbers (denoted as *n*), respectively. This suggests that a rise in n results in the destabilization of the site where the substitution occurs. To corroborate this assumption, we reevaluated the relative site energies to establish a new definition for the Na-Mg interaction energies considering the Na<sup>+</sup> coordination number as a variable. The values were meticulously adjusted using a first-order linear function for clarity (Figure B.1c). The fitted Na-Mg interaction energy values closely align with the computed values, suggesting that Mg<sup>2+</sup> site stability is primarily decided by the Na<sup>+</sup> coordination number in Na-based layered oxides. On the other hand, Li ions demonstrate coordination with six Na<sup>+</sup>

ions (n = 6) at all substitution sites, which agrees with the coordination number assumption observed in the 2c and 4h outcomes. Nonetheless, the relatively stable 2b site cannot be entirely explained by the coordination number hypothesis alone, despite having a coordination number of 6 at the 2b site. In principle, charge neutrality is primarily governed by cationic and anionic species in an oxide system. Consequently, the Mn ion's valence state, acting as a variable component, may undergo alterations to preserve charge balance, depending on the type of alkali metal ions present. As a result, the presence of Mg<sup>2+</sup> ions leads to the reduction of Mn<sup>4+</sup> valence state to that of Mn<sup>3+</sup>, a behavior not observed in the case of Li<sup>+</sup> ions, which align with the behavior of Na<sup>+</sup> ions in the Mn-layered oxide.



Figure B.1 (a) Comparison of relative site energies for  $Li^+$  and  $Mg^{2+}$  ions regarding crystallographic sites such as 2b, 4h, and 2c, based on Wyckoff positions in Na[Na<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> (Na: yellow, Li: green, Mn: violet, Mg: orange, and O: red). (b) Analysis of local atomic structures, considering Na<sup>+</sup>-Mg<sup>2+</sup> and Na<sup>+</sup>-Li<sup>+</sup> bonds within a cutoff distance (< 3.2 Å) at 2c, 4h, and 2b sites in Li<sup>+</sup>and Mg<sup>2+</sup>-incorporated Mn-based layered oxides. (c) Computed and fitted Na-Mg interaction energies varying with the Na<sup>+</sup> coordination number

Considering the preferred sites for divalent Mg<sup>2+</sup>, Figure B.2a presents the

mixing enthalpy's formation energies, examining all potential configurations of Na and Mg ion as the normalized Mg content (y) in  $Na_{(1-y)/2}[Mg_{y/2}Mn_{1/2}]O_{3/2}$  across the full range  $(0.0 \le v \le 1.0)$ .[60] Energy values were calculated using 256 different atomic configurations of binary mixtures with varying y contents of  $Na_2MnO_3$  and Mg<sub>2</sub>MnO<sub>3</sub>. For better comprehension of the energy diagram, the configurations with the lowest energy for each Mg content were identified as pseudo-ground (gray-filled circle) and ground (red-filled circle) states, and their values were divided into three areas: 1st  $(0.0 \le y \le 0.25)$ , 2nd  $(0.25 \le y \le 0.5)$ , and 3rd  $(0.5 \le y \le 1.0)$ . In the first region, a single-phase reaction is observed. As additional Mg is inserted up to y =0.5, a two-phase reaction is observed in the second region. Lastly, an extra biphasic reaction comprising the Mg-rich and Mg-poor phases at y = 0.5 and 1.0 is discovered in the third region. According to the thermodynamic phase-stability, the structure with Mg inserted at y = 0.25 is considered the most stable in Na<sub>(1-y)/2</sub>[Mg<sub>y/2</sub>Mn<sub>1/2</sub>]O<sub>3/2</sub>, and its atomic arrangement is depicted in the inset. Furthermore, all Na ions are located at the 2c and 4h sites in the alkali metal layer, while all Mg ions are found at the 2b site in the TM layer; thus, this oxide can be indicated as Na[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> (NMMO). The optimized structure aligns with the  $Mg^{2+}$  site preference in Figure B.1a and the experimentally and theoretically investigated atomic structures of full Na stoichiometry  $Na[Li_{1/3}Mn_{2/3}]O_2$  cathodes, which exhibit a honeycomb-ordered superstructure with O3-type in the C2/m space group.[13] Moreover, the created O3stacking Na[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> has been experimentally seen.[169]



Figure B.2 (a) Mixing enthalpy formation energies considering Na and Mg configurations varying with the amount of Mg content (v)in  $Na_{(1-\nu)/2}[Mg_{\nu/2}Mn_{1/2}]O_{3/2}$ . (b) Mixing enthalpy formation energies, examining Na ions and their vacancies while varying the vacancy content (x) in O-type Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> for FS (solid blue line) and FR (solid red line) modes and P-type Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> (solid black line), divided into three areas (1st  $0.0 \le$  $x \le 0.33$ , 2nd  $0.33 \le x \le 0.67$ , and 3rd  $0.67 \le x \le 1.0$ ). (c) O–O bond populations in Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> within the oxygen redox range ( $0.33 \le x \le 1.0$ ) depending on FS (white bar) and FR (blue bar) conditions. Chemical potential (left graphs) and phase transition contours (right graphs) of  $Na_{1-x}[Mg_{1/3}Mn_{2/3}]O_2$  in the third area for both (e) FR (lower graphs) and (d) FS (upper graphs) modes. The colored area in the lower left graph represents the voltage hysteresis gap

To comprehend the thermodynamic phase stabilities during charging in NMMO, Figure B.2b presents the mixing enthalpy's formation energies, examining all potential Na ions and their vacancies while varying the vacancy content (*x*) in Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> across the entire range ( $0.0 \le x \le 1.0$ ) (Equation (2.2)). Moreover, their values are divided into three areas using reference points at *x* = 0.33 and *x* = 0.67: (i)  $0.0 \le x \le 0.33$ , (ii)  $0.33 \le x \le 0.67$ , and (iii)  $0.67 \le x \le 1.0$ . The

calculations were performed with two different types of O<sup>2-</sup> optimization conditions: i) fully relaxed (FR) and ii) fixed structure (FS), wherein the former and latter modes permit and restrict the formation of O–O dimers, respectively.[19] The convex hull in the FR mode indicates that the first monophasic reaction takes place for values lower than x = 0.33, and further desodiation to x = 0.67 in Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> results in the second monophasic reaction. While monophasic reactions are present in the first and second vacancy content ranges, their phase behaviors seem to differ based on the dominant species in the oxide that compensates for the charge disparity upon desodiation. As redox-capable cations (such as TM in typical oxide cathodes) undergo oxidation, the thermodynamic phase stability is enhanced in CFT energetics. Based on this hypothesis, the first monophasic reaction, characterized by an increase in phase stability, is thought to be governed by the cationic redox of  $Mn^{3+}(3d) - O(2p)$ . Subsequently, the second reaction is accompanied by a decline in phase stability, indicating the onset of oxygen redox reactions after the inflection point at x = 0.33in  $Na_{1-x}[Mg_{1/3}Mn_{2/3}]O_2$ . These redox mechanisms can be attributed to changes in the Mn–O bond length (Figure B.3a), further elaboration on this matter will be provided in the subsequent section. In the third area, a biphasic reaction occurs, consisting of the Na-poor and non-Na phases at x = 0.67 and x = 1.0, as a pseudo-ground phase at x = 0.83 is identified. Specifically, the incorporation of O–O dimers in slab gliding contributes to the thermodynamic stabilization of NMMO, as Figures B.3b and c illustrate. In other words, the thermodynamic driving force triggers the formation of oxygen dimers in NMMO, leading to the biphasic reaction in the third area. Dimerization of oxygen ions results in irreversible oxygen capacities upon discharge following the initial charging process. In the FS mode, the convex hull displays a clearly discernible monophasic reaction in the third zone, indicating nonpolarizing
oxygen capacity in the vacancy content from x = 0.67 to 1.0 and even for  $0.33 \le x \le$ 0.67 in  $Na_{1-x}[Mg_{1/3}Mn_{2/3}]O_2$ . To support the argument that O–O dimerization instigates a biphasic reaction in the third zone, the O-O bond distributions were counted based on their lengths in the oxygen redox range  $(0.33 \le x \le 1.0)$  depending on the FS and FR modes in  $Na_{1-x}[Mg_{1/3}Mn_{2/3}]O_2$ , as displayed in Figure B.2c. In the second region of NMMO, under the FR condition, the most prevalent O-O bond lengths are concentrated between 2.5 and 2.6 Å. Nevertheless, a notable reduction in O–O bond length transpires after the breakpoint (x = 0.67), with the shortest bonds at x = 0.67 and x = 1.0 determined to be ~2.50 and 2.36 Å in Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub>, respectively. The shorter bonds are found within the  $[Mg_{1/3}Mn_{2/3}]O_2$  intralayer, while the longer bonds are observed between the  $[Mg_{1/3}Mn_{2/3}]O_2$  layers (insets in Figure B.2c). Unlike the FR condition, under the FS mode, no short O–O bonds are detected below 2.4 Å throughout the entire vacancy range ( $0.0 \le x \le 1.0$ ). Considering the widely accepted concept that an O–O dimer with a length below 2.5 Å is indicative of a peroxo-like dimer, it appears that NMMO in both FS and FR modes contains several peroxo-like O-O dimers.[88] However, as illustrated in Figures B.3d and e, O-O bonds with lengths between 2.4 and 2.5 Å in both FS and FR modes form within the  $[Mg_{1/3}Mn_{2/3}]O_2$  intralayer and are reversible, exerting minimal influence on the hysteretic oxygen capacity.[19] These findings suggest that the O–O bond formation is a crucial factor in initiating the biphasic reaction, leading to the hysteretic oxygen capacity observed in NMMO. Furthermore, the formation energy under the FR condition was calculated by altering the vacancy content (x) in P-type  $Na_{1-x}[Mg_{1/3}Mn_{2/3}]O_2$  across the entire range  $(0.0 \le x \le 1.0)$  to decide the more favorable structure type upon charging (black tie line in Figure B.2b) (Equation (2.2)). According to the convex hull analysis, the P-type structure is found to be less

thermodynamically stable than the O-type structure throughout the entire deintercalation range in NMMO.



Figure B.3 (a) Mn–O's bonding length variation for  $Na_{1-x}[Mg_{1/3}Mn_{2/3}]O_2$  from x = 0.0 to 1.0. Atomic structures and stacking sequences with [010] projection view included  $[Mg_{1/3}Mn_{2/3}]O_2$  intra- or interlayer O–O dimer of O3-Na<sub>1-x</sub> $[Mg_{1/3}Mn_{2/3}]O_2$  at x = 0.83 and 1.0 in (b) FR and (c) FS calculation modes. Atomic structures included  $[Mg_{1/3}Mn_{2/3}]O_2$  intra- or interlayer O–O dimer (< 2.5Å) of  $Na_{1-x}[Mg_{1/3}Mn_{2/3}]O_2$  from x = 0.5 to 1.0 in (d) FR and (e) FS calculation modes

Theoretically, a two-phase reaction during discharging and charging in intercalation compounds is governed by ground states linked via a tie line, with pseudo-ground states in the two-phase region playing a pivotal role in activating the hysteretic oxygen capacities in different oxygen redox oxides.[43] A comprehensive understanding of voltage hysteresis can be attained by examining the intercalating charge carriers' chemical potential.[170] Grounded on this principle, we calculated the chemical potentials for both the FS and FR conditions varying with the amount of vacancies content (x) in Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> over the third area at 300 K, with the

findings illustrated in the left panels of Figures B.2d and e, respectively (Equation (2.10)). In the FS mode, there is no thermodynamic chemical potential hysteresis observed in NMMO. In contrast, the FR mode demonstrates a substantial hysteresis, indicating the variance between the minima and maxima in chemical potential. This certifies that the oxygen ion dimerization driven by thermodynamic forces significantly influences the hysteretic anion capacity during subsequent discharging after the initial desodiation from the Mg<sup>2+</sup>-Mn oxide. To extend this understanding at the atomic level to nanoscale phenomena, phase field simulations were performed to describe the system's phase stability in the nanodomain under both FR and FS modes in the third area (Figure B.4) (Equation (2.8), (2.9), (2.16), and (2.14)). The phase distribution for the oxygen redox reaction results are depicted by the colored contour in the right panels of Figures B.2d and e, illustrating the lower (FR) and upper (FS) graphs, respectively. To enable a straightforward comparison, the physical values were normalized using characteristic values, and the phase-transition simulations were conducted at intermediate concentration. Under the FS mode, there is no indication of a phase transition, while the FR condition reveals the occurrence of a biphasic reaction during the charging process. This finding serves as compelling evidence supporting the driving force responsible for the phase transition, which can be attributed to the occurrence of O-O dimerization. As observed in the mixing enthalpy's formation energies, the O–O dimerization  $(O^{2-}/O_2^{2-})$  becomes energetically unfavorable, leading to the occurrence of the biphasic phase transition. This indicates that the presence of the peroxide-like dimer during charging plays a pivotal role in triggering the voltage hysteresis and irreversibility characteristics associated with the oxygen redox capacity involving the divalent species.



Figure B.4 (a) Combined-phase mixing enthalpy fitted from the pseudoground/ground states from first-principles mixing enthalpy's formation energies and (b) the homogeneous free energy ( $\mathscr{F}_{homo}$ ) over the third region (0.67  $\leq x \leq 1.0$ ) for Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> in both FS (upper) and FR (lower) modes, from Figure B.2b using the quadratic double-well function. The colored regions (light magenta in the FR mode) indicate the spinodal decomposition regions

Essentially, the electronic structure offers insights into understanding the origins of the redox mechanism and the redox-active materials' atomic bonding nature. To elucidate NMMO's charge compensation mechanism in the two calculation modes, we computed the PDOSs of Mn 3*d*-electron, Mg 2*s*-electron, and O 2*p*-electron at x = 0.0, 0.333, 0.667, and 1.0 in Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> under the FR mode (Figure B.5a). Under the energetics of CFT, the PDOSs of Mn at x = 0.0 and 0.333 display the charge states of Mn<sup>3+</sup> and Mn<sup>4+</sup>, respectively. This indicates that within the vacancy content range from x = 0.0 to 0.333, the Mn<sup>3+</sup> species function as a redox center, undergoing a Mn<sup>3+</sup>/Mn<sup>4+</sup> redox transformation. Nevertheless, for values above x = 0.333, Mn retains its Mn<sup>4+</sup> charge state, while the valence band originating from O(2*p*), experiences a shift to the conduction band due to the

presence of mobile oxygen electrons in the Mg–O–Na linear atomic structure (as depicted in Figure B.6). The observed PDOS results suggest that, after x = 0.333 in NMMO (as depicted in Figure B.7a), electrons originating from the  $O^{2-}$  species play a dominant role in charge compensation. These findings align with predictions based on phase stability, Mn-O bonding length variation, and experimentally analyzed the compound's electrochemical properties.[169] To represent the redox process, an averaged equilibrium voltage curve for Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub>, accompanied by a schematic illustration depicting the energy versus PDOS at each O and Mn charge compensation area, is displayed in Figures B.7b and c. The graph demonstrates the engagement of the Mn 3d-electron in charge compensation, exhibiting an average redox potential of approximately 2.02 V within the region from x = 0.0 to 0.333. The redox reaction is mainly driven by the O 2*p*-electron, contributing around 4.26 V in the remaining region. Analogous to the totally optimized mode, NMMO under the FS mode without O-O dimerization exhibits a comparable charge-compensation mechanism (i.e., Mn and O serve as redox centers for the ranges of  $0.0 \le x \le 0.333$ and  $0.333 \le x \le 1.0$ , respectively) since an equal amount of Na is extracted from the host material (Figure B.5b). Moreover, Mn and O's Bader net charge changes offer quantitative confirmation that an identical amount of charge is utilized to balance the charge deficit arising from Na extraction in both NMMOs under the two calculation modes (Figure B.7a).[153] As a result, Irrespective of the extent of oxygen redox reversibility, the quantity of charge required for capacity or charge compensation would remain constant. To investigate the relationship between phase stability and oxygen-redox-inducing O-O dimerization, we separated the oxygen's electronic structures based on their sites in the totally desodiated state at x = 1.0 in NMMO under the FS and FR modes (Figures B.5a and b at x = 1.0). In NMMO under the FR mode, which experiences a biphasic reaction in the third area, the conduction band for  $0.0 \le \text{E-E}_{\text{f}} \le 2.0$  (green-shaded PDOS) is primarily occupied by O(2*p*) holes forming the bond in the peroxide-like  $O_2^{2^2}$  dimer; specifically, the oxygen atoms are located at the sites marked with green circles, as depicted in Figure B.5e. This discovery provides strong evidence for the occurrence of O-O dimer formation during the charge compensation (O<sup>2-</sup>/O<sub>2</sub><sup>2-</sup>) mechanism. Furthermore, a chemical bond is detected between the [Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> layers (interlayer O–O). Nevertheless, in the case of NMMO under the FS mode, which demonstrates a monophasic reaction in the third area, the conduction band for  $0.0 \le \text{E-E}_{f} \le 2.0$  is occupied by O(2p) holes originating from  $O^{n-}$  without the involvement of an interlayer O-Odimer during the lattice-based oxygen redox (O<sup>2-</sup>/O<sup>n-</sup>) (Figure B.5f). A comparison of the FS and FR modes suggests that the oxygen ions dimerization in the redox reaction triggers a biphasic reaction, leading to hysteretic anionic capacity. As illustrated in Figures B.5c and d, the formation of O-O dimerization, particularly within the interlayer, is crucial to hysteretic oxygen capacities. This phenomenon may be a significant cause of voltage hysteresis when divalent species  $(Mg^{2+})$  are introduced into Mn-layered-oxide cathodes.



Figure B.5 (a) Combined graphs of the PDOSs for Mn 3*d*-electron, Mg 2*s*-electron, and O 2*p*-electron at x = 0.0, 0.333, 0.667, and 1.0 for Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> in (a) FR and (b) FS modes. Schematic representation of the oxygen redox reaction for (c) FR and (d) FS modes. Top and side perspectives of spatial electron density across the conduction bands ( $0.0 \le E - E_f \le 2.0$ ) of Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> at x = 0.0 under (e) FR and (f) FS modes



Figure B.6 Spatial arrangement of electrons in the occupied band from -2 to -1 eV of Na[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> (left) and the local spatial electron distribution for Mg–O–Na linear configuration (right)



Figure B.7 (a) Average Bader net charges of Mn (upper) and O (lower) across all vacancy levels ( $0.0 \le x \le 1.0$ ) in Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> for both FS (solid blue line with the cross) and FR (solid red line with the circle) modes. (b) Averaged equilibrium voltage curve for Na<sub>1-x</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> with (c) the corresponding diagram illustrating the energy versus DOS at each Mn (left) and O (right) charge compensation region

In order to compare, we simulated the Ti-based O3-type Na[Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub> (NMTO) using the crystal structure of NMMO and conducted a similar investigation using a method analogous to the one used for the Mn-based oxide. Specifically, O3-type NMTO is primarily examined in this study, as it has been experimentally synthesized and detected to prevail in the O3-type.[171,172] Figure B.8a shows that the site energy of Mg<sup>2+</sup> in Na<sub>2</sub>TiO<sub>3</sub> is smaller than that in Mn oxide when compared to the Mg<sup>2+</sup> site energy in Na<sub>2</sub>MnO<sub>3</sub>. However, the trends of destabilization from 2b to 2c sites exhibit similarities. The atomic structures, provided as insets, offer better clarity and understanding. Likewise, this outcome is supported by analyzing the columbic repulsion between Mg<sup>2+</sup> and Na<sup>+</sup> bonds with a cutoff distance below 3.2 Å, and the corresponding electrostatic interactions are depicted in Figure B.8b. In the case of the 2b site, the Mg<sup>2+</sup> ion also possesses n = 0, which aligns with the number observed in Mn oxide. In contrast, the coordination numbers at the 4h and 2c sites in Na<sub>2</sub>TiO<sub>3</sub> (n = 4 and, respectively) were 2 less compared to those in Na<sub>2</sub>MnO<sub>3</sub>. As displayed in Figure B.8c, to strengthen the hypothesis regarding the impact of the

 $Na^+$  coordination number on the degree of destabilization caused by  $Mg^{2+}$  substitution, we reanalyzed and presented the Mg–Na interaction energies based on the Na<sup>+</sup> coordination number. Moreover, we accurately fit their values using a first-order linear function with respect to n in the Ti oxide. Likewise, in Na<sub>2</sub>TiO<sub>3</sub>, the fitted values closely resemble the Mg–Na interaction energies obtained through first-principles calculations, thereby supporting the relevance of the *n* premise in Nabased layered oxides.



Figure B.8 (a) Relative site energies of  $Mg^{2+}$  in comparison to the crystallographic sites, such as 2b, 4h, and 2c, based on Wyckoff positions in Na[Na<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub> (Mg: orange, Na: yellow, Ti: blue, and O: red). (b) Local atomic arrangements considering Na<sup>+</sup>-Mg<sup>2+</sup> bonds within the cutoff length (< 3.2 Å) at the 2b, 4h, and 2c sites in Mg<sup>2+</sup>-incorporated Ti-based layered oxides (Na: yellow). (c) Calculated and fitted Na-Mg interaction energies varying with changes in the Na<sup>+</sup> coordination number

As shown in Figure B.9a, we computed the mixing enthalpy's formation energies, taking into account all vacancies and Na ions by altering the vacancy content (x) in Na<sub>1-x</sub>[Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub> across all vacancy levels ( $0.0 \le x \le 1.0$ ) for an indepth examination of the thermodynamic phase stability during the charging (Equation (2.2)). Figure B.9b illustrates the atomic arrangement corresponding to the NMMO's structure. Analogous to NMMO, the NMTO's energy diagram was separated into three zones, and the formation energies were derived under two calculation means: (i) FR and (ii) FS. Under the first calculation mode, the convex hull shows distinct first and second monophasic reactions occurring at Na<sub>1</sub> $x[Mg_{1/3}Ti_{2/3}]O_2$  with  $0.0 \le x \le 0.33$  and  $0.33 \le x \le 0.67$ . Interestingly, the thermodynamic phase stabilities in these regions are consistent with those observed in Mg-inserted Mn oxide (i.e., an increase in the former and a decrease in the latter). This indicates that in the first region of Na<sub>1-x</sub>[Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub>, the cationic redox involving  $Ti^{3+}(3d)$ -O(2p) occurs, while the oxygen redox occurs after the inflection point (x = 0.33) in the Ti-based oxide. The redox mechanism predictions can be clarified by examining the variations in Ti-O bond length (Figure B.10a). A more comprehensive comprehension, along with the Mn-based oxide, will be presented in the following part. Contrary to NMMO, extra desodiation to x = 1.0 in Na<sub>1</sub>- $_x[Mg_{1/3}Ti_{2/3}]O_2$  results in a pseudo-ground state at x = 0.83 under the FR mode. Its value is analogous to the energy required for activation at room temperature (~25 meV) to the tie line.[173] This suggests that NMTO experiences a single-phase reaction throughout the third range of vacancy content under real-world conditions. Furthermore, the FS mode shows a single-phase reaction throughout the third range of vacancy content in NMTO, examining the thermal activation energy at 300 K. Moreover, the FS mode also reveals single-phase reactions across the other two regions of vacancy content. This implies that the FS and FR modes exhibit a singlephase reaction across the complete range of vacancy content. Building on the earlier assumption regarding the relationship between phase stability and O-O dimerization in the NMMO region, we examined the O-O bond distributions based on their lengths within the range of oxygen redox reactions  $(0.33 \le x \le 1.0)$  under both FS and FR conditions (Figure 3.20c). In both modes, the shortest O-O bond distributions are found to cluster within the O–O bond length of 2.6 Å to 2.7 Å in the second zone for NMTO. In the third zone  $(0.67 \le x \le 1.0)$ , the majority of O–O

bond lengths decrease by merely ~0.1 Å, suggesting a minimal alteration in the O–O bond length during NMTO's redox reaction. Nevertheless, at x = 0.67 and 0.83, a minor portion of the O–O bond length rapidly drops to under 2.4 Å. In general, these short O–O bonds emerge within the [Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub> intralayer, which is reversible and has minimal impact on the hysteretic oxygen capacity (Figures B.10b, c, and d).[92,171,174] As a result, NMTO does not exhibit interlayer O–O dimerization, leading to a monophasic reaction during the oxygen redox reaction. In line with the earlier assumption made for NMMO, the formation of O–O bonds play a crucial role in initiating the biphasic reaction, which causes the hysteretic oxygen capacity for NMTO and the O-type Mg<sup>2+</sup>-incorporated oxide cathodes.



Figure B.9 (a) Mixing enthalpy's Formation energies considering vacancies and Na ions varying with the degree of vacancy (x) in O-type Na<sub>1-x</sub>[Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub> for FS (solid blue line) and FR (solid red line) modes, divided into three areas (1st  $0.0 \le x \le 0.33$ , 2nd  $0.33 \le x \le 0.67$ , and 3rd  $0.67 \le x \le 1.0$ ). (b) The atomic arrangement of O-type Na[Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub>. (c) The O–O bond distributions of Na<sub>1-x</sub>[Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub> in the oxygen redox scope ( $0.33 \le x \le 1.0$ ) depending on the FS (white bar) and FR (blue bar) conditions. Chemical potential (left graphs) and the phase-distribution contours (right graphs) of Na<sub>1-x</sub>[Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub> in the third area for both the (e) FR (lower graphs) and (d) FS (upper graphs) modes



Figure B.10 (a) Ti–O's bonding length variation for  $Na_{1-x}[Mg_{1/3}Ti_{2/3}]O_2$  from x = 0.0 to 1.0. (b) The O–O bonds formed within the  $[Mg_{1/3}Ti_{2/3}]O_2$  intralayer (black dotted lines) for both FS and FR conditions at x = 0.67 and 0.83 for the  $Mg^{2+}$ –Ti oxide. (c) Average and individual TM–O bonding lengths in the TMO<sub>6</sub> octahedrons with varying vacancy concentration over the entire vacancy range  $(0.0 \le x \le 1.0)$  in  $Na_{1-x}[Mg_{1/3}TM_{2/3}]O_2$ , where TM = Ti (dark cyan) and Mn (purple). Corresponding TM–O bonds are described in the inset figures. (d) Average and individual short O–O bonding lengths in TiO<sub>6</sub> and MnO<sub>6</sub> as functions of vacancy concentration (x) from x = 0.0 to 1.0 in  $Na_{1-x}[Mg_{1/3}TM_{2/3}]O_2$ . Corresponding short O–O bonds are described in the inset figures in the inset figures.

In a manner akin to NMMO, the formation energies and chemical potentials of Na<sub>1-x</sub>[Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub> under the FR and FS computation conditions were calculated varying with the degree of vacancy (*x*) to investigate the thermodynamic phase stability and voltage hysteresis (Figure B.9d) (Equation (2.10)). The analysis considered that at 300 K, the pseudo-ground state is present within the thermal activation energy scope from the tie line across the third area. In contrast to NMMO, NMTO does not show any significant thermodynamic chemical potential hysteresis in both the calculation conditions. Voltage hysteresis arises due to phase transitions; thus, the extent of phase transitions demonstrates the extent of voltage hysteresis. Considering this close relationship, phase field simulations for NMTO were carried out under both FS and FR conditions to investigate the hysteretic oxygen capacity (Figure B.11 and Equation (2.8), (2.9), (2.16), and (2.14)). The right panels of Figure B.9d and e exhibit the colored phase distribution contours for both outcomes over the third area, with the upper (FS) and lower (FR) graphs displayed, respectively. The computational findings do not demonstrate evidence of phase transition, suggesting that the impact of phase-transition-induced hysteretic oxygen capacity, attributable to O–O dimerization, a vital feature for NMMO, is negligible in both NMTO conditions.



Figure B.11 (a) combined-phase mixing enthalpy fitted from the pseudoground/ground states from first-principles mixing enthalpy's formation energies and (b) the homogeneous free energy ( $\mathscr{F}_{homo}$ ) over the third region (0.67  $\leq x \leq 1.0$ ) for Na<sub>1-x</sub>[Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub> in both FR (lower) and FS (upper) modes, from Figure B.9a using the quadratic double-well function

The  $Mg^{2+}$ -incorporated systems, NMTO and NMMO, demonstrate distinct potential hysteresis despite having identical  $O^{2-}$  relaxation conditions. NMMO

exhibits interlayer O-O dimerization in the FR mode, causing hysteretic oxygen capacity, whereas NMTO does not show any voltage hysteresis. To investigate the redox mechanism, the electronic configurations for NMTO were computed. Like NMMO, the PDOSs of Ti 3d-electron, Mg 2s-electron, and O 2p-electron were calculated for  $Na_{1-x}[Mg_{1/3}Ti_{2/3}]O_2$  at x = 0.0, 0.333, 0.667, and 1.0 in the FR condition (Figure B.12a). Consistent with NMMO, Mn served as a redox center in the initial stages. The PDOSs reveal that  $Ti^{3+}$  species acts as a redox center  $(Ti^{3+}/Ti^{4+})$  in the vacancy range from x = 0.0 to 0.333, whereas after x = 0.333, Ti keeps its charge state of  $Ti^{4+}$  and the valence band of O(2p) transfers to the conduction band. The results show that for vacancy content above x = 0.333, the O<sup>2-</sup> species do a significant function in the process of charge compensation in  $Na_{1-x}[Mg_{1/3}Ti_{2/3}]O_2$ . This aligns with the forecasts based on the phase stability and Ti-O bonding length variations. Furthermore, the electronic structure calculations indicate that NMTO and NMMO possess identical types of redox centers corresponding to the redox potential depending on the vacancy concentration (Figures B.13a and b). Precisely, under the FR mode, Ti and O act as a redox center within the specified range of  $0.0 \le x \le 0.333$ and  $0.333 \le x \le 1.0$ , respectively. The FS condition in NMTO demonstrates identical charge compensation behavior, indicating that the identical quantity of Na is removed from the host material (Figure B.12b). Moreover, O and Ti's Bader net charges measurably show that an equal quantity of charge is utilized to balance the charge under both FS and FR modes in NMTO (Figure B.13c). As a result, the charge compensation mechanism is found to be similar between NMTO and NMMO, regardless of the two types of computation conditions or the presence of cation-redox centers (Mn or Ti).



Figure B.12 Combined graphs of the PDOSs for Ti 3*d*-electron, Mg 2*s*-electron, and O 2*p*-electron at x = 0.0, 0.333, 0.667, and 1.0 for Na<sub>1-x</sub>[Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub> in (a) FR and (b) FS conditions are presented. Schematic representations of the oxygen redox reaction for (c) FR and (d) FS conditions are provided. Top and side perspectives of spatial electron density across the conduction bands ( $0.0 \le E-E_f \le 2.0$ ) of Na<sub>1-x</sub>[Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub> at x = 0.0 are depicted under the (e) FR and (f) FS conditions



Figure B.13 (a) Averaged equilibrium voltage curve for  $Na_{1-x}[Mg_{1/3}Ti_{2/3}]O_2$  with (b) the corresponding schematic illustration that depicts the energy versus DOS at each Ti (left) and O (right) charge compensation area. (c) Average Bader net charges of Ti (upper) and O (lower) throughout the entire range ( $0.0 \le x \le 1.0$ ) in  $Na_{1-x}[Mg_{1/3}Ti_{2/3}]O_2$  for both FS (solid blue line with the cross) and FR (solid red line with the circle) modes

Nevertheless, the reason of distinct chemical properties in the context of

potential hysteresis, incited by the O-O dimerization, amid the Ti and Mn oxide cathodes, remains ambiguous. To elucidate its provenance, we meticulously examined the electronic configurations of O(2p) corresponding to its locations in the totally desodiated state (x = 1.0) NMTO under both the FS and FR conditions (Figures B.12a and b at x = 1.0). For the two-type of computation modes for NMTO encountering the monophasic reactions within the third domain, it was corroborated that the conduction bands for  $0.0 \le E - E_f \le 2.0$  are populated by O(2p) holes originating from  $O^{n-}$  in the absence of O–O dimerization throughout the oxygen redox processes (Figures B.12e and f). This suggests that the formation of oxygen ion dimers between layers is improbable in NMTO. As depicted in Figures B.12c and d, in the FR mode of NMTO, the oxygen redox involves a nonhysteretic oxygen capacity through the lattice-based O<sup>2-</sup>/O<sup>n-</sup> reaction, culminating in the absence of potential hysteresis in the succeeding discharging following the initial charging. In other words, while NMMO tends to form the O–O dimer  $(O^2/O_2^2)$  during charging due to thermodynamic favorability, NMTO, on the other hand, exhibits greater stability with the O<sup>2-</sup>/O<sup>n-</sup> configuration. Given that the sole distinction between NMTO and NMMO lies in the transition metal (Ti or Mn), the reason of the disparate oxygen redox scenarios  $(O^2/O_2^2)$  or  $O^2/O^{n-}$  stems from the transition metal. In general, Ti generates comparatively stronger ionic Ti-O bonding characteristics, whereas Mn produces a comparably stronger covalent Mn-O bond. Given the prevailing understanding, we propose that the covalent nature of oxygen ions favors the formation of O-O dimers, especially interlayer O-O dimers, as part of the oxygen redox process, while ions with ionic bonding tendencies are less likely to form such dimers during the relevant extent of oxygen redox involvement. This is attributable to the fact that fully exploiting the oxygen redox in Ti-based oxide

materials precipitates rapid structural destabilization due to the formation of the O–O dimer.[19] Consequently, it is expected that the potential hysteresis arising from the degree of O–O dimerization or the oxygen redox, in the O-type  $Mg^{2+}$ -integrated system is ultimately dictated by the TM–O bonding character being covalent or ionic, which can be modulated by the specific transition metal utilized.

Incorporating divalent species (specifically Mg<sup>2+</sup>) into O-type layered oxide cathodes,  $AM[Mg_{x}TM_{1-x}]O_{2}$ , reliably facilitates reversible oxygen redox reactions. Furthermore, these oxide systems do not indicate O<sub>2</sub> gas evolution or divalent species migration to the Na layers. Nevertheless, the Mg<sup>2+</sup>-including oxides continue to struggle with hysteretic potential production. To ascertain the hysteretic oxygen capacity, we investigated O3-Na[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> and O3-Na[Mg<sub>1/3</sub>Ti<sub>2/3</sub>]O<sub>2</sub> based on three physicochemical aspects: (i) the stability of the Mg<sup>2+</sup>-site based on the coordination number of Na<sup>+</sup>, (ii) the potential hysteresis caused by the phase transition triggered by O-O dimerization, and (iii) the connection between TM-O bonding properties and O–O dimer formation. Initially, the study validated that the thermodynamically stable Mg<sup>2+</sup> site is determined by the Na<sup>+</sup> coordination number to  $Mg^{2+}$ , which favors  $Mg^{2+}$  stabilization at the site with the lowest  $Na^+$  coordination, i.e., the TM layer. Secondly, the interlayer O-O dimerization demonstrably facilitated the phase transition, resulting in the hysteretic oxygen capacity. Lastly, the covalent or ionic TM-O bonding characteristics regulate the extent of O-O dimerization, which is immediately correlated with potential hysteresis. Our discoveries unveil the enigmatic determinants of the hysteretic oxygen capacity for the O-type Mg<sup>2+</sup>-integrated oxide system and offer insights for effectively harnessing the oxygen redox reaction for divalent species-including cathodes to promote advancements in LIBs and SIBs.

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## 국문 초록

지난 수십 년 간 많은 노력으로 리튬 이온 이차전지의 전기화학 성능은 크게 개선되었지만, 에너지 저장 시스템에 대한 수요 증가로 보다 저렴한 이차전지 개발 필요성이 강조되고 있다. 이를 위해 상대적으로 매장량이 풍부한 소듐 산화물을 활용한 소듐 이온 이차전지 같은 다양한 차세대 이차전지가 제안되고 있다. 그러나, 이런 차세대 이차전지도 전극 소재의 내재적 한계로 전기화학 성능을 온전히 발휘하지 못하는 실정이며 그 근본적인 원인에 대한 이해도 부족한 상황이다. 특히, 전극 고체 소재 내 이온 전하 운반체 (e.g. Li+ or Na+) 수송으로 전기화학 에너지를 저장하는 차세대 이차전지의 성능 저하 원인을 파악하기 위해서는 복합적으로 발생하는 전기화학적·기계적 현상들에 대한 정확한 이해가 필요하다. 이를 위해서 여러 스케일에 걸쳐 이차전지 소재의 물리적 거동을 해석할 수 있는 멀티스케일 해석기법이 필수적이다.

본 연구에서는 이차전지 고체 소재에서 이온 수송으로 인한 전기화학적 성능 저하를 분석하기 위해 제일원리 계산 기반 멀티스케일 해석기법을 정립하였다. 특히, 전자-원자 스케일에서의 밀도 함수 이론, 열역학적 분석, 전기화학적 분석, 및 운동학적 분석, 단일 입자 스케일에서의 화학역학적 상 장 모델, 그리고 마이크로 스케일에서의 유한요소 해석과 같이 다양한 시뮬레이션 기법을 통합하여 미시스케일에서의 현상들을 반영하고 거시스케일에서의 이차전지 소재의

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거동을 분석하여 차세대 이차전지의 에너지 밀도 향상, 수명 연장 및 안전성 개선을 위해 직면한 다양한 문제들의 원인을 밝혔다.

특히 본 학위논문에서는 소듐 이온 이차전지 양극 활물질에 집중하여 연구를 수행하였다. 먼저, 소듐 양극 활물질은 고체 산화물 내에서 리튬 이온보다 상대적으로 크기가 큰 소듐 이온의 수송을 동반하는 산화환원 반응으로 에너지를 저장한다. 리튬 이온보다 상대적으로 큰 소듐 이온이 전하 운반체로써 역할을 하기 때문에 소듐 양극 홬물질이 갖는 내재적 하계가 존재하다. 이를 극복하고 고에너지 밀도를 안정적으로 긴 수명동안 유지하기 위한 물리화학적 요인을 밝히기 위해 망간기반 층상계 산화물의 열역학적 상 안정도와 상 전이 혀상을 본 방법론으로 분석하였다. 본 방법론으로 계산된 균일 자유 에너지를 분석한 결과 양이온 산화환원 반응 구간에서 망간-니켈 층상계 산화물이 망간 층상계 산화물보다 더 빠른 상 전이 현상을 보여주어 상대적으로 감소된 충방전 수명 특성을 보여준다. 그러나, 음이온 산화환원 반응 구간에서는 망간-니켈 층상계 산화물에서만 존재하는 소듐 이온 극소량 상 덕분에 더 높은 에너지 밀도를 안정적으로 유지할 수 있다. 또한, 소듐 이온 극소량 상 덕분에 망간-니켈 층상계 산화물에서 음이온 산화환원 반응 구간에서 전압 이력 현상이 감소한 것을 발견하였다. 이를 통해, (i) 양이온 산화환원 반응 구간에서 망간-니켈 층상계 산화물 내 소듐 이온과 공극의 용해도를 높여주고 (ii) 음이온 산화화원 반응 구간에서는 망간-니켈 층상계 산화물의 상 전이 발생을 완화해주는 소듐 이온이 극소량 있는 상을 잘

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활용하면 높은 에너지 밀도를 안정적으로 긴 수명동안 유지할 수 있음을 제시하였다.

또한, 본 방법론을 적용하여 망간-니켈 층상계 산화물 일차 입자가 충방전동안 비등방성 구조적 변형을 겪는 것을 보였으며, 일차 입자의 비등방성 구조 변형으로 일반적인 이차 입자 내부에 탄성 응력이 쌓여 이차 입자의 부분적 파괴를 야기하며 이로 인해 이차 전지 수명 저하를 유발함을 발견하였다. 반면, 방사형 이차 입자의 경우 일차 입자의 비등방성 구조 변형이 발생하더라도 탄성 응력 집중이 완화되어 이차 입자 파괴가 억제되고, 이차 전지 수명을 향상시킬 수 있음을 제시하였다.

결론적으로 위와 같이 정립된 제일원리 계산 기반 멀티스케일 해석기법을 차세대 이차전지용 고체 양극 활물질 적용하여, 전기화학적 성능이 저하되는 근본적인 원인을 밝히는 연구를 계산을 통해 이론적으로 밝히고, 이를 극복할 수 있는 방안을 제시하는 연구를 성공적으로 수행하였다. 이는 제안된 멀티스케일 방법론의 효용성을 증명하는 것뿐만 아니라, 경험에 의존하여 차세대 전극 소재를 개발하던 기존의 방향과 더불어 이론에 기반하여 전기화학 성능을 개선할 수 있는 신뢰도 높은 방향을 제시할 수 있을 것으로 기대한다. 또한, 제안된 멀티스케일 해석기법은 실험적 매개 변수가 없는 경우에도 복잡한 전기화학적 반응과 기계적 거동을 포함하는 다양한 전극 시스템 해석에 적용할 수 있을 것으로 기대한다.

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Keyword : 이차전지, 소듐 이온 전지, 고체 양극 활물질, 전기화학 성능 저하, 제일원리 계산, 멀티스케일 역학 Student Number : 2017-26678