



EXPLORATION OF NOVEL CATHODE ACTIVE MATERIALS FOR SODIUM-ION BATTERIES

Dem Fachbereich Biologie und Chemie
der Justus-Liebig-Universität Gießen
vorgelegte Dissertation zur Erlangung
des akademischen Grades
Doktor der Naturwissenschaften
– Dr. rer. nat. –

Siyu An
from Hebei, China

July 2025

Dekan / Dean

Prof. Dr. Thomas Wilke

1. Gutachter / 1st Reviewer

Prof. Dr. Jürgen Janek
(Justus-Liebig-Universität Gießen)

2. Gutachter / 2nd Reviewer

Prof. Dr. Philipp Adelhelm
(Humboldt-Universität zu Berlin)

Eingereicht / submitted

05.2025

Disputation / disputation

07.2025

Eidesstattliche Erklärung

Die vorliegende Arbeit wurde im Zeitraum von November 2022 bis Mai 2025 am Battery and Electrochemistry Laboratory (BELLA) des Instituts für Nanotechnologie am Karlsruher Institut für Technologie unter der Betreuung von Prof. Dr. Jürgen Janek erstellt.

Ich erkläre:

Ich versichere, dass ich die vorliegende Dissertation selbstständig und ohne unzulässige Hilfe Dritter angefertigt und ausschließlich die in der Arbeit aufgeführten Hilfsmittel verwendet habe. Sämtliche wörtlich oder sinngemäß übernommenen Passagen aus veröffentlichten Quellen sowie alle auf mündlichen Auskünften beruhenden Angaben sind kenntlich gemacht. Zudem erkläre ich mich mit einer möglichen Überprüfung der Dissertation mittels Antiplagiat-Software einverstanden. Bei allen durchgeführten und in der Dissertation beschriebenen Untersuchungen habe ich die Grundsätze guter wissenschaftlicher Praxis beachtet, wie sie in der 'Satzung der Justus-Liebig-Universität Gießen zur Sicherung guter wissenschaftlicher Praxis' festgelegt sind.

Siyu An, Karlsruhe, 05.2025

Abstract

Lithium-ion batteries (LIBs) have led the energy storage market for decades due to their excellent performance. However, the increasing scarcity and cost of lithium resources have shifted research interest toward alternative technologies. Sodium-ion batteries (SIBs), with their abundant sodium resources and competitive electrochemical properties, have emerged as promising candidates. In particular, O3-type layered oxide cathodes are attractive for practical applications due to their high sodium content and potential for high reversible capacity.

This dissertation focuses on optimizing Ni- and Mn-rich O3-type layered oxide cathodes for SIBs. Using NaNiO_2 (NNO) as a prototype material, the work first addresses the challenges associated with irreversible phase transitions caused by Na^+ -de/intercalation-induced interlayer gliding and Jahn-Teller (JT) distortion from Ni^{3+} . To improve the structural reversibility and electrochemical performance, Ti^{4+} was introduced to produce $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NNTO), which was successfully synthesized via a solid-state reaction for the first time. NNTO exhibited a high specific capacity of 190 mAh/g, but suffered from chemo-mechanical degradation and irreversible lattice oxygen loss. To further address these limitations, Ca^{2+} was introduced as a pillaring ion. Among the various substitution levels explored, $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) exhibited the largest interlayer spacing, along with best capacity retention and rate performance. *In situ* X-ray diffraction (XRD), scanning electron microscopy (SEM), acoustic emission (AE), and differential electrochemical mass spectrometry (DEMS) analyses confirmed that Ca^{2+} effectively mitigates interlayer gliding and volume collapse, thereby enhancing the reversibility of both nickel and oxygen redox reactions and increasing the structural and interfacial stability during electrochemical cycling.

The study was further extended to Mn-rich O3-type layered oxides. NaMnO_2 (NMO), a cost-effective and environmentally friendly cathode candidate, is also known to undergo complex and irreversible phase transitions, along with significant manganese migration at high potentials. In this work, precipitated Mn_3O_4 was employed as a precursor for NMO synthesis. To enhance its structural and electrochemical properties, Ti^{4+} was introduced to form $\text{NaMn}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NMTO). Titanium substitution effectively stabilized the O3 phase, suppressed the JT distortion associated with Mn^{3+} , and facilitated the transformation from polycrystalline to quasi-single-crystalline morphology. The optimized NMTO also exhibited an enlarged interlayer spacing, enhanced capacity retention ([42-70] % after 50 cycles), and suppressed oxygen evolution, while effectively preventing the formation of the O1 phase, as confirmed by *in situ* XRD and DEMS measurements.

In conclusion, this dissertation demonstrates effective strategies for improving the structural and electrochemical stability of both Ni-rich and Mn-rich O3-type layered oxides. The mechanistic insights and material design principles presented herein provide valuable guidance for the development of high-performance sodium-ion cathode materials.

Zusammenfassung

Lithium-Ionen-Batterien (LIBs) haben den Energiespeichermarkt über Jahrzehnte hinweg aufgrund ihrer hervorragenden Leistung dominiert. Mit der zunehmenden Verknappung und den steigenden Kosten von Lithiumressourcen richtet sich das Forschungsinteresse jedoch verstärkt auf alternative Technologien. Natrium-Ionen-Batterien (NIBs) gelten aufgrund der reichlich verfügbaren Natriumressourcen und ihrer wettbewerbsfähigen elektrochemischen Eigenschaften als vielversprechende Kandidaten. Besonders O3-Typ Schichtgitter-Kathoden sind für praktische Anwendungen attraktiv, da sie einen hohen Natriumgehalt und eine hohe reversible Kapazität ermöglichen.

Diese Dissertation beschäftigt sich mit der Optimierung von Ni- und Mn-reichen, O3-Typ Schichtgitter-Oxidkathoden für SIBs. Ausgehend von NaNiO_2 (NNO) werden zunächst die Herausforderungen im Zusammenhang mit irreversiblen Phasenübergängen untersucht, welche durch die Na^+ -Ein-/Auslagerung sowie die Jahn-Teller (JT)-Verzerrung von Ni^{3+} verursacht werden. Um die strukturelle Stabilität und elektrochemische Leistung zu verbessern, wurde Ti^{4+} eingeführt (substituiert), um $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NNTO) zu bilden. Letzteres wurde erstmals erfolgreich mittels Festkörperreaktion synthetisiert. NNTO lieferte eine hohe spezifische Kapazität von 190 mAh/g, litt jedoch unter chemo-mechanischer Degradation und irreversiblen Sauerstoffverlusten. Zur weiteren Verbesserung wurde Ca^{2+} als „pillaring ion“ eingeführt. Unter den untersuchten Substitutionsgraden zeigte $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) den größten Schichtabstand sowie den besten Kapazitätserhalt und Ratenverhalten. *In situ* Röntgendiffraktometrie (XRD), Rasterelektronenmikroskopie (SEM), akustische Emissionsmessungen (AE) und differentielle elektrochemische Massenspektrometrie (DEMS) bestätigten, dass Ca^{2+} effektiv die Schichtverschiebung und den Volumenkollaps unterdrückt, die Reversibilität der Redoxprozesse von Nickel und Sauerstoff verbessert und die strukturelle Stabilität während des Lade-/Entladevorgangs erhöht.

Die Studie wurde anschließend auf Mn-reiche, O3-Typ Kathodenmaterialien ausgeweitet. NaMnO_2 (NMO) stellt zwar eine kostengünstige und umweltfreundliche Kathodenoption dar, weist jedoch bei hohen Spannungen komplexe und irreversible Phasenübergänge sowie eine erhebliche Migration von Mangan auf. In dieser Arbeit wurde erstmals gefälltes Mn_3O_4 als Präkursor zur Synthese von NMO eingesetzt. Um die strukturellen und elektrochemischen Eigenschaften zu verbessern, wurde wiederum Ti^{4+} eingeführt (substituiert), wodurch $\text{NaMn}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NMTO) entstand. Die Ti^{4+} -Substitution stabilisierte effektiv die O3-Phase, unterdrückte die durch Mn^{3+} verursachte JT-Verzerrung und förderte den Übergang von einer polykristallinen zu einer quasi-einkristallinen Partikelmorphologie. Das optimierte NMTO-Kathodenmaterial zeigte zudem einen vergrößerten Schichtabstand, einen verbesserten Kapazitätserhalt ([42-70] % nach 50 Zyklen) sowie eine unterdrückte Sauerstofffreisetzung und verhinderte effektiv die Bildung der O1-Phase, wie durch *in situ* XRD- und DEMS-Analysen bestätigt wurde.

Zusammenfassend zeigt diese Dissertation wirkungsvolle Strategien zur Verbesserung der strukturellen und elektrochemischen Stabilität von sowohl Ni- als auch Mn-reichen, O3-Typ Schichtgitteroxiden auf. Die gewonnenen mechanistischen Erkenntnisse und Materialdesignprinzipien bieten wertvolle Ansätze für die zukünftige Entwicklung leistungsfähiger Natrium-Ionen-Kathodenmaterialien.

List of Abbreviations

LIBs	Lithium-ion batteries
EVs	Electric vehicles
HEVs	Hybrid electric vehicles
ESSs	Energy-storage systems
LCO	Lithium cobalt oxide (LiCoO_2)
CAM	Cathode active material
NCM	Lithium nickel cobalt manganese oxide ($\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$)
NCA	Lithium nickel cobalt aluminum oxide ($\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$)
LNO	Lithium nickel oxide (LiNiO_2)
SIBs	Sodium-ion batteries
PBAs	Prussian blue analogues
NNO	Sodium nickel oxide (NaNiO_2)
NMO	Sodium manganese oxide (NaMnO_2)
NNTO	Sodium nickel titanium oxide ($\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$)
LFP	Lithium iron phosphate (LiFePO_4)
CaNNTO	Sodium calcium nickel titanium oxide ($\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$)
α -NMO	α - NaMnO_2
O	Octahedral
P	Prismatic
JT	Jahn-Teller
S.G.	Space group
XRD	X-ray diffraction
TXM	Transmission X-ray microscopy
XANES	X-ray absorption near-edge structure
DFT	Density functional theory

HF	Hydrofluoric acid
PVDF	Polyvinylidene difluoride
SOC	States of charge
CEI	Cathode-electrolyte interphase
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
AE	Acoustic emission
DEMS	Differential electrochemical mass spectrometry
XAS	X-ray absorption spectroscopy
NMTO	Sodium manganese titanium oxide ($\text{NaMn}_{0.9}\text{Ti}_{0.1}\text{O}_2$)
TM	Transition metal
ccp	Cubic close-packed

Table of Contents

1. Introduction.....	1
2. Fundamentals.....	4
2.1. Structural Classification and Prototype Materials of Layered Oxide Cathodes	4
2.1.1 Crystal Structures of Layered Oxide Cathodes for Sodium-Ion Batteries ...	4
2.1.2 Advantages and Limitations of O3- and P2-Type Layered Oxides	5
2.1.3. NaNiO_2 and NaMnO_2	6
2.2. Structure, Electrochemical Properties, and Degradation Behavior of NaNiO_2 and NaMnO_2	9
2.2.1. Structure and Electrochemistry of NaNiO_2	9
2.2.2. Phase Evolution of NaNiO_2	9
2.2.3. Structure and Electrochemistry of NaMnO_2	10
2.2.4. Phase Evolution of O'3-Type NaMnO_2	11
2.2.5. Degradation of NaNiO_2 and NaMnO_2	13
2.3. Synthesis Parameters of Solid-State Reaction and Resulting Properties	18
2.3.1. Calcination Temperature	18
2.3.2. Cooling Process	19
2.3.3. Na/TM Ratio	20
2.3.4. Calcination Atmosphere and Precursor Selection	20
2.4. Chemical Modification of NaNiO_2 and NaMnO_2	22
2.4.1. Substitution on the Ni-Site of NaNiO_2	22
2.4.2. Substitution on the Mn-Site of NaMnO_2	23
2.4.3. Substitution on the Na-Site	25
2.4.4. Interfacial Stability Optimization.....	26
3. Results.....	28
3.1. Publication I: Improving Cycling Performance of the NaNiO_2 Cathode in Sodium-Ion Batteries by Titanium Substitution.....	28
3.2. Publication II: Exploring Calcium Pillaring of O3-Type $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ Cathodes to Advance Na-Ion Battery Technology.....	47
3.3. Publication III: Titanium Substitution to Advance the Prospect of NaMnO_2 Cathodes for Practical Application in Sodium-Ion Batteries	58
4. Conclusions and Outlook.....	81
5. Bibliography.....	84
6. Appendix.....	94

6.1. Supporting Information.....	94
6.1.1. Supporting Information of Publication I.....	94
6.1.2. Supporting Information of Publication II.....	105
6.1.3. Supporting Information of Publication III.....	115
6.2. Scientific Contributions.....	121
6.2.1. List of Publications.....	121
6.2.2. List of Patents.....	121
7. Acknowledgements.....	122

1. Introduction

The development and utilization of fossil fuels played a pivotal role in driving the First and Second Industrial Revolutions, undoubtedly contributing indispensably to the advancement of industry and technology in human society. However, in recent decades, the excessive exploitation of fossil energy has led to severe environmental consequences on a global scale, such as global warming and ozone layer depletion. To address these pressing issues, the exploration of cleaner and more sustainable energy sources has become imperative.^[1–5]

Among the promising alternatives, nuclear reactors stand out. Nevertheless, the challenge of managing radioactive nuclear waste remains a major concern.^[4] Renewable energy sources, such as wind, solar, and tidal energy have garnered increasing attention due to their environmentally friendly and renewable nature. Yet, their inherent intermittency in both spatial and temporal dimensions significantly limit direct utilization.^[6–10]

To overcome this limitation, secondary rechargeable batteries have emerged as an ideal solution. Among them, lithium-ion batteries (LIBs) have been extensively studied for their high energy density.^[7,8,11,12] Since the successful commercialization of LIBs by Sony Corporation in 1991, they have dominated the field of electricity storage for decades and have significantly propelled the development of various sectors, including portable electronic devices, such as laptops and smartphones, electric vehicles (EVs), hybrid electric vehicles (HEVs), and large-scale energy-storage systems (ESSs).^[9,13]

LiCoO₂ (LCO), the first cathode active material (CAM) used in LIBs, was developed by Mizushima *et al.*^[14] However, due to the high cost and limited abundance of cobalt, alternative CAMs with different compositions were subsequently developed, including LiNi_xCo_yMn_{1-x-y}O₂ (NCM) and LiNi_xCo_yAl_{1-x-y}O₂ (NCA).^[15–17] In the field of EVs, the continuous demand for higher capacities to ensure longer driving ranges has driven the evolution of NCM and NCA materials toward higher nickel content, ultimately approaching LiNiO₂ (LNO).^[13,17,18] LNO, as an isostructural compound of LCO, also offers a high theoretical capacity and working potential. Nevertheless, its commercialization has been hindered by several issues, such as interfacial and structural instabilities during cycling.^[19,20]

In summary, the development and commercialization of various LIB CAMs have undoubtedly accelerated the advancement of EVs and other energy-storage applications. However, the finite and uneven distribution of lithium resources has raised concerns regarding the long-term sustainability of lithium-based technologies.^[21–24] Sodium, by contrast, is abundantly available in nature, widely distributed across the globe, and significantly less expensive.^[22,25] Moreover, since sodium-ion batteries (SIBs) share similar storage mechanisms with LIBs, they are considered one of the most promising next-generation energy-storage technologies. Unlike LIBs, which are limited to the choice of a narrow range of transition metal (TM) species, layered sodium-ion cathodes can be synthesized using a broader spectrum of 3d TMs, ranging from titanium to copper, allowing for the incorporation of more

1. Introduction

abundant and sustainable elements.^[26–30] This compositional flexibility not only enhances the material availability, but also contributes to lowering the overall production cost. In addition, sodium does not form alloys with aluminum, which enables the use of aluminum foil as a current collector on both electrodes, potentially reducing production cost further by replacing copper.^[31,32] Despite the fact that sodium has a higher atomic mass and larger ionic radius ($r = 1.02 \text{ \AA}$) compared to lithium ($r = 0.76 \text{ \AA}$), ultimately leading to a lower energy density, these characteristics make SIBs particularly well-suited for applications where volumetric or gravimetric energy density is less critical, such as electric two-wheelers, utility vehicles, and grid ESSs.^[12,22]

As a critical component of SIBs, the CAMs play a key role in determining the overall energy density of the system. Therefore, research on CAMs is of paramount importance. Currently, a variety of cathodes are being extensively investigated, including layered oxides,^[9,33–36] Prussian blue analogues (PBAs),^[37–40] and polyanionic frameworks.^[41–43] Among them, layered oxides have attracted significant attention due to their high theoretical specific capacities and high operating potentials.^[9,34,44]

Layered oxides typically fall into two structural categories, namely Na-rich O3-type and Na-deficient P2-type, which will be discussed in detail in section 2.1. The O3-type structure, in particular, is considered more suitable for practical full cell applications due to its higher sodium content.^[1,45] Nevertheless, further optimization of O3-type CAMs is required to meet the demands of various application scenarios. For instance, high-energy-density variants are desirable for EV batteries, while lower-energy-density but more stable variants are better suited for stationary ESSs.

This doctoral project focuses on the development of high-performance O3-type oxide CAMs. The main strategy employed is ion substitution to enhance the reversible capacity and cycling stability of NaNiO_2 (NNO) and NaMnO_2 (NMO), which served as prototype materials.

The first part of this dissertation, inspired by LNO, investigates the electrochemical performance of NNO as a prototype cathode material for SIBs, with the goal of developing a high-performance Ni-based layered oxide. Previous studies have shown that NNO possesses a high theoretical specific capacity of up to 235 mAh/g. However, it suffers from several drawbacks during cycling, including low reversible capacity, complex phase transitions, and irreversible high-voltage phase changes.^[46–48] To address these issues, d^0 transition metal Ti^{4+} was introduced to substitute Ni^{3+} . By systematically optimizing the solid-state synthesis parameters, including temperature, Na/TM ratio, cooling rate, O_2 flow rate, and Ni/Ti ratio, $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NNTO) was successfully synthesized for the first time. Notably, NNTO exhibited a high reversible specific capacity of 190 mAh/g with an average voltage of 3.2 V, yielding an energy density comparable to that of commercial LiFePO_4 (LFP). However, due to chemo-mechanical degradation and irreversible lattice oxygen loss, further improvements in cycling stability were necessary.^[12]

In a follow-up study, Ca^{2+} was introduced as a pillaring ion to mitigate these issues. Through systematic optimization of the Ca^{2+} fraction, $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$

1. Introduction

(CaNNTO) was successfully synthesized. Structural and electrochemical analyses of the CaNNTO system clearly revealed the positive role of Ca^{2+} as a pillaring ion in enhancing the stability of NNTO.^[10]

The third part of the dissertation shifted focus to the more cost-effective and environmentally friendly NMO. Interestingly, a similar substitution of Ti^{4+} was applied, but its function differed significantly from that in the NNO system. In this case, Ti^{4+} not only alleviated the Jahn-Teller (JT) distortion and modified the primary particle morphology and size, but also stabilized the polymorphic α -phase of NMO, ultimately improving cycling stability.^[49,50]

In conclusion, this work presents both Ni-based layered cathodes with potential for EV applications and more sustainable Mn-based layered oxides as promising alternatives.

2. Fundamentals

2.1. Structural Classification and Prototype Materials of Layered Oxide Cathodes

2.1.1 Crystal Structures of Layered Oxide Cathodes for Sodium-Ion Batteries

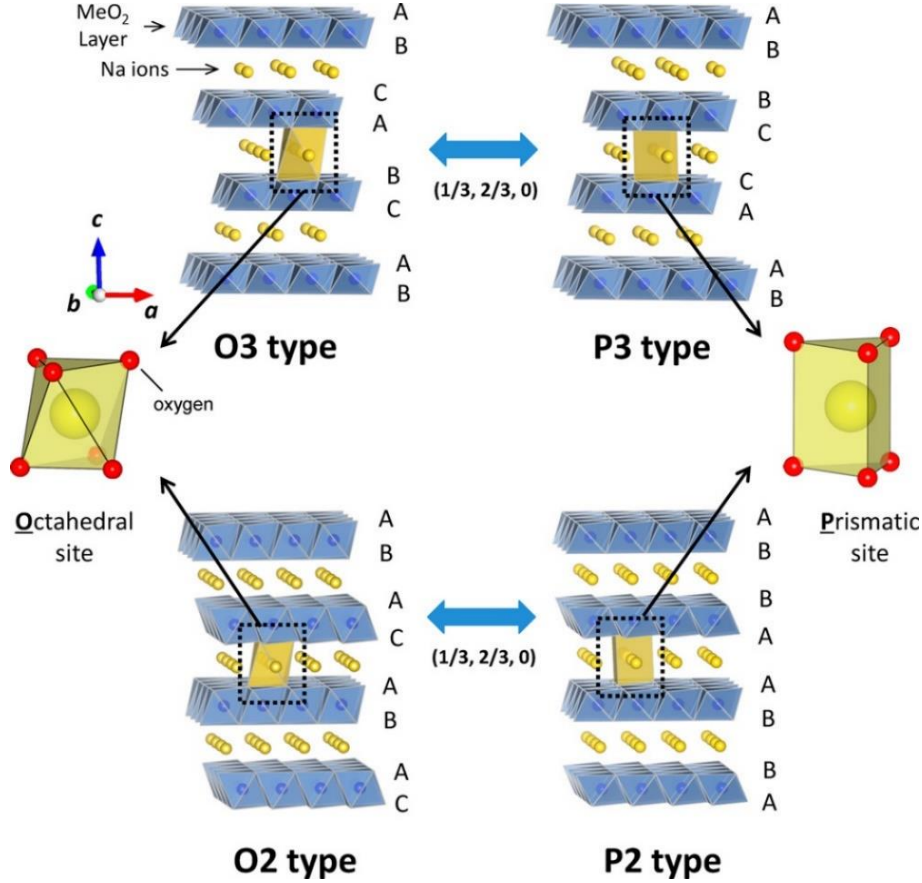


Figure 1. Schematic illustrations of O3, P3, O2, and P2 crystal structures and the phase transition processes triggered by sodium extraction.^[51]

Layered transition metal oxides are generally described by the formula $A_x\text{TMO}_2$, where A represents an alkali metal (such as Li or Na), x denotes its content, and TM stands for one or more transition metals with variable oxidation states.^[52] In the case of layered sodium oxides, these materials can be typically categorized into two main types, which are O3 and P2, according to the classification introduced by Delmas *et al.*^[52] In this nomenclature, the letter (O and P) indicates the coordination environment of Na⁺ ions, with “O” referring to octahedral sites and “P” to prismatic sites, and the accompanying number corresponding to the minimum number of repeating oxide layers in the unit cell.^[45,51,52] For instance, O3-type structures exhibit a stacking sequence of AB, CA, and BC, while P2-type structures follow an AB, BA order, as illustrated in **Figure 1**.

O3-type NaTMO_2 share many structural features with their lithium counterparts LiTMO_2 , particularly the cubic close-packed (ccp) stacking of oxygen atoms.^[51] In both types of materials, the alkali metal and transition metal ions are each coordinated in edge-sharing octahedra, which alternate to form a layered structure. These materials typically crystallize in the hexagonal crystal system with space group (S.G.)

2. Fundamentals

$R\bar{3}m$.^[9,34,44,53] However, one key distinction is the difference in ionic radii, as Na^+ ($r = 1.02 \text{ \AA}$) is significantly larger than Li^+ ($r = 0.76 \text{ \AA}$), thereby effectively avoiding cation mixing between the Na^+ and TM ions in NaTMO_2 .^[12,54] In addition, the larger size of Na^+ also enables it to occupy prismatic sites, giving rise to the formation of P2-type structures. In this configuration, the TM ions remain octahedrally coordinated and alternate with NaO_2 layers, and the resulting structures typically belong to the hexagonal S.G. $P63/mmc$.^[3,55,56] This structural diversity, encompassing both O3- and P2-type materials, provide valuable design flexibility for optimizing CAMs in SIBs. Furthermore, structural variations such as in-plane distortion, which arise from JT distortion, are often denoted by the use of a prime symbol (') in the phase notation.^[51,57] For example, NaNiO_2 (NNO) exhibits a monoclinic lattice (S.G. $C2/m$), while P'2-type Na_xMnO_2 adopts an orthorhombic structure (S.G. $Cmcm$).^[46,48,56]

It is also important to note that both O3- and P2-type materials often undergo phase transitions during sodium extraction. In O3-type structures, the extraction of Na^+ ions can induce slab gliding within the TMO_2 layers, leading to a transformation into the P3 phase (**Figure 1**), in which Na^+ occupies prismatic sites that are thermodynamically more favorable. In contrast, for P2-type materials, Na^+ extraction destabilizes the prismatic environment, prompting the TMO_2 slabs to shift towards octahedral coordination, thereby converting the structure into the O2 phase.^[45,51,57] This behavior plays a crucial role in determining the electrochemical performance and long-term stability of sodium cathodes.

2.1.2 Advantages and Limitations of O3- and P2-Type Layered Oxides

Due to their inherent structural characteristics, O3- and P2-type layered oxides exhibit distinct electrochemical properties. One of the most significant differences lies in their sodium content per unit cell. Specifically, O3-type materials exhibit the highest sodium content (typically $0.7 \leq x(\text{Na}) \leq 1$), whereas P2-type compounds are intrinsically sodium-deficient, with typical contents ranging from $0.6 \leq x(\text{Na}) \leq 0.8$.^[3,58–60] This inherent advantage in sodium content makes O3-type materials more favorable for use in practical full cell configurations. In contrast, P2-type materials generally require pre-sodiation or the addition of sacrificial salts, such as Na_2CO_3 , to compensate for their lower initial sodium content.^[61–63]

In addition, the sodium ions in O-type structures are coordinated octahedrally by six oxygen atoms. As illustrated in **Figure 2**, Na^+ migration in this structure involves a transition through a tetrahedral site located between two adjacent octahedra, resulting in relatively high diffusion barriers.^[64] In contrast, in P-type structures, Na^+ ions occupy prismatic sites, and their migration occurs directly through face-sharing prisms, facilitating ion transport.^[51] Consequently, P-type materials generally exhibit superior rate performance compared to their O-type counterparts.

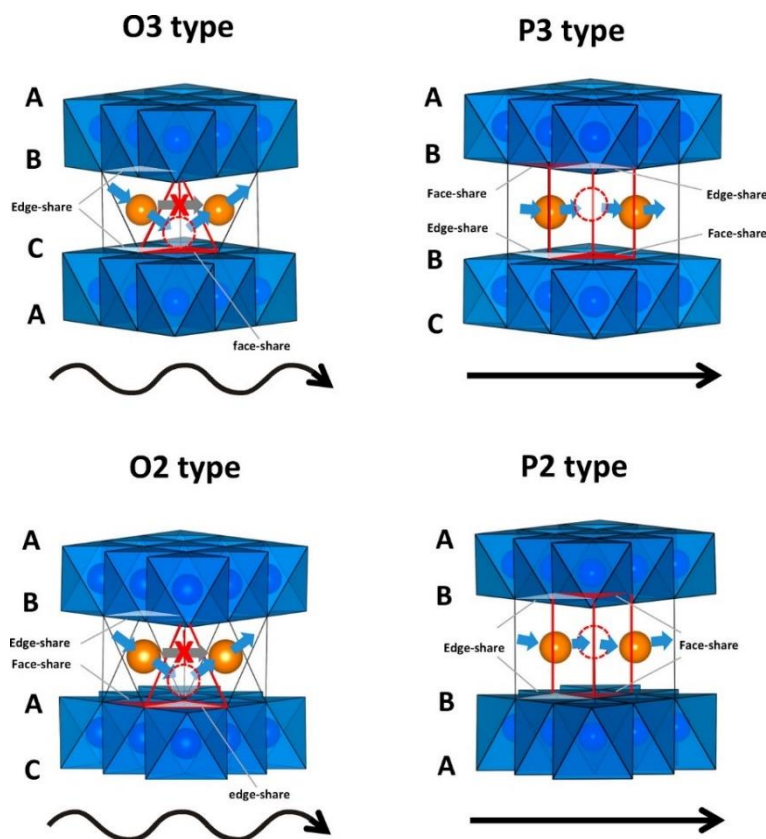


Figure 2. Sodium diffusion paths in different structures.^[51]

While both O3- and P-type materials have their respective advantages and have been extensively investigated in academic research, challenges remain when it comes to large-scale industrial applications. For P2-type materials, the need for pre-sodiation and/or the use of sacrificial salts can lead to gas generation and higher production cost, limiting their practical feasibility. In contrast, O3-type materials, with their higher sodium content and simpler processing requirements, are considered more suitable for industrial deployment. Nonetheless, O3-type cathodes still face critical challenges, including complex phase transitions during cycling and relatively poor rate capability.^[59,65,66] Therefore, this doctoral thesis focused on in-depth study and optimization of O3-type oxide CAMs, aiming to address the above limitations and enhance their applicability in SIBs.

2.1.3. NaNiO_2 and NaMnO_2

Due to the larger ionic radius of Na^+ compared to that of Li^+ , Na_xTMO_2 compounds can form layered structures with a broader range of transition metals than their Li_xTMO_2 counterparts, as shown in **Figure 3**.^[67] Although titanium can produce layered oxides, such as NaTiO_2 , its low redox potential limits any applications to the anode side, and thus it is not discussed in detail here.^[68] Nevertheless, Ti^{4+} is frequently employed as a structural stabilizer in layered oxide cathodes for SIBs.^[69–73]

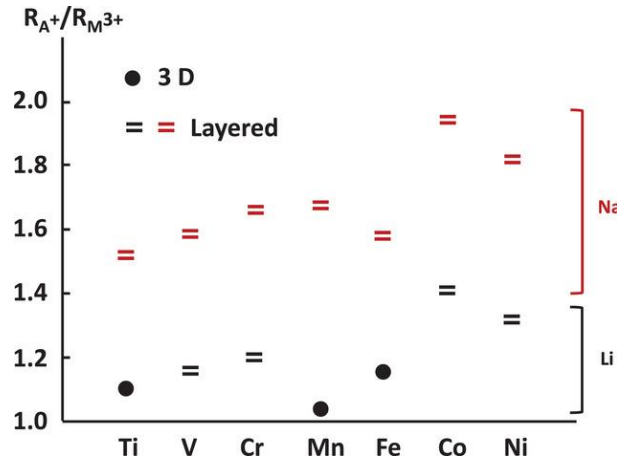


Figure 3. 2D or 3D structural formation of $A_x\text{TMO}_2$ determined by the ratio of alkali to transition metal ionic radii.^[67]

Vanadium- and chromium-based layered oxides (e.g., V: ~120 mAh/g, 1.2-2.4 V vs. Na^+/Na ; Cr: ~120 mAh/g, 2.0-3.6 V vs. Na^+/Na) have shown electrochemical activity in Na_xTMO_2 systems.^[74,75] However, their inherent toxicity makes them unsuitable for large-scale ESSs from a sustainability perspective.^[76] Although LCO was the first commercialized layered CAM for LIBs, its sodium analogue, NaCoO_2 , has not achieved comparable practical success.^[77,78] O3-type NaCoO_2 suffers from complex phase transitions (O3-O'3-P'3-P3), resulting in unsatisfactory electrochemical performance.^[78] Additionally, the high cost and toxicity of cobalt reduce the likelihood of layered Co-rich oxides being used in future applications.

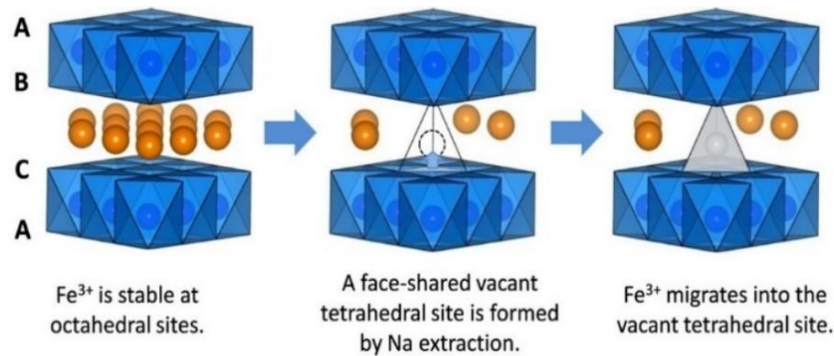


Figure 4. Proposed mechanism of iron migration upon sodium extraction.^[79]

In contrast, NaFeO_2 has drawn increasing attention due to its low cost and environmental friendliness. It is often considered the model compound for O3-type layered oxides, crystallizing in the *S.G. R-3m*, and can be readily synthesized via conventional solid-state reactions.^[80] Unlike in LIBs, the similar ionic radii of Li^+ and Fe^{3+} hinder the formation of layered Fe-based oxides through high-temperature synthesis, often resulting in rock-salt structures.^[51] Despite NaFeO_2 having a high theoretical specific capacity (241.8 mAh/g), its reversible capacity is limited to around 80 mAh/g.^[81] The reason is that a fraction of Fe^{3+} ions can migrate into adjacent tetrahedral sites, as depicted in **Figure 4**. During sodium extraction, vacancies are generated at the face-sharing tetrahedral sites neighboring the FeO_6 octahedra. Owing

2. Fundamentals

to the thermodynamic stabilization of trivalent iron in tetrahedral coordination, Fe^{3+} ions readily migrate into these sites, thereby obstructing sodium diffusion and deteriorating the electrochemical performance.^[79,81] Thus, the development of layered Fe-rich oxides remains a considerable challenge.

O'3-type Mn-based oxides typically crystallize in a monoclinic lattice (S.G. $C2/m$), primarily attributed to the JT distortion induced by Mn^{3+} ions.^[59,82] The initial electrochemical investigation of O'3- NaMnO_2 (O'3-NMO) has been reported in 1985, although at that time, only approximately 0.2 of Na^+ could be reversibly extracted.^[83] A subsequent study in 2011 demonstrated enhanced performance, with reversible sodium extraction increasing to around 0.8 of the total sodium content.^[82] Despite these improvements, the limited cycling stability of O'3-NMO remains a significant challenge. Moreover, the synthesis of O3-type Mn-rich oxides with practical applicability continues to encounter considerable difficulties, which will be discussed in detail in a later section. Nevertheless, Mn-rich materials, owing to their relatively low cost and promising reversible capacity, represent a compelling subject for further investigation and development.

LNO, regarded as a benchmark, high-capacity CAM for LIBs, has attracted considerable research interest, which has also extended to its sodium analogue, NNO.^[54] NNO has attracted growing interest due to its high theoretical capacity. Previous studies have shown that NNO can deliver an initial specific charge capacity of up to 199 mAh/g in the potential window of 2.0-4.5 V vs. Na^+/Na , although the corresponding discharge capacity was limited to 147 mAh/g. Notably, when cycled between 1.25 and 3.75 V at a rate of C/10, NNO exhibited good capacity retention, with the Coulomb efficiency increasing to 99.2 % after 20 cycles.^[46] To elucidate the origin of irreversible capacity loss, Wang *et al.* conducted *in situ* XRD studies and attributed the performance degradation to complex phase transitions and irreversible gliding of the NiO_2 slabs under high-voltage conditions.^[48] These structural instabilities are likely associated with the JT distortion induced by Ni^{3+} , suggesting that mitigating this distortion is essential for enhancing the electrochemical stability of layered Ni-rich oxides. Given the intrinsically high theoretical specific capacity and significant research potential of Ni-rich systems, NNO and related materials remain promising candidates for further in-depth investigations.

Based on the above analysis, layered Ni- and Mn-rich oxides possess considerable research potential. Therefore, in this doctoral research, NNO and NMO were selected as prototype materials for systematic optimization and detailed investigations.

2.2. Structure, Electrochemical Properties, and Degradation Behavior of NaNiO_2 and NaMnO_2

2.2.1. Structure and Electrochemistry of NaNiO_2

NNO exhibits two thermodynamically stable polymorphs, a high-temperature rhombohedral phase (S.G. $R\bar{3}m$) and a low-temperature monoclinically distorted phase (S.G. $C2/m$). In the low-temperature structure, Ni^{3+} ions occupy edge-sharing octahedral sites. However, due to the low-spin electronic configuration of Ni^{3+} ($t_{2g}^6e_g^1$), a pronounced JT distortion occurs, leading to elongation of the NiO_6 octahedra along the z-axis and resulting in significant structural distortion. Upon heating to about 450 K, the static JT distortion is thermally relaxed, allowing the structure to transition into the more symmetric rhombohedral phase.^[84–86]

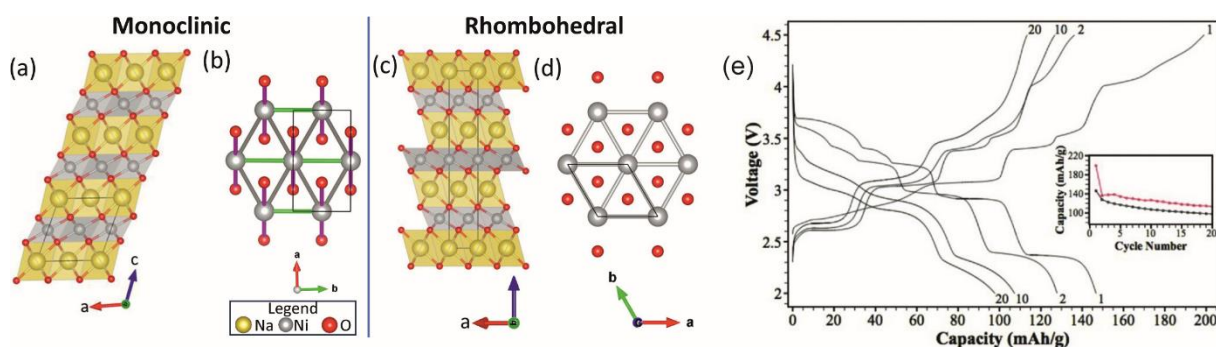


Figure 5. Crystal structures of NNO: (a) monoclinic phase and (c) rhombohedral phase. Panels (b) and (d) illustrate the Ni–Ni bond lengths (gray representing non-elongated, green representing elongated) and the JT-elongated Ni–O bonds (pink) in the respective structures. In the rhombohedral phase, no elongation of Ni–Ni or Ni–O bonds is observed.^[84] (e) Voltage profiles of NNO cycled between 2.0 and 4.5 V vs. Na^+/Na at a rate of C/10.^[46]

The crystal structure of NNO has been determined first in 1954 using film-based techniques.^[87] However, its electrochemical properties were not thoroughly explored until 1982, when it was reported that only 0.2 equivalents of Na^+ can be reversibly extracted within the potential range of 1.8–3.4 V vs. Na^+/Na .^[88] Considerable progress has been made in a later study in 2013, which demonstrated that up to 0.85 Na^+ can be extracted and 0.62 Na^+ re-inserted per formula unit during the first cycle within a wider potential window of 2.0–4.5 V vs. Na^+/Na .^[46] Although the material exhibited limited capacity retention, these findings renewed interest in NNO, particularly due to its high theoretical specific capacity and potential as a model system for the study and development of layered Ni-based cathodes.

2.2.2. Phase Evolution of NaNiO_2

Due to the larger ionic radius of Na^+ , NNO undergoes in-plane gliding of the NiO_2 slabs during sodium-ion intercalation and de-intercalation, which may induce multiple phase transitions. In early studies, Braconnier *et al.* first reported the presence of multiple

2. Fundamentals

phase transformations in NNO ($O'3$ - $P'3$ - $P''3$ - $O''3$) upon electrochemical cycling.^[88] However, due to the limited sodium extraction (around 0.2 Na^+ in the potential range of 1.8-3.4 V vs. Na^+/Na), the understanding of structural evolution in NNO remained incomplete at that time.

Subsequent studies employing *in situ* transmission X-ray microscopy-XANES (TXM-XANES) and *in situ* high-energy X-ray diffraction (HEXRD) have provided a more comprehensive picture of the structural evolution of NNO. As shown in **Figure 6**, a series of complex phase transitions occurs within the potential window of 2.0-4.5 V vs. Na^+/Na , including $O'3 \rightarrow P'3$ ($O''3$) $\rightarrow P''3 \rightarrow O'''3 \rightarrow O''''3$.^[48]

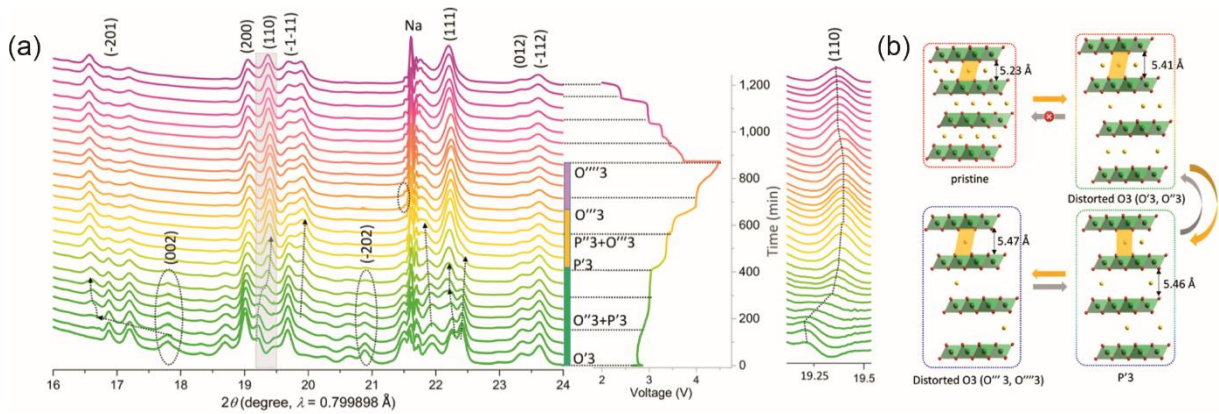


Figure 6. (a) *In situ* HEXRD patterns of NNO collected in the initial cycle (2.0-4.5 V vs. Na^+/Na at C/10 rate). (b) Schematic illustration of the structural evolution of NNO during charge and discharge.^[48]

Notably, the high-voltage transition (above 4.0 V vs. Na^+/Na) to the $O''''3$ phase is associated with substantial capacity loss. This is attributed to the irreversible gliding of the NiO_2 slabs, which leads to a permanent change in the c -axis parameter after the first charge, preventing the structure from returning to its original state upon discharge. Therefore, strategies such as tailoring the upper cut-off potential to avoid irreversible phase transitions or introducing dopants to stabilize the framework have been proposed to enhance the electrochemical reversibility of NNO. The latter approach will be discussed in detail in sections 2.4.1. and 2.4.3.

2.2.3. Structure and Electrochemistry of $NaMnO_2$

Stoichiometric NMO typically exists in two distinct polymorphic forms, as illustrated in **Figure 7**, a low-temperature monoclinic phase (α -NMO), formed within the temperature range of (600-900) °C, and a high-temperature orthorhombic phase (β -NMO) with a corrugated-layer structure, which is stabilized above 900 °C.^[50,65,82] The α -NMO phase is isostructural with NNO discussed in section 2.2.1., and its monoclinic distortion originates from the JT effect associated with Mn^{3+} , leading to elongated MnO_6 octahedra.^[82,83,89]

Despite their distinct crystal symmetries, density functional theory (DFT) calculations have shown that the formation energies of the α - and β -phases are nearly identical,

2. Fundamentals

suggesting comparable thermodynamic stability.^[49] However, synthesizing phase-pure β -NMO remains experimentally challenging. In a notable breakthrough, Shishkin *et al.* reported the successful preparation of single-phase β -NMO in 2018 by substituting 10 mol.% of manganese with copper, thereby stabilizing the orthorhombic structure.^[49]

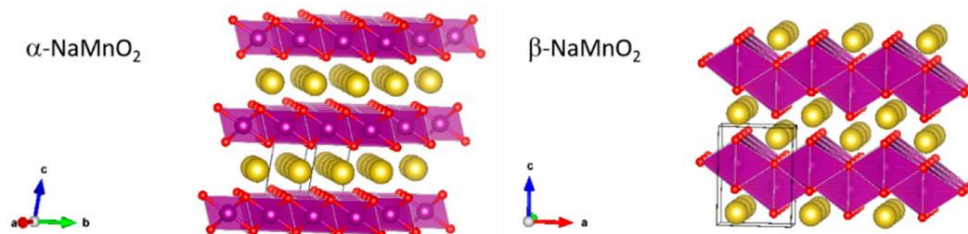


Figure 7. Representation of the structure of the two polymorphs of NaMnO_2 (red = oxygen, purple: MnO_6 octahedra, yellow: sodium).^[50]

In terms of electrochemical performance, both polymorphs demonstrate high operating potentials and relatively large specific capacities.^[50,65,66,82] Nevertheless, due to the synthetic difficulty and the inherent tendency of β -NMO to gradually transform into the α -phase during cycling, most research has concentrated on α -NMO.^[90] While the initial electrochemical study of α -NMO has been conducted in 1985, the first clear demonstration of efficient and reversible Na^+ (de)intercalation has not been reported until 2011.^[82,83] Although α -NMO can deliver a high initial specific capacity approaching 200 mAh/g, its capacity retention over extended cycling remains unsatisfactory. Moreover, α -NMO exhibits an unusual degradation behavior at low current densities, which is hypothesized to arise from prolonged exposure to high potentials during slow cycling. This extended residence time at elevated potentials may facilitate interfacial reactions and structural degradation.^[82] To overcome these limitations, several strategies can be exploited, including surface coating, electrolyte formulation optimization, and cation doping, all aiming at mitigating side reactions and improving long-term performance of α -NMO.^[59,91–93]

2.2.4. Phase Evolution of O'3-Type NaMnO_2

Despite the appealing working potential and reversible capacity of NMO, its highly complex phase transitions present significant challenges for further optimization.^[50,82] In comparison to NNO, which shares the same monoclinic structure, NMO exhibits up to nine distinct structural phases during cycling, as illustrated in **Figure 8**. However, due to the low crystallinity and weak diffraction intensity of the final manganese-based migration phase O'3-O1(9), only eight phases can typically be identified using *in situ* XRD.^[65]

The nine phases, labeled sequentially as O'3(1), O'3(2), O'3(3), O'3(4), O'3(5), O'3(6), O'3(7), O'3-O1(8), and O'3-O1(9), exhibit various symmetries. Among them, O'3(1), O'3(2), O'3(4), O'3(6), and O'3(7) adopt a monoclinic structure, while O'3(3) and O'3(5) crystallize in a triclinic system.^[65,66] Interestingly, although layered Mn-based oxides are often prone to forming the P3 phase during solid-state synthesis, NMO does not

2. Fundamentals

exhibit a P3-type transition during electrochemical (de)sodiation.^[94] This behavior contrasts with other O3- or O'3-type materials such as NaCrO₂, NaCoO₂, NaNiO₂, and NaNi_{0.5}Mn_{0.5}O₂, which typically undergo P3 phase formation upon Na⁺ extraction.^[12,78,95,96] The absence of a P3 phase in NMO highlights its distinct structural evolution during cycling.

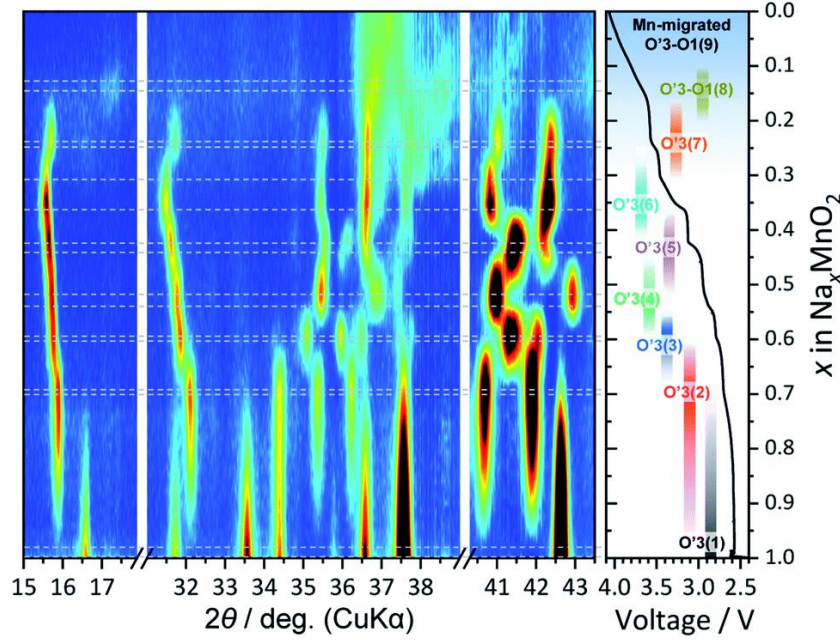


Figure 8. 2D XRD contour plot of NMO during charging at 6 mA/g in the first cycle.^[65]

To further understand the structural complexity of NMO, several studies have investigated the origin of specific intermediate phases observed during cycling.^[59,65,66,92,94] It has been proposed that the formation of phases such as O'3(2), O'3(4), and O'3(6) is closely related to sodium-vacancy ordering, which is likely driven by Mn^{3+/4+} charge ordering or correlated interactions.^[66] A particularly notable phase in this sequence is O'3-O1(8), which is believed to result from stacking faults between the O'3(7) and O1-type layers.^[65] This phase transition also involves partial migration of manganese from the TM layer into sodium sites located within the interlayer region. These migrated ions are considered to occupy tetrahedral coordination environments in the O3-type interlayer space or octahedral sites in the O1-type stacking sequence, which can markedly reduce the crystallinity of the resulting O'3-O1(8) phase.^[65,94] As a result, this phase exhibits weak diffraction intensity and is considerably more difficult to detect compared to the earlier monoclinic and triclinic phases.

Moreover, the structural evolution of NMO during discharge displays unique characteristics too. When NMO is discharged within the potential range of 2.0-3.8 V vs. Na⁺/Na, only O'3(2) and O'3(1) phases can be clearly observed, while the remaining phases give rise to ill-defined reflections. This behavior is attributed to the formation of the low-crystallinity O'3-O1(8) phase at high potentials, which disrupts long-range ordering and hinders structural recovery. In contrast, when the upper cut-off potential is limited to 3.476 V, a full sequence of transitions from O'3(1) to O'3(7) can be identified. Notably, the O'3(3) phase typically appears concurrently with O'3(4),

2. Fundamentals

resulting in asymmetric redox features observed in differential capacity plots.^[50,59,65,82,91]

Taken together, this rather detailed phase transition analysis indicates that a straightforward strategy to improve the capacity retention of NMO is to avoid the formation of the poorly crystalline O'3-O1(8) phase. More discussion on this strategy will be presented in sections 2.4.2. and 3.3.

2.2.5. Degradation of NaNiO_2 and NaMnO_2

I. Phase Transitions

One of the most critical origins of degradation in both NNO and NMO lies in their complex phase transitions, leading to three major consequences. As discussed in sections 2.2.2. and 2.2.4., among others, this involves irreversible changes to the crystal structure. This includes, for instance, the irreversible gliding of NiO_2 slabs near 4.0 V in NNO, and the severe migration phase(s) observed around 3.8 V in NMO.^[48,65] Second, phase transitions are often accompanied by significant changes in unit-cell volume, typically manifested as a large contraction along the *c*-parameter.^[28,57,72,97] This volume variation introduces severe lattice stress, which subsequently results in intergranular cracking, particularly when Na-deficient O1-type phases are involved.^[60,97–99] Third, during the coexistence of multiple phases, the mismatch in lattice parameters between adjacent phases can generate large coherency strain at the phase boundaries, thus giving rise to intragranular particle fracture.^[100–102] Both intergranular and intragranular cracks expose fresh cathode surfaces to the electrolyte, accelerating parasitic reactions.^[96] Over time, such degradation leads to the loss of electrode integrity, including particle pulverization and loss of electrical contact with the current collector, as well as depletion of active Na^+ ions, ultimately resulting in capacity fading.^[103,104] Therefore, chemo-mechanical degradation induced by phase transitions is recognized as one of the primary degradation mechanisms in NNO and NMO.

II. Jahn-Teller Distortion

JT distortion not only triggers complex phase transitions (e.g., O3 to O'3 and P3 to P'3), but also contributes to TM dissolution, ion migration, and surface reconstruction. To elucidate the underlying mechanisms, the electronic structures of NNO and NMO are discussed as representative examples.

In an ideal octahedral coordination environment formed by six surrounding oxygens, the five degenerate 3d orbitals of a TM ion (each capable of accommodating two electrons of opposite spin) are split into two subsets due to crystal field effects, namely the e_g orbitals (d_{z^2} and $d_{x^2-y^2}$), which point directly toward the oxygen ligands, and the t_{2g} orbitals (d_{xy} , d_{xz} , and d_{yz}), which are oriented between the oxygen ligands, as shown in **Figure 9a**.^[29,105–107]

2. Fundamentals

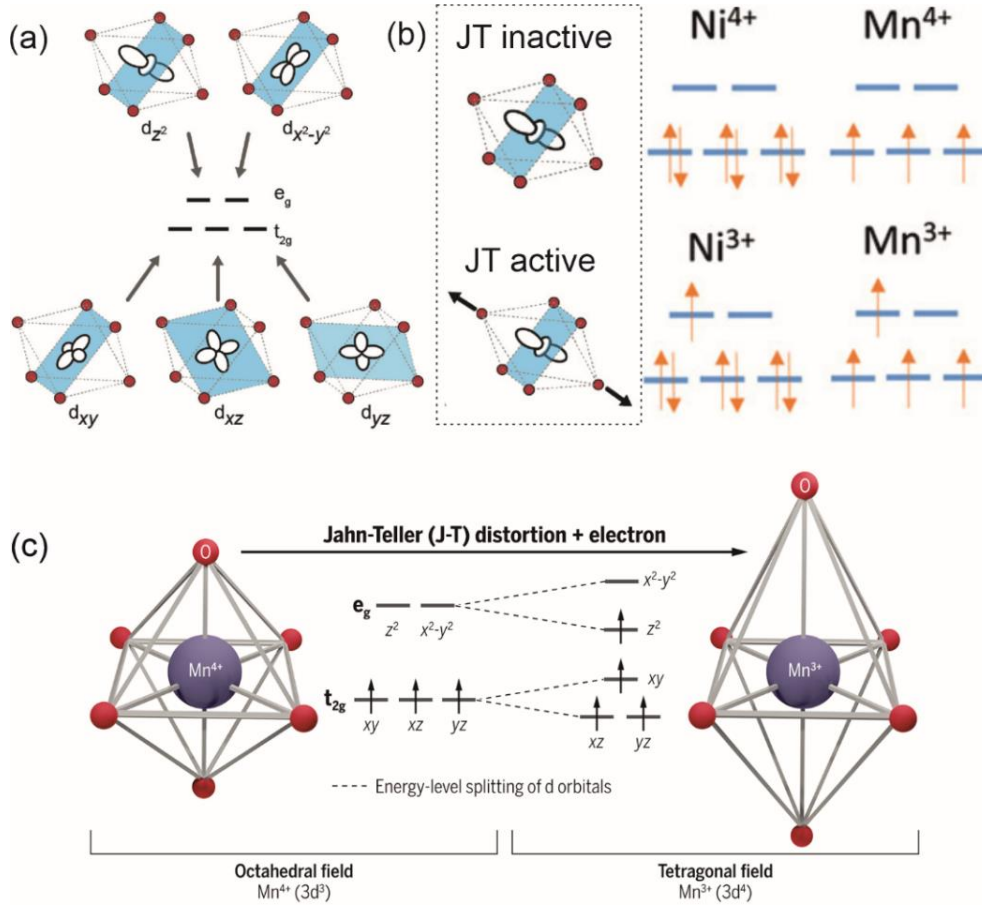


Figure 9. (a) Crystal field splitting of d orbitals in an octahedral environment.^[105] (b) Electronic structures of JT inactive (top row) and active (bottom row) octahedra of nickel and manganese.^[29,105] (c) The ligand field in NMO distorts the six equivalent metal-oxygen bonds (left) into two longer axial bonds and four shorter equatorial bonds (right). Charge is transferred from the metal cation to the axial oxygens, thus becoming more basic.^[106]

TM cations in layered oxides typically adopt octahedral (O_h) coordination. For low-spin Ni^{3+} and high-spin Mn^{3+} , there is a single electron occupying the e_g orbital. This configuration is particularly susceptible to JT distortion, which lowers the total energy of the system by removing the degeneracy of the e_g orbitals. As illustrated in **Figures 9b** and **c**, elongation along one of the octahedral axes causes the e_g levels to split, such that the occupied orbital lies at lower energy and the unoccupied orbital at higher energy.^[106,107]

This distortion leads to the formation of longer TM–O bonds along the axial direction. These bonds exhibit increased ionic character, rendering the axial oxygen atoms more negatively charged.^[102,106] From a Lewis acid-base perspective, the oxygen atoms become more basic, making them more prone to react with protons to produce H_2O .^[102,108–110] However, since the oxygen in TM–O bonds is less negatively charged than in free H_2O , an additional electron must be transferred from the TM d_{z^2} orbital to the axial oxygen to facilitate this reaction. As a result, the TM ion is oxidized to a higher oxidation state (e.g., Ni^{3+} to Ni^{4+} , Mn^{3+} to Mn^{4+}).^[106,110,111] These high-valent cations

2. Fundamentals

can then oxidize the electrolyte, leading to the evolution of CO_2 , and are subsequently reduced to lower oxidation states (e.g., Ni^{2+} , Mn^{2+}).^[112,113] The divalent cations may then undergo several degradation pathways:

1. Dissolution into the electrolyte, contributing to the formation of intergranular and intragranular cracks that promote sodium loss and further degradation;^[48,111,114]
2. Migration to tetrahedral sites in the NaO_2 layer, thereby initiating surface reconstruction and formation of spinel or rock-salt phases;^[111,115]
3. Retention at tetrahedral positions, where they obstruct the sodium diffusion channels.^[105]

These degradation processes are generally more pronounced in layered Mn-based oxides, but several reports also indicate the occurrence of ion migration and surface reconstruction in Ni-rich systems.^[48,116,117]

III. Interfacial Stability

The interfacial stability of O3-type CAMs is a critical factor governing their structural reversibility, particularly in terms of both air|cathode and electrolyte|cathode interfaces. This section first focuses on the stability of the air|cathode interface.

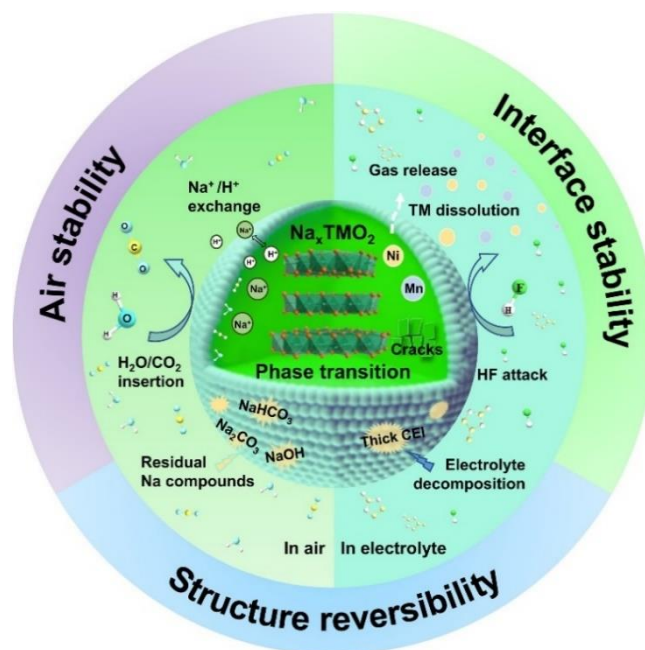
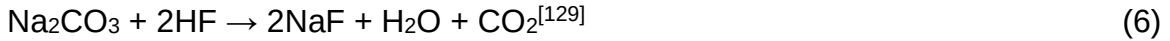
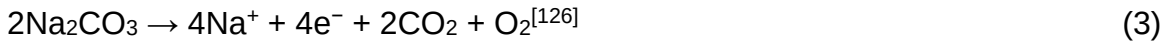
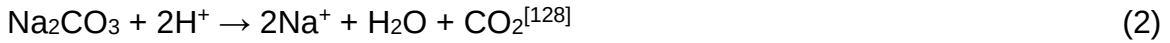
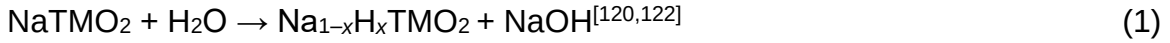


Figure 10. A schematic representation of the various degradation mechanisms affecting layered oxide cathodes, including air sensitivity, interfacial instability, and structural irreversibility.^[102]

Due to the sensitivity of SIB cathodes to ambient moisture and CO_2 , these materials must be handled and stored under dry or vacuum conditions.^[118,119] For O3-type Na_xTMO_2 materials, several degradation mechanisms have been proposed upon exposure to humid air.^[120,121] One of the primary processes involves the spontaneous

2. Fundamentals

extraction of Na⁺ ions from the layered structure, which can occur either via redox reactions between the particles and water or through a Na⁺/H⁺ exchange mechanism.^[122,123] Ultimately, this leads to the formation of protonated phases. The hydrolysis reaction can be represented as shown in **Equation 1**.^[120] The resulting NaOH can further react with atmospheric CO₂ to produce a residual layer of carbonate species, such as Na₂CO₃ and NaHCO₃, which are detrimental to surface stability.^[120] These reactions are typically accompanied by TM (Ni or Mn) dissolution at the surface, facilitating the formation of a dense rock-salt phase that impedes sodium transport.^[111] Additionally, the basicity of Na₂CO₃ and NaHCO₃ can trigger the defluorination of the PVDF binder, thus leading to particle agglomeration and gelation of the electrode slurry.^[124,125] Moreover, carbonate species formed on the surface may undergo chemical decomposition or electrochemical oxidation during cycling (**Equations 2 and 3**).^[126] The latter process generates reactive oxygen, which readily attacks the electrolyte, causing further gas evolution and significantly compromising the cycling performance and stability of battery.^[127]



The stability of the electrolyte|cathode interface remains a critical issue in SIBs. This includes not only TM dissolution and surface reconstruction, as previously discussed in relation to JT distortion, but also electrolyte decomposition and gassing.^[130–132] While the outgassing behavior of cathodes has been extensively studied in LIBs, the corresponding mechanisms in SIBs are still underexplored. Nevertheless, due to the similarities between LIBs and SIBs, gas evolution observed in LIB systems is often used as a reference for SIBs.^[128,133]

At the cathode side, the predominant gaseous species are CO₂ and O₂.^[40,126,134] Oxygen release is typically attributed to the irreversible loss of lattice oxygen. Given its high reactivity, this released oxygen tends to oxidize the electrolyte directly, producing CO₂ as a gaseous byproduct.^[126,135–137] Carbon dioxide, however, can also originate from other sources, including decomposition of residual carbonates present on the particle surface (**Equations 2 and 3**) and electrochemical oxidation of the electrolyte at high potentials.^[126,138]

The irreversible lattice oxygen loss frequently results in the formation of an oxygen-deficient surface layer, which promotes TM dissolution and phase transformation.^[111] These effects are closely linked to the structural instability described earlier in the

2. Fundamentals

context of JT distortion. In addition, when NaPF_6 is used as the conducting salt, it can decompose to form hydrofluoric acid (HF), as shown in **Equations 4** and **5**. HF not only accelerates the decomposition of carbonate species (**Equation 6**), but also enhances the dissolution of transition metals, further degrading the electrolyte|cathode interface.^[139]

Improving interfacial stability therefore requires not only structural and surface optimization of CAMs, but also careful design of stable electrolyte formulations. This integrated approach is essential to suppress parasitic reactions, minimize degradation, and enhance the long-term performance of SIBs.

2.3. Synthesis Parameters of Solid-State Reaction and Resulting Properties

Solid-state synthesis is one of the most commonly employed methods for preparing layered oxides, owing to its simplicity and suitability for large-scale industrial production.^[140] The successful formation of layered structures is often dependent on specific synthesis parameters used during the solid-state process, such as calcination temperature, Na/TM ratio, cooling process, and atmosphere. These parameters not only determine whether the desired phase can be obtained, but also significantly influence critical material properties, including particle size, purity, and crystallinity, all of which directly affect the electrochemical performance of the final product. Therefore, this section will provide a detailed discussion of each synthesis parameter and its potential impact on structure and properties of the resulting materials.

2.3.1. Calcination Temperature

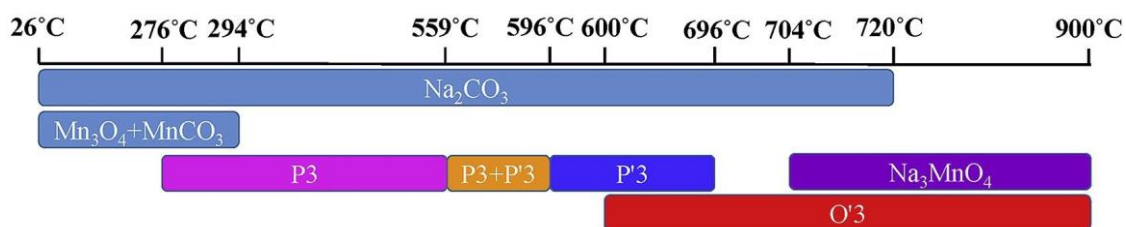


Figure 11. Phase evolution of Na_xMnO₂ during calcination.^[141]

The calcination temperature is one of the most critical parameters in solid-state synthesis, not only for LIBs, but also for SIBs. In the case of LIBs, for the layered Li-rich oxide CAM, Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂, it was found that increasing the calcination temperature from 850 to 900 °C, while maintaining the same crystal structure (S.G. *R-3m*), significantly increases both grain size and crystallinity. Moreover, the sample calcined at 900 °C exhibited superior cycling stability, whereas the material treated at 850 °C delivered higher reversible capacities.^[142] These findings indicate that the calcination temperature not only influences the particle size and crystallinity of the material, but also has distinct effects on the electrochemical properties.

For SIBs, in addition to the phenomena observed in LIBs, the calcination temperature can also lead to the formation of different crystal structures from the same chemical composition. For instance, the P-type Na-deficient oxide Na_xMn_{0.5}Co_{0.5}O₂ was synthesized at 650, 800, and 900 °C. The results revealed that pure P3 and P2 phases can be obtained at 650 and 900 °C, respectively, while a mixed phase was formed at 800 °C. Electrochemical testing demonstrated that the P2-type sample exhibits the best overall performance, while the mixed-phase material showed the highest Na⁺ diffusion coefficient.^[143]

A similar phenomenon was observed for the synthesis of Na_xMnO₂. As shown in **Figure 11**, distinct phases such as P3, P'3, O'3, and Na₃MnO₄ can be identified at different temperatures.^[141] It is worth noting that the O'3 phase represents the low-temperature α -phase, while the high-temperature β -phase is typically obtained at

2. Fundamentals

synthesis temperatures above 900 °C (see section 2.2.3.)^[51] In terms of electrochemical performance, the α -phase exhibits better reversibility in the sodium insertion/extraction reactions compared to the β -phase.^[50] As a result, most studies have focused on the α -phase of NaMnO₂ (O'3-type).

It should be noted that for most layered materials, lower reaction temperatures are insufficient to produce well-defined layered structures or the desired phase, whereas excessively high temperatures can lead to thermal decomposition of the material. In addition, elevated temperatures may also promote grain growth or sintering, which can increase the diffusion path length for charge transport and consequently deteriorate the rate capability.

Therefore, calcination temperature is a critical parameter that fundamentally affects the phase composition, microstructural characteristics, and electrochemical behavior of layered oxide CAMs. Hence, systematic tailoring of this parameter is indispensable for the rational design and development of high-performance SIB electrode materials. In section 3.1., a systematic study on the optimization of calcination temperature is presented.

2.3.2. Cooling Process

Although the calcination temperature is pivotal in establishing well-ordered layered structures, the subsequent cooling process can also play a critical role in preserving the structural integrity of the synthesized material. A well-documented example involves the orthorhombic P'2-Na_{2/3}MnO₂ and its P2 counterpart. The P'2 phase is typically obtained via rapid quenching, whereas a slower cooling process favors the formation of the P2 phase. However, neither method yields a single-phase material.^[144–146] To address this challenge, the synthesis route was systematically optimized, demonstrating that a pure P2 phase can be obtained from a well-defined P'2 phase. Notably, the P'2 phase, which exhibits JT distortion, has been shown to provide superior electrochemical performance.^[56] These results indicate that the cooling rate not only determines the resulting crystal structure, but also impacts the electrochemical properties of the material.

Furthermore, the cooling rate also plays a decisive role in the defect chemistry of layered Mn-based oxides. Slow or uncontrolled cooling often induces the formation of manganese vacancies, which may facilitate the oxidation of Mn³⁺ to Mn⁴⁺, thereby decreasing the number of redox-active centers and adversely affecting the reversible capacity.^[51] Liu *et al.* conducted a comparative study involving three different cooling strategies, namely natural cooling, air quenching, and liquid nitrogen quenching, and concluded that liquid nitrogen quenching is most effective in suppressing vacancy formation, thus leading to superior electrochemical performance.^[147]

In addition to its effects on crystal structure and cation vacancy concentration, the cooling rate may also introduce internal lattice strain. For example, in the NaNi_{0.4}Mn_{0.4}Co_{0.2}O₂ system, residual strain introduced during the quenching process

2. Fundamentals

facilitated the formation of electrochemically inactive rock-salt NiO phases, compromising the cycling stability of the material. Notably, this degradation mechanism was independent of the electrochemical window, but could be accelerated at elevated temperatures and high current densities.^[148]

Beyond the influence of cooling rate, the atmosphere during cooling also affects the synthesis of layered oxides. In the case of O3-type NMO, cooling can be carried out in air or under an inert gas (e.g., argon). While rapid quenching is required in air, slow cooling is sufficient in an inert atmosphere. However, both approaches aim at preventing the further oxidation of Mn^{3+} to Mn^{4+} , thereby suppressing the formation of the P2 phase.^[94]

Taken together, these findings underscore the critical role of the cooling process in the synthesis of high-performance layered oxide CAMs. A comprehensive understanding and tailoring of cooling protocols are therefore essential for advancing the structural design and practical application of SIB electrode materials. In section 3.1., a detailed study on the optimization of cooling rate is presented.

2.3.3. Na/TM Ratio

Precise control over the Na/TM ratio is crucial for determining the final phase composition of layered oxide cathode materials. This effect is especially pronounced in SIB CAMs, where variations in sodium content can selectively promote the formation of P2- or O3-type phases.^[149] When the Na/TM ratio is below 2/3, prismatic coordination becomes more thermodynamically favorable. Within this context, prismatic sites can be further categorized into face-sharing and edge-sharing types. Owing to the higher electrostatic repulsion associated with face-sharing sites, Na^+ ions preferentially occupy edge-sharing prismatic positions. However, when the Na/TM ratio exceeds 2/3, octahedral coordination becomes unavoidable, thereby favoring the formation of the O3-type phase.^[51,56,145] Hence, tailoring the Na/TM ratio can enable precise control over phase selection.

In addition to its influence on phase selection, the Na/TM ratio exerts a direct impact on the electrochemical properties of the material. For example, synthesizing O3-type materials with a Na/TM ratio below 1 can introduce sodium vacancies in a controlled manner, which can facilitate sodium diffusion and thus improve rate capability.^[150] Furthermore, during solid-state synthesis, it is common practice to introduce an excess of sodium precursor in order to compensate for sodium loss at elevated temperatures, thereby ensuring the desired final stoichiometry and phase purity.^[96]

2.3.4. Calcination Atmosphere and Precursor Selection

The selection of calcination atmosphere is closely related to the chemical nature of the target material and the oxidation behavior of the transition metals involved. For layered Ni-rich oxides, such as LNO and NNO, NiO or $\text{Ni}(\text{OH})_2$ is typically used as the TM

2. Fundamentals

precursor.^[12,13,47] In these cases, an oxygen-rich environment (e.g., pure O₂) is required to ensure complete oxidation of Ni²⁺ to Ni³⁺ during calcination, which is critical for obtaining a well-defined structure.^[48,54] In contrast, for Mn-rich compositions, air is often sufficient as the reaction atmosphere, as it provides a moderate oxidizing environment that prevents the over-oxidation of Mn³⁺ to Mn⁴⁺, thereby minimizing the formation of undesirable impurity phases.^[59,65,92] In particular, during the synthesis of O'3-type NMO, the precursor and reaction atmosphere must be chosen carefully. When Mn₂O₃ is used as the starting material, employing an inert gas atmosphere, such as argon, can effectively prevent the oxidation of Mn³⁺ to Mn⁴⁺.^[94] This approach may help to preserve the desired oxidation state and phase composition without the need for additional quenching steps, thereby simplifying the synthesis process. Hence, selecting an appropriate atmosphere based on the oxidation state of precursor is essential for obtaining phase-pure layered Mn-based oxides with stable electrochemical properties.

In addition to the reaction atmosphere, precursor homogeneity also plays a vital role in determining the quality and electrochemical performance of the final material. In conventional solid-state synthesis, nano- or micron-sized precursors are typically mixed mechanically, which often results in uneven elemental distribution and ill-defined particle morphology. To overcome these limitations, co-precipitation has been widely adopted as an alternative synthesis route. This technique enables atomic-level mixing of multiple cations and yields precursors of uniform (secondary particle) morphology, low surface area, and reduced internal porosity.^[151,152] Such characteristics are highly beneficial for improving the tap density of the final CAMs.^[153,154] Moreover, the scalability, operational simplicity, and tunable particle morphology make co-precipitation particularly attractive for large-scale production of battery materials.^[154,155] Accordingly, in this doctoral research, Ni(OH)₂ and Mn₃O₄ precursors synthesized via co-precipitation were employed for the preparation of layered Ni-rich and Mn-rich oxide cathodes, respectively, ensuring both compositional uniformity and structural stability in the final products.

2.4. Chemical Modification of NaNiO_2 and NaMnO_2

As discussed in section 2.2, both NNO and NMO suffer from several degradation mechanisms, including irreversible phase transitions, JT distortion, and interfacial instability. To address these challenges, one of the most widely adopted strategies is cation substitution, which can be implemented at either the alkali metal or TM sites. In particular, issues related to interfacial degradation can be further alleviated by optimizing the electrolyte composition and applying surface coatings to improve chemical and electrochemical stability.

Since Ni- and Mn-based CAMs respond differently to TM substitution in terms of structure and performance, the following sections will examine each system separately to provide a clearer analysis of their behavior and optimization strategies.

2.4.1. Substitution on the Ni-Site of NaNiO_2

Owing to the relatively large ionic radius of Na^+ , the Ni site in NNO can accommodate a variety of TM or alkali metal substitutions. Although NNO exhibits two polymorphs, only one is thermodynamically stable at room temperature. Therefore, when synthesizing substituted NNO, a sodium content in the range of 0.8 to 1 typically leads to the formation of either an O3 or O'3 structure.

Among various substitution strategies, Fe^{3+} has been considered one of the most promising candidates to replace Ni^{3+} , due to its lack of JT distortion, low cost, environmental friendliness, and non-toxicity.^[149] When a small amount of Fe^{3+} is introduced, the cycling stability of NNO can be moderately improved. This enhancement is attributed to two key factors. First, the substitution of Ni^{3+} with Fe^{3+} alleviates the lattice distortion induced by JT-active Ni^{3+} , thereby stabilizing the O3 phase over O'3 and reducing structural complexity during cycling. Second, since both Fe^{3+} and Ni^{3+} participate in redox reactions, with the $\text{Ni}^{3+}/4+$ redox couple playing a dominant role, the JT distortion induced by a small amount of Fe^{4+} is effectively suppressed, thereby mitigating the risk of irreversible iron migration. However, the average operating voltage decreases to about 2.7 V, and the relatively low reversible capacity (~60 % of the theoretical specific capacity) remains a major limitation for practical applications.^[156–158] Increasing the iron substitution level further is also not ideal, as it tends to promote Fe^{4+} migration at high potential (above 3.9 V vs. Na^+/Na), leading to more severe structural degradation.^[149]

Although Co-rich materials are generally avoided in SIB research due to their high cost and environmental concerns, partial cobalt substitution has been commonly employed in LIB systems to enhance structural and electrochemical stability.^[121,140,159] In layered Ni-based sodium oxides, introducing a moderate fraction of cobalt (e.g., ~0.5 molar ratio) can similarly stabilize the O3-type structure by suppressing JT distortion. Nevertheless, these materials still exhibit complex phase transitions during cycling, which are likely driven by sodium-vacancy ordering rather than lattice distortion. As a

2. Fundamentals

result, the use of cobalt as a substituent/dopant in SIB cathodes is generally not favored, given its limited benefits and sustainability drawbacks.^[149,158]

The incorporation of d^0 metal ions, such as Ti^{4+} , has also emerged as a widely used strategy to substitute TMs in layered oxides.^[72,73] Owing to its redox-inactive nature, Ti^{4+} primarily acts as a structural stabilizer rather than an electrochemically active species.^[70] Specifically, it can suppress the JT distortion associated with Ni^{3+} , thereby reducing interlayer gliding and enhancing reversibility of phase transitions.^[71] Notably, although titanium is generally considered inert during cycling, XANES studies comparing the fully charged and discharged states often reveal no shift in the first derivative of the absorption edge (indicating no change in oxidation state), yet subtle differences near the white line may be observed. These discrepancies are typically attributed to pseudo JT distortions.^[71] Recent studies suggest that while Ti^{4+} does not undergo redox reactions itself, it can facilitate local charge redistribution by interacting with neighboring electrochemically active species. This interaction alters the local structural environment and can lead to pseudo JT effects.^[160] In addition, Ti^{4+} has been reported to promote oxygen redox, thus contributing to increased capacity, although the reversibility of this contribution remains under investigation.^[160] For example, one study has demonstrated that substituting 50 mol.% of nickel in NNO with Ti^{4+} significantly reduces the complexity of phase transitions by stabilizing the Ni^{2+} oxidation state. However, the resulting reversible capacity reached only half of the theoretical value, indicating that further optimization is necessary.^[26,69–71]

It is worth emphasizing that most research on layered Ni-rich oxide CAMs involves the synergistic effect of multiple dopants. In addition to iron, cobalt, and titanium, elements such as aluminum, copper, and zirconium have also been explored.^[161–164] Notably, aluminum and copper have been reported to not only modulate phase transition behavior, but also enhance air stability of the materials. Nevertheless, a common limitation persists: many of these studies achieve enhanced cycling stability at the cost of reduced reversible capacity, ultimately failing to fully exploit the intrinsic energy density of Ni-based materials.

The central objective of this doctoral research was therefore to develop high-capacity O3-type CAMs by employing TM substitution strategies while maintaining a high nickel content and maximizing reversible capacity, enabling both structural stability and superior electrochemical performance.

2.4.2. Substitution on the Mn-Site of $NaMnO_2$

At present, research on O3-type Mn-rich CAMs remains limited, with the majority of studies focusing on P2-type compounds.^[63,165] This trend is not only due to the generally superior rate performance of P2-type materials, but more importantly due to the significant synthetic challenges associated with stabilizing the O3 phase. Two primary obstacles have been identified in this regard.^[49,50] The first challenge arises from the phase purity of NMO upon partial substitution. Even when stoichiometric

2. Fundamentals

amounts of sodium ($\text{Na/TM} = 1$) are employed during synthesis, the incorporation of small fractions of aliovalent or isovalent substituents/dopants often leads to the formation of P2-phase impurities.^[57,63] The second difficulty relates to polymorphism. As discussed in section 2.2.3., NMO exists in two polymorphic forms at room temperature. Upon substituting even ~ 10 mol.% of manganese, the resulting material tends to form a mixture of these polymorphs, thereby complicating structural control and reproducibility.^[49]

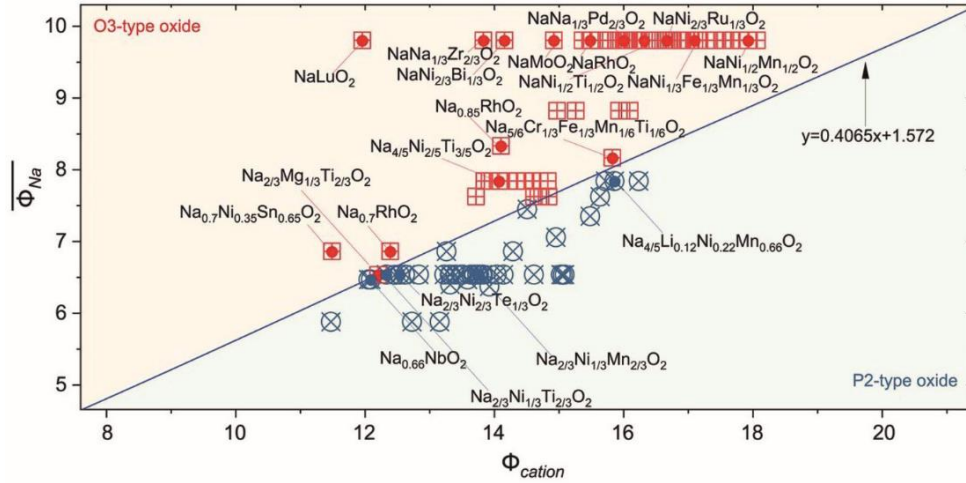


Figure 12. Cationic potential of representative P2- and O3-type layered oxides.^[166]

To rationalize the structural outcomes of substitution, the concept of cationic potential (**Equation 7**) has been proposed. $\overline{\Phi_{\text{TM}}}$ refers to the weighted average of the ionic potential (defined as the ratio of oxidation state to ionic radius, $\overline{\Phi_{\text{TM}}} = \sum \frac{wn}{r}$) of all transition metals occupying the TM site. Note that w denotes the molar fraction of each TM with charge n and ionic radius r . $\overline{\Phi_{\text{Na}}}$ refers to the weighted average ionic potential of sodium, which is defined accordingly. Charge neutrality in the Na_xTMO_2 composition requires that the total oxidation state of the cation species balances the negative charge from the oxygen ions $\sum wn = 4 - x$, meaning that the sum of all cationic charges must equal 4, where x denotes the sodium content.^[166] The value of $\overline{\Phi_{\text{Na}}}$ is calculated to be 9.8 when $x = 1$. According to the empirical boundary described in **Figure 12**, an O3-type structure is thermodynamically favored when Φ_{cation} is less than 20.2. This model has been shown to correctly predict the structure of a wide range of reported O3- and P2-type CAMs.

$$\Phi_{\text{cation}} = \frac{\overline{\Phi_{\text{TM}}} \overline{\Phi_{\text{Na}}}}{\overline{\Phi_{\text{O}}}} \quad (7)$$

However, several deviations from this model have been observed. For instance, $\text{NaMn}_{0.9}\text{Cu}_{0.1}\text{O}_2$ has a calculated Φ_{cation} of 16.29, which falls within the predicted O3 stability range. Nevertheless, experimental results show that it is nearly impossible to synthesize a O3 structure for this composition.^[167,168] A similar issue is found in the $\text{NaNi}_x\text{Mn}_{1-x}\text{O}_2$ system. Although adequate sodium source ($\text{Na/TM} \approx 1$) is used, P2-type

2. Fundamentals

phases still dominate the structure when the nickel content is below 33 %.^[165] These findings indicate that while the cationic potential model can offer useful predictions, it does not universally capture the complex phase behavior of substituted Mn-based systems.

Despite these limitations, several compositions have been successfully stabilized in the O3 phase and demonstrate promising cycling performance. For instance, $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ forms a non-distorted O3 structure and delivers a reversible specific capacity approaching 200 mAh/g.^[72,73,96,169,170] This compound has therefore attracted considerable research attention. Similarly, in the $\text{NaFe}_x\text{Mn}_{1-x}\text{O}_2$ system, although high manganese contents generally destabilize the O3 framework, compositions such as $\text{Na}_{0.8}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ have been reported to adopt an O3-type structure and deliver specific capacities of up to 180 mAh/g.^[150] Based on the combination of the above two types of materials, $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ has been developed, which can deliver a specific capacity of 136 mAh/g within a voltage window of 2.0-4.0 V vs. Na^+/Na . Subsequently, various optimization strategies for this material have been proposed, including the adjustment of cut-off voltage and substitution with Li^+ or Ca^{2+} ions.^[1,111] These findings highlight the possibility of obtaining high-performance O3-type Mn-rich CAMs through careful compositional design.

A further obstacle in the synthesis of O3-type Mn-rich cathodes is the stabilization of the α -polymorph of NMO. In a comprehensive study involving the substitution of manganese with 10 mol.% of twelve different elements (Mg, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn), both DFT calculations and experimental results indicated that only Ti^{4+} effectively stabilizes the α -phase. All other dopants tended to induce the formation of P2 or β -type impurity phases.^[49] Nevertheless, detailed investigations into (O3-type) Ti^{4+} -stabilized Mn-rich systems remain limited, and further studies are necessary to understand the underlying stabilization mechanisms.

In view of these considerations, the present research aimed to develop Mn-rich layered CAMs by introducing Ti^{4+} as a stabilizing substituent. This approach was designed to preserve high manganese content while suppressing the JT distortion associated with Mn^{3+} , thereby improving both structural stability and electrochemical reversibility. More details about this strategy and the experimental implementation are provided in section 3.3.

2.4.3. Substitution on the Na-Site

While TM-site substitution has been shown to improve the performance of layered oxide cathodes by mitigating JT distortion and mitigating phase transitions, this strategy alone is often insufficient, particularly at high states of charge (SOC). At high SOC, substantial sodium extraction from the NaO_2 layers can lead to slab gliding and collapse of the interlayer spacing, resulting in significant volume variations and structural degradation.

2. Fundamentals

To address these issues, substitution at the sodium site has become a common approach to enhance the electrochemical performance of layered oxide cathodes in SIBs. Among the most studied substituents, often referred to as "pillaring ions," are K^+ , Mg^{2+} , and Ca^{2+} .^[53,171–176] Despite considerable differences in ionic radii compared to Na^+ (K^+ : 1.38 Å, Mg^{2+} : 0.72 Å, Ca^{2+} : 1.00 Å vs. Na^+ : 1.02 Å), all three species have been successfully incorporated into the sodium site within layered structures. More importantly, these pillaring ions have demonstrated beneficial effects across various types of CAMs, including P2-, O3-, and P3-type materials. Their presence can prevent the collapse of the NaO_2 interlayer by reducing the extent of interlayer gliding, suppress the formation of irreversible sodium-deficient phases, and enhance sodium diffusion by increasing the interslab distance. Collectively, these effects contribute to improved cyclability and rate performance.^[171–175]

Among them, Mg^{2+} is particularly notable for its dual occupancy at both the TM- and Na-sites. This results in the formation of structural motifs such as Na–O–Mg and Mg–O–Mg, which introduce localized O 2p states. These states can interact with the TM–O orbitals and facilitate reversible oxygen redox, thereby enhancing capacity and stability.^[172,175] Ca^{2+} , in addition to offering similar structural benefits, has also been reported to improve air stability. In studies on $NaNi_{0.33}Mn_{0.33}Fe_{0.33}O_2$ and $NaNi_{0.5}Mn_{0.5}O_2$, the introduction of Ca^{2+} was found to effectively suppress Na^+/H^+ exchange (as described in **Equation 1**), reducing sodium loss and preventing subsequent TM dissolution and surface reconstruction.^[9,34,36] Furthermore, DFT calculations suggest that Ca^{2+} promotes the expansion of O 2p and Ni 3d orbitals toward lower energy levels, which ultimately stabilizes the electronic states of oxygen coordinated with calcium. This stabilization facilitates oxygen redox reactions, thus helping to preserve the structural integrity of the cathode during cycling.^[36,177]

Taken together, substitution at both the TM and sodium sites can provide a synergistic framework for tailoring structural stability, phase evolution, and electrochemical reversibility of layered oxide CAMs. This integrated approach is therefore critical for the rational design of structurally stable Ni- and Mn-rich cathode materials and plays a vital role in enabling the development of high-energy-density and long-cycle-life SIBs.

2.4.4. Interfacial Stability Optimization

As discussed in section 2.2.5., interfacial stability issues in layered oxide CAMs primarily involve two distinct interfaces, namely the air|cathode and electrolyte|cathode interfaces. The first case, air sensitivity, has been addressed in sections 2.4.1. and 2.4.2., where it was demonstrated that partial substitution with elements such as copper, aluminum, or calcium can significantly improve air stability. These dopants suppress moisture-induced Na^+/H^+ exchange and reduce the formation of surface carbonate species, thereby preserving the structural and chemical integrity of the cathode upon exposure to ambient atmosphere.^[102,123]

2. Fundamentals

In contrast, improving the stability of the electrolyte|cathode interface typically requires alternative strategies, including electrolyte formulation, morphological optimization, and the application of protective coatings. For instance, fluorine-rich electrolytes can induce the formation of robust cathode-electrolyte interphases (CEIs) composed of metal fluorides. These CEI layers effectively passivate the electrode surface, suppressing further electrolyte decomposition during cycling and improving long-term stability.^[178,179]

Morphology also plays a crucial role in interfacial reactivity. In LIBs, it has been shown that polycrystalline particles, due to their higher specific surface area and susceptibility to cracking, tend to undergo more extensive side reactions with the electrolyte compared to single-crystalline counterparts, resulting in increased gas evolution and interfacial degradation.^[15] This insight suggests that, in SIBs, the development of single-crystal morphologies, without compromising electrochemical performance, may offer a promising route to enhance interfacial robustness and prolong cycle life.

Surface coatings have attracted significant attention as a direct method to modify the electrolyte|electrode interface. Commonly studied coatings include Al_2O_3 , MgO , ZnO , and ZrO_2 .^[180–184] Among them, Al_2O_3 has been widely recognized for its dual functionality. It acts as an acid scavenger, preventing the chemical degradation of residual sodium carbonate induced by acidic electrolyte components.^[134] In addition, Al_2O_3 provides mechanical reinforcement that helps maintain the integrity of the layered structure and mitigates particle detachment during cycling.^[180] Similarly, ionically conductive NaPO_3 surface coatings have demonstrated the ability to scavenge HF and H_2O from the electrolyte, thereby suppressing parasitic reactions and improving cycling stability.^[185] The use of MgO coatings is particularly interesting, as Mg^{2+} can simultaneously diffuse into the bulk material, enabling doping that further enhances structural and electrochemical stability.^[181]

Aside from these strategies, attention must also be paid to surface carbonate species that form during synthesis. Excess Na_2CO_3 on the surface can decompose during the initial charge, releasing large amounts of CO_2 and potentially triggering singlet oxygen evolution. Such reactive intermediates may initiate further oxidation of the electrolyte, thereby accelerating interfacial degradation.^[126,127,129] As such, careful control of sodium precursor content and processing conditions is essential to minimize carbonate formation and maintain interfacial integrity.

3. Results

3.1. Publication I: Improving Cycling Performance of the NaNiO_2 Cathode in Sodium-Ion Batteries by Titanium Substitution

Publication I demonstrated the enhancement of electrochemical performance in the prototype material NNO through partial substitution of Ni^{3+} with redox-inactive Ti^{4+} . To achieve the optimal effect of Ti^{4+} incorporation, a systematic tailoring of the solid-state synthesis parameters was conducted, including calcination temperature, cooling rate, oxygen flow rate, as well as the Na/TM and Ti/Ni molar ratios. As a result, the optimized composition of NNTO was successfully synthesized. Compared to pristine NNO, NNTO exhibited a significantly improved reversible specific capacity, increasing from about 120 to 190 mAh/g, along with an increase in average operating voltage by approximately 0.2 V. However, NNTO still exhibits limitations in long-term cycling stability and rate capability. The degradation mechanisms were systematically investigated using a combination of XRD, electrochemistry, microscopy, XANES, AE, and DEMS.

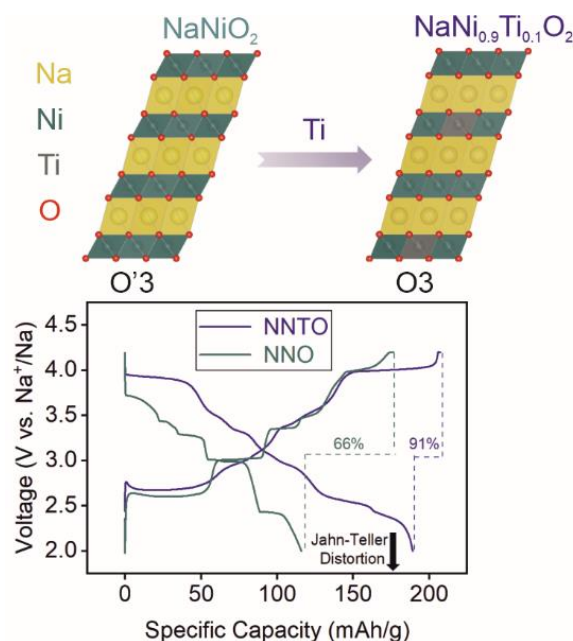


Figure 13. Table of contents graphic of publication I. Adapted from reference [12].

The experiments were designed by the first author under the supervision of A. Kondrakov, J. Janek, and T. Brezesinski. The first author planned and optimized the synthesis of NNTO, conducted XRD, electrochemical tests, DEMS, and performed the data analysis. L. Karger and S.L. Dreyer carried out *in situ* (*operando*) XRD and AE measurements, respectively, and analyzed the data together with the first author. SEM imaging was performed by E. Barbosa and R. Zhang, with data analysis by the first author. XANES measurements were conducted by Y. Hu and M. Fichtner and analyzed by the first author and J. Lin. TEM and ICP-OES measurements were performed by P. Müller and T. Bergfeldt, respectively, with TEM data analysis by both the first author

3. Results

and P. Müller. The manuscript was written by the first author and edited by all co-authors.

Reprinted with permission from S. An, L. Karger, S.L. Dreyer, Y. Hu, E. Barbosa, R. Zhang, J. Lin, M. Fichtner, A. Kondrakov, J. Janek, T. Brezesinski, *Mater. Futures* 2024, 3, 035103. Copyright © 2024 The Author(s). Published by IOP Publishing Ltd on behalf of the Songshan Lake Materials Laboratory.



PAPER • OPEN ACCESS

Improving cycling performance of the NaNiO_2 cathode in sodium-ion batteries by titanium substitution

To cite this article: Siyu An *et al* 2024 *Mater. Futures* 3 035103

View the [article online](#) for updates and enhancements.

You may also like

- [The Alternative Voltammetric Method for the Determination of Nicotine and Its Metabolite Nicotine N-Oxide](#)
Olha Dushna, Liliya Dubenska, Serhiy Plotyca *et al.*
- [Hybridization Effects of Nitrogen-Doped Graphene–Carbon Nanotubes and Nano-Onion Carbons on the Electrocatalytic Activity of the Oxygen Reduction Reaction](#)
Eun Yeob Choi, Somin Lee and C. K. Kim
- [Xylometazoline-induced change in aspirated nasal nitric oxide detects obstructed paranasal ostia](#)
Pekka Tamminen, Ilkka Kivekäs, Jura Numminen *et al.*

OPEN ACCESS

IOP Publishing | Songshan Lake Materials Laboratory

Materials Futures

Mater. Futures 3 (2024) 035103 (16pp)

<https://doi.org/10.1088/2752-5724/ad5faa>

Improving cycling performance of the NaNiO_2 cathode in sodium-ion batteries by titanium substitution

Siyu An¹, Leonhard Karger¹, Sören L Dreyer¹, Yang Hu², Eduardo Barbosa¹, Ruizhuo Zhang¹, Jing Lin¹, Maximilian Fichtner², Aleksandr Kondrakov^{1,3}, Jürgen Janek^{1,4,*} and Torsten Brezesinski^{1,*} 

¹ Battery and Electrochemistry Laboratory (BELLA), Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

² Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Helmholtzstr. 11, 89081 Ulm, Germany

³ BASF SE, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany

⁴ Institute of Physical Chemistry & Center for Materials Research (ZfM/LaMa), Justus-Liebig-University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

E-mail: juergen.janek@kit.edu and torsten.brezesinski@kit.edu

Received 12 April 2024, revised 18 June 2024

Accepted for publication 26 June 2024

Published 25 July 2024



CrossMark

Abstract

O3-type layered oxide cathodes, such as $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, have garnered significant attention due to their high theoretical specific capacity while using abundant and low-cost sodium as intercalation species. Unlike the lithium analog (LiNiO_2), NaNiO_2 (NNO) exhibits poor electrochemical performance resulting from structural instability and inferior Coulomb efficiency. To enhance its cyclability for practical application, NNO was modified by titanium substitution to yield the O3-type $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NNTO), which was successfully synthesized for the first time via a solid-state reaction. The mechanism behind its superior performance in comparison to that of similar materials is examined in detail using a variety of characterization techniques. NNTO delivers a specific discharge capacity of $\sim 190 \text{ mAh g}^{-1}$ and exhibits good reversibility, even in the presence of multiple phase transitions during cycling in a potential window of 2.0–4.2 V vs. Na^+/Na . This behavior can be attributed to the substituent, which helps maintain a larger interslab distance in the Na-deficient phases and to mitigate Jahn–Teller activity by reducing the average oxidation state of nickel. However, volume collapse at high potentials and irreversible lattice oxygen loss are still detrimental to the NNTO. Nevertheless, the performance can be further enhanced through coating and doping strategies. This not only positions NNTO as a promising next-generation cathode material, but also serves as inspiration for future research directions in the field of high-energy-density Na-ion batteries.

* Authors to whom any correspondence should be addressed.



Original content from this work may be used under the terms of the [Creative Commons Attribution 4.0 licence](https://creativecommons.org/licenses/by/4.0/). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Supplementary material for this article is available [online](#)

Keywords: Ni-rich layered oxide, cathode material, substitution, doping, electro-chemo-mechanical degradation, Na-ion battery

1. Introduction

With the rapid development of lithium-ion batteries (LIBs), both electric vehicles and large-scale energy storage systems have experienced significant advancements [1–3]. However, due to the uneven distribution of lithium resources and cost considerations, there is an urgent need for novel, more sustainable solutions to meet future demands. Because of similarities in the storage mechanisms between sodium-ion batteries (SIBs or NIBs) and LIBs and the higher abundance and widespread distribution of sodium in the Earth's crust, as well as in the seawater, SIBs have the potential to become a next-generation (low-cost) technology in the field of electrochemical energy storage [4–6]. Among numerous SIB cathode materials, layered transition metal oxides, Na_xTMO_2 (TM = Ni, Co, Mn, Fe, Cr, etc), stand out as the most promising candidates due to their high theoretical specific capacities and high operation potentials, similar to the successfully utilized LiTMO_2 (e.g. $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, referred to as NCMs or NMCs) in LIBs [6–10].

Transition metal oxide cathode materials in SIBs exist mostly in two thermodynamically stable structures, known as O3 (Na^+ on octahedral sites coordinated by oxygen) and P2 (Na^+ on prismatic sites) [3, 11–13]. In the O3-type structure, Na^+ diffuses between adjacent NaO_6 octahedra through interstitial tetrahedral sites, leading to a relatively higher energy barrier compared to P2-type structures, and therefore to inferior rate capability. In the P2-type structure, sodium transport occurs via face-shared trigonal prismatic sites, resulting in better diffusivity. Nevertheless, the higher sodium content of O3-type compounds and the resulting higher storage capacity make them more attractive for practical (full cell) applications [6, 7, 13, 14].

In LIBs, to achieve high specific capacities ($q_{\text{ch/dis}} \geq 200 \text{ mAh g}^{-1}$) in a reasonable potential range, the focus is strongly placed on layered Ni-rich oxides (>80% Ni fraction), such as LiNiO_2 (LNO) [15–19]. However, due to the relatively close ionic radii of Li^+ ($r = 0.76 \text{ \AA}$) and Ni^{2+} ($r = 0.69 \text{ \AA}$), Ni_{Li} point defects (Ni^{2+} occupying crystallographic Li sites) form during calcination, which is generally believed to be detrimental to the electrochemical behavior [20–23]. Inspired by the high capacity achievable with LNO, O'3-type NaNiO_2 (NNO) in SIBs is also widely investigated (owing to both its high operating potential and high theoretical specific capacity of 235 mAh g^{-1}) [24–26]. Na^+ ($r = 1.02 \text{ \AA}$) has a significantly different ionic radius compared to Ni^{2+} and Ni^{3+} ($r = 0.56 \text{ \AA}$), which prevents the formation of substitutional (interlayer) defects, but causes larger volume variations during cycling [22, 27–29].

Due to the larger ionic radius of Na^+ , NNO experiences in-plane TMO_2 slab gliding during the intercalation and extraction of sodium ions, which in turn can lead to multiple, poorly reversible phase transitions ($\text{O}'3 \rightarrow \text{P}'3 \rightarrow \text{P}''3 \rightarrow \text{O}''3 \rightarrow \text{O}'''3$). Aside from that, low-spin Ni^{3+} ($t_{2g}^6 e_g^1$) induces strong Jahn–Teller distortion, leading to strain and ultimately resulting in capacity fading [7, 13, 14, 24, 25]. In 2013, Vassilaras *et al* reported on the extraction of 0.85 Na^+ (equivalent to $q_{\text{ch}} \approx 199 \text{ mAh g}^{-1}$) and re-insertion of 0.62 Na^+ (equivalent to $q_{\text{dis}} \approx 147 \text{ mAh g}^{-1}$) in NNO during the initial cycle in a potential window of 2.0–4.5 V vs. Na^+/Na [24]. However, the low Coulomb efficiency indicates that further research is required to address the challenges associated with the potential use of NNO. Komaba *et al* conducted a comprehensive study on $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, where divalent Ni^{2+} is oxidized to tetravalent Ni^{4+} during charging, and the electrochemically inactive Mn^{4+} contributes to structural stability [30]. Inspired by this work, Yu *et al* proposed that Ti^{4+} could play a similar role to Mn^{4+} and successfully incorporated Ti^{4+} into the crystallographic Ni position, resulting in the formation of rhombohedral (α - NaFeO_2 -type) $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$. Electrochemical testing revealed a reversible specific capacity of 121 mAh g^{-1} at a rate of 0.2C [31]. Maletti *et al* further probed $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ using *operando* synchrotron x-ray diffraction measurements, demonstrating that titanium remains tetravalent throughout cycling and the gliding of TMO_2 slabs is strongly suppressed. This led to a reversible transition between the O3 and P3 phases (1.5–4.2 V vs. Na^+/Na), exhibiting a much smoother voltage profile than that of NNO [32]. Even though $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ shows superior cycling stability over NNO, the low reversible capacity leaves room for improvements.

In addition to doping/substitution, the synthesis conditions for layered oxides, particularly the calcination temperature, play a significant role in the material's performance. In the case of LIBs, it has been found that the calcination temperature has a critical influence on the electrochemical performance of $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$ [33]. Similarly, for SIBs, the choice of synthesis temperature can lead to the formation of either α - NaMnO_2 at a lower temperature or β - NaMnO_2 at a higher temperature [34, 35]. Moreover, the Na/TM ratio also has a notable effect on the material's performance. Some studies have proposed using excess sodium to compensate for losses during calcination, thereby achieving the desired stoichiometry [36, 37]. However, Zhou *et al* discovered that a slight sodium deficiency can have beneficial effects on the initial capacity and capacity retention [38]. Furthermore, layered oxides are sensitive to the cooling rate (as part of the synthesis). In LIBs, Liu *et al* explored the

correlation between cooling rate, calcination conditions, and the generation of Ni/Mn disorder and oxygen vacancies in the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [39]. Their research demonstrated that a slow cooling rate, combined with annealing steps, effectively mitigates the formation of oxygen vacancies and impurity phases. However, the findings indicate that a certain fraction of oxygen vacancies is required for achieving high performance. Similarly, in SIBs, the cooling rate plays a pivotal role. Liu *et al* enhanced the capacity by quenching the Mn-based material $\text{Na}_{2/3}\text{M}_x\text{Mn}_{1-x}\text{O}_2$ (M = dopant) in liquid nitrogen to achieve a vacancy-free structure [40]. Xu *et al* also proposed the significance of native lattice stress induced by quenching on the fading behavior [41]. In general, variations of parameters during the calcination process appear to have a significant impact on both the material's structure and performance, yet quantitative knowledge is lacking.

In the present work, we consider $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NNTO) as a potentially new cathode material for application in SIBs. We have investigated different synthesis conditions in a systematic manner and analyzed the resulting structures, particle morphologies, and electrochemical properties of the obtained samples. Through optimization of the preparation conditions, NNTO of high purity (>98%) was produced, which delivered higher specific capacity ($\sim 190 \text{ mAh g}^{-1}$ at C/30 rate in the potential window of 2.0–4.2 V vs. Na^+/Na) and showed better cycling stability than NNO and titanium-rich $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ [25, 26, 31, 32, 37]. However, NNTO still suffers from degradation upon battery operation. By combining physical and electrochemical characterization techniques, we gain insight into the potential reasons behind the capacity fading, which provides new avenues for tailoring this promising cathode material.

2. Experimental section

2.1. Synthesis

$\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ was prepared by a two-step solid-state reaction from $\text{Ni}(\text{OH})_2$ ($d_{50} \approx 4 \mu\text{m}$, BASF SE), nanoscale TiO_2 , and reagent-grade NaOH powder (97%; Sigma-Aldrich). For the initial pre-calcination, the reactants were homogenized under Ar atmosphere for 10 min with different molar equivalents of NaOH , namely 1.0, 1.025, and 1.05, i.e. $n(\text{TM})/n(\text{Na}) = 1:1$, 1:1.025, and 1:1.05, respectively, using a laboratory blender (Kinematica). The precursor mixture was then heated in an alumina crucible under O_2 flow (1.4 l h^{-1}) in a tube furnace (Nabertherm P330) at 300°C for 10 h with 3 K min^{-1} heating and cooling rates. After cooling to room temperature, the intermediate product was homogenized again for 10 min, followed by transfer to an alumina crucible for the main calcination under different O_2 flow rates of 1.4 and 7 l h^{-1} at temperatures ranging from 600°C to 900°C for 12 h with 3 K min^{-1} heating rate and different cooling rates of 2 K min^{-1} , 0.5 K min^{-1} , and quenching. For quenching, the quartz tube containing the sample was directly removed from the furnace and rapidly cooled to room temperature.

For the study of different molar Ni/Ti ratios (95:5, 90:10, 85:15, and 80:20), the molar TM/Na ratio was set to

1:1. Powder mixtures were prepared by blending and pre-calcination, as described above. The homogenized mixtures were calcined under O_2 flow (7 l h^{-1}) at 800°C for 12 h with 3 K min^{-1} heating rate and 2 K min^{-1} cooling rate.

NaNiO_2 was also prepared by solid-state reaction from $\text{Ni}(\text{OH})_2$ and NaOH (10 mol.% excess) at 700°C for 12 h using the above-mentioned conditions.

2.2. Surface coating

An oven-dried Schlenk flask with a magnetic stirring bar was transferred into the glovebox, and 7 ml of dry toluene (Sigma-Aldrich) was added to the flask. Subsequently, 2 M trimethylaluminum (TMA) in toluene (Sigma-Aldrich) was added dropwise (given in equivalents of a base amount of $100 \mu\text{mol}$ TMA per 1 g of cathode material), and the solution was stirred for 1 h before adding 1 g of cathode material. After 2 h, the flask was transferred to a Schlenk line equipped with a cold trap between the line and flask to remove the solvent under vacuum. Once no liquid phase was visible anymore, the flask was directly connected to the Schlenk line, and the cathode material was dried at room temperature and 1×10^{-3} mbar overnight. Lastly, the product was heated at 300°C for 1 h under oxygen flow in a tube furnace (Nabertherm P330). The heating and cooling rates were set to 3 K min^{-1} .

2.3. Electrochemical testing

Electrodes were prepared by casting an N-methyl-pyrrolidone (NMP) slurry with 94 wt.% cathode material, 3 wt.% Super C65 carbon, and 3 wt.% polyvinylidene difluoride (Solef 5130; Solvay) binder onto 0.03 mm Al foil as the current collector. The slurry was prepared by combining all components with 20 wt.% additional NMP in a planetary centrifuge mixer (Thinky ARE-250), applying a two-step program with 3 min at 2000 rpm and 3 min at 400 rpm. The slurry was spread onto the current collector using a film applicator (Coatmaster 510; Erichsen) at a rate of 5 mm s^{-1} . The as-made tapes were dried overnight in a vacuum at 120°C and then calendared at 14 N mm^{-1} (Sumet Messtechnik). Electrodes of 13 mm diameter and $9\text{--}12 \text{ mg cm}^{-2}$ areal loading were punched out. $95 \mu\text{l}$ of a 1 M solution of NaClO_4 in ethylene carbonate (EC), dimethyl carbonate (DMC), and propylene carbonate (PC), 1:1:1 by vol., containing 5 vol.% fluoroethylene carbonate (FEC) as additive was used as the electrolyte. In a variation, the electrolyte contained no FEC. Subsequently, the prepared electrodes, GF/D glass fiber separator, Na metal, and electrolyte were assembled into 2032-type coin half-cells in an Ar glovebox. Electrochemical testing was done in a potential window of 2.0–4.2 V vs. Na^+/Na at various C-rates ($1\text{C} = 200 \text{ mA g}^{-1}$).

2.4. X-ray diffraction

XRD data were collected in Debye–Scherrer geometry using a STOE STADI-P diffractometer equipped with a DECTRIS MYTHEN 1K strip detector and a Mo anode ($\lambda = 0.70926 \text{ \AA}$,

50 kV, 40 mA). The instrumental contribution to peak broadening was determined by measuring a NIST 660c LaB₆ standard as a line broadening reference. The samples for XRD were flame-sealed in borosilicate capillaries of 0.5 mm inner diameter and 0.01 mm wall thickness (Hilgenberg).

2.5. Operando XRD

The positive and negative caps and the spacers of the coin-cell casings were subject to modification by electro-erosion machining for *operando* XRD measurements, resulting in a 5 mm diameter hole in the center. The outer holes were sealed with Kapton windows of 6 mm diameter. The cells were cycled at a rate of C/20 utilizing a Gamry Interface 1000 potentiostat. XRD patterns were collected within an angular range of $5^\circ < 2\theta < 37^\circ$ with an acquisition time of about 10 min utilizing the aforementioned STOE Stadi-P diffractometer. The patterns were analyzed according to the Rietveld method using the GSAS-II software [42].

2.6. In situ XRD

XRD using a customized diffractometer was used to study the main calcination process; the setup is reported elsewhere [43]. For sample preparation, the pre-calcination mixture for NaNi_{0.9}Ti_{0.1}O₂ with 1:1 TM/Na ratio was employed. The mixture was heated at a rate of 1 K min⁻¹ under an O₂ atmosphere, with each pattern being the accumulated signal over 5 min. Temperature calibration was performed by comparison with the cell volume of Al₂O₃, which was measured in a separate experiment.

2.7. Scanning electron microscopy

SEM analysis was performed at an accelerating voltage of 10 kV using a LEO-1530 microscope (Carl Zeiss AG) with a field emission source. For cross-sectional imaging, an IB-19510CP polisher (JEOL Ltd) with an Ar-gas source was employed.

2.8. Transmission electron microscopy

Samples for low-magnification TEM imaging and energy-dispersive x-ray spectroscopy (EDS) analysis were embedded in resin in an Ar glovebox to prevent sample degradation. The material was then cut by ultramicrotomy under dry conditions and directly investigated. During preparation, the samples were exposed to air for about 10 min. Samples for atomic resolution analysis were prepared by Ga-focused ion beam (FIB) milling using a Helios 5 CX DualBeam (Thermo Fisher Scientific) and directly transferred to the microscope to minimize exposure to air. The samples were examined using a probe-corrected Themis Z (3.1; Thermo Fisher Scientific) in high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) mode at 300 kV. The chemical composition was examined with the integrated SuperX G2 EDS detector. The data were analyzed using the Velox 3.10 software.

2.9. Inductively coupled plasma-optical emission spectroscopy

The elemental composition was studied by ICP-OES using a Thermo Fisher Scientific ICAP 7600 DUO instrument. Powder samples were dissolved in an acid digester within a graphite furnace. Mass fractions were derived from three independent measurements for each sample of which about 10 mg were dissolved in a mixture of 6 ml hydrochloric acid and 2 ml nitric acid at 353 K for 4 h. The digested samples were diluted for analysis utilizing four different calibration solutions and an internal standard (Sc). The oxygen content was determined by carrier gas hot extraction with a commercial oxygen/nitrogen analyzer TC600 (LECO Corp.). Certified standard KED-1025 was employed for calibration.

2.10. X-ray absorption spectroscopy

XAS at the Ni K-edge was performed in transmission mode using a laboratory Rowland-circle based instrument (easyXAFS300+; easyXAFS, LLC). The Ag x-ray tube was operated at 35 kV, and a Si(444) crystal analyzer was employed [44]. Pristine powder samples were diluted with cellulose and pelletized by a hydraulic press in an Ar glovebox. The prepared pellets were sealed with Kapton tape and then taken out for XAS measurements under ambient atmosphere. Reference NiO and Ni(OH)₂ were prepared in a similar fashion. Cycled electrodes (two cycles at C/30 and 8 cycles at C/10) were measured by pre-sealing them in the glovebox using Kapton tape. Energy grids of 2 eV, 0.25 eV, and 0.05 Å⁻¹ were used for the pre-edge, near-edge, and post-edge regions, respectively. Multiple scans were collected for the reference Ni foil (Goodfellow or Exafs Materials) and each sample. The absorption spectra were obtained using a Python-based software with integrated dead-time correction (easyXAFS, LLC), according to the relation $\mu(E) \approx \ln(I_0/I_t)$. Energy calibration was based on the first peak in the first derivative of $\mu(E)$ of the Ni reference foil. XAS data were further analyzed using the Demeter package. The normalization energy range was set up to 8800 eV, employing the normalization order 2 within $k = 0-12$ Å⁻¹.

2.11. Acoustic emission

AE signals were acquired using a differential wideband sensor (125–1000 kHz; MISTRAS Group) mounted to the bottom of coin cells using vacuum grease to improve contact. The experimental setup also incorporated an in-line pre-amplifier and a data acquisition system (USB AE Node; MISTRAS Group). The pre-amplifier gain, analog filter, and sampling rate were set to 40 dB, 20–1000 kHz, and 5 MSPS, respectively. Sensor coupling was verified by the pencil-lead break test [45, 46]. A minimum of two samples was tested to ensure reproducibility. Initially, the recorded data underwent pre-processing via the AEwin software (MISTRAS Group), involving removal of background noise by excluding all hits with less than two counts, peak frequencies below 100 kHz, and/or amplitudes of less than 27 dB. Subsequently, the data were analyzed in

conjunction with the corresponding electrochemical measurements (one cycle at C/30 and four cycles at C/10).

2.12. Differential electrochemical mass spectrometry

Customized DEMS cells using a 30 mm diameter cathode (with 10 mg cm^{-2} areal loading) were cycled at a rate of C/10. A 4 mm diameter hole in the center of the cathode allowed for gas flow. GF/D, Na metal, and $700 \mu\text{l}$ of 1.0 M NaClO_4 in EC:DMC:PC with FEC were used as the separator, anode, and electrolyte, respectively. During cycling, a constant stream of He carrier gas (purity 6.0, 2.5 ml min^{-1}) was passed through the cells. The extracted gas mixture was probed using a mass spectrometer (OmniStar GSD 320, Pfeiffer Vacuum GmbH). More details can be found in the literature [47, 48].

3. Results and discussion

Since the calcination temperature is crucial for the synthesis of layered oxides, a systematic study of its influence was first carried out. Prior to the main calcination step, a well-blended mixture of $4 \mu\text{m}$ Ni(OH)_2 particles (figure S1(a)), NaOH, and nano-sized TiO_2 was heated at 300°C under O_2 atmosphere for 10 h (see Experimental section for more details) to facilitate dehydration and ensure good contact between the reactants. The resultant sample was probed using XRD (figure S1(b)). The main reflections matched the rocksalt-type NiO phase. The remaining weaker reflections did neither match the pattern of NaOH nor that of TiO_2 . Instead, they can be attributed to a layered structure of $\text{Na}_x\text{Ti}_{1-x}\text{O}_2$ (referred to as $\text{Na}_x\text{Ti}_y\text{O}_z$ in the following) formed by solid-state reaction between NaOH and TiO_2 [49]. Notably, the latter side phase was largely amorphous, due to the relatively low pre-calcination temperature.

To determine the optimal temperature range for the main calcination step, an *in situ* XRD measurement was conducted on the pre-heated precursor mixture. The setup used is illustrated in figure S2(a) [43]. During the continuous heating process, $C2/m$, $R-3m$, and $Fm-3m$ phases were identified. Figure 1 shows that NiO ($Fm-3m$) remains the dominant phase up to 630°C . However, alongside NiO, the above-mentioned $\text{Na}_x\text{Ti}_y\text{O}_z$ was observed, with its structure exhibiting temperature-dependent variations. From 630°C on, the formation of the layered structure of NNTO with the space group $R-3m$ is apparent, which persists until 870°C . As shown in figures 1 and S2(b), with further temperature increase, the reflections of both NNO ($C2/m$), such as (20–2), (111), (021), and (221), and NiO become dominant. Additionally, the intensity of the (104) reflection of NNTO decreases. This indicates that NNTO undergoes decomposition into NNO and NiO at higher temperatures. As a result, we determined that the desired $R-3m$ phase (NNTO) can be achieved in the temperature range of about 630°C – 870°C .

For verification of the phase evaluation, four distinct temperatures, namely 700°C , 750°C , 800°C , and 850°C , were selected from the range acquired from the *in situ* XRD experiment,

plus 600°C and 900°C . All other synthesis parameters remained constant: $n(\text{Na})/n(\text{TM}) = 1/1$, $n(\text{Ni})/n(\text{Ti}) = 9/1$, 7 l h^{-1} O_2 flow rate, and 2 K min^{-1} cooling rate. As evident from the phase fractions (table S1) from Rietveld refinement analysis of the XRD data shown in figure 2, there is an obvious trend. As the temperature increases from 600°C to 800°C , the phase purity of NNTO increases from 79.5 to 98.5 wt.% while the fractions of the NNO and NiO impurities decrease. This is highlighted by the red dashed rectangle in figure 2. At temperatures above 800°C , the intensity of the NNTO (104) reflection diminishes while that of the NiO (002) and NNO (111)/(20–2) reflections increases. By 900°C , NNTO largely decomposes into NNO and NiO, which is consistent with the *in situ* XRD results.

Next, SEM images were collected from the different samples to examine the particle morphology (figures 3(a)–(e)). The flower-shaped structure of $\text{Na}_x\text{Ti}_y\text{O}_z$ was observed on the surface of the secondary particles in figures 3(a) and (b), which is likely due to incomplete reaction at calcination temperatures $\leq 750^\circ\text{C}$. To gain a better understanding of the structure of the samples prepared at a lower temperature and their elemental distribution, STEM and EDS measurements were conducted on NNTO obtained at 700°C . EDS mapping (figure S3(a)) indicated a uniform distribution of Ni. In contrast, the Na and Ti signals revealed signs of inhomogeneities, which agrees with the presence of $\text{Na}_x\text{Ti}_y\text{O}_z$ as an impurity phase. The latter apparently segregates on the surface of the secondary particles at lower calcination temperatures. HAADF images at different magnifications of a FIB-prepared specimen are shown in figures S3(b)–(d). Some minor variations in contrast are clearly visible, which may be indicative of local non-uniformities. However, the high-resolution image in figure S3(d) indicates that a well-layered structure is already present at 700°C .

A smooth particle surface was observed upon reaching 800°C (figure 3(c)). EDS mapping confirmed the uniform distribution of Ni, Na, and Ti on different length scales (figures 4(a) and S4), while cross-sectional STEM imaging (figures 4(b)–(d)) revealed a well-defined secondary/primary particle morphology and a distinct layered structure. This demonstrates that the diffusion kinetics of titanium and sodium, which is correlated to the reaction between NNO and $\text{Na}_x\text{Ti}_y\text{O}_z$, is enhanced as the temperature rises from 700°C to 800°C . It should be noted that an uneven distribution of Na was observed in a few secondary particles (figure S(5)), which is due to sodium loss during the solid-state reaction (see discussion below). The latter leads to the formation of Na-deficient NNTO, along with trace amounts of NiO impurities (table S1). With further temperature increase beyond 800°C , NNTO seems to first sinter into larger particles (figure 3(d)) and then to decompose into NiO and NNO, which helps explain the ill-defined particle morphology seen in figure 3(e) [8, 24–26, 31, 32, 37].

Since the NNTO samples obtained at 700°C , 750°C and 800°C had a higher overall purity, their electrochemical behavior was further investigated. To this end, all three materials were incorporated into electrodes and cycled against Na metal

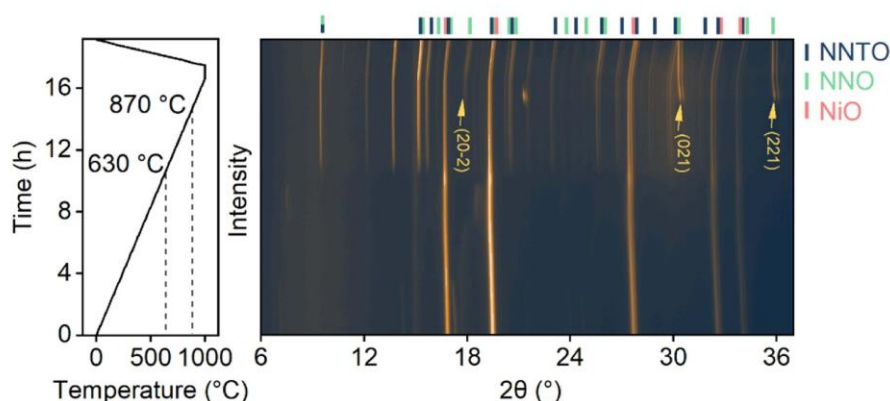


Figure 1. Contour plot of *in situ* XRD data collected from the pre-heated NNTO mixture during calcination under O₂ atmosphere.

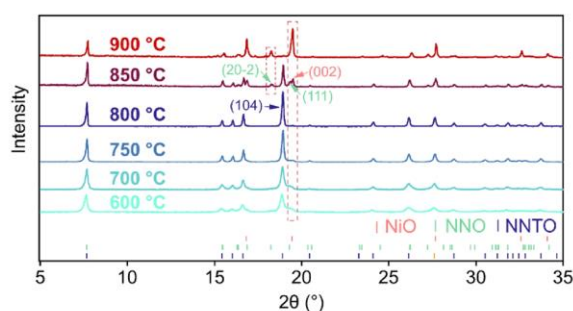


Figure 2. XRD patterns of NNTO prepared at different calcination temperatures.

in the potential range between 2.0 and 4.2 V vs. Na⁺/Na at C-rates ranging from C/30 to 1C. As evident from the voltage profiles shown in figures S6(a)–(c), they exhibit promising initial Coulomb efficiencies of 91% (700 °C), 93% (750 °C), and 94% (800 °C). This is indicative of improved Na⁺ diffusivity in NNTO as compared to NNO (first-cycle Coulomb efficiency of 69%) and NaNi_{0.5}Ti_{0.5}O₂ (first-cycle Coulomb efficiency of 74%). By comparing the cycling performance, NNTO prepared at 800 °C, which also had the highest purity, was found to exhibit the least polarization, as well as the best stability and rate capability (figures 3(f) and S6(d)–(f)). Therefore, the calcination temperature of 800 °C was applied throughout the rest of this study.

In addition to the calcination temperature, the molar Na/TM ratio can also strongly affect the material's performance. For this reason, three different ratios, namely 1, 1.025, and 1.05, which should theoretically produce Na-deficient, stoichiometric, and Na-excess NNTO, respectively, were explored in this study. As evident from the XRD patterns in figure 5(a) and the phase fractions given in table S2,

all three ratios yield high-purity NNTO (>97 wt.%). ICP-OES (table S3) revealed an average sodium loss in the range of 1–3 mol.% for the different samples, which agrees with reported findings [50, 51]. Notably, it seems that the formation of NNO becomes more energetically favorable with increasing sodium excess.

SEM was then applied to visualize the influence of the molar Na/TM ratio on the NNTO properties. The images in figures 5(b) and (c) (see also figure 3(c)), as well as the particle size distributions acquired from the SEM data (figure 5(d)), clearly indicate the growth of primary particles from $d_{50} = 355$ nm for $n(\text{Na})/n(\text{TM}) = 1.0$ to 516 nm for 1.05. This finding can be ascribed to the excess NaOH serving as a flux during calcination. Note that the primary particle size usually has a profound effect on the cycling performance. Accordingly, electrochemical tests were performed under the same conditions to verify this hypothesis. The different voltage profiles for the initial cycle (figures S6(c) and S7(a) and (b)) were similar—the materials delivered comparable specific capacities at C/30. However, the discharge capacity of NNTO prepared with molar Na/TM ratios of 1.025 and 1.05 decreased strongly with increasing C-rate (figure 5(e)), thus pointing toward slower diffusion kinetics with increasing primary particle size. This is in agreement with the higher polarization apparent from the dq/dV curves in figures S7(c) and (d) compared to figure S6(f). The superior performance of NNTO prepared with $n(\text{Na})/n(\text{TM}) = 1.0$ could also be attributed to the slight sodium deficiency, as vacancy sites likely facilitate sodium transport [38]. Regardless, the ratio was set to 1 hereafter.

In addition to the previously mentioned calcination temperature and the molar Na/TM ratio, the cooling rate has varying effects on the performance and morphology of layered oxides too. Here, we have investigated NNTO by using three different cooling rates, namely 0.5 K min^{−1}, 2 K min^{−1}, and quenching in O₂ atmosphere (see Experimental section for more details). All other synthesis parameters remained constant: $n(\text{Na})/n(\text{TM}) = 1/1$, $n(\text{Ni})/n(\text{Ti}) = 9/1$, 7 l h^{−1} O₂ flow

3. Results

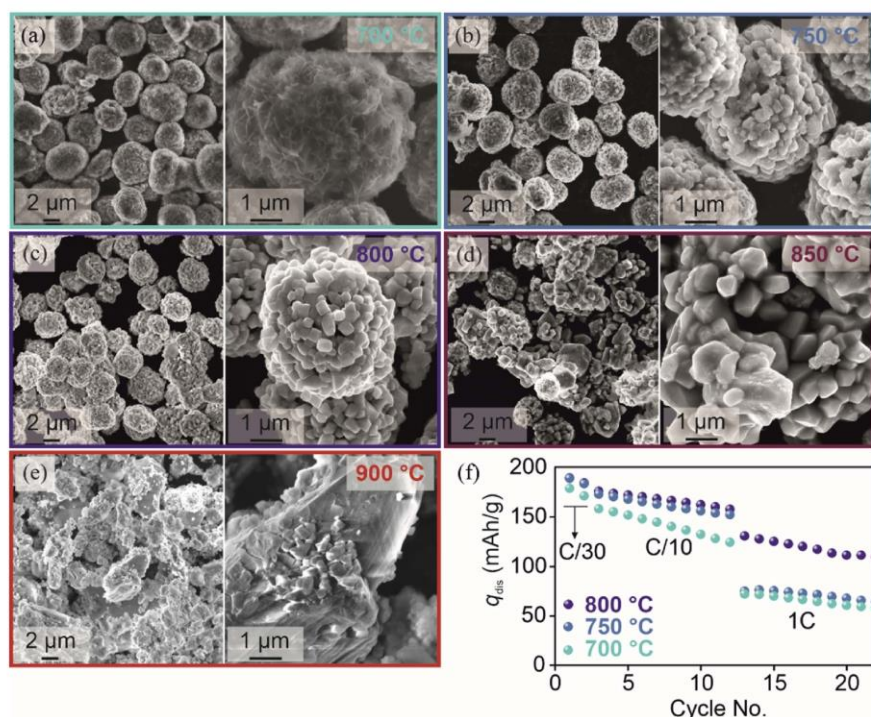


Figure 3. (a)–(e) Low- and high-magnification SEM images of NNTO prepared at different calcination temperatures. (f) Cycling performance of samples obtained at 700, 750, and 800 °C.

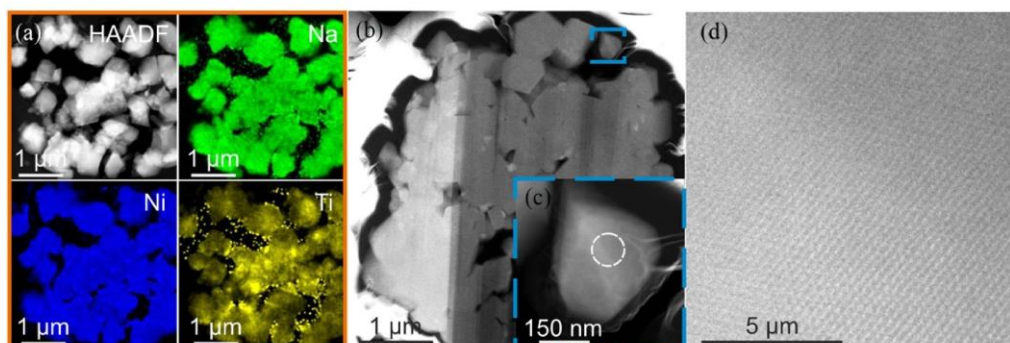


Figure 4. (a) STEM-EDS mapping of NNTO (800 °C). The random dots in the Ti map are artifacts. (b), (c) Low- and high-magnification cross-sectional HAADF STEM images of a FIB-prepared NNTO (800 °C) particle. (d) High-resolution image of the area indicated by the white dashed circle in (c).

rate, and 800 °C calcination temperature. XRD analysis was first conducted on the obtained samples. Figure 6(a) and table S4 demonstrate that only NNTO prepared at a cooling rate of 0.5 K min^{−1} exhibits relatively lower purity (96.1 wt.%). This can be attributed to the longer annealing time caused by the slower cooling, which apparently leads to partial decomposition of NNTO and further induces growth and sintering of the primary particles (figure 6(b)). The subsequent electrochemical testing (figures 6(e) and (f)) indicated that the larger primary particles, resulting from slow cooling, negatively

affect the rate capability. Notably, despite the comparable primary particle size between the quenched and 2 K min^{−1} samples (figures 6(d) and 5(d)), with $d_{50} = 403$ and 355 nm, respectively, the quenched NNTO experienced much stronger capacity fading. This discrepancy seems to be due to the presence of cracks (see magnified SEM image in figure 6(c)) on the primary particle level produced by quenching, which apparently leads to more serious degradation during cycling [41]. Therefore, a cooling rate of 2 K min^{−1} was maintained in the following.

3. Results

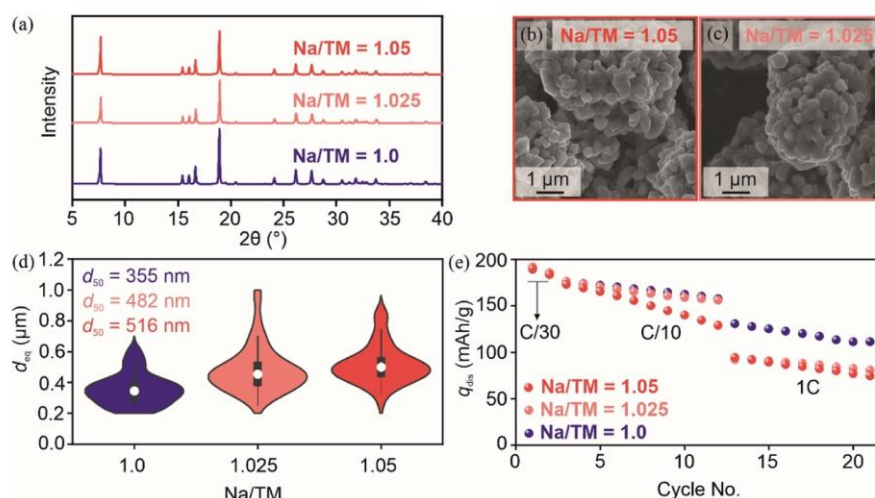


Figure 5. (a) XRD patterns, (b), (c) SEM images, (d) primary particle size distributions, and (e) cycling performance of NNTO prepared with different molar Na/TM ratios.

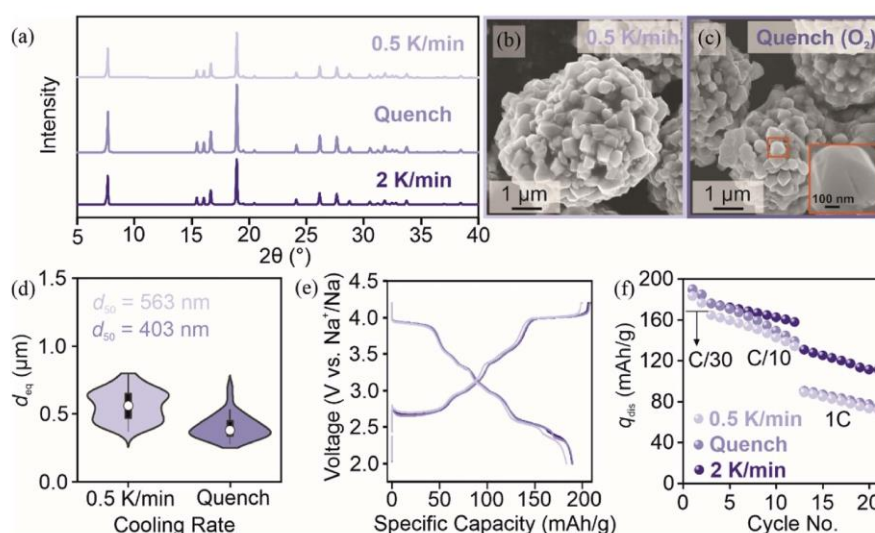


Figure 6. (a) XRD patterns, (b), (c) SEM images, (d) primary particle size distributions, (e) first-cycle voltage profiles, and (f) cycling performance of NNTO prepared with different cooling rates.

To explore the effect that the flow rate of O_2 has on the morphology and purity of NNTO, calcinations were performed at high (7 l h^{-1}) and low rates (1.4 l h^{-1}). XRD analysis (figure 7(a)) revealed that the phase fraction of NiO decreases while that of NNTO increases with increasing rate (table S5). This observation indicates that sufficient O_2 supply facilitates the oxidation of Ni^{2+} to Ni^{3+} to generate the layered structure. Figure 7(b) presents SEM images of NNTO prepared with the lower O_2 flow rate. Notably, the primary particle size was found to be markedly larger in this case (SEM images at different magnifications of NNTO prepared with the higher O_2 flow rate are shown in figure 3(c)). This can potentially be

attributed to the following reasons. In the synthesis of NNO, particle sizes of $d_{50} \approx 1.4$ and $3.6 \mu\text{m}$ are achieved at 600 and 700 $^\circ\text{C}$, respectively [23]. However, the polycrystalline morphology of the $Ni(OH)_2$ precursor (figure S1(a)) used here was retained by introducing Ti^{4+} into the NNO, which demonstrates the profound effect that titanium substitution has on the primary particle size in NNTO. When the O_2 flow rate is reduced, the relatively slower NiO oxidation can impede the reaction of the precursor particles with the titanium source. Consequently, these incompletely reacted precursor particles undergo growth (to larger NNO grains) and are then slowly sodiated by the $Na_xTi_yO_z$ present on the surface, resulting in

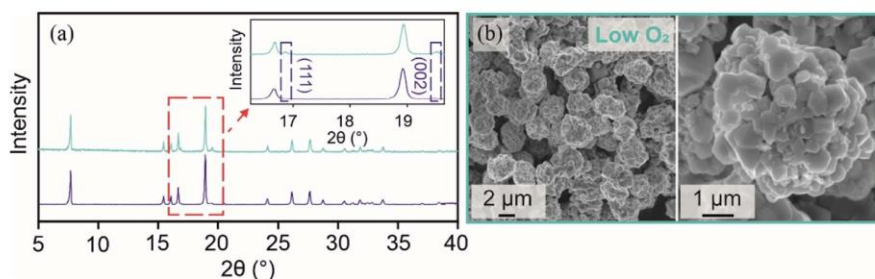


Figure 7. (a) XRD patterns of NNTO prepared with different O_2 flow rates of 1.4 l h^{-1} (cyan) and 7 l h^{-1} (purple). (b) SEM images at different magnifications of the 1.4 l h^{-1} sample.

the formation of bigger NNTO primary particles. However, local cooling effects with increasing flow rate cannot be ruled out. In agreement with the phase purity and primary particle size, the electrochemical testing (figure S(8)) confirmed that NNTO prepared with the higher O_2 flow rate delivers higher specific capacities, independent of the C-rate.

Furthermore, experiments were performed to examine the effect of varying molar Ni/Ti ratios on the material's performance. For a titanium content of 5 mol.%, the $R-3m$ phase fraction from Rietveld refinement analysis (table S6) was found to be only 46.6 wt.%, while the $C2/m$ fraction was 49.4 wt.%. We attribute the higher proportion of residual NNO to an insufficient titanium content for proper suppression of the Jahn–Teller distortion in NNO. Likewise, we attempted the synthesis with 15 and 20 mol.% titanium. However, under the same calcination conditions, the fraction of $R-3m$ phase decreased with increasing degree of substitution. Despite applying the optimized preparation route for NNTO, as well as literature known ones for synthesizing $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$, we were not able to obtain phase-pure materials for the intermediate stoichiometries [31, 37]. The SEM images presented in figures S9(a)–(c), especially those in figure S9(a), suggest that the morphology of the primary particles resembles that of NNO [23], albeit they are smaller in size due to the presence of titanium, the latter preventing sintering of grains. Furthermore, as can be seen from figures S9(b) and (c), the surface of the secondary particles is increasingly covered with nano-scale particles with increasing titanium content. This might be attributed to Ti^{4+} reaching its solubility limit. However, it should be noted that for $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$, an $R-3m$ phase fraction of 93 wt.% (7 wt.% NiO) has been reported in the literature [31, 37]. Overall, the synthesis variables were tailored using the one parameter at a time approach, yielding the following optimal conditions: $n(\text{Na})/n(\text{TM}) = 1/1$, $n(\text{Ni})/n(\text{Ti}) = 9/1$, 800°C , 2 K min^{-1} , and $7 \text{ l}_{\text{oxygen}} \text{ h}^{-1}$. The structural parameters from Rietveld analysis of NNTO prepared with these optimized conditions are given in table S7.

When compared with $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and NNO, the reversible specific capacity of NNTO is greatly enhanced [25, 26, 31, 32]. However, due to the relatively larger ionic radius of Na^+ , NNTO, like most O3-type cathodes in SIBs, undergoes complex phase transitions resulting from the gliding of

TMO_2 slabs. This can be clearly seen from the voltage profiles and dq/dV curves shown in figures S6(c) and (f), respectively. Even though the introduction of Ti^{4+} into the Ni sites helps mitigate the phase transitions to some extent, fading issues persist.

To further investigate the charge-storage properties of NNTO, electrochemical testing was done on half-cells. To this end, NNTO was fabricated into electrodes, as described in the Experimental section, and cycled against Na metal as the counter electrode in coin cells in the potential window of 2.0–4.2 V vs. Na^+/Na . The electrolyte was a mixture of 1 M NaClO_4 in EC:PC:DMC (1:1:1 by vol.) with 5 vol.% FEC additive. FEC was used to enhance the reversibility of the Na^+ insertion/extraction reactions (figure S(10)) [31, 52]. For long-term cycling, initially five cycles at C/30 were performed to ensure formation of a robust cathode solid-electrolyte interphase (cSEI). Subsequently, the cells were cycled at C/2 in the following 200 cycles. It should be noted that the latter C-rate is comparatively higher and more realistic than those (C/20 or C/10) often applied in the study of other O3-type cathode materials in SIBs [31, 53]. The cycling data (figure 8(a)) revealed an average Coulomb efficiency of 99.2% at C/2 and a capacity retention of 26.4% after 200 cycles. In comparison to $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$, which exhibits a capacity retention of only ~53% after 50 cycles at C/5 in the potential range between 2.0 and 4.7 V, NNTO demonstrates improved stability, maintaining 64% after 50 cycles at C/2 [31]. Nevertheless, the fading of NNTO cannot be ignored. The voltage profiles and dq/dV curves in figures S11(a) and (b), respectively, indicate severe impedance buildup with cycling. Rate performance testing was also conducted (figure 8(b)), revealing distinct capacity decay with increasing C-rate. This can be attributed to the diffusion resistance in O3-type cathodes, which is amplified with increasing current density, leading to severe polarization. However, NNTO still managed to deliver a specific discharge capacity of 89 mAh g^{-1} at 2C. Upon reducing the C-rate back to C/30, the capacity failed to reach that achieved in the initial cycles ($\sim 190 \text{ mAh g}^{-1}$). Compared to the extensively studied $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ [31], NNTO exhibits superior rate capability. This highlights that the inclusion of Ti^{4+} in NNTO improves the sodium transport properties.

To determine the oxidation state of nickel in the pristine and cycled states, representative NNTO and NNO cathodes

3. Results

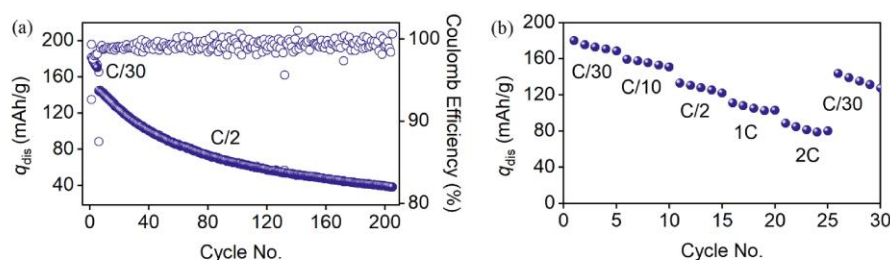


Figure 8. (a) Long-term cycling performance of NNTO in coin half-cells and (b) corresponding rate capability.

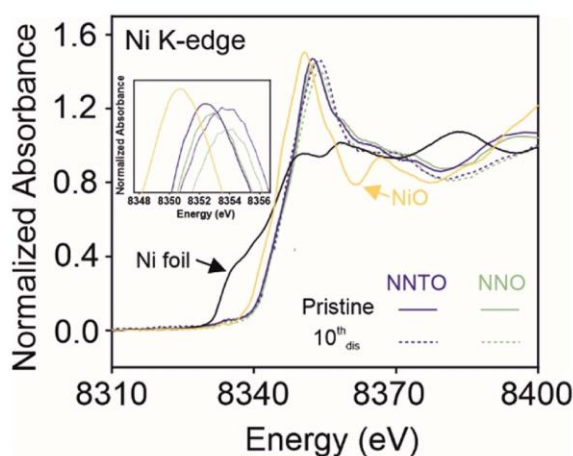


Figure 9. Ex situ XANES spectra at the Ni K-edge of NNTO and NNO in the pristine and discharged states (after 10 cycles).

were probed using XAS. We note that due to the limited resolution of the laboratory spectrometer used in this study, accurate testing of the oxidation state of the titanium substituent was not possible. To ensure comparability of the electrodes across various states, both NNTO and NNO were subject to electrochemical testing under the same conditions (figure S(12)). Subsequently, XAS measurements were conducted on both the pristine electrodes and those collected in the discharged state after 10 cycles. As can be seen from figure 9, the Ni K-edge of pristine NNTO lies between that of NNO and NiO, indicating the coexistence of Ni^{2+} and Ni^{3+} , as expected from the titanium substitution. After 10 cycles, because of localized structural alterations, both NNTO and NNO exhibit varying degrees of rightward shifts at the Ni K-edge. However, the energy position of NNO was about 1 eV higher than that of NNTO, indicating that NNTO has a better structural stability.

For a more detailed understanding of the structural changes occurring in NNTO during cycling, *operando* XRD was conducted on the cathodes. The contour plot in figure 10(a) reveals four reversible phase transitions. Due to the low intensity (laboratory diffractometer), continuous refinement was not possible. Therefore, individual XRD patterns were refined to describe the structural evolution. As shown in figure S(13),

the Ni^{2+} ions undergo oxidation to Ni^{3+} upon Na^+ extraction, which enhances the Jahn–Teller distortion and leads to the emergence of monoclinic distortion and formation of the O'3 phase. The most prominent feature was a splitting of the (104) reflection into (20–2) and (111) for O'3. However, the (20–2) reflection was barely visible (low intensity). With further desodiation, the repulsion within the oxygen layers increases, causing gliding of the TMO₂ slabs and formation of the P3 phase. The most noticeable change was a significant enhancement of the (105), (102), (006), and (003) reflections [7]. As the sodium content depleted further, P3 transitioned toward O''3, causing less lattice distortion. The latter is evident from the decrease in a/b value from O'3 (1.86) to O''3 (1.83) [25]. Nevertheless, the cubic volume of O''3 is slight larger than that of P3 (table S8). Similar results have been reported for other (charged) Ni-rich O3-type layered oxides in SIBs, such as O'3-NaNiO₂ and O3-NaNi_{0.5}Co_{0.5}O₂ [25, 53–57]. With progressing desodiation, the Ni^{3+} ions undergo further oxidation to Ni^{4+} , accompanied by the formation of the O1 phase. The hypothesis is that O1 is thermodynamically more stable at high states of charge, similar to the O3–O1 transition occurring in LiCoO₂ (LCO) [58]. The different transitions (based on the discharge data in table S8) are indicated in the dq/dV curve for the second cycle in figure S(14), aiming at providing a more intuitive understanding of the phase changes. Due to significant overpotentials in the initial charge cycle, an accurate comparison is not feasible. It should be noted that the peaks at about 3.1, 3.4, and 3.5 V (figure S(14)) cannot be unambiguously correlated with features in the XRD data; they can likely be attributed to Na^+ /vacancy ordering or reversible reactions involving the Ni^{2+} – Ni^{3+} and/or Ni^{3+} – Ni^{4+} redox couples, with the former potentially stabilizing the monoclinic O'3 phase and facilitating its formation [56, 59–62].

The structural parameters from Rietveld refinements of the individual XRD patterns are given in table S8. All unit-cell volumes were translated into values analogous to the primitive cubic cell for easier comparison between different phases. As can be seen, prior to the formation of the O1 phase, the volume changes are minor, irrespective of the transitions from O3 → O'3 → P3 → O''3 (figure 10(b)). However, upon O1 formation at potentials above 4.0 V vs. Na^+/Na (equivalent to ~80% state of charge), the volume collapses to about 70% of the initial O3 volume, eventually resulting in the formation of cracks (figures 10(c) and (d)) and leading to mechanical

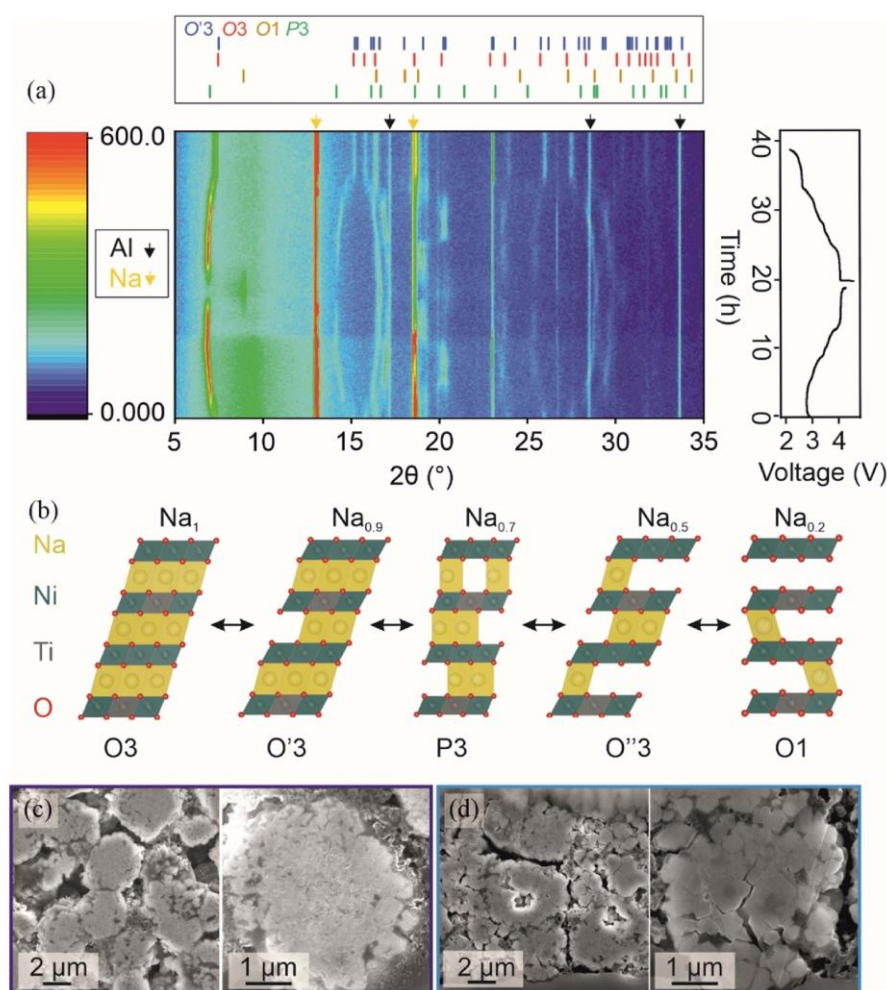


Figure 10. (a) 2D contour plot of *operando* XRD data collected during the first cycle at C/10 rate. (b) Illustration of crystal structures for O3, O'3, P3, O''3, and O1. Cross-sectional SEM images of NNTO (c) in the pristine state and (d) after 200 cycles.

degradation. A similar fading behavior has been observed for the O3-type $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ [36]. Notably, although the P3 phase is in a Na-deficient state, its c parameter was found to not deviate much from that of the initial O3 phase. This can be explained by weakening of the oxygen–oxygen shielding effect upon Na^+ extraction [63].

To gain further insight into crack formation during cycling of NNTO, *operando* AE as a non-destructive technique was employed. AE is widely used for monitoring the fatigue and mechanical damage of construction materials [64]. Regarding batteries, AE has been employed both to monitor cell health and predict cycle life, and as a characterization tool for individual electrodes [65–67]. While (bulk) phase evolution can be studied via XRD, information about microscopic structural changes, such as particle fracture, are not easily obtained in *operando* mode [68]. By monitoring the AE of NNTO, particle cracking can be examined. In general, AE directly detects

the generation and propagation of cracks, thereby indirectly providing information about structural changes on the material and/or electrode level. Nevertheless, other acoustically active processes can be monitored as well, such as SEI formation [46, 64, 68, 69]. As shown in figures 11(a) and (b), acoustic activity accumulated early in the initial cycle, due to formation of the cSEI [68, 70–73]. This has also been found for LCO and LNO cathodes [68, 70]. Near the end of charge and in subsequent cycles, the majority of acoustic activity was detected at potentials associated with particle fracture due to phase transitions and the corresponding unit-cell volume changes during desodiation [68, 70, 71, 74–76]. The number of new hits per cycle gradually decreased, which is reflected in the hit density shown in figure 11(b) and highlighted for the later cycles in figure S15(a). A similar observation of AE being closely related to particle fracture has recently been reported for a P2-type SIB CAM [46].

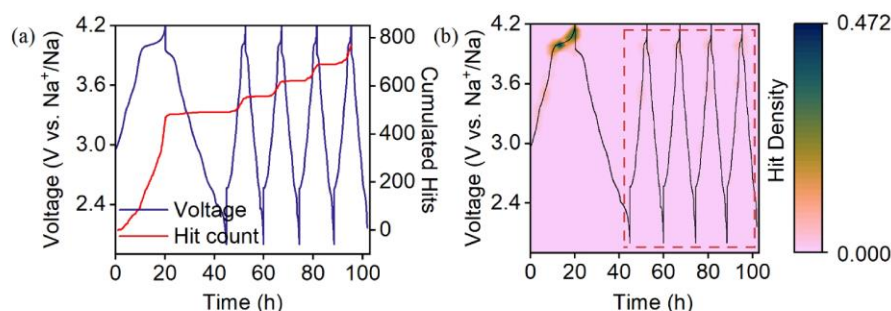


Figure 11. (a) Voltage profiles for the first five cycles (at C/30 rate followed by C/10 cycling) and corresponding cumulated hits. (b) Contour plot of acoustic activity (hit density) as a function of time and potential.

Since the AE is concentrated in the phase-transition regions, dq/dV curves of the first two cycles are displayed in figures S15(b) and (c). In the beginning of the initial cycle, which corresponds to the (acoustically active) cSEI formation stage, the acoustic behavior associated with phase transitions was relatively weak, but strong activity caused by the O³-O1 transition at about 4.0 V vs. Na⁺/Na was clearly observed. In the second cycle, two distinct peaks, centered around 3.5 V, led to acoustic activity. A possible reason might be Na⁺/vacancy ordering, leading to a reduction in Jahn–Teller distortion and further resulting in strain concentration, plastic deformation, and/or intragranular cracking [53]. While Jahn–Teller distortion can be observed by XRD, the latter effects may only be detected in real-time by AE or advanced electron microscopy techniques. However, other peaks in the dq/dV curves were not associated with distinct acoustic behavior. Overall, the volume collapse at high potentials can be correlated with specific AE signals, strongly suggesting crack formation. Therefore, it seems that chemo-mechanical degradation is one of the main factors contributing to the NNTO fading.

Finally, *in situ* DEMS measurements were performed to study the gassing behavior of NNTO. Figures 12(a)–(d) illustrates the relationship between voltage profile and gas evolution rate and total amount of the three species detected, namely hydrogen (H₂, $m/z = 2$), oxygen (O₂, $m/z = 32$), and carbon dioxide (CO₂, $m/z = 44$). The evolution of these gases can be seen in analogy to their generation in LIBs. CO₂ originates from the chemical oxidation of electrolyte associated with the release of lattice oxygen or from electrochemical oxidation of the electrolyte (or, mainly during the initial cycle, from surface carbonates) [77–82]. In LIBs, the O₂ released from layered oxide cathode materials is reactive oxygen and is seldom directly detected in the form of molecular oxygen. Instead, it is indirectly detected in the form of the electrolyte oxidation product CO₂ [83, 84]. However, small amounts of O₂ were observed in this study. H₂ is initially generated through the reduction of trace water at the anode. Its release at higher potentials is typically attributed to the formation of protic species as secondary products, stemming from oxidation reactions involving the electrolyte, at the cathode. These species then migrate to the anode, where they undergo reduction processes under the release of H₂ (figure 12(b)) [81, 82, 85]. In

the first cycle, a small amount of O₂ ($\sim 2.9 \mu\text{mol g}^{-1}$) evolved (figure 12(c)), which can be attributed to NNTO undergoing oxygen redox activation, as known for O3-type layered oxides containing redox-inactive transition metals [86, 87]. This in turn can lead to anion oxidation at higher potentials, resulting partially in irreversible O₂ evolution [82, 87, 88]. The main evolved gas was CO₂ (figure 12(d)), with the highest rate at about 4.0 V vs. Na⁺/Na. Generally, residual carbonates can explain much of the CO₂ evolution in the initial cycle [78]. However, no carbonate vibrational bands were detected by Fourier-transform infrared spectroscopy (figure S(16)), indicating a largely carbonate-free surface of the NNTO secondary particles. Because the H₂ evolution exhibited a similar behavior (figure 12(b)), we attribute the generation of H₂ and a major portion of CO₂ at 4.0 V to the reaction between released lattice oxygen and electrolyte. A smaller portion of CO₂, explaining the gas evolution shoulder at 4.2 V, may be attributed to the decomposition of trace carbonates and/or electrochemical oxidation of the electrolyte, which however is commonly observed only at potentials above 4.7 V vs. Li⁺/Li (equivalent to ~ 4.4 V vs. Na⁺/Na), and thus considered less likely [82]. In the second cycle, due to the formation of the cSEI and an oxygen-depleted surface, the gas generated by chemical oxidation of electrolyte significantly decreased. Yet, small amounts of H₂ and CO₂ were observed, implying the persistence of lattice oxygen loss and subsequent electrolyte degradation. In conclusion, the gassing behavior infers that irreversible oxidation of lattice oxygen is, next to the phase transitions and resulting particle fracture, another underlying mechanism of the continuous degradation of NNTO.

In addressing the two degradation mechanisms mentioned above, a preliminary optimization was performed. For mitigating chemo-mechanical degradation induced by continuous cracking, an Al₂O₃ coating was applied to the NNTO secondary particles [89–92]. The purpose was to prevent adverse side reactions from occurring between newly formed (reactive) interfaces and electrolyte. As shown in figure S(17), the Al₂O₃ coating indeed helps stabilize the NNTO surface, improving the cycling stability, although some degradation remains. In the future, dopants may be employed, along with protective coatings. This approach is expected to not only alleviate the volume collapse of NNTO at high potentials, but also to

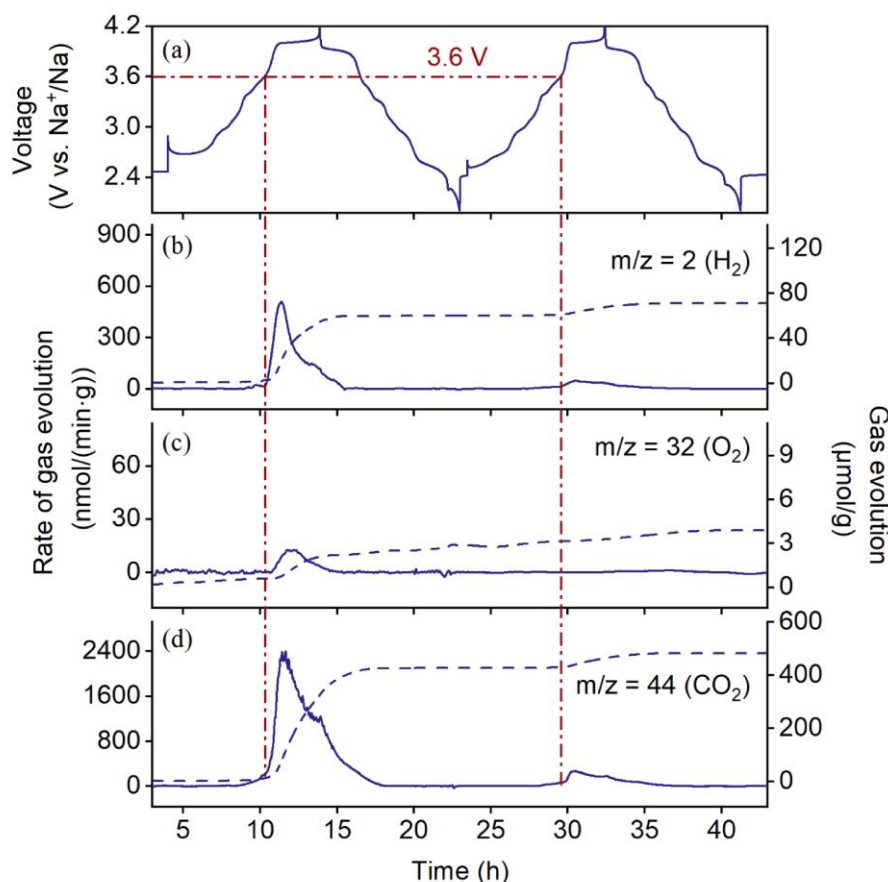


Figure 12. (a) Voltage profiles at C/10 rate and corresponding time-resolved evolution rates (left y-axis) and cumulative amounts (right y-axis) of (b) H_2 , (c) O_2 , and (d) CO_2 measured by DEMS.

suppress lattice oxygen loss to ultimately enhancing the overall cycling performance.

4. Conclusions

In summary, in the present work, we have reported about $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NNTO), which is superior to NaNiO_2 and $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ when used as a cathode material in sodium-ion cells. By systematic exploration of the synthesis conditions, high-purity NNTO was prepared through a solid-state route. The material is capable of delivering a reversible specific capacity of $q_{\text{dis}} \approx 190 \text{ mAh g}^{-1}$ in the electrochemical window of 2.0–4.2 V vs. Na^+/Na at an average operating potential of 3.2 V. Compared to NaNiO_2 and $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$, NNTO demonstrates increased cycling stability even at higher C-rates (maintaining $\sim 64\%$ of the capacity after 50 cycles at C/2). However, significant fading is still observed upon long-term cycling. Through *operando* XRD, we found that NNTO undergoes an O'3-O1 phase transition at around 4.0 V, causing a $\sim 30\%$ volume collapse and resulting in crack initiation and propagation during battery operation. This observation

was verified through *post mortem* SEM imaging and *operando* AE measurements. Furthermore, *in situ* gas analysis via DEMS revealed irreversible lattice oxygen loss, contributing to structural instability and fading. To address these degradation mechanisms, we have implemented an alumina surface coating, and intend to introduce dopants into the Na sites [93], or further to the transition metal sites of NNTO, to mitigate the volume variation at high potentials.

5. Future perspectives

The rapid advancement of LIBs has significantly propelled the electric and hybrid vehicle industry in recent years. SIBs, as a promising alternative to LIBs, are particularly suitable for large-scale electrochemical energy storage, due to their lower cost and the abundant availability of raw materials. However, recent research on layered oxide cathodes has revealed that favorable operating potentials and high theoretical specific capacities make SIBs also viable for high-performance applications. Among the existing layered oxides, sodium-rich O3-type materials generally exhibit a higher

theoretical specific capacity than sodium-deficient P2-type materials, making the former more promising for practical application. Nonetheless, the multiple phase transitions and Jahn–Teller distortion associated with O3-type structures can severely affect the cycling performance and stability. Doping transition metal sites with tetravalent metal species (such as Ti^{4+}) has been shown to effectively mitigate some of the issues. Despite these advances, further investigation into the material's stability/reactivity (bulk/surface) at high potentials is required to fully realize the potential of this promising class of cathode materials.

Acknowledgments

This study was supported by BASF SE. The authors thank Dr Thomas Bergfeldt (KIT) and Dr Philipp Müller (BASF SE) and their teams for collecting the ICP-OES and TEM data, respectively. J J and M F acknowledges funding by the German Research Foundation (DFG) under project ID 390874152 (POLiS Cluster of Excellence). This work contributes to the research performed at CELEST (Center for Electrochemical Energy Storage Ulm-Karlsruhe).

Conflict of interest

The authors declare no conflict of interest.

ORCID iD

Torsten Brezesinski  <https://orcid.org/0000-0002-4336-263X>

References

- [1] Manthiram A 2020 A reflection on lithium-ion battery cathode chemistry *Nat. Commun.* **11** 1550
- [2] Chang U, Lee J T, Yun J-M, Lee B, Lee S W, Joh H-I, Eom K and Fuller T F 2019 *In situ* self-formed nanosheet MoS_3 /reduced graphene oxide material showing superior performance as a lithium-ion battery cathode *ACS Nano* **13** 1490–8
- [3] Yuan T *et al* 2022 A high-rate, durable cathode for sodium-ion batteries: sb-doped O3-type Ni/Mn-based layered oxides *ACS Nano* **16** 18058–70
- [4] Chayambuka K, Mulder G, Danilov D L and Notten P H L 2018 Sodium-ion battery materials and electrochemical properties reviewed *Adv. Energy Mater.* **8** 1800079
- [5] Gao R-M, Zheng Z-J, Wang P-F, Wang C-Y, Ye H and Cao F-F 2020 Recent advances and prospects of layered transition metal oxide cathodes for sodium-ion batteries *Energy Storage Mater.* **30** 9–26
- [6] Li S, Sun Y, Pang Y, Xia S, Chen T, Sun H, Zheng S and Yuan T 2022 Recent developments of layered transition metal oxide cathodes for sodium-ion batteries toward desired high performance *Asia-Pac. J. Chem. Eng.* **17** e2762
- [7] Wang P-F, Yao H-R, Liu X-Y, Zhang J-N, Gu L, Yu X-Q, Yin Y-X and Guo Y-G 2017 Ti-substituted $\text{NaNi}_{0.5}\text{Mn}_{0.5-x}\text{Ti}_x\text{O}_2$ cathodes with reversible O3-P3 phase transition for high-performance sodium-ion batteries *Adv. Mater.* **29** 1700210
- [8] Guo S, Yu H, Liu P, Ren Y, Zhang T, Chen M, Ishida M and Zhou H 2015 High-performance symmetric sodium-ion batteries using a new, bipolar O3-type material, $\text{Na}_{0.8}\text{Ni}_{0.4}\text{Ti}_{0.6}\text{O}_2$ *Energy Environ. Sci.* **8** 1237–44
- [9] Wang P-F, You Y, Yin Y-X, Wang Y-S, Wan L-J, Gu L and Guo Y-G 2016 Suppressing the P2-O2 phase transition of $\text{Na}_{0.67}\text{Mn}_{0.67}\text{Ni}_{0.33}\text{O}_2$ by magnesium substitution for improved sodium-ion batteries *Angew. Chem., Int. Ed.* **128** 7571–5
- [10] Han M H, Gonzalo E, Singh G and Rojo T 2015 A comprehensive review of sodium layered oxides: powerful cathodes for Na-ion batteries *Energy Environ. Sci.* **8** 81–102
- [11] Guo S, Liu P, Yu H, Zhu Y, Chen M, Ishida M and Zhou H 2015 A layered P2- and O3-type composite as a high-energy cathode for rechargeable sodium-ion batteries *Angew. Chem., Int. Ed.* **54** 5894–9
- [12] Xie Y *et al* 2021 Role of lithium doping in $\text{P2-Na}_{0.67}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$ for sodium-ion batteries *Chem. Mater.* **33** 4445–55
- [13] Delmas C, Fouassier C and Hagemmuller P 1980 Structural classification and properties of the layered oxides Physica B+C **99** 81–85
- [14] Delmas C, Braconnier J-J, Fouassier C and Hagemmuller P 1981 Electrochemical intercalation of sodium in Na_xCoO_2 bronzes *Solid State Ion.* **3–4** 165–9
- [15] Nitta N, Wu F, Lee J T and Yushin G 2015 Li-ion battery materials: present and future *Mater. Today* **18** 252–64
- [16] Blomgren G E 2017 The development and future of lithium ion batteries *J. Electrochem. Soc.* **164** A5019–25
- [17] Noh H-J, Youn S, Yoon C S and Sun Y-K 2013 Comparison of the structural and electrochemical properties of layered $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$ ($x=1/3, 0.5, 0.6, 0.7, 0.8$ and 0.85) cathode material for lithium-ion batteries *J. Power Sources* **233** 121–30
- [18] Kim J-H, Ryu H-H, Kim S J, Yoon C S and Sun Y-K 2019 Degradation mechanism of highly Ni-rich $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$ cathodes with $x > 0.9$ *ACS Appl. Mater. Interfaces* **11** 30936–42
- [19] Bianchini M, Roca-Ayats M, Hartmann P, Brezesinski T and Janek J 2019 There and back again—the journey of LiNiO_2 as a cathode active material *Angew. Chem., Int. Ed.* **58** 10434–58
- [20] Li W, Reimers J N and Dahn J R 1992 Crystal structure of $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$ and a lattice-gas model for the order-disorder transition *Phys. Rev. B* **46** 3236–46
- [21] Reimers J N, Li W and Dahn J R 1993 Short-range cation ordering in $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$ *Phys. Rev. B* **47** 8486–93
- [22] Shannon R D 1976 Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides *Acta Crystallogr.* **32** 751–67
- [23] Karger L *et al* 2023 Low-temperature ion exchange synthesis of layered LiNiO_2 single crystals with high ordering *Chem. Mater.* **35** 648–57
- [24] Vassilaras P, Ma X, Li X and Ceder G 2013 Electrochemical properties of monoclinic NaNiO_2 *J. Electrochem. Soc.* **160** A207–11
- [25] Han M H, Gonzalo E, Casas-Cabanas M and Rojo T 2014 Structural evolution and electrochemistry of monoclinic NaNiO_2 upon the first cycling process *J. Power Sources* **258** 266–71
- [26] Wang L, Wang J, Zhang X, Ren Y, Zuo P, Yin G and Wang J 2017 Unravelling the origin of irreversible capacity loss in NaNiO_2 for high voltage sodium ion batteries *Nano Energy* **34** 215–23
- [27] Kang K, Meng Y-S, Breger J, Grey C P and Ceder G 2006 Electrodes with high power and high capacity for rechargeable lithium batteries *Science* **311** 977–80

- [28] Luo Y *et al* 2022 Towards Ni-rich layered oxides cathodes with low Li/Ni intermixing by mild molten-salt ion exchange for lithium-ion batteries *Nano Energy* **102** 107626
- [29] Cao X, Qiao Y, Jia M, He P and Zhou H 2022 Ion-exchange: a promising strategy to design li-rich and li-excess layered cathode materials for Li-ion batteries *Adv. Energy Mater.* **12** 2003972
- [30] Komaba S, Yabuuchi N, Nakayama T, Ogata A, Ishikawa T and Nakai I 2012 Study on the reversible electrode reaction of $\text{Na}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ for a rechargeable sodium-ion battery *Inorg. Chem.* **51** 6211–20
- [31] Yu H, Guo S, Zhu Y, Ishida M and Zhou H 2014 Novel titanium-based O3-type $\text{NaTi}_{0.5}\text{Ni}_{0.5}\text{O}_2$ as a cathode material for sodium ion batteries *Chem. Commun.* **50** 457–9
- [32] Maletti S, Sarapulova A, Schökel A and Mikhailova D 2019 Operando studies on the $\text{NaTi}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode for Na-ion batteries: elucidating titanium as a structure stabilizer *ACS Appl. Mater. Interfaces* **11** 33923–30
- [33] Ma Q, Peng F, Li R, Yin S and Dai C 2016 Effect of calcination temperature on microstructure and electrochemical performance of lithium-rich layered oxide cathode materials *Mater. Sci. Eng.* **213** 123–30
- [34] Manzi J, Paolone A, Palumbo O, Corona D, Massaro A, Cavaliere R, Muñoz-García A B, Trequattrini F, Pavone M and Brutti S 2021 Monoclinic and orthorhombic NaMnO_2 for secondary batteries: a comparative study *Energies* **14** 1230
- [35] Kubota K, Miyazaki M, Kim E J, Yoshida H, Barpanda P and Komaba S 2021 Structural change induced by electrochemical sodium extraction from layered $\text{O}'3\text{-NaMnO}_2$ *J. Mater. Chem. A* **9** 26810–9
- [36] Yu T-Y, Ryu H-H, Han G and Sun Y-K 2020 Understanding the capacity fading mechanisms of O3-type $\text{Na}[\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2]$ cathode for sodium-ion batteries *Adv. Energy Mater.* **10** 2001609
- [37] Wang H, Xiao Y, Sun C, Lai C and Ai X 2015 A type of sodium-ion full-cell with a layered $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ cathode and a pre-sodiated hard carbon anode *RSC Adv.* **5** 106519–22
- [38] Zhou D, Huang W, Zhao F and Lv X 2019 The effect of Na content on the electrochemical performance of the O3-type $\text{Na}_x\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ for sodium-ion batteries *J. Mater. Sci.* **54** 7156–64
- [39] Liu H *et al* 2018 Truncated octahedral high-voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode materials for lithium ion batteries: positive influences of Ni/Mn disordering and oxygen vacancies *J. Electrochem. Soc.* **165** A1886–96
- [40] Liu X *et al* 2020 Al and Fe-containing Mn-based layered cathode with controlled vacancies for high-rate sodium ion batteries *Nano Energy* **76** 104997
- [41] Xu G-L *et al* 2022 Native lattice strain induced structural earthquake in sodium layered oxide cathodes *Nat. Commun.* **13** 436
- [42] Toby B H and Von Dreele R B 2013 GSAS-II: the genesis of a modern open-source all purpose crystallography software package *J. Appl. Crystallogr.* **46** 544–9
- [43] Geßwein H, Stübke P, Weber D, Binder J R and Mönig R 2022 A multipurpose laboratory diffractometer for operando powder x-ray diffraction investigations of energy materials *J. Appl. Crystallogr.* **55** 503–14
- [44] Jahrman E P *et al* 2019 An improved laboratory-based x-ray absorption fine structure and x-ray emission spectrometer for analytical applications in materials chemistry research *Rev. Sci. Instrum.* **90** 024106
- [45] Schweidler S, Dreyer S L, Breitung B and Brezesinski T 2021 Operando acoustic emission monitoring of degradation processes in lithium-ion batteries with a high-entropy oxide anode *Sci. Rep.* **11** 23381
- [46] Dreyer S L, Zhang R, Wang J, Kondrakov A, Wang Q, Brezesinski T and Janek J 2023 The effect of configurational entropy on acoustic emission of P2-type layered oxide cathodes for sodium-ion batteries *J. Phys. Energy* **5** 035002
- [47] Berkes B B, Jozwiuk A, Sommer H, Brezesinski T and Janek J 2015 Simultaneous acquisition of differential electrochemical mass spectrometry and infrared spectroscopy data for in situ characterization of gas evolution reactions in lithium-ion batteries *Electrochem. Commun.* **60** 64–69
- [48] Berkes B B, Jozwiuk A, Vračar M, Sommer H, Brezesinski T and Janek J 2015 Online continuous flow differential electrochemical mass spectrometry with a realistic battery setup for high-precision, long-term cycling tests *Anal. Chem.* **87** 5878–83
- [49] Rudola A, Saravanan K, Mason C W and Balaya P 2013 $\text{Na}_2\text{Ti}_3\text{O}_7$: an intercalation based anode for sodium-ion battery applications *J. Mater. Chem. A* **1** 2653–62
- [50] Yuan T *et al* 2023 Moisture stable and ultrahigh-rate Ni/Mn-based sodium-ion battery cathodes via K^+ decoration *Nano Res.* **16** 6890–902
- [51] Darga J and Manthiram A 2022 Facile synthesis of O3-type $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ single crystals with improved performance in sodium-ion batteries *ACS Appl. Mater. Interfaces* **14** 52729–37
- [52] Komaba S, Ishikawa T, Yabuuchi N, Murata W, Ito A and Ohsawa Y 2011 Fluorinated ethylene carbonate as electrolyte additive for rechargeable Na batteries *ACS Appl. Mater. Interfaces* **3** 4165–8
- [53] Kubota K, Fujitani N, Yoda Y, Kuroki K, Tokita Y and Komaba S 2021 Impact of Mg and Ti doping in O3 type $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ on reversibility and phase transition during electrochemical Na intercalation *J. Mater. Chem. A* **9** 12830–44
- [54] Yabuuchi N, Kubota K, Dahbi M and Komaba S 2014 Research development on sodium-ion batteries *Chem. Rev.* **114** 11636–82
- [55] Braconnier J-J, Delmas C, Fouassier C and Hagenmuller P 1980 Comportement électrochimique des phases Na_xCoO_2 *Mater. Res. Bull.* **15** 1797–804
- [56] Li X, Wang Y, Wu D, Liu L, Bo S-H and Ceder G 2016 Jahn–Teller assisted Na diffusion for high performance Na ion batteries *Chem. Mater.* **28** 6575–83
- [57] Vassilaras P, Kwon D-H, Dacek S T, Shi T, Seo D-H, Ceder G and Kim J C 2017 Electrochemical properties and structural evolution of O3-type layered sodium mixed transition metal oxides with trivalent nickel *J. Mater. Chem. A* **5** 4596–606
- [58] Van der Ven A, Aydinol M K and Ceder G 1998 First-principles evidence for stage ordering in Li_xCoO_2 *J. Electrochem. Soc.* **145** 2149–55
- [59] Kaufman J L and Van Der Ven A 2019 Na_xCoO_2 phase stability and hierarchical orderings in the O3/P3 structure family *Phys. Rev. Mater.* **3** 015402
- [60] Kubota K, Asari T, Yoshida H, Yabuuchi N, Shiiba H, Nakayama M and Komaba S 2016 Understanding the structural evolution and redox mechanism of a $\text{NaFeO}_2\text{–NaCoO}_2$ solid solution for sodium-ion batteries *Adv. Funct. Mater.* **26** 6047–59
- [61] Yabuuchi N, Ikeuchi I, Kubota K and Komaba S 2016 Thermal stability of Na_xCrO_2 for rechargeable sodium batteries; studies by high-temperature synchrotron x-ray diffraction *ACS Appl. Mater. Interfaces* **8** 32292–9
- [62] Didier C, Guignard M, Suchomel M R, Carlier D, Darriet J and Delmas C 2016 Thermally and electrochemically driven topotactical transformations in sodium layered oxides Na_xVO_2 *Chem. Mater.* **28** 1462–71
- [63] Ding F-X, Rong X-H, Wang H-B, Yang Y, Hu Z-L, Dang R-B, Lu Y-X and Hu Y-S 2022 Phase transitions of Na-ion

- layered oxide materials and their influence on properties *Acta Phys. Sin.* **71** 108801
- [64] Enoki M, Inaba H, Mizutani Y, Nakano M and Ohtsu M 2016 Principles of the acoustic emission (AE) method and signal processing *Practical Acoustic Emission Testing* (Springer)
- [65] Beganovic N and Söffker D 2019 Estimation of remaining useful lifetime of lithium-ion battery based on acoustic emission measurements *J. Energy Resour. Technol.* **141** 041901
- [66] Wang K, Chen Q, Yue Y, Tang R, Wang G, Tang L and He Y 2023 Cyclic aging monitoring of lithium-ion battery based on acoustic emission *Nondestruct. Test. Eval.* **38** 480–99
- [67] Zhang K, Yin J and He Y 2021 Acoustic emission detection and analysis method for health status of lithium ion batteries *Sensors* **21** 712
- [68] Schweidler S, Bianchini M, Hartmann P, Brezesinski T and Janek J 2020 The sound of batteries: an operando acoustic emission study of the LiNiO₂ cathode in Li-ion cells *Batter. Supercaps* **3** 1021–7
- [69] Majasan J O, Robinson J B, Owen R E, Maier M, Radhakrishnan A N P, Pham M, Tranter T G, Zhang Y, Shearing P R and Brett D J L 2021 Recent advances in acoustic diagnostics for electrochemical power systems *J. Phys. Energy* **3** 032011
- [70] Choe C-Y, Jung W-S and Byeon J-W 2015 Damage evaluation in lithium cobalt oxide/carbon electrodes of secondary battery by acoustic emission monitoring *Mater. Trans.* **56** 269–73
- [71] Schweidler S, Dreyer S L, Breitung B and Brezesinski T 2022 Acoustic emission monitoring of high-entropy oxyfluoride rock-salt cathodes during battery operation *Coatings* **12** 402
- [72] Tranchot A, Etienneble A, Thivel P-X, Idrissi H and Roué L 2015 In-situ acoustic emission study of Si-based electrodes for Li-ion batteries *J. Power Sources* **279** 259–66
- [73] Matsuo T, Uchida M and Cho H 2011 Development of acoustic emission clustering method to detect degradation of lithium ion batteries *J. Solid Mech. Mater. Eng.* **5** 678–89
- [74] Kircheva N, Genies S, Chabrol C and Thivel P-X 2013 Evaluation of acoustic emission as a suitable tool for aging characterization of LiAl/LiMnO₂ cell *Electrochim. Acta* **88** 488–94
- [75] Rhodes K, Dudney N, Lara-Curzio E and Daniel C 2010 Understanding the degradation of silicon electrodes for lithium-ion batteries using acoustic emission *J. Electrochem. Soc.* **157** A1354
- [76] Didier-Laurent S, Idrissi H and Roué L 2008 In-situ study of the cracking of metal hydride electrodes by acoustic emission technique *J. Power Sources* **179** 412–6
- [77] Jung R, Metzger M, Maglia F, Stinner C and Gasteiger H A 2017 Chemical versus electrochemical electrolyte oxidation on NMC111, NMC622, NMC811, LNMO, and conductive carbon *J. Phys. Chem. Lett.* **8** 4820–5
- [78] Hatsukade T, Schiele A, Hartmann P, Brezesinski T and Janek J 2018 Origin of carbon dioxide evolved during cycling of nickel-rich layered NCM cathodes *ACS Appl. Mater. Interfaces* **10** 38892–9
- [79] Papp J K, Li N, Kaufman L A, Naylor A J, Younesi R, Tong W and McCloskey B D 2021 A comparison of high voltage outgassing of LiCoO₂, LiNiO₂, and Li₂MnO₃ layered Li-ion cathode materials *Electrochim. Acta* **368** 137505
- [80] Strauss F, Payandeh S, Kondrakov A and Brezesinski T 2022 On the role of surface carbonate species in determining the cycling performance of all-solid-state batteries *Mater. Futures* **1** 023501
- [81] Dreyer S L, Kondrakov A, Janek J and Brezesinski T 2022 In situ analysis of gas evolution in liquid- and solid-electrolyte-based batteries with current and next-generation cathode materials *J. Mater. Res.* **37** 3146–68
- [82] Wang J et al 2022 P2-type layered high-entropy oxides as sodium-ion cathode materials *Mater. Futures* **1** 035104
- [83] Jung R, Metzger M, Maglia F, Stinner C and Gasteiger H A 2017 Oxygen release and its effect on the cycling stability of LiNi_xMn_yCo_zO₂ (NMC) cathode materials for Li-ion batteries *J. Electrochem. Soc.* **164** A1361–77
- [84] Wandt J, Freiberg A T S, Ogronik A and Gasteiger H A 2018 Singlet oxygen evolution from layered transition metal oxide cathode materials and its implications for lithium-ion batteries *Mater. Today* **21** 825–33
- [85] Metzger M, Strehle B, Solchenbach S and Gasteiger H A 2016 Origin of H₂ evolution in LIBs: H₂O reduction vs. electrolyte oxidation *J. Electrochem. Soc.* **163** A798–809
- [86] Yu Y, Ning D, Li Q, Franz A, Zheng L, Zhang N, Ren G, Schumacher G and Liu X 2021 Revealing the anionic redox chemistry in O3-type layered oxide cathode for sodium-ion batteries *Energy Storage Mater.* **38** 130–40
- [87] Voronina N, Yaqoob N, Kim H J, Lee K-S, Lim H-D, Jung H-G, Guillon O, Kaghazchi P and Myung S-T 2021 A new approach to stable cationic and anionic redox activity in O3-layered cathode for sodium-ion batteries *Adv. Energy Mater.* **11** 2100901
- [88] Guo Y-J et al 2021 Boron-doped sodium layered oxide for reversible oxygen redox reaction in Na-ion battery cathodes *Nat. Commun.* **12** 5267
- [89] Hwang J-Y, Myung S-T, Choi J U, Yoon C S, Yashiro H and Sun Y-K 2017 Resolving the degradation pathways of the O3-type layered oxide cathode surface through the nano-scale aluminum oxide coating for high-energy density sodium-ion batteries *J. Mater. Chem. A* **5** 23671–80
- [90] Dreyer S L, Kretschmer K R, Tripković Đ, Mazilkin A, Chukwu R, Azmi R, Hartmann P, Bianchini M, Brezesinski T and Janek J 2022 Multi-element surface coating of layered Ni-rich oxide cathode materials and their long-term cycling performance in lithium-ion batteries *Adv. Mater. Interfaces* **9** 2101100
- [91] Neudeck S, Strauss F, Garcia G, Wolf H, Janek J, Hartmann P and Brezesinski T 2019 Room temperature, liquid-phase Al₂O₃ surface coating approach for Ni-rich layered oxide cathode material *Chem. Commun.* **55** 2174–7
- [92] Peng B, Wan G, Ahmad N, Yu L, Ma X and Zhang G 2023 Recent progress in the emerging modification strategies for layered oxide cathodes toward practicable sodium ion batteries *Adv. Energy Mater.* **13** 2300334
- [93] Peng B, Chen Y, Wang F, Sun Z, Zhao L, Zhang X, Wang W and Zhang G 2022 Unusual site-selective doping in layered cathode strengthens electrostatic cohesion of alkali-metal layer for practicable sodium-ion full cell *Adv. Mater.* **34** 2103210

3.2. Publication II: Exploring Calcium Pillaring of O3-Type $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ Cathodes to Advance Na-Ion Battery Technology

Publication II, as a follow-up to publication I (see section 3.1.), explores the enhancement of NNTO performance through partial substitution of Na^+ with Ca^{2+} as a pillaring ion. Ten different Ca^{2+} concentrations were systematically investigated, and the resulting materials were characterized by XRD and electrochemical measurements. Among these, the composition with 2.5 mol.% Ca^{2+} exhibited the largest interslab distance, along with the best capacity retention and rate capability. Subsequent *in situ* XRD, *post-mortem* SEM, and AE measurements confirmed that calcium incorporation effectively mitigates electro-chemo-mechanical degradation. Hard and soft XAS revealed more reversible $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$ redox processes in CaNNTO, while DEMS demonstrated that Ca^{2+} substitution suppresses lattice oxygen loss, thereby contributing to the stabilization of the cathode|electrolyte interface.

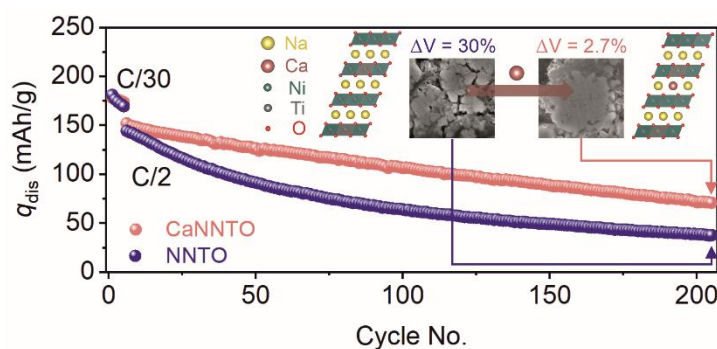


Figure 14. Table of contents graphic of publication II. Adapted from reference [10].

The experiments were planned and designed by the first author under the supervision of A. Kondrakov, J. Janek, and T. Brezesinski. All sample preparation, XRD, electrochemical measurements, and DEMS testing were carried out by the first author. TEM measurements were performed by P. Müller and analyzed in collaboration with the first author. Laboratory *in situ* XRD was conducted by L. Karger, and the data were analyzed by the first author. AE measurements were carried out by S.L. Dreyer and jointly analyzed with the first author. SEM imaging was performed by F. Ulusoy and R. Zhang, with data analysis completed by the first author. Synchrotron *in situ* XRD was conducted by both the first author and J. Lin at beamline P02.1, DESY, with support from V. Baran (data analysis was performed by the first author). Hard XAS was carried out by the first author and J. Lin at ID26, ESRF, with assistance from S. Vasala. Soft XAS was conducted by J. Lin at ID32, ESRF, with support from K. Kummer. The resulting data were analyzed by the first author. The manuscript was written by the first author and revised by all co-authors.

Reprinted with permission from S. An, L. Karger, P. Müller, J. Lin, S. Vasala, V. Baran, S.L. Dreyer, R. Zhang, F. Ulusoy, A. Kondrakov, J. Janek, T. Brezesinski, *Chem. Eng. J.* 2025, 509, 160939. Copyright © 2025 The Authors. Published by Elsevier B.V.

3. Results

Chemical Engineering Journal 509 (2025) 160939



Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej



Exploring calcium pillaring of O3-type $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ cathodes to advance Na-ion battery technology[☆]

Siyu An^a, Leonhard Karger^{a,✉}, Philipp Müller^{b,✉}, Jing Lin^a, Sami Vasala^c, Volodymyr Baran^d, Sören L. Dreyer^{a,✉}, Ruizhuo Zhang^a, Fatih Ulusoy^a, Aleksandr Kondrakov^{a,b,*}, Jürgen Janek^{a,e,*}, Torsten Brezesinski^{a,*}

^a Battery and Electrochemistry Laboratory (BELLA), Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

^b BASF SE, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany

^c European Synchrotron Radiation Facility (ESRF), avenue des Martyrs 71, 38000 Grenoble, France

^d Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany

^e Institute of Physical Chemistry & Center for Materials Research (ZfM/LaMa), Justus-Liebig-University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

ARTICLE INFO

Keywords:

Sodium-ion battery
Cathode active material
Layered oxide
Substitution
Pillaring effect
Electro-chemo-mechanical degradation

ABSTRACT

$\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NNTO), a promising sodium-ion cathode material, is capable of delivering high specific capacities but is compromised by structural degradation at high potentials and poor redox stability. Herein, we introduced varying amounts of Ca^{2+} as pillaring ions into the intercalation sites of NNTO to examine their effect on structure and electrochemical performance. Laboratory X-ray diffraction and charge/discharge testing identified $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) as the optimal composition in terms of interlayer spacing, rate capability, and cycling stability. Specifically, the capacity retention after 200 cycles improved from 27 to 48 %. To elucidate the role of Ca^{2+} , synchrotron X-ray diffraction was performed, revealing that CaNNTO undergoes only about 3 % volume change in the initial cycle, compared to about 30 % for NNTO. This reduced volume variation was confirmed by cross-sectional electron microscopy and acoustic emission measurements. Hard and soft X-ray absorption spectroscopy further indicated a more reversible nickel redox ($\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$) in CaNNTO, and differential electrochemical mass spectrometry demonstrated that Ca^{2+} incorporation helps suppress oxygen loss from the lattice, thereby directly stabilizing the cathode|electrolyte interface. Overall, calcium pillaring is found to effectively mitigate structural collapse and redox instabilities, making CaNNTO a more viable candidate for practical sodium-ion battery applications.

The significant challenges posed by the temporal and spatial discontinuities of renewable energy in practical applications require effective energy-storage devices that can be deployed at a mass scale. Since the 1990s, the development and commercialization of lithium-ion batteries (LIBs), pioneered by Sony Corp., significantly accelerated the progress of energy-storage technologies, which in turn has catalyzed the rapid growth of electric vehicles, including hybrid and plug-in hybrid vehicles [1–4]. However, the geographic distribution and relatively high costs of lithium resources have fueled the pursuit of a more sustainable solution. Sodium-ion batteries (SIBs) have therefore emerged as a promising next-generation technology, mainly because of their similarity to LIBs in many respects while using abundant sodium as the shuttling ion and also offering alternative concepts for cathode materials

[5–7].

Among the various sodium intercalation and insertion compounds, layered oxides have garnered significant attention due to their favorable electrochemical properties and similarity to high-capacity LiTMO_2 (e.g., $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, NCM or NMC) cathode materials employed in LIBs [6,8–11]. In contrast to LIBs, which are constrained by a limited selection of transition metal (TM) species, layered sodium-ion cathodes can be synthesized from a broader range of 3d TMs – from Ti to Cu [9–13]. This flexibility allows for the use of more abundant and sustainable elements, which can further reduce production costs.

O3 and P2 are known as two different thermodynamically stable structures of TM oxide cathode materials in SIBs. P2-type layered oxides have been widely studied due to their face-shared trigonal prismatic

[☆] This article is part of a special issue entitled: 'Electrochemical Energy' published in Chemical Engineering Journal.

* Corresponding authors.

E-mail addresses: aleksandr.kondrakov@basf.com (A. Kondrakov), juergen.janek@kit.edu (J. Janek), torsten.brezesinski@kit.edu (T. Brezesinski).

<https://doi.org/10.1016/j.cej.2025.160939>

Available online 23 February 2025

1385-8947/© 2025 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

3. Results

S. An et al.

Chemical Engineering Journal 509 (2025) 160939

alkali-metal sites, offering superior sodium transport properties compared to O3-type layered oxides [6,8,14,15]. O3-type oxides, by contrast, have a larger sodium inventory and are thus more suitable for full-cell applications. However, Na^+ extraction/intercalation from/into O3 phases typically leads to complex transitions and significant volume changes, which can induce microcracking and structural degradation [16–19]. Therefore, exploring strategies to improve the cycling performance of O3-type SIB cathode materials is of great importance.

A commonly employed strategy to enhance the performance of NaTMO_2 phases is elemental substitution. In our previous work, we successfully synthesized $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NNTO) by substitution of the nickel ions in NaNiO_2 (NNO) with 10 mol.% Ti^{4+} [20]. Although NNTO demonstrated significantly improved cycling stability and specific capacity compared to NNO, the prevailing $\text{O}^{2-} \rightarrow \text{O}^{1-}$ phase transition at potentials above 4.0 V vs. Na^+/Na led to volume collapse and irreversible lattice oxygen loss, which ultimately compromised its cyclability. To address these issues, we implemented a pillaring strategy aimed at stabilizing the cathode material through the substitution of intercalation sites with Ca^{2+} , which has been shown to be an effective method for enhancing the electrochemical performance of layered oxides [21–28]. In this study, NNTO was substituted with varying amounts of Ca^{2+} . By comparing results from Rietveld refinements of X-ray diffraction (XRD) data and electrochemical testing, we identified 2.5 mol.% as the optimal Ca^{2+} fraction. Subsequently, further physical and electrochemical characterization techniques were employed to gain insight into the stabilization mechanism.

To explore the impact of different calcium contents on the structure and performance of NNTO, as well as to determine the solubility limit, a relatively wide range of concentrations was selected for investigation. To substitute NNTO with Ca^{2+} , different amounts of $\text{Ca}(\text{OH})_2$ were added during the pre-calcination step to NaOH , $\text{Ni}(\text{OH})_2$, and TiO_2 , according to the stoichiometry of $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (with $x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045, \text{ and } 0.05$). The mixture was then heated at 300 °C for 10 h under O_2 atmosphere to facilitate dehydration and ensure good contact between the reactants. The resulting product was homogenized and calcined at 800 °C for 12 h to obtain the layered material (see Experimental section for more details).

Subsequently, all ten samples were subjected to XRD analysis. The respective patterns are presented in Fig. 1a, and phase fractions from Rietveld refinements are shown in Fig. S1 and further given in Table S1. It is evident that the main phase of all samples is of $R\bar{3}m$ symmetry, accompanied by varying fractions of an impurity phase with space group $Fm\bar{3}m$, which can be attributed to the presence of rock salt-like NiO and/or CaO. As the degree of substitution increases, the impurity

fraction also increases, although CaO is not clearly visible in Fig. 1a. In the study of NNTO, the NiO content increased with a decreasing Na/TM ratio, and this trend also applies to the $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ samples employed in the present work [20]. The introduction of Ca^{2+} results in a sodium-deficient state, making the formation of NiO energetically more favorable. Notably, a significant increase in phase fraction of CaO is observed when the Ca^{2+} fraction reaches 2.5 mol.%, suggesting that this may be the solubility limit in the alkali-metal (intercalation) sites of NNTO.

Fig. 1b shows the refined structural parameters for the different materials (see also Table S2). The lattice parameters a and c , as well as the unit-cell volume, seemingly reach a local maximum at 2.5 mol.%. Subsequently, they exhibit a decreasing trend up to a Ca^{2+} fraction of about 4.0 mol.%, after which they increase again. It is worth noting that when Ca^{2+} is introduced as a pillaring ion into P2-type oxides, the c -parameter typically shows a contraction due to the smaller ionic radius of calcium and higher charge compared to sodium [27,28]. However, for O3-type oxides reported in the literature, the results are more complex. For example, in the study of Yu et al. on $\text{Na}_{0.98}\text{Ca}_{0.01}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$, the c -parameter decreased upon Ca^{2+} introduction, due to enhanced $\text{O}^{2-}\text{--Ca}^{2+}\text{--O}^{2-}$ bonding in the layered lattice compared to $\text{O}^{2-}\text{--Na}^+\text{--O}^{2-}$. In contrast, for both $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{Na}_{0.9}\text{Ca}_{0.05}\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$, increases in c with Ca^{2+} substitution have been attributed to the formation of sodium vacancies [4,21,22,24]. The results of the current study align with the latter scenario, as the introduction of Ca^{2+} apparently leads to the generation of an equivalent number of sodium vacancies, thus resulting in an expansion of the interlayer spacing.

For the trend of an increasing a -parameter up to $x \approx 0.025$ in $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$, the following hypothesis can be proposed. With increasing Ca^{2+} concentration, the fraction of NiO impurity phase also increases, which may lead to the formation of vacancies at the nickel sites. To compensate for the charge imbalance, more nickel ions are likely to be oxidized to Ni^{3+} . Unlike $\text{O}^{2-}\text{--TM--O}^{2-}$, in the vacancy configuration, the lack of shielding against O–O repulsion by the transition metals results in an increase in a . Considering that Ni^{3+} has a smaller ionic radius than Ni^{2+} (0.56 Å vs. 0.69 Å), the expansion effect dominates, leading to the observed increase in a -parameter.

In the range of $0.025 < x < 0.04$, the lattice parameters exhibit a decreasing trend, which may be attributed to Ca^{2+} reaching its solubility limit, leading to the formation of more sodium vacancies. As shown in Fig. S1 and Table S1, the fraction of NiO impurity phase clearly increases within this range, leading to the oxidation of Ni^{2+} to Ni^{3+} for charge compensation. Consequently, the smaller ionic radius of Ca^{2+} (1.00 Å vs. 1.02 Å), along with its higher charge relative to Na^+ , leads to

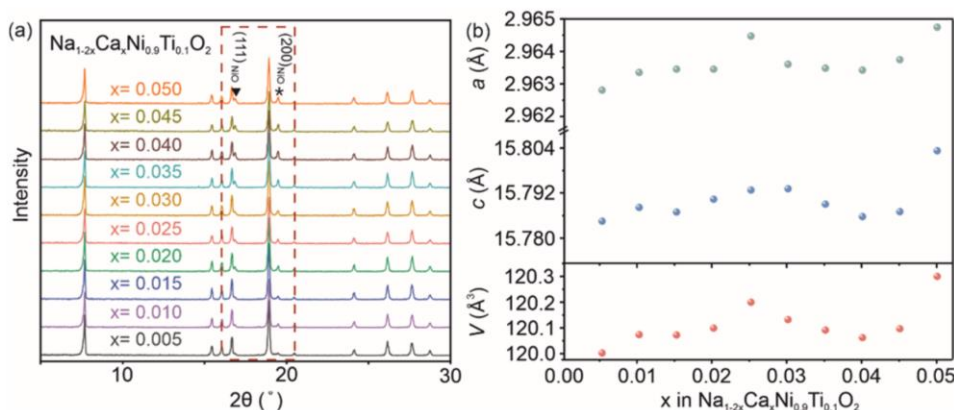


Fig. 1. (a) Laboratory XRD patterns collected from the $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ samples and (b) corresponding lattice parameters and unit-cell volumes from Rietveld refinement analyses.

3. Results

a contraction of the interlayer spacing, and the increasing concentration of Ni^{3+} contributes to the decrease in a -parameter, thus resulting in a decrease in unit-cell volume. However, for $x > 0.04$, we hypothesize that further reduction in sodium content in the $\text{O}^{2-}\text{--Na}^+\text{--O}^{2-}$ layers creates more vacancies, leading to the increase of O–O repulsion that outweighs the effects of Ca^{2+} . This results in an increase in lattice parameters a and c , as well as in unit-cell volume. A similar trend is also reflected in the interlayer spacing, as shown in Fig. S2 (see also Table S2). Therefore, we selected the five samples with fractions below the apparent solubility limit, as well as that containing 5.0 mol.% Ca^{2+} , for subsequent scanning electron microscopy (SEM) analysis and electrochemical testing.

Fig. S3 shows SEM images of the aforementioned materials. As can be seen from this data, the primary particle size of all five samples is somewhat larger than that of NNTO, indicating that the introduction of Ca^{2+} promotes grain growth. However, among them, there is no significant difference in either primary particle size or morphology. In contrast, the sample with 5.0 mol.% Ca^{2+} exhibits a distinct morphology, characterized by the presence of nanoscale particles, which may be attributed to the deposition of excess CaO on the free surface of the primary and secondary particles, corroborating our hypothesis that the solubility limit of Ca^{2+} in NNTO is reached at $x \approx 0.025$.

Electrochemical performance testing in the potential window of 2.0–4.2 V vs. Na^+/Na was conducted to investigate differences between these samples. Table S3 gives the results from inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements. Considering 2–3 mol.% sodium loss during calcination, all samples exhibit the expected stoichiometric ratios. The cyclability of SIB half-cells using the $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ cathodes is displayed in Fig. 2. It is noteworthy that, except for the 5.0 mol.% Ca^{2+} sample, the initial specific discharge capacities (see Fig. 2a) are similar. This indicates that similar amounts of Na^+ ions are de/intercalated at a rate of C/30, which in turn suggests that moderate Ca^{2+} substitution barely affects the capacity. The fact that the sample with a Ca^{2+} fraction of 5.0 mol.% delivers a lower specific capacity can be attributed to two main factors. First, as mentioned earlier, the formation of NiO impurities (see also Fig. S1) may lead to vacancies at the nickel sites and defects in the $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ lattice. For maintaining charge balance, both the originally present 0.1 mol of Ni^{2+} and 0.8 mol of Ni^{3+} are getting oxidized, thereby reducing the number of available redox-active species. Additionally, the presence of CaO on the particle surface may hinder sodium diffusion (higher cathode|electrolyte impedance, etc.), which would ultimately negatively affect cyclability.

Fig. 2b presents the long-term performance at C/2, after formation at C/30 for five cycles. The capacity retentions after 200 cycles are about 32, 36, 42, 44, 48, and 42 % for the $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ cathodes with $x = 0.005, 0.010, 0.015, 0.020, 0.025$, and 0.050, respectively, much improved compared to NNTO (about 26 %). This may be attributed to the pillaring effect of Ca^{2+} , which helps maintain the interlayer spacing at high states of charge or, in other words, at high degrees of

desodiation, thus preserving sodium diffusivity in the bulk phase. This is also reflected in the changes in overpotential during cycling. The overpotential decreases with increasing degree of Ca^{2+} substitution (up to $x = 0.025$), which agrees with the trend in capacity degradation seen in Fig. S4.

Furthermore, analysis of differential capacity curves (see Fig. S5) reveals that cells using the 2.5 mol.% Ca^{2+} sample exhibit a much lower polarization than those with NNTO, with the redox peaks being largely maintained after 200 cycles. In contrast, the curves for NNTO are virtually featureless from the 150th cycle onward. This indicates that Ca^{2+} incorporation not only facilitates sodium diffusion but also improves stability. The mechanisms underlying this behavior were probed, among others, using soft X-ray absorption spectroscopy (sXAS) and differential electrochemical mass spectrometry (DEMS).

Fig. 2c presents the rate-performance data. At the initial low rate of C/30, all samples are capable of delivering similar specific discharge capacities. However, with increasing rate, from C/10 to 2C, the $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ materials with $x = 0.010, 0.015, 0.020, 0.025$, and 0.050 reveal an overall better performance. Among them, those having Ca^{2+} fractions of 2.0 and 2.5 mol.% exhibit the best performance, characterized by higher specific capacities across various rates. NNTO and the sample containing 5.0 mol.% Ca^{2+} have inferior sodium diffusivity at rates $\geq \text{C}/2$, leading to increased overpotential and poor performance. Surprisingly, the nanoscale particles detected on the surface of the 5.0 mol.% Ca^{2+} sample do not strongly affect its rate capability. When the SIB half-cells are returned to cycling with C/30 rate, the $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ materials recover toward high discharge capacities.

To better illustrate the effect of calcium pillaring on kinetics, the differential capacity curves for cells using the 2.5 mol.% Ca^{2+} sample and NNTO at rates ranging from C/30 to 2C are compared in Fig. S6. The data clearly demonstrate the enhanced rate performance of NNTO enabled by Ca^{2+} substitution, with consistently lower overpotentials across all current densities.

In summary, the 2.5 mol.% Ca^{2+} sample exhibits favorable structural parameters, the best capacity retention, and good rate capability. Therefore, this sample was selected for in-depth analysis and is referred to as CaNNTO in the following.

Fig. 3a presents the XRD data for CaNNTO obtained using synchrotron radiation, with the refined lattice parameters and phase fractions given in Tables S4 and S5. The data are of better quality than those acquired by laboratory XRD, making them ideal for comparison with NNTO. Notably, the a - and c -parameters and the unit-cell volume are slightly larger compared to the laboratory XRD results, while the phase fractions are similar. The interslab distances, 5.2675 Å for CaNNTO and 5.2590 Å for NNTO, are indicated in Fig. 3b. As expected, calcium pillaring leads to an increase by about 0.16 %, which helps explain the superior cycling performance of CaNNTO.

Fig. 3c shows the results from energy-dispersive X-ray spectroscopy (EDS) analysis. The elemental maps indicate a relatively uniform

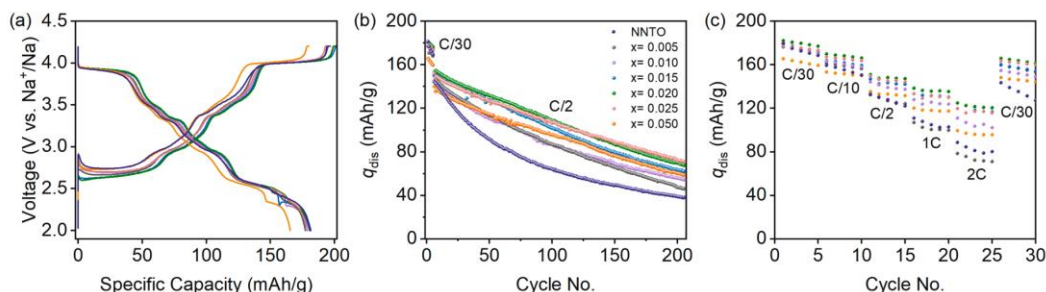


Fig. 2. (a) Voltage profiles at C/30, (b) long-term cycling performances at C/2, and (c) rate capabilities of $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ and NNTO cathodes in SIB half-cells.

3. Results

S. An et al.

Chemical Engineering Journal 509 (2025) 160939

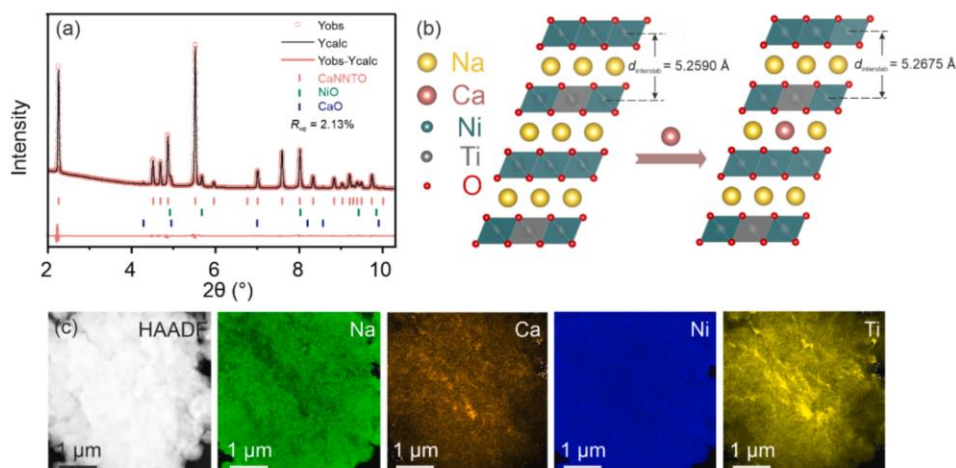


Fig. 3. (a) Rietveld refinement profile of synchrotron XRD data for CaNNTO. (b) Schematic representations of the crystal structures of CaNNTO and NNTO. The interlayer spacings are indicated. (c) STEM-EDS mapping of CaNNTO.

distribution of sodium and nickel. In contrast, some inhomogeneities are visible for calcium and titanium, increasing toward the center of the secondary particles. This finding is supported by the line scan results presented in Fig. S7. However, low-magnification EDS mapping (see Fig. S8) demonstrates a more uniform distribution of the respective elements. Aside from that, the measured stoichiometry (see Table S3) agrees well with the expected ratios, suggesting only local inhomogeneities in some of the particles. To address this issue in future studies, the co-precipitation method could be employed for achieving a more uniform distribution of calcium and titanium.

Figs. 4 and S9 present atomic-resolution scanning transmission electron microscopy (STEM) images of CaNNTO taken in high-angle annular dark-field (HAADF) mode. Specifically, top- and side-view

images are shown in Figs. 4a and S9a, clearly revealing the layered structure. This is confirmed by the fast Fourier transform (FFT) patterns extracted from the HAADF-STEM images (see Figs. 4b and S9b), indicating that the bulk structure is of well-ordered O3-type nature. Furthermore, the intensity line scans in Figs. 4c and S9c reveal lattice plane distances of 0.21 nm {104} and 0.26 nm {006}, respectively, which are in good agreement with the XRD results.

To provide a clearer comparison of the cyclability between CaNNTO and NNTO, their first-cycle voltage profile, long-term cycling performance, and rate capability are shown in Fig. S10. These aspects were already discussed above in detail, so they will not be elaborated further here.

To gain a better understanding of the structural evolution of

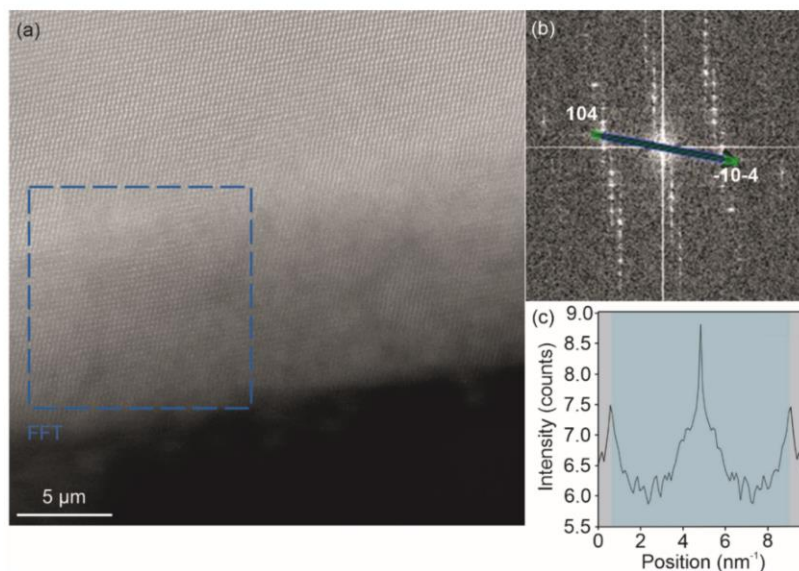


Fig. 4. (a) Atomic-resolution HAADF-STEM image of CaNNTO. (b) FFT pattern from the region indicated by the dashed blue box in (a). It should be noted that additional intensities are present along the vertical direction due to sample vibration artifacts. (c) Intensity line scan along the direction indicated by the arrow in (b). The distance of 0.21 nm corresponds to the {104} lattice planes of the layered phase. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results

S. An et al.

Chemical Engineering Journal 509 (2025) 160939

CaNNTO during charging and discharging, *operando* synchrotron XRD measurements were conducted on the SIB half-cells, which resulted in the 2D contour plot shown in Fig. 5a. Starting from the initial O3 phase, the extraction of Na^+ ions leads to increased O–O repulsion in the $\text{O}^{2-}\text{--Na}^+\text{--O}^{2-}$ layers, eventually resulting in the formation of a P3 phase at about 3.2 V in the first cycle at C/10 rate, as evidenced by the appearance of (003), (006), (101), (012), and (015) reflections. With further increase in state of charge, the P3 phase transitions toward an O'3 phase at about 4.0 V, which remains stable even at higher potentials, and then reverts back to P3 during discharge, ultimately returning to the initial O3 phase at low potentials. It is important to note that due to limitations during the synchrotron experiments, we were unable to capture the diffraction patterns at the final stages of discharge (resodiation). To address this, additional *operando* laboratory XRD measurements were conducted, and the results, as shown in Fig. S11, confirm the reversible phase transitions of $\text{O3} \rightarrow \text{P3}$ and $\text{P3} \rightarrow \text{O'3}$. Unlike for NNTO, no O'3 (or O''3) $\rightarrow$ O1 transition is observed at potentials > 4.0 V, indicating that calcium pillaring effectively prevents structural collapse in the sodium-deficient state of CaNNTO.

Fig. 5b presents the volume variation associated with the different phase transitions. For easier comparison, all unit-cell volumes were converted to cubic cell volumes. The data demonstrate that the maximum change during cycling is only about 3 % for CaNNTO, representing a significant improvement over NNTO (about 30 %) [20].

Subsequently, cross-sectional SEM imaging was employed to probe the chemo-mechanical behavior of CaNNTO and NNTO. Fig. 5c and e indicates that both materials in the pristine state exhibit relatively dense structures without any visible particle fracture. However, only the secondary particles of CaNNTO are well preserved after 200 cycles (see Fig. 5d and f), revealing hardly any signs of intergranular cracking. This observation can presumably be attributed to the minor “electrode breathing” during battery operation and further suggests that the introduction of Ca^{2+} into NNTO helps mitigate mechanical degradation.

Both X-ray absorption near-edge structure (XANES) spectroscopy at the Ni and Ti K-edges and sXAS at the Ni L_3 -edge were also performed to explore the redox behavior (reaction mechanism) during cycling. As

evident from Fig. S12a, the Ni K-edge of pristine CaNNTO is positioned between that of NiO and NiO , indicating that nickel adopts a mixed oxidation state of Ni^{2+} and Ni^{3+} . Fig. 6a illustrates the evolution of the Ni K-edge in the initial cycle at a rate of C/10. As charging progresses, the spectra gradually shift to higher energies by about 3 eV, which is indicative of nickel oxidation. During discharge, the spectra shift back to the original energy position. For a more intuitive comparison, Fig. S13a shows the spectra recorded at open circuit voltage (OCV) and in the fully charged (4.2 V) and discharged states (2.0 V). Fig. S12a further presents *ex situ* spectra recorded after 20 cycles. Notably, even after 20 cycles, the spectra return to their original energy position, indicating good reversibility. By contrast, XANES data collected from NNTO reveal irreversible redox processes already after 10 cycles, highlighting that calcium pillaring has a positive effect on nickel redox, too [20]. Oxidized Ni species may migrate to the octahedral and/or tetrahedral sites (Na vacancies) in the alkali-metal layer upon cycling, [29,30] providing an explanation as to why the nickel ions in NNTO do not reach their pristine energy states after discharge. In addition, nickel migration is likely to obstruct the sodium diffusion pathways (see also Figs. S5 and S6). However, the introduction of Ca^{2+} has been shown to suppress nickel migration, [30] thus ensuring fast ion transport. Aside from that, calcium pillaring helps stabilize the cathode|electrolyte interface and further enhances redox stability (see also section on DEMS below).

Figs. 6b and S13b illustrate the evolution of the Ti K-edge during the first cycle. Although slight shifts are seemingly apparent in the spectra, a comparison of first derivatives reveals no major changes, indicating that Ti^{4+} rather acts as a structural stabilizer than a redox-active ion [8,31,32]. This conclusion is further supported by the higher-quality (*ex situ*) XANES data presented in Fig. S12b. Note that a similar observation has been made in studies on $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ [32].

To examine the nickel oxidation state(s) in the bulk as well as on the surface of CaNNTO, sXAS measurements were performed *ex situ* in inverse partial fluorescence yield (IPFY) and total electron yield (TEY) modes. The Ni L_3 -spectra from Massel *et al.* displayed at the bottom of Fig. 6c were collected from compounds in which the nickel ions are in a relatively defined oxidation state, namely NiF_2 (Ni^{2+}), K_2NiF_6 (Ni^{3+}), and KNiO_6 (Ni^{4+}) [33]. Across all TEY spectra, a strong Ni^{2+} fingerprint is observed, with some indications of Ni^{3+} formation at the end of charge. This finding suggests the presence of NiO impurities on the particle surface, in agreement with the XRD results. The IPFY spectra with their much larger probing depth capture the redox behavior of the bulk material more accurately. In the pristine state, nickel is present as a mixture of Ni^{2+} and Ni^{3+} , consistent with the XANES results. With increasing desodiation, the intensity of the Ni^{2+} fingerprint strongly diminishes, while the characteristic fingerprints of Ni^{3+} and Ni^{4+} increase gradually. However, Ni^{3+} is clearly present at the end of charge (4.2 V vs. Na^+/Na), which is due to the fact that CaNNTO cannot be completely desodiated. With an actual initial specific charge capacity of 190 mAh/g, compared to the theoretical specific capacity of 226 mAh/g, about 19 % of Ni^{3+} per formula unit remain unoxidized. During discharge, CaNNTO undergoes a reversible change in intensity ratio between the high- and low-energy features, further supporting the conclusions derived from XANES analysis.

Non-destructive acoustic emission (AE) measurements were then conducted on the SIB half-cells using the CaNNTO and NNTO cathode materials. The advantage of AE testing is its ability to detect crack formation and propagation that may not be captured by XRD or other *operando* techniques [34,35]. Fig. 7 shows representative contour plots of acoustic activity (hit density) as a function of time and potential. Both CaNNTO and NNTO undergo phase transitions toward P3 and O'3 (or O''3) during cycling. However, the key differences are the absence of the $\text{O3} \rightarrow \text{O'3}$ transition at low potentials (about 2.5 V) and the $\text{O''3} \rightarrow \text{O1}$ transition at high potentials (> 4.0 V) in CaNNTO. These differences can also be noticed in the AE results. Because of the introduction of Ca^{2+} , the $\text{O}^{2-}\text{--Na}^+\text{--O}^{2-}$ slab spacing is well maintained in the sodium-deficient state, resulting in a maximum volume change of only about 3 %,

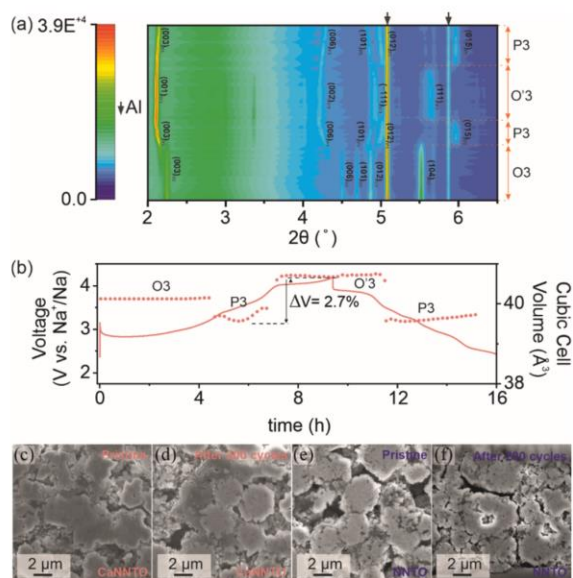


Fig. 5. (a) 2D contour plot of *operando* synchrotron XRD data collected from CaNNTO during the initial cycle at C/10 and (b) corresponding volume variation. (c–f) Cross-sectional SEM images of CaNNTO and NNTO in the pristine state and after 200 cycles at C/2.

3. Results

S. An et al.

Chemical Engineering Journal 509 (2025) 160939

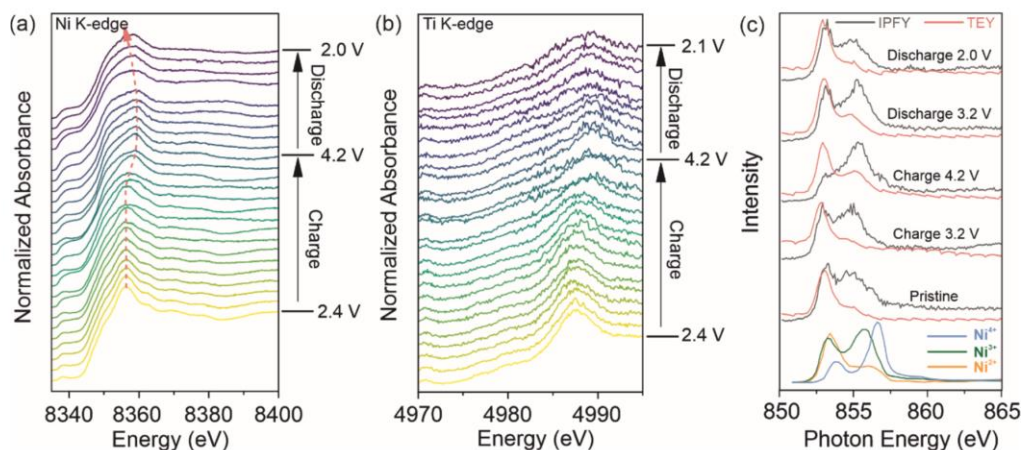


Fig. 6. (a) *In situ* XANES at the Ni K-edge and (b) Ti K-edge of CaNNTO during the initial cycle at C/10. (c) *Ex situ* Ni L₃-edge sXAS in IPFY and TEY modes of CaNNTO at different states of charge.

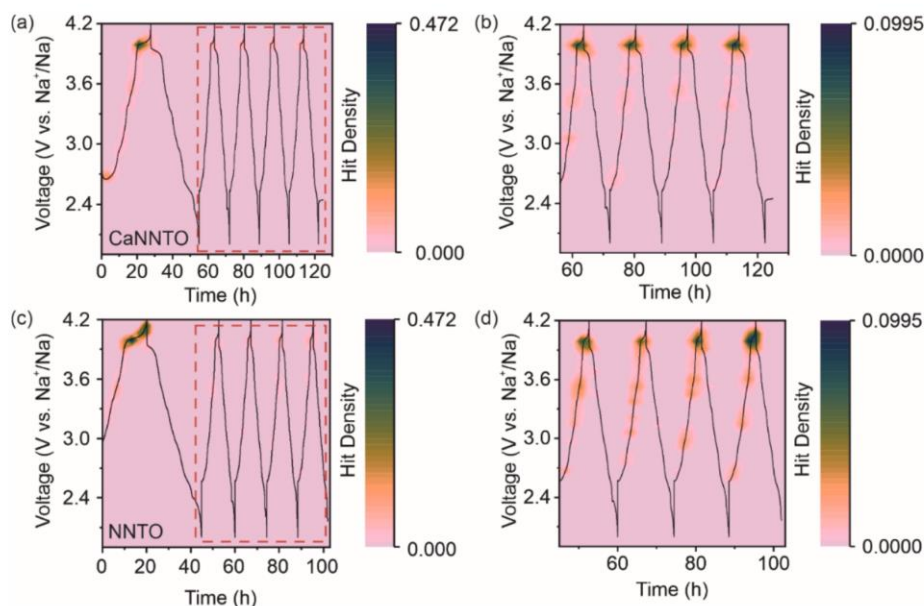


Fig. 7. Contour plots of acoustic activity (hit density) versus the time and potential for CaNNTO and NNTO. (a, c) Cycles 1–5 and (b, d) cycles 2–5.

compared to $> 4\%$ for NNTO prior to the phase transition toward O1. As a result, even though both cathodes exhibit similar signals, the acoustic activity of CaNNTO is significantly lower than that of NNTO. The latter material shows a much higher hit density around 4.0 V, with additional signals appearing at even higher potentials. This is due to the transition to the O1 phase near 4.0 V in NNTO, which is accompanied by a 30 % volume collapse. Although CaNNTO does not undergo a phase transition at that potential, the overall small volume change still generates some acoustic activity. Aside from that, the hit density for both CaNNTO (see Fig. 7a and b) and NNTO (see Fig. 7c and d) decreases with increasing cycle number. This behavior is consistent with recent reports on P2-type SIB cathode materials, where a similar trend has been observed [36].

Finally, *in situ* gas analysis via DEMS was utilized to monitor gas evolution in the SIB half-cells during cycling operation. The cells containing either CaNNTO or NNTO were cycled in a customized setup in

the same potential window of 2.0–4.2 V vs. Na⁺/Na at a rate of C/10 for two cycles while simultaneously tracking the outgassing (see Fig. 8a–h). Typically, lattice oxygen is oxidized and released as reactive oxygen, which then reacts with the electrolyte to produce CO₂. Therefore, O₂ ($m/z = 32$) is often only detected in trace amounts or in the form of CO₂ [37–41]. In the case of NNTO, anionic redox activity has been suggested in previous work, and indeed, trace amounts of oxygen (about 2.9 $\mu\text{mol/g}$) are detected, whereas CaNNTO exhibits no apparent O₂ evolution. This indicates that the introduction of Ca²⁺ possibly also reduces irreversible lattice oxygen loss. As can be seen, both NNTO and CaNNTO generate H₂ ($m/z = 2$) and CO₂ ($m/z = 44$), with onset potentials of about 3.6 V. However, CaNNTO produces significantly lower amounts during the first cycle, namely 28 $\mu\text{mol/g}$ of H₂ and 324 $\mu\text{mol/g}$ of CO₂, compared to 59 $\mu\text{mol/g}$ of H₂ and 428 $\mu\text{mol/g}$ of CO₂ for NNTO. The H₂ evolution presumably stems from the reduction of protic species

3. Results

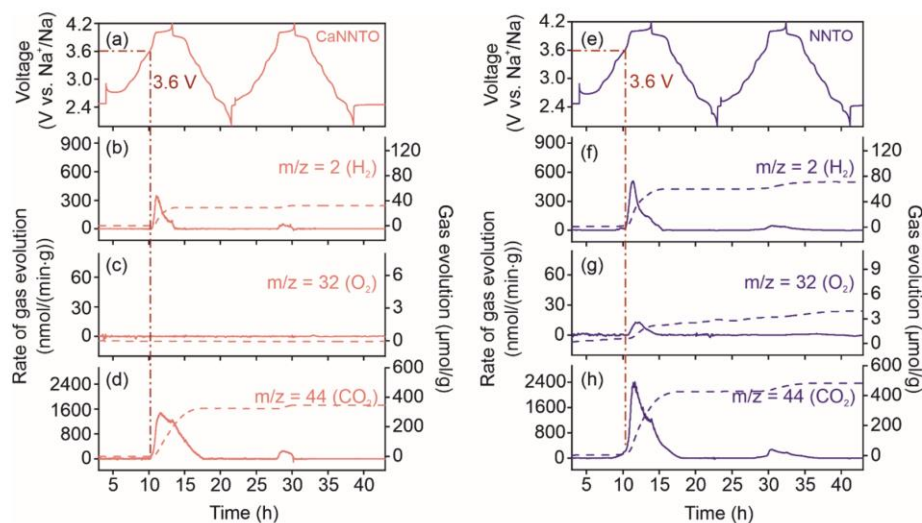


Fig. 8. (a, e) Voltage profiles at C/10 and corresponding time-resolved evolution rates (left y-axis) and cumulative amounts (right y-axis) of (b, f) H_2 , (c, g) O_2 , and (d, h) CO_2 measured by DEMS.

released by the oxidative electrolyte decomposition at the cathode side [42]. The lower gas evolution rates observed with CaNNTO can be attributed to several factors. One suggested contributing factor is differences in specific surface area. Another important aspect is the smaller volume variation of CaNNTO upon cycling, leading to less particle fracture and keeping the reactive surface area (available for side reactions with the electrolyte) at a minimum.

Fu *et al.* studied the effect of Ca^{2+} substitution in P2-type $\text{Na}_{0.67}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$ and found through density functional theory (DFT) calculations that it leads to an expansion of the O 2p and Ni 3d orbitals (to deeper energy levels), thereby stabilizing the electronic states of oxygen bonded to calcium. We assume that a similar effect may occur in CaNNTO [30]. Therefore, less outgassing is observed.

Irreversible lattice oxygen loss is typically accompanied by surface reconstruction, ultimately leading to the formation of a rock salt-like NiO phase, which negatively affects performance. As demonstrated by Mu *et al.*, surface nickel reduction may occur at all states of charge in sodium layered oxides [43]. Overall, the formation of NiO lowers the number of redox-active centers, causing a decrease in reversible specific capacity. Additionally, the loss of lattice oxygen may lead to a reduction in interlayer spacing. Overall, while mitigating irreversible oxygen loss, Ca^{2+} incorporation also helps maintain high redox activity and enhances the cathode|electrolyte stability.

Furthermore, O K-edge sXAS spectra were recorded in TEY mode to better understand the gassing behavior of CaNNTO. In Fig. S14, a peak characteristic of Na_2CO_3 (at about 534 eV) is clearly visible for both the pristine material and after charging to 3.2 V [33,44]. The presence of carbonates is also confirmed by Fourier-transform infrared (FT-IR) spectroscopy (see Fig. S15) [45]. However, as charging progresses to 4.2 V, the Na_2CO_3 peak vanishes, indicating that the surface carbonate species are electrochemically and/or chemically decomposed in the initial cycle. The former reaction typically produces CO_2 and O_2 , while the latter may yield CO_2 and H_2O [42]. Both can contribute to the total amount of evolved CO_2 mentioned above. The peak located at about 532 eV corresponds to NiO, which further supports the XRD and Ni L₃-edge sXAS findings. In the second cycle, both CaNNTO and NNTO continue to produce H_2 and CO_2 , suggesting that oxygen redox and electrolyte degradation still occur, but much less pronounced in the case of CaNNTO. It is noteworthy that the photon energy region below 534 eV typically represents the density of hole states above the Fermi level

[33]. However, since the FEY mode is surface-sensitive, the information that can be gained is biased by the carbonate signal and the hole density of NiO. Nevertheless, qualitatively, the peak around 528.5 eV increases strongly during charging, likely due to oxidation reactions involving nickel.

Finally, to gain insight into the structural stability of CaNNTO and NNTO, *ex situ* XRD measurements were conducted on the cathodes both in their pristine state and after 200 cycles (see Fig. S16). The data provide clear evidence that both materials initially exhibit an O3-type ($R\bar{3}m$) structure. However, upon cycling, they undergo a phase transition from O3 to O'3 ($C2/m$). The key distinction is that the (001) peak shift is less pronounced [relative to the (003) peak in the pristine state] for CaNNTO, indicating that it maintains a larger interslab distance during battery operation. The smaller peak shift further suggests that more Na^+ can be reinserted into CaNNTO, which agrees with its superior performance (see Fig. S10). Additionally, as highlighted by the dashed box in Fig. S16, some fraction of O3 phase is preserved after cycling, confirming the better structural stability of CaNNTO.

In summary, Ca^{2+} was successfully introduced into the alkali-metal (intercalation) sites of NNTO, serving as pillaring ions. Cathode materials with varying Ca^{2+} contents were systematically studied, and the optimal fraction was determined to be 2.5 mol.%. XRD indicated that Ca^{2+} substitution increases the interlayer distance. Furthermore, results from *operando* XRD and AE analyses demonstrated that the issue of volume collapse at high potentials is effectively addressed by the presence of Ca^{2+} . As a result, CaNNTO exhibits strongly improved cycling performance. sXAS and XANES measurements further confirmed the superior stability of CaNNTO, while DEMS indicated that the presence of Ca^{2+} also contributes to mitigating irreversible oxygen redox and to enhancing the cathode|electrolyte stability.

Experimental section

Synthesis. $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$, with x varying from 0.005 to 0.05, was prepared by a two-step solid-state reaction from $\text{Ni}(\text{OH})_2$ ($d_{50} \approx 4 \mu\text{m}$; BASF SE), nanoscale TiO_2 , $\text{Ca}(\text{OH})_2$ (Sigma-Aldrich), and NaOH (97 %; Sigma-Aldrich). For the initial pre-calcination, the reactants were homogenized under Ar atmosphere for 10 min using a laboratory blender (Kinematica). The precursor mixture was then heated in an alumina crucible under O_2 flow (7 L/h) in a tube furnace (Nabertherm

3. Results

P330) at 300 °C for 10 h, with 3 K/min heating and cooling rates. After cooling to room temperature, the intermediate product was homogenized again for 10 min, followed by transfer to an alumina crucible for the main calcination under O₂ flow (7 L/h) at 800 °C for 12 h with 3 K/min heating rate and 2 K/min cooling rate.

Battery Testing. Electrodes were prepared by casting an N-methylpyrrolidone (NMP) slurry with 94 wt.% cathode material, 3 wt.% Super C65 carbon additive, and 3 wt.% polyvinylidene difluoride (PVDF, Solef 5130; Solvay) binder onto an Al foil current collector of 0.03 mm thickness. The slurry was prepared by blending the different components using 20 wt.% additional NMP in a planetary centrifuge mixer (Thinky ARE-250) at 2000 and 400 rpm, each for 3 min. The slurry was then spread onto the Al foil using a Coatmaster 510 film applicator (Erichsen) at 5 mm/s. The resultant electrodes were dried overnight at 120 °C and under dynamic vacuum, followed by calendaring at 14 N/mm (Sumet Messtechnik). Finally, 13 mm-diameter electrodes with areal loadings of 9–12 mg/cm² were punched out and assembled into 2032-type coin half-cells in an Ar glovebox, using GF/D glass fiber and Na metal as separator and anode, respectively. 95 μ L of a 1 M solution of NaClO₄ in ethylene carbonate (EC), dimethyl carbonate (DMC), and propylene carbonate (PC), 1:1:1 by vol., containing 5 vol.% fluoroethylene carbonate (FEC) was used as electrolyte. In a variation, the electrolyte contained no FEC additive. Electrochemical testing was done in a potential range between 2.0 and 4.2 V vs. Na⁺/Na at various current rates (1C = 200 mA/g) and with a constant voltage step at 4.2 V, either for 30 min or until the current dropped below C/100, using a battery test system (MACCOR Inc.).

Laboratory X-ray Diffraction. XRD patterns were collected from the samples in 0.5 mm-diameter borosilicate capillaries with 0.01 mm wall thickness (Hilgenberg) in Debye-Scherrer geometry using a STOE STADI-P diffractometer equipped with a DECTRIS MYTHEN 1 K strip detector and a Mo anode (λ = 0.70926 Å, 50 kV, 40 mA). The instrumental contribution to peak broadening was determined by measuring a NIST 660c LaB₆ standard as line broadening reference.

Operando Laboratory X-ray Diffraction. Customized cells with Kapton windows in the center were cycled at C/20, utilizing a Gamry Interface 1000 potentiostat. XRD patterns were collected on the aforementioned STOE Stadi-P diffractometer between 5° and 37° 2 θ and with an acquisition time of about 10 min.

Operando Synchrotron X-ray Diffraction. Measurements were performed at the Powder Diffraction and Total Scattering beamline P02.1 at PETRA-III, DESY, Hamburg, Germany [46]. The same coin-cell design as that used in the *operando* laboratory XRD testing was employed, along with a customized holder, as detailed in the work by Herklotz *et al.* [47]. The wavelength was determined to be 0.20726 Å by refinement of a NIST 660c LaB₆ standard. The electrochemical cycling was started only after recording the first pattern to ensure proper characterization of the initial material. The cells were charged and discharged galvanostatically at C/10, and XRD data were collected using the VAREX 4343CT detector (150 $\times$ 150 μ m² pixel size, 2880 $\times$ 2880 pixel area; CsI scintillator directly deposited onto amorphous Si photo-diodes) with an acquisition time of 130 s per pattern. Detector calibration was accomplished using the LaB₆ 660c standard placed in the coin cell. Data integration was done using the pyFAI software, [48] and further analysis was carried out using the Rietveld method within FullProf Suite.

Scanning Electron Microscopy. SEM images were recorded at an accelerating voltage of 10 kV using a LEO-1530 microscope (Carl Zeiss AG) with a field emission source. An IB-19510CP polisher (JEOL Ltd.) with Ar source was utilized in the specimen preparation for cross-sectional imaging.

Transmission Electron Microscopy. Specimens for low-magnification TEM imaging and EDS analysis were embedded in a resin in an Ar glovebox to prevent degradation. They were cut by ultramicrotomy under dry conditions and directly investigated. During preparation, the samples were exposed to ambient air for about 10 min.

Specimens for atomic resolution analysis were prepared by Ga-focused ion beam milling using a Helios 5 CX DualBeam (Thermo Fisher Scientific) and directly transferred to the microscope to minimize exposure to ambient air. They were probed using a probe-corrected Themis Z (3.1; Thermo Fisher Scientific) in HAADF STEM mode at 300 kV. The chemical composition was examined using the integrated SuperX G2 EDS detector, and the data were analyzed using the Velox 3.10 software.

Inductively Coupled Plasma-Optical Emission Spectroscopy. The elemental composition was examined by ICP-OES using an ICAP 7600 DUO (Thermo Fisher Scientific). The samples (about 10 mg) were dissolved in an acid digester within a graphite furnace, specifically in a mixture of hydrochloric acid and nitric acid at 353 K for 4 h. Mass fractions were determined from three independent measurements. The digested samples were diluted for analysis using four calibration solutions and an internal standard (Sc). Carrier gas hot extraction was employed for determining the oxygen content using a TC600 (LECO Corp.) oxygen/nitrogen analyzer and the certified standard KED-1025 for calibration.

High-energy-resolution Fluorescence Detected X-ray Absorption Near-edge Structure Spectroscopy. HERFD XANES was performed at the ID26 high brilliance X-ray spectroscopy beamline at ESRF, Grenoble, France. This beamline is an undulator beamline of high intensity. *In situ* XAS data at the Ni and Ti K-edges of CaNNTO were collected from coin cells with Kapton windows with total acquisition times of 5 and 7.5 min, respectively. The coin cells were cycled at C/10 in the potential window of 2.0–4.2 V vs. Na⁺/Na and probed in HERFD mode using Si (620) for Ni and Ge (440) for Ti and a DECTRIS PILATUS 100 K detector system. For *ex situ* analysis, the pristine and cycled (two cycles at C/30 and 18 cycles at C/10) electrodes were sealed using Kapton tape in an Ar glovebox and then taken out for XANES measurements under ambient atmosphere. Multiple scans were collected for each sample to avoid beam damage. Energy calibration was done based on the first peak in the first derivative of $\mu(E)$ of Ni and Ti reference foils. All spectra were normalized and averaged (15 spectra) using the PyMca 5.9.2 software [49].

Acoustic Emission. AE signals were recorded using a differential wideband sensor (125–1000 kHz; MISTRAS Group) placed at the bottom of coin cells. The experimental setup comprised an in-line pre-amplifier and a data acquisition system (USB AE Node; MISTRAS Group). The pre-amplifier gain, analog filter, and sampling rate were set to 40 dB, 20–1000 kHz, and 5 MSPS, respectively. The sensor coupling was verified by the pencil-lead break test [20,36,50]. At least two samples were tested to ensure data reliability. Removal of background noise, using the AEwin software (MISTRAS Group), involved excluding hits of less than two counts and those with peak frequencies below 100 kHz and/or amplitudes of less than 27 dB.

Differential Electrochemical Mass Spectrometry. Customized DEMS half-cells with a 30 mm-diameter cathode of areal loading 10 mg/cm² were cycled at C/10. 700 μ L of a 1 M solution of NaClO₄ in EC, DMC, and PC, 1:1:1 by vol., containing 5 vol.% FEC served as electrolyte. During cycling, a constant stream of He carrier gas (purity 6.0, 2.5 mL/min) was passed through the cell, and the extracted gas mixture was analyzed via a mass spectrometer (OmniStar GSD 320, Pfeiffer Vacuum GmbH) [51,52].

Fourier-transform Infrared Spectroscopy. Spectra were acquired on an ALPHA FT-IR spectrometer (Bruker) equipped with a Ge crystal. The measurements were performed in an Ar glovebox.

Soft X-ray Absorption Spectroscopy. sXAS measurements were performed at the ID32 beamline at ESRF, Grenoble, France [53]. The Ni L-edge was examined in TEY and IPFY modes, with an energy range from 850 to 870 eV. O K-edge XAS measurements were performed in TEY mode, with an energy range from 520 to 570 eV. IPFY spectra were recorded using the recently commissioned XES spectrometer of the ID32 beamline.

3. Results

S. An et al.

Chemical Engineering Journal 509 (2025) 160939

CRedit authorship contribution statement

Siyu An: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **Leonhard Karger:** Writing – review & editing, Investigation, Formal analysis. **Philipp Müller:** Writing – review & editing, Investigation, Formal analysis. **Jing Lin:** Writing – review & editing, Investigation, Formal analysis. **Sami Vasala:** Writing – review & editing, Investigation, Formal analysis. **Volodymyr Baran:** Writing – review & editing, Investigation, Formal analysis. **Sören L. Dreyer:** Writing – review & editing, Investigation, Formal analysis. **Ruizhuo Zhang:** Writing – review & editing, Investigation, Formal analysis. **Fatih Ulusoy:** Writing – review & editing, Investigation, Formal analysis. **Aleksandr Kondrakov:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Jürgen Janek:** Writing – review & editing, Supervision, Funding acquisition. **Torsten Brezesinski:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was supported by BASF SE. The authors would like to thank Thomas Bergfeldt (KIT) and Yang Hu (Helmholtz Institute Ulm) and their teams for helping collect the ICP-OES and XANES data, respectively. J. L. acknowledges the Fonds der Chemischen Industrie (FCI) for financial support. We acknowledge the ESRF for provision of synchrotron radiation facilities under proposal nos. MA-6219 (DOI: 10.15151/ESRF-ES-1550923205) and MA-6348 (DOI: 10.15151/ESRF-ES-1830838169). We also would like to thank Sami Vasala and Kurt Kummer for assistance and support in using beamlines ID26 and ID32. We acknowledge DESY, a member of the Helmholtz Association (HGF), for the provision of experimental facilities. Parts of this research were carried out at PETRA III, using beamline P02.1. Beamtime was allocated for proposal I-20230867.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2025.160939>.

Data availability

Data will be made available on request.

References

- [1] B. Scrosati, J. Hassoun, Y.-K. Sun, Lithium-ion batteries. A look into the future, *Energy Environ. Sci.* 4 (2011) 3287–3295, <https://doi.org/10.1039/c1ee01388b>.
- [2] A. Manthiram, A reflection on lithium-ion battery cathode chemistry, *Nat. Commun.* 11 (2020) 1550, <https://doi.org/10.1038/s41467-020-15355-0>.
- [3] T. Yuan, S. Li, Y. Sun, J.-H. Wang, A.-J. Chen, Q. Zheng, Y. Zhang, L. Chen, G. Nam, H. Che, J. Yang, S. Zheng, Z.-F. Ma, M. Liu, A. High-Rate, Durable Cathode for Sodium-Ion Batteries: Sb-Doped O3-Type Ni/Mn-Based Layered Oxides, *ACS Nano* 16 (2022) 18058–18070, <https://doi.org/10.1021/acsnano.2c04702>.
- [4] T.-Y. Yu, J. Kim, J.-Y. Hwang, H. Kim, G. Han, H.-G. Jung, Y.-K. Sun, High-energy O3-Na_{1-2x}Ca_x[Ni_{0.5}Mn_{0.5}]O₂ cathodes for long-life sodium-ion batteries, *J. Mater. Chem. A* 8 (2020) 13776–13786, <https://doi.org/10.1039/d0ta04847j>.
- [5] K. Chayambuka, G. Mulder, D.L. Danilov, P.H.L. Notten, Sodium-Ion Battery Materials and Electrochemical Properties Reviewed, *Adv. Energy Mater.* 8 (2018) 1800079, <https://doi.org/10.1002/aenm.201800079>.
- [6] S. Li, Y. Sun, Y. Pang, S. Xia, T. Chen, H. Sun, S. Zheng, T. Yuan, Recent developments of layered transition metal oxide cathodes for sodium-ion batteries toward desired high performance, *Asia-Pac. J. Chem. Eng.* 17 (2022) e2762.
- [7] R.-M. Gao, Z.-J. Zheng, P.-F. Wang, C.-Y. Wang, H. Ye, F.-F. Cao, Recent advances and prospects of layered transition metal oxide cathodes for sodium-ion batteries,

- Energy Storage Mater.* 30 (2020) 9–26, <https://doi.org/10.1016/j.ensm.2020.04.040>.
- [8] P.-F. Wang, H.-R. Yao, X.-Y. Liu, J.-N. Zhang, L. Gu, X.-Q. Yu, Y.-X. Yin, Y.-G. Guo, Ti-Substituted NaNi_{0.5}Mn_{0.5-x}Ti_xO₂ Cathodes with Reversible O3–P3 Phase Transition for High-Performance Sodium-Ion Batteries, *Adv. Mater.* 29 (2017) 1700210, <https://doi.org/10.1002/adma.201700210>.
 - [9] S. Guo, H. Yu, P. Liu, Y. Ren, T. Zhang, M. Chen, M. Ishida, H. Zhou, High-performance symmetric sodium-ion batteries using a new, bipolar O3-type material, Na_{0.8}Ni_{0.4}Ti_{0.6}O₂, *Energy Environ. Sci.* 8 (2015) 1237–1244, <https://doi.org/10.1039/c4ee03361b>.
 - [10] P.-F. Wang, Y. You, Y.-X. Yin, Y.-S. Wang, L.-J. Wan, L. Gu, Y.-G. Guo, Suppressing the P2–O2 Phase Transition of Na_{0.67}Mn_{0.67}Ni_{0.33}O₂ by Magnesium Substitution for Improved Sodium-Ion Batteries, *Angew. Chem., Int. Ed.* 128 (2016) 7571–7575, <https://doi.org/10.1002/ange.201602202>.
 - [11] M.H. Han, E. Gonzalo, G. Singh, T. Rojo, A comprehensive review of sodium layered oxides: powerful cathodes for Na-ion batteries, *Energy Environ. Sci.* 8 (2015) 81–102, <https://doi.org/10.1039/c4ee03192j>.
 - [12] X. Li, Y. Wang, D. Wu, L. Liu, S.-H. Bo, G. Ceder, Jahn–Teller Assisted Na Diffusion for High Performance Na Ion Batteries, *Chem. Mater.* 28 (2016) 6575–6583, <https://doi.org/10.1021/acs.chemmater.6b02440>.
 - [13] S. Kim, X. Ma, S.P. Ong, G. Ceder, A comparison of destabilization mechanisms of the layered Na₂MO₂ and Li₂MO₂ compounds upon alkali de-intercalation, *Phys. Chem. Chem. Phys.* 14 (2012) 15571–15578, <https://doi.org/10.1039/c2cp43377j>.
 - [14] C. Delmas, C. Fouassier, P. Hagenmuller, Structural classification and properties of the layered oxides, *Physica b-c* 99 (1980) 81–85, [https://doi.org/10.1016/0378-4363\(80\)90214-4](https://doi.org/10.1016/0378-4363(80)90214-4).
 - [15] C. Delmas, J.-J. Braconnier, C. Fouassier, P. Hagenmuller, Electrochemical intercalation of sodium in Na₂CoO₂ bronzes, *Solid State Ion.* 3–4 (1981) 165–169, [https://doi.org/10.1016/0167-2738\(81\)90076-X](https://doi.org/10.1016/0167-2738(81)90076-X).
 - [16] J.-H. Kim, H.-H. Ryu, S.J. Kim, C.S. Yoon, Y.-K. Sun, Degradation Mechanism of Highly Ni-Rich Li[Ni_{1-x}Co_xMn_{1-x-y}]O₂ Cathodes with x > 0.9, *ACS Appl. Mater. Interfaces* 11 (2019) 30936–30942, <https://doi.org/10.1021/acsami.9b09754>.
 - [17] H.-H. Ryu, K.-J. Park, C.S. Yoon, Y.-K. Sun, Capacity Fading of Ni-Rich Li[Ni_{1-x}Co_xMn_{1-x-y}]O₂ (0.6 ≤ x ≤ 0.95) Cathodes for High-Energy-Density Lithium-Ion Batteries: Bulk or Surface Degradation? *Chem. Mater.* 30 (2018) 1155–1163, <https://doi.org/10.1021/acs.chemmater.7b05269>.
 - [18] G.W. Nam, N.-Y. Park, K.-J. Park, J. Yang, J. Liu, C.S. Yoon, Y.-K. Sun, Capacity Fading of Ni-Rich NCA Cathodes: Effect of Microcracking Extent, *ACS Energy Lett.* 4 (2019) 2995–3001, <https://doi.org/10.1021/acsenenergylett.9b02302>.
 - [19] T.-Y. Yu, H.-H. Ryu, G. Han, Y.-K. Sun, Understanding the Capacity Fading Mechanisms of O3-Type Na[Ni_{0.5}Mn_{0.5}]O₂ Cathode for Sodium-Ion Batteries, *Adv. Energy Mater.* 10 (2020) 2001609, <https://doi.org/10.1002/aenm.202001609>.
 - [20] S. An, L. Karger, S.L. Dreyer, Y. Hu, E. Barbosa, R. Zhang, L. Jing, M. Fichtner, A. Kondrakov, J. Janek, T. Brezesinski, Improving cycling performance of the NaNiO₂ cathode in sodium-ion batteries by titanium substitution, *Mater. Futures* 3 (2024) 035103, <https://doi.org/10.1088/2752-5724/ad5faa>.
 - [21] L. Sun, Y. Xie, X.-Z. Liao, H. Wang, G. Tan, Z. Chen, Y. Ren, J. Gim, W. Tang, Y.-S. He, K. Amine, Z.-F. Ma, Insight into Ca-Substitution Effects on O3-Type NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ Cathode Materials for Sodium-Ion Batteries Application, *Small* 14 (2018) 1704523, <https://doi.org/10.1002/sml.201704523>.
 - [22] Q. Tao, H. Ding, H. Zhao, J. Huang, B. Dai, J. Li, Ca-doped Na-site NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ as a high-performance cathode material for sodium ion batteries, *J. Alloys Compd.* 976 (2024) 172977, <https://doi.org/10.1016/j.jallcom.2023.172977>.
 - [23] M. Matsui, F. Mizukoshi, H. Hasegawa, N. Imanishi, Ca-substituted P3-type Na₂Ni_{1/3}Mn_{1/3}Co_{1/3}O₂ as a potential high voltage cathode active material for sodium-ion batteries, *J. Power Sources* 485 (2021) 229346, <https://doi.org/10.1016/j.jpowsour.2020.229346>.
 - [24] J. Zhou, Y. Zhang, W. Xu, X. Li, W. Zhou, W. Zhang, N. Wang, M. Liu, K. Dai, Enhancing electrochemical performance of sodium-ion batteries: Optimal Ca²⁺ doping in O3-Na_{0.33}Mn_{0.33}Fe_{0.33}O₂ layered oxide cathode materials, *J. Electroanal. Chem.* 969 (2024) 118541, <https://doi.org/10.1016/j.jelechem.2024.118541>.
 - [25] S.-B. Wei, Y.-J. He, Y. Tang, H.-W. Fu, J. Zhou, S.-Q. Liang, X.-X. Cao, A Ca-substituted air-stable layered oxide cathode material with facilitated phase transitions for high-performance Na-ion batteries, *Rare Met.* 43 (2024) 5701–5711, <https://doi.org/10.1007/s12598-024-02819-1>.
 - [26] L. Zhang, J. Deshmukh, H. Hijazi, Z. Ye, M.B. Johnson, A. George, J.R. Dahn, M. Metzger, Impact of Calcium on Air Stability of Na[Ni_{1/3}Fe_{1/3}Mn_{1/3}]O₂ Positive Electrode Material for Sodium-Ion Batteries, *J. Electrochem. Soc.* 170 (2023) 070514, <https://doi.org/10.1149/1945-7111/ace55a>.
 - [27] M. Matsui, F. Mizukoshi, N. Imanishi, Improved cycling performance of P2-type layered sodium cobalt oxide by calcium substitution, *J. Power Sources* 280 (2015) 205–209, <https://doi.org/10.1016/j.jpowsour.2015.01.044>.
 - [28] S.C. Han, H. Lim, J. Jeong, D. Ahn, W.B. Park, K.-S. Sohn, M. Pyo, Ca-doped Na₂CO₂ for improved cyclability in sodium ion batteries, *J. Power Sources* 277 (2015) 9–16, <https://doi.org/10.1016/j.jpowsour.2014.11.150>.
 - [29] L. Wang, J. Wang, X. Zhang, Y. Ren, P. Zuo, G. Yin, J. Wang, Unravelling the origin of irreversible capacity loss in NaNiO₂ for high voltage sodium ion batteries, *Nano Energy* 34 (2017) 215–223, <https://doi.org/10.1016/j.nanoen.2017.02.046>.
 - [30] H. Fu, Y.-P. Wang, G. Fan, S. Guo, X. Xie, X. Cao, B. Lu, M. Long, J. Zhou, S. Liang, Synergistic stability enhancement with magnesium and calcium ion substitution for Ni/Mn-based P2-type sodium-ion battery cathodes, *Chem. Sci.* 13 (2022) 726–736, <https://doi.org/10.1039/d1sc05715d>.

3. Results

- [31] K. Kubota, N. Fujitani, Y. Yoda, K. Kuroki, Y. Tokita, S. Komaba, Impact of Mg and Ti doping in O3 type $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ on reversibility and phase transition during electrochemical Na intercalation, *J. Mater. Chem. A* 9 (2021) 12830–12844, <https://doi.org/10.1039/D1TA01164B>.
- [32] S. Maletti, A. Sarapulova, A. Schökel, D. Mikhailova, Operando Studies on the $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ Cathode for Na-Ion Batteries: Elucidating Titanium as a Structure Stabilizer, *ACS Appl. Mater. Interfaces* 11 (2019) 33923–33930, <https://doi.org/10.1021/acsami.9b10352>.
- [33] F. Massel, B. Aktekin, Y.-S. Liu, J. Guo, M.H. Sorby, D. Brandell, R. Younesi, M. Hahlin, L.-C. Duda, The role of anionic processes in $\text{Li}_{1-x}\text{Ni}_{0.44}\text{Mn}_{1.56}\text{O}_4$ studied by resonant inelastic X-ray scattering, *Energy Adv.* 2 (2023) 375–384, <https://doi.org/10.1039/d2ya00321j>.
- [34] M. Enoki, H. Inaba, Y. Mizutani, N. Nakano, M. Ohtsu, Practical Acoustic Emission Testing (2016) Tokyo: Springer, doi:10.1007/978-4-431-55072-3.
- [35] S. Schweidler, M. Bianchini, P. Hartmann, T. Brezesinski, J. Janek, The Sound of Batteries: An Operando Acoustic Emission Study of the LiNiO_2 Cathode in Li-Ion Cells, *Batteries Supercaps* 3 (2020) 1021–1027, <https://doi.org/10.1002/batt.202000099>.
- [36] S.L. Dreyer, R. Zhang, J. Wang, A. Kondrakov, Q. Wang, T. Brezesinski, J. Janek, The effect of configurational entropy on acoustic emission of P2-type layered oxide cathodes for sodium-ion batteries, *J. Phys. Energy* 5 (2023) 035002, <https://doi.org/10.1088/2515-7655/acd41a>.
- [37] R. Jung, M. Metzger, F. Maglia, C. Stinner, H.A. Gasteiger, Oxygen Release and Its Effect on the Cycling Stability of $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) Cathode Materials for Li-Ion Batteries, *J. Electrochem. Soc.* 164 (2017) A1361–A1377, <https://doi.org/10.1149/2.0021707jes>.
- [38] J. Wandt, A.T.S. Freiberg, A. Ogródnik, H.A. Gasteiger, Singlet oxygen evolution from layered transition metal oxide cathode materials and its implications for lithium-ion batteries, *Mater. Today* 21 (2018) 825–833, <https://doi.org/10.1016/j.mattod.2018.03.037>.
- [39] R. Jung, M. Metzger, F. Maglia, C. Stinner, H.A. Gasteiger, Chemical versus Electrochemical Electrolyte Oxidation on NMC111, NMC622, NMC811, LNMO, and Conductive Carbon, *J. Phys. Chem. Lett.* 8 (2017) 4820–4825, <https://doi.org/10.1021/acs.jpclett.7b01927>.
- [40] J.K. Papp, N. Li, L.A. Kaufman, A.J. Naylor, R. Younesi, W. Tong, B.D. McCloskey, A comparison of high voltage outgassing of LiCoO_2 , LiNiO_2 , and Li_2MnO_3 layered Li-ion cathode materials, *Electrochim. Acta* 368 (2021) 137505, <https://doi.org/10.1016/j.electacta.2020.137505>.
- [41] S.L. Dreyer, A. Kondrakov, J. Janek, T. Brezesinski, In situ analysis of gas evolution in liquid- and solid-electrolyte-based batteries with current and next-generation cathode materials, *J. Mater. Res.* 37 (2022) 3146–3168, <https://doi.org/10.1557/s43578-022-00586-2>.
- [42] L. Zhang, C. Tzolakidou, S. Mariyappan, J.-M. Tarascon, S. Trabesinger, Unraveling gas evolution in sodium batteries by online electrochemical mass spectrometry, *Energy Storage Mater.* 42 (2021) 12–21, <https://doi.org/10.1016/j.ensm.2021.07.005>.
- [43] L. Mu, X. Feng, R. Kou, Y. Zhang, H. Guo, C. Tian, C.-J. Sun, X.-W. Du, D. Nordlund, H.L. Xin, F. Lin, Deciphering the Cathode-Electrolyte Interfacial Chemistry in Sodium Layered Cathode Materials, *Adv. Energy Mater.* 8 (2018) 1801975, <https://doi.org/10.1002/aenm.201801975>.
- [44] I. Moez, D. Susanto, W. Chang, H.-D. Lim, K.Y. Chung, Artificial cathode electrolyte interphase by functional additives toward long-life sodium-ion batteries, *Chem. Eng. J.* 425 (2021) 130547, <https://doi.org/10.1016/j.cej.2021.130547>.
- [45] T. Hatsukade, A. Schiele, P. Hartmann, T. Brezesinski, J. Janek, Origin of Carbon Dioxide Evolved during Cycling of Nickel-Rich Layered NCM Cathodes, *ACS Appl. Mater. Interfaces* 10 (2018) 38892–38899, <https://doi.org/10.1021/acsami.8b13158>.
- [46] A.-C. Dippel, H.-P. Liermann, J.T. Delitz, P. Walter, H. Schulte-Schrepping, O. H. Seeck, H. Franz, Beamline P02.1 at PETRA III for high-resolution and high-energy powder diffraction, *J. Synchrotron Radiat.* 22 (2015) 675–687, <https://doi.org/10.1107/S1600577515002222>.
- [47] M. Herklotz, J. Weiß, E. Ahrens, M. Yavuz, L. Mereacre, N. Kiziltas-Yavuz, C. Dräger, H. Ehrenberg, J. Eckert, F. Fauth, L. Giebler, M. Knapp, A novel high-throughput setup for in situ powder diffraction on coin cell batteries, *J. Appl. Cryst.* 49 (2016) 340–345, <https://doi.org/10.1107/S1600577515022165>.
- [48] G. Ashiotis, A. Deschilde, Z. Nawaz, J.P. Wright, D. Karkoulis, F.E. Picca, J. Kieffer, The fast azimuthal integration Python library: PyFAI, *J. Appl. Cryst.* 48 (2015) 510–519, <https://doi.org/10.1107/S1600577515004306>.
- [49] V.A. Solé, E. Papillon, M. Cotte, Ph. Walter, J. Susini, A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra, *Spectrochim. Acta Part B, At. Spectrosc.* 62 (2007) 63–68, <https://doi.org/10.1016/j.sab.2006.12.002>.
- [50] S. Schweidler, S.L. Dreyer, B. Breitung, T. Brezesinski, Operando acoustic emission monitoring of degradation processes in lithium-ion batteries with a high-entropy oxide anode, *Sci. Rep.* 11 (2021) 23381, <https://doi.org/10.1038/s41598-021-02685-2>.
- [51] B.B. Berkes, A. Jozwiuk, H. Sommer, T. Brezesinski, J. Janek, Simultaneous acquisition of differential electrochemical mass spectrometry and infrared spectroscopy data for in situ characterization of gas evolution reactions in lithium-ion batteries, *Electrochem. Commun.* 60 (2015) 64–69, <https://doi.org/10.1016/j.elecom.2015.08.002>.
- [52] B.B. Berkes, A. Jozwiuk, M. Vračar, H. Sommer, T. Brezesinski, J. Janek, Online Continuous Flow Differential Electrochemical Mass Spectrometry with a Realistic Battery Setup for High-Precision, Long-Term Cycling Tests, *Anal. Chem.* 87 (2015) 5878–5883, <https://doi.org/10.1021/acs.analchem.5b01237>.
- [53] N.B. Brookes, F. Yakhou-Harris, K. Kummer, A. Fondacaro, J.C. Cezar, D. Betto, E. Velez-Fort, A. Amorese, G. Ghiringhelli, L. Braicovich, R. Barrett, G. Berruyer, F. Cinciosi, L. Eybert, P. Marion, P. van der Linden, L. Zhang, The beamline ID32 at the ESRF for soft X-ray high energy resolution resonant inelastic X-ray scattering and polarisation dependent X-ray absorption spectroscopy, *Nucl. Instrum. Methods Phys. Res., Sect. A* 903 (2018) 175–192, <https://doi.org/10.1016/j.nima.2018.07.001>.

3.3. Publication III: Titanium Substitution to Advance the Prospect of NaMnO₂ Cathodes for Practical Application in Sodium-Ion Batteries

Publication III reports, for the first time, the successful synthesis of NMO using precipitated Mn₃O₄ as the manganese precursor. By introducing varying fractions of Ti⁴⁺ to partially substitute manganese, a series of Mn-rich layered O'3-type CAMs were obtained. Among them, NaMn_{0.9}Ti_{0.1}O₂ (NMTO) was identified as the optimal composition. The incorporation of Ti⁴⁺ not only stabilized the α -phase of NMO, but also effectively suppressed the formation of undesirable P2-type secondary phases. XRD and electrochemical analyses revealed that Ti⁴⁺ substitution also mitigates the JT distortion from Mn³⁺, thereby enhancing cycling stability and improving capacity retention. SEM imaging indicated a significant morphology transformation upon Ti⁴⁺ incorporation, shifting from polycrystalline to quasi-single-crystalline particles. *Post-mortem* SEM further confirmed that this morphology contributes to improved chemo-mechanical stability during cycling. *In situ* XRD demonstrated that NMTO effectively suppresses the formation of the O1 phase, thereby maintaining structural integrity and reducing degradation caused by interlayer collapse and volume changes. Notably, this work also presented the first comparative investigation of gas evolution in NMO and NMTO. DEMS revealed that Ti⁴⁺ incorporation helps effectively reduce irreversible lattice oxygen loss, contributing to enhanced interfacial and structural stability.

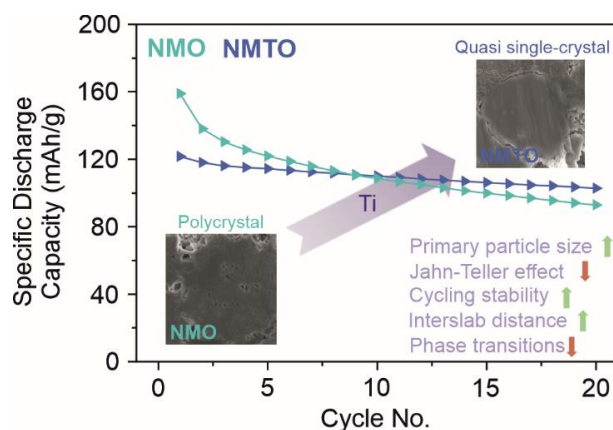


Figure 15. Table of contents graphic of publication III.

The experimental work was conceived and designed by the first author under the supervision of A. Kondrakov, J. Janek, and T. Brezesinski. The first author carried out all sample preparation, XRD characterization, electrochemical testing, and DEMS measurements, as well as the corresponding data analyses. SEM imaging was performed by F. Ulusoy and R. Zhang, with data interpretation by the first author. TEM measurements were conducted by R. Sahu and C. Kübel, and the data were jointly analyzed by the first author and R. Sahu. XANES experiments were carried out by the first author, J. Lin, and Y. Hu at beamline ID26, ESRF, with support from S. Vasala. The resulting data were processed by the first author. *In situ* XRD was performed by the first author and J. Lin at beamline P02.1, DESY, with support from V. Baran. Data analysis was completed by the first author. The manuscript was written by the first author and revised with input from all co-authors.

Titanium Substitution to Advance the Prospect of NaMnO₂ Cathodes for Practical Application in Sodium-Ion Batteries

Siyu An¹, Rajib Sahu^{1,2}, Ruizhuo Zhang¹, Fatih Ulusoy¹, Christian Kübel^{2,3}, Aleksandr Kondrakov^{1,4*}, Jürgen Janek^{1,5} and Torsten Brezesinski^{1*}

¹Battery and Electrochemistry Laboratory (BELLA), Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

²Karlsruhe Nano Micro Facility (KNMFi), Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

³Institute of Materials Research, Technical University Darmstadt (TUDa), Peter-Grünberg-Str. 2, 64287 Darmstadt, Germany

⁴BASF SE, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany

⁵Institute of Physical Chemistry & Center for Materials Research (ZfM/LaMa), Justus-Liebig-University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

*Corresponding authors: aleksandr.kondrakov@basf.com,
torsten.brezesinski@kit.edu

Abstract

O3-type layered oxides stand out among various Na-ion battery cathodes due to their unparalleled theoretical specific capacities. As a representative of low-cost, Mn-based cathode materials, α -NaMnO₂ (NMO) has attracted great attention. However, its practical application is hindered by poor reversibility. Compared to other O3 or O'3-type layered oxides, such as NaNiO₂, NMO undergoes multiple phase transitions, with the final O1 phase negatively affecting cycling performance. In this study, precipitated Mn₃O₄ was employed, to our knowledge for the first time, as a precursor in the synthesis of NMO, and the cathode material was systematically optimized through incremental improvement via titanium substitution. NaMn_{0.9}Ti_{0.1}O₂ was found to exhibit enhanced stability, with the capacity retention increasing from 42 to 70 % after 50 cycles, along with superior rate capability over NMO. This is due in part to titanium's role in facilitating primary particle (grain) growth and suppressing O1 phase formation, thereby preserving structural integrity and mitigating degradation caused by volume variations and irreversible oxygen redox during battery operation. This work not only provides valuable insights into the development of next-generation NMO cathodes but also advances their potential for practical applications.

Introduction

Electrochemical energy-storage devices (EESDs) are now widely employed across various applications, ranging from small-scale electronic products to large-scale electric vehicles and grid energy-storage systems, and have become indispensable in modern society. Lithium-ion batteries (LIBs), as the one of the most widely used type of EESD, have been extensively studied and applied.^{1–5} However, the uneven distribution of lithium resources and their increasing demand highlight the urgent need for alternative and more sustainable solutions to address these challenges.^{6–8}

Nowadays, attention has been re-directed toward various alkali-metal batteries.^{9–12} Among them, sodium-ion batteries (SIBs) offer exceptional advantages in terms of reversible capacity, kinetics, thermo-chemical stability, and ease of storage and transportation. Given the conceptual and functional similarities between SIBs and LIBs, the development and production of SIBs face fewer technical barriers.^{13–16} As a result, SIBs have re-gained attention, particularly in applications where energy density constraints related to volume or weight are less critical.

Among the cathode materials for SIBs, layered sodium transition-metal (TM) oxides (NaTMO_2) have emerged as the most promising candidates due to their high theoretical specific capacities. Unlike lithium in layered oxides, occupying only octahedral sites, Na^+ ions can reside on prismatic or octahedral sites coordinated by six oxygen ions, thus forming two primary structure types, namely P2 and O3.^{17–20} Mn-based layered oxides are particularly attractive for cost reasons (abundant raw material availability).^{8,21,22} Among them, the P2-type $\text{Na}_{0.7}\text{MnO}_2$ has been widely explored for its excellent rate performance. However, the intrinsic sodium deficiency of the P2 structure poses challenges for practical applications.^{23,24} To address this issue, researchers have proposed employing sacrificial salts, such as Na_2CO_3 , to compensate for sodium deficiencies.^{25,26} However, the large quantities of CO_2 generated by Na_2CO_3 during electrochemical cycling render this approach impractical.²⁶ Therefore, O3-type layered oxides with relatively higher sodium contents, such as NaMnO_2 (NMO), hold greater potential for practical deployment.^{2,27}

Stoichiometric NMO exists in two polymorphs, the low-temperature alpha phase and the high-temperature beta phase. The alpha phase undergoes structural distortion, from $R\bar{3}m$ to monoclinic $C2/m$ symmetry, due to the Jahn-Teller effect of high-spin Mn^{3+} , forming an O'3-type structure. By contrast, the beta phase adopts a zigzag structure.^{28–30} Density functional theory (DFT) calculations by Shishkin *et al.* indicate that the formation energies of both phases are nearly identical, making it challenging to obtain a single-phase material.²⁹

Regarding cycling performance, Ma *et al.* demonstrated a reversible specific capacity of about 200 mAh/g for α -NMO in 2011.² Further work by Manzi *et al.* on both the high- and low-temperature phases revealed that α -NMO exhibits better reversibility for the sodium insertion/extraction reactions.²⁸ Consequently, the α -phase, which is easier to synthesize with high purity, has more potential to be studied. Nevertheless, the poor cyclability of α -NMO remains a critical issue. To investigate the underlying reasons,

Kubota *et al.* carried out *in situ* and *ex situ* X-ray diffraction (XRD) analyses on α -NMO and identified the formation of an O'3-O1 (mixed) phase with reduced interlayer distance at higher potentials. Based on the phase evolution, further studies on the potential window revealed that a narrower range of 2–3.476 V, compared to 2–3.8 V, increases stability by preventing the formation of the O'3-O1 phase. Additionally, cycling in a wider range of 2–3.8 V was found to lead to (irreversible) changes in crystallinity, which can further compromise performance.³⁰ Thus, suppressing or avoiding O1 phase formation is critical to enhancing stability.

One common strategy to suppress phase transitions is the substitution of TM ions in NaTMO₂.^{31–33} The same holds for LIB cathode materials. For NMO, TM substitution not only helps suppress phase transitions but also to stabilize specific polymorphs. Shishkin *et al.* investigated the substitution of Mn in NaMnO₂ with 12 different elements and found that titanium and copper are able to effectively stabilize α -NMO and β -NMO, respectively.²⁹ However, systematic studies on Ti-substituted, Mn-rich O'3-type NMO are lacking.

In the present work, we substituted Mn in NMO with varying fractions of Ti⁴⁺ and systematically investigated the structure, morphology, and electrochemical performance of the respective cathode materials. Ultimately, we identified NaMn_{0.9}Ti_{0.1}O₂ (NMTO) as the optimal composition. Results from XRD and differential electrochemical mass spectrometry (DEMS) measurements demonstrate that the introduction of titanium successfully suppresses the formation of the O1 phase at high potentials and partially inhibits irreversible lattice oxygen redox. Furthermore, it facilitates grain growth and coarsening during calcination, resulting in the formation of quasi single-crystal particles with enhanced cycling stability.

Results and Discussion

In contrast to most studies that typically employ Mn₂O₃ as a precursor in the synthesis, Mn₃O₄ precipitated from solution (see scanning electron microscopy [SEM] image and XRD pattern in **Figure S1**, Supporting Information) was used here to improve the electrode's tap density.^{2,28–30,34} First, NMO was prepared to validate the feasibility of the experimental conditions for the new precursor. To this end, Mn₃O₄ and Na₂CO₃ (5 mol.% excess) were thoroughly mixed, followed by calcination at 800 °C for 12 h under air. Finally, the material was quenched to room temperature, yielding NMO. The XRD pattern collected from the as-synthesized NMO is presented in **Figure 1a**. Rietveld analysis confirmed that the material is single phase and crystallizes in a monoclinic (*C2/m*) structure, with lattice parameters $a = 5.66565$ Å, $b = 2.86019$ Å, $c = 5.80334$ Å, and $\beta = 113.174^\circ$ (**Table S1**, Supporting Information) in agreement with reports available in the literature.^{2,30} An SEM image of NMO is shown in **Figure 1b**, revealing that the primary particles exhibit a rod-like shape and the secondary particles maintain a well-defined spherical morphology.

3. Results

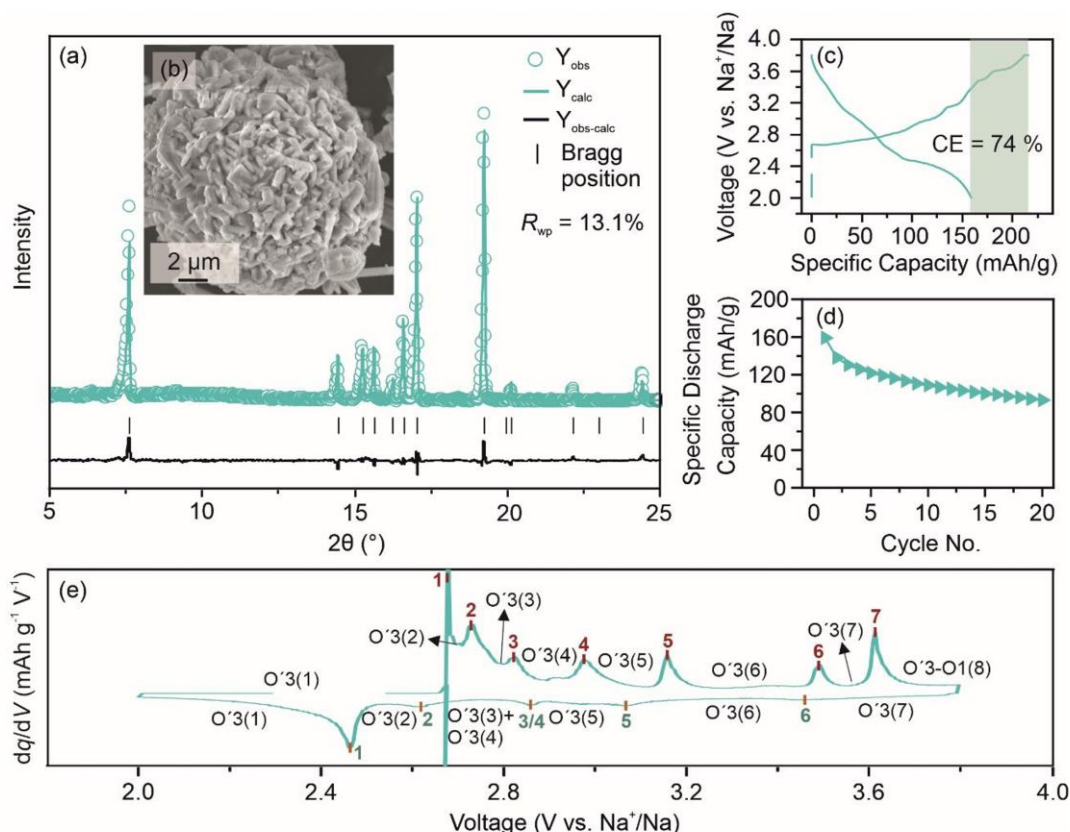


Figure 1. (a) Rietveld refinement profile, (b) SEM image, (c) first-cycle voltage profile, (d) cycling performance at C/10 rate, and (e) first-cycle differential capacity curve of NaMnO₂ (NMO). Peaks for the oxidation process (1–7) are marked in red and those for the reduction process (1–6) in green in panel (e).

The first-cycle voltage profile of NMO is displayed in **Figure 1c**. The initial specific charge and discharge capacities reached 216 and 160 mAh/g, respectively, corresponding to a Coulomb efficiency of 74 % (2.0–3.8 V vs. Na⁺/Na, C/10). Notably, the first discharge capacity was slightly lower than previously reported.^{30,35} This discrepancy may be attributed to the larger size of primary particles, which may negatively affect sodium diffusion. However, the electrolyte used may also have an impact.³⁶ It should be noted that large primary particles may contribute to a less distinct voltage profile, due to larger inhomogeneities.³⁰

The cycling stability over 20 cycles (58 % capacity retention) and the first-cycle differential capacity (dq/dV) curve are shown in **Figures 1d** and **e**, respectively. Notably, the dq/dV data successfully reproduce the seven oxidation peaks and five reduction peaks reported in the literature. Both O'3(3) and O'3(5) correspond to triclinic phases, while the remaining six phases are monoclinic. Although the third oxidation peak does not have a (distinct) respective reduction peak, Komaba and co-workers observed the presence of some O'3(3) at the O'3(4) position in **Figure 1e**. Therefore, the XRD and electrochemical results are highly consistent with previous reports,

confirming the successful synthesis of single-phase NMO using precipitated Mn_3O_4 as precursor.

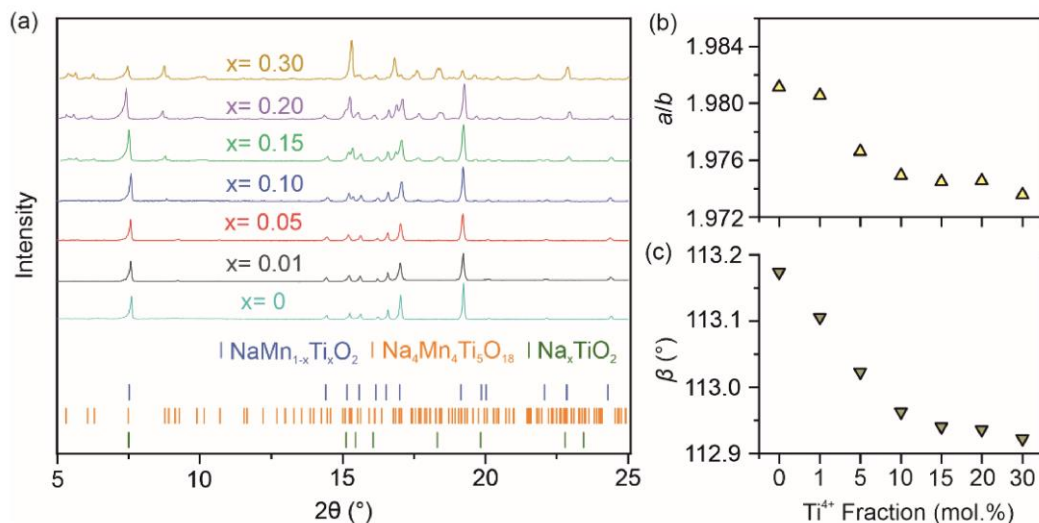


Figure 2. (a) XRD patterns of NaMnO_2 (NMO) and $\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$, with $x = 0.01, 0.05, 0.10, 0.15, 0.20$, and 0.30 . Corresponding (b) a/b and (c) β values from Rietveld analyses.

Ti^{4+} -substituted NMO ($\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$) was prepared under identical conditions by substituting manganese with titanium. In this study, six different titanium fractions, namely 1, 5, 10, 15, 20, and 30 mol.%, were systematically investigated to explore the effect that Ti^{4+} substitution has both on the structure and on the cycling performance of NMO. **Figure 2a** presents the XRD patterns for the different samples prepared, and the phase fractions from Rietveld analyses are given in **Table S2** (Supporting Information). With increasing degree of substitution, impurity phases, such as $\text{Na}_4\text{Mn}_4\text{Ti}_5\text{O}_{18}$ (*Pbam*) or Na_xTiO_2 (*R-3m*), start to appear (at about 5 mol.% Ti^{4+}). When the titanium fraction reaches 30 mol.%, the target phase $\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$ (*C2/m*) only accounts for 10.4 wt.%. These results indicate that moderate substitution levels effectively stabilize the α -NMO, while excessive Ti^{4+} incorporation promotes the formation of secondary phases.³⁴

Table S1 (Supporting Information) summarizes the structural parameters derived from Rietveld refinements, and **Figures 2b** and **c** display the trends in a/b ratio and β with increasing titanium fraction. The a/b ratio is commonly used to quantify the degree of in-plane distortion in layered materials, where an undistorted hexagonal structure has a value of $\sqrt{3}$.^{30,33} As can be seen from **Figure 2b**, the a/b ratio decreases with increasing degree of substitution and stabilizes around 10 mol.% Ti^{4+} . A similar trend is observed for β in **Figure 2c**. These results indicate that the Jahn-Teller distortion caused by high-spin Mn^{3+} is effectively mitigated. A possible reason for this is that the introduction of Ti^{4+} induces the formation of an equivalent amount of Mn^{2+} , a phenomenon we also observed in a previous study on $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$.³³ The plateau in the a/b and β data beyond 10 mol.% Ti^{4+} is likely due to the solubility limit being reached.

Table S3 presents the inductively coupled plasma-optical emission spectroscopy (ICP-OES) results for $\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$ with $x = 0, 0.01, 0.05, \text{ and } 0.10$, indicating that all samples had the intended composition with minimal sodium losses.

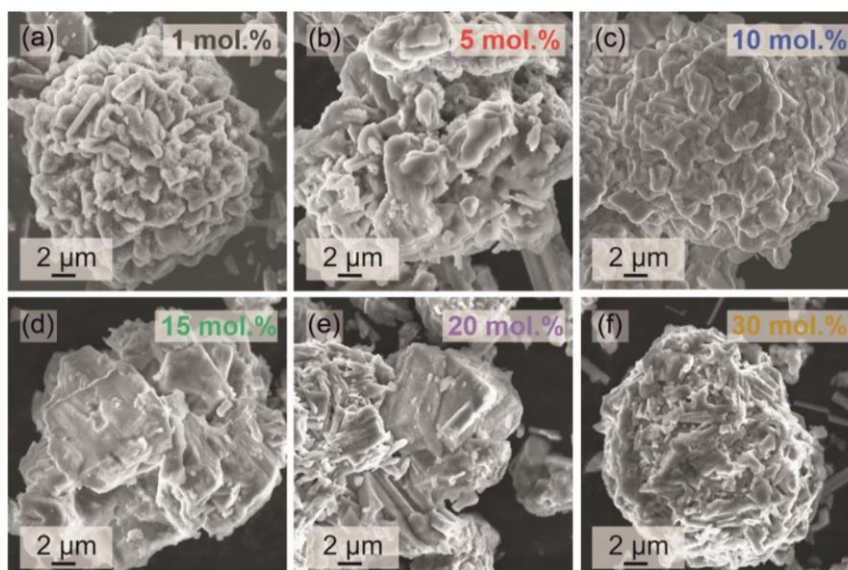


Figure 3. (a–f) SEM images of $\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$, with $x = 0.01, 0.05, 0.10, 0.15, 0.20, \text{ and } 0.30$.

Figures 3a–f show SEM images of the $\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$ samples. All of them retained, to some extent, their secondary particle morphology. However, significant differences were observed in the size and morphology of primary particles (grains). With increasing titanium fraction, the grains grow much larger, evolving from elongated shapes into quasi single-crystal particles. Similar observations have been made for layered oxide LIBs cathodes. For example, cobalt doping tends to increase the particle size, whereas selenium or tungsten doping can suppress grain growth of lithium transition-metal oxides.^{37–39} This can be attributed to the ability of different dopants/substituents to affect the surface energy, thereby regulating the grain growth orientation during synthesis.³⁷ Note that in **Figures 3e** and **f**, the smaller particles present on the surface are likely impurity phases, such as $\text{Na}_4\text{Mn}_4\text{Ti}_5\text{O}_{18}$ or Na_xTiO_2 . Overall, these findings demonstrate that Ti^{4+} substitution has a profound effect on both the morphology and size of NMO grains.

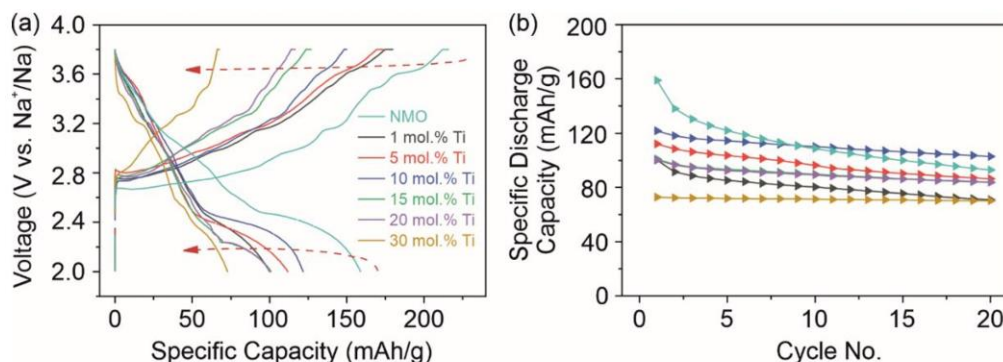


Figure 4. (a) First-cycle voltage profiles of half-cells using either NaMnO₂ (NMO) or NaMn_{1-x}Ti_xO₂, with $x = 0.01, 0.05, 0.10, 0.15, 0.20$, and 0.30 and (b) corresponding cycling performances at C/10 rate.

Subsequently, the electrochemical performance of the NaMn_{1-x}Ti_xO₂ samples was evaluated to further investigate the influence of Ti⁴⁺ substitution on NMO. **Figure 4a** presents the first-cycle voltage profiles, showing that the specific charge capacity decreases with increasing titanium fraction. Due to the differences in phase purity, further discussion needs to be divided into the following cases. For ≤ 10 mol.% Ti⁴⁺, two potential reasons may explain the observed capacity decline. First, the larger primary particles may slow down sodium diffusion. Second, varying degrees of lattice distortion, as indicated by the changes in a/b ratio, may affect the Na⁺ extraction. For example, previous studies have shown that P'2-Na_xMnO₂ (with lattice distortion) achieves higher reversible capacities than pristine P2-Na_xMnO₂.²³ For > 10 mol.% Ti⁴⁺, the capacity is strongly determined by the impurity phase Na₄Mn₄Ti₅O₁₈, which itself is electrochemically active (with a smaller contribution from NaMn_{1-x}Ti_xO₂).

As can be seen from **Figure 4a** and **Figure S2** (Supporting Information), the first-cycle specific discharge capacity exhibits a more intriguing trend. It decreased gradually upon exceeding 10 mol.% Ti⁴⁺ due to the increasing fraction of impurity phases. For ≤ 10 mol.% Ti⁴⁺, the specific discharge capacity first decreased and then increased with increasing titanium fraction, reaching a local maximum around 10 mol.%. Interestingly, the sample containing 1 mol.% Ti⁴⁺ delivered the lowest capacity, which is likely related to the primary particle size. However, the 5 and 10 mol.% Ti⁴⁺ samples with even larger grains exhibited superior discharge capacities. This is also evident from the dq/dV plots presented in **Figure S3** (Supporting Information). It is worth noting that due to the large polarization in the initial cycle, the differential capacity curves for the second cycle are presented instead. With increasing titanium fraction, additional peaks emerged, especially so for the sample containing 10 mol.% Ti⁴⁺. Guo *et al.* reported that Na₄Mn₄Ti₅O₁₈ shows redox peaks at 3.4/3.3 and 2.4/2.3 V vs. Na⁺/Na, indicating that it is electrochemically active in the potential range of 2.0–3.8 V employed here for cycling of the NaMn_{1-x}Ti_xO₂ cathodes.⁴⁰ Nevertheless, comparative analysis revealed that the redox peaks of Na₄Mn₄Ti₅O₁₈ do not correspond to any of the features observed in **Figure S3** (Supporting Information). Furthermore, the phase fraction of Na₄Mn₄Ti₅O₁₈ only accounted for 4.1 wt.% (**Table S2**, Supporting Information), making

3. Results

it unlikely to significantly contribute to the overall capacity. This suggests that the newly observed peaks mainly originate from the $\text{NaMn}_{0.9}\text{Ti}_{0.1}\text{O}_2$ itself.

The *ex situ* Ti K-edge X-ray absorption near-edge structure spectroscopy (XANES) data in **Figure S4** (Supporting Information) provide further insights. For the 10 mol.% Ti^{4+} sample, the energy positions during charging and discharging remained unaltered upon electrochemical cycling, thus indicating that titanium only serves as a structural stabilizer without exhibiting redox activity. This can imply that the above observations may be due to variations in local manganese environment and/or sodium/vacancy ordering. Indeed, previous studies on NMO have revealed the presence of $\text{Mn}^{3+/4+}$ ordering and Na^+ /vacancy ordering.²⁷ Therefore, the additional peaks in the dq/dV curves seem to directly result from the Ti^{4+} incorporation, affecting the manganese valence-state distribution and leading to distinct $\text{Mn}^{2+/3+/4+}$ ordering and/or Na^+ /vacancy ordering. Of note, as expected, similar peak patterns were observed in samples with higher titanium fractions (**Figure S3**, Supporting Information).

Figure 4b depicts the cycling stability of the $\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$ samples. The sample with 10 mol.% Ti^{4+} exhibited the best overall performance, maintaining a high specific discharge capacity of > 100 mAh/g and achieving a capacity retention of 85 % after 20 cycles, compared to only 58 % observed for NMO. Based on these results, further investigations focused on the 10 mol.% Ti^{4+} sample, which will be referred to as NMTO in subsequent discussions.

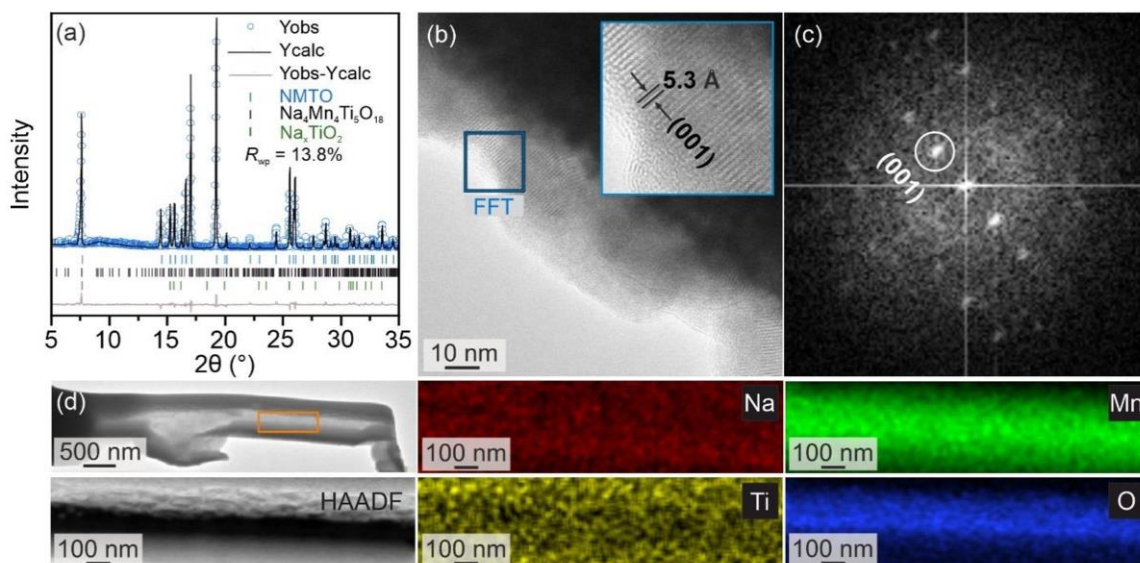


Figure 5. (a) Rietveld refinement profile, (b) HRTEM image, and (c) FFT pattern from the region highlighted by the blue box in (b) of $\text{NaMn}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NMTO). (d) Corresponding STEM EDS mapping analysis.

XRD and transmission electron microscopy (TEM) measurements were conducted on NMTO to examine its structural and chemical characteristics in some more detail (**Figures 5a–d**). **Figure 5b** presents a high-resolution TEM (HRTEM) image, clearly revealing its layered nature. Fast Fourier transformation (FFT) analysis of the region

3. Results

highlighted in **Figure 5b** identified characteristic lattice planes of spacing 5.3 Å (**Figure 5c**), consistent with the results from Rietveld refinement of XRD data. **Figure 5d** shows scanning TEM (STEM) images of a focused ion beam (FIB)-cut cross-section of an NMTO particle and corresponding energy dispersive X-ray spectroscopy (EDS) mapping data, with the latter suggesting homogeneous distribution of elements across the sample. However, we note that non-uniformities in composition were also observed (**Figure S5**, Supporting Information). This result agrees with the presence of Na_xTiO_2 as an impurity phase (**Figure 5a**). Nevertheless, due to the similar elemental composition of $\text{Na}_4\text{Mn}_4\text{Ti}_5\text{O}_{18}$ and the NMTO phase, distinguishing their spatial distribution via EDS alone remains challenging.

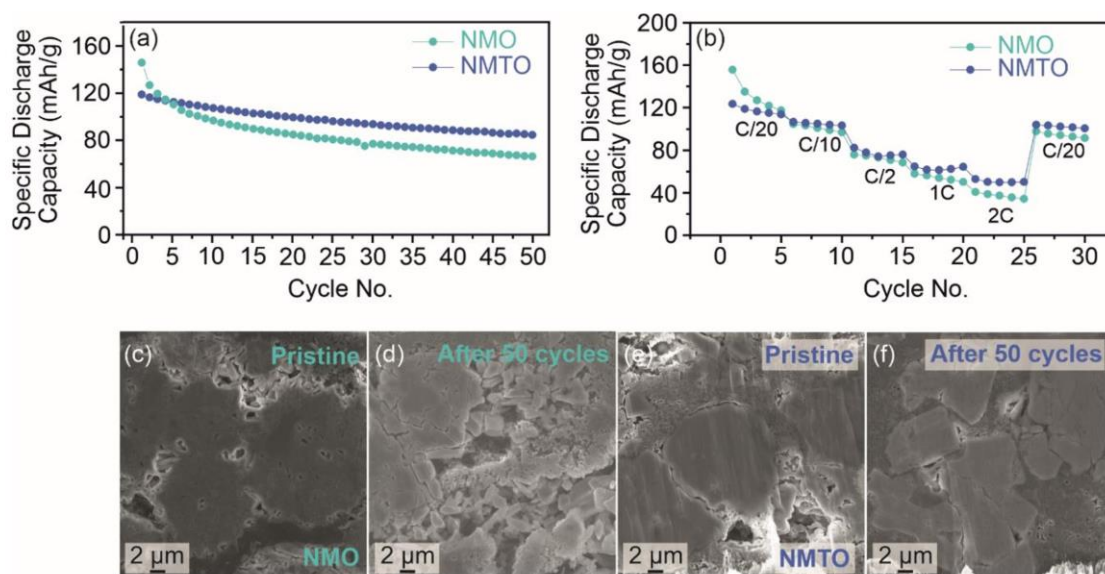


Figure 6. Comparisons of (a) cycling performance at C/10 and (b) rate capability of NaMnO_2 (NMO) and $\text{NaMn}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NMTO). Cross-sectional SEM images of (c, e) pristine and (d, f) cycled cathodes (50 cycles).

The cycling performance of the NMO and NMTO cathodes over 50 cycles is shown in **Figure 6a**. In the case of NMTO, the capacity retention was about 70 %, compared to 42 % for NMO, indicating that the introduction of Ti^{4+} enhances the overall stability. **Figure 6b** presents the rate capabilities of NMTO and NMO. Notably, an initial current rate of C/20 was employed to investigate whether this helps extract more capacity. However, the first-cycle specific discharge capacities were found to be similar to those achieved with the same cathodes at C/10. This observation agrees with previous reports on NMO,² indicating that the sodium diffusion kinetics is not the primary factor limiting the accessible (reversible) capacity. It is worth noting that, apart from the initial five cycles at C/20, NMTO consistently delivered higher capacities, with lower polarization (**Figure S6**, Supporting Information) across various current rates compared to NMO. This can be explained by the interslab distances given in **Table S1** (Supporting Information). However, it should be noted that calculations were only made for samples with ≤ 10 mol.% Ti^{4+} because of their relatively higher phase purity. The

results demonstrate that the interslab distance increases with increasing titanium fraction, which in turn facilitates sodium diffusion and enhances rate performance. Note that the latter increase is not due to changes in ionic radius (Ti^{4+} : $r = 0.605 \text{ \AA}$, Mn^{3+} : $r = 0.645 \text{ \AA}$, Mn^{2+} : $r = 0.83 \text{ \AA}$) but reduced Jahn-Teller distortion.

Figures 6c–f show cross-sectional SEM images of NMO and NMTO cathodes before and after long-term cycling. In **Figure 6c**, the primary particles within the secondary particles of NMO can be clearly distinguished, and they appear closely packed. However, after 50 cycles (**Figure 6d**), severe intergranular cracking was evident. This suggests that, during battery operation, reactive surfaces are formed and continuously exposed to the electrolyte, thereby accelerating degradation. By contrast, NMTO with its quasi single-crystalline morphology exhibited fewer cracks after electrochemical cycling (**Figures 6e and f**). This kind of structural robustness apparently results in less chemo-mechanical degradation compared to NMO, contributing to its enhanced stability.

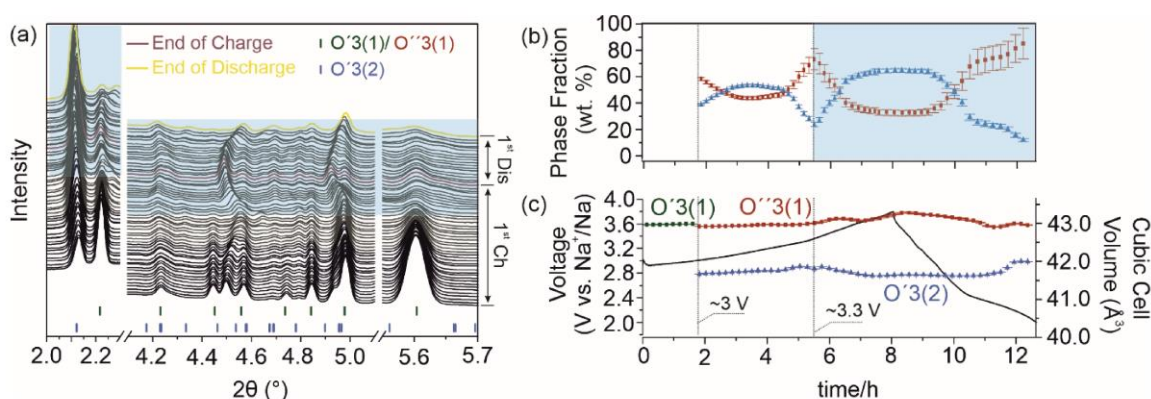


Figure 7. (a) *In situ* XRD patterns of $\text{NaMn}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NMTO) during electrochemical cycling at C/10 rate shown in the form of a contour plot. (b) Phase fractions beyond 3.0 V vs. Na^+/Na and (c) corresponding volume variations.

To explore the structural changes occurring with NMTO during electrochemical cycling, *in situ* (synchrotron) XRD measurements were performed, as shown in **Figure 7a**. It is noteworthy that NMO (**Figure 1e**) exhibits eight distinct phases during cycling, following the sequence $\text{O}'3(1) \rightarrow \text{O}'3(2) \rightarrow \text{O}'3(3) \rightarrow \text{O}'3(4) \rightarrow \text{O}'3(5) \rightarrow \text{O}'3(6) \rightarrow \text{O}'3(7) \rightarrow \text{O}'3\text{-O}1(8)$. As mentioned previously, among these, $\text{O}'3(3)$ and $\text{O}'3(5)$ correspond to triclinic phases, while the others are monoclinic. In contrast, for NMTO, only three monoclinic phases, namely $\text{O}'3(1)$, the Na-deficient phase of $\text{O}'3(1)$, and $\text{O}'3(2)$ —were detected, with no P-type phase being present. This observation is consistent with Kobota *et al.*'s previous study on the structural evolution of NMO.³⁰ They argue that P-type phases are commonly observed in Ni-, Cr-, Co-, or NiMn-based O3 and O'3-type NaTMO_2 cathodes during electrochemical cycling but are typically introduced into Mn-based systems through solid-state synthesis.^{41–44} Although Ma *et al.* reported on the presence of P-type phases in their study on NMO, the current results align with earlier findings.⁴⁵ For clarity, the Na-deficient phase of $\text{O}'3(1)$ is hereafter referred to as $\text{O}''3(1)$.

As shown in **Figure 7a**, the initial phase during charging up to about 3.0 V vs. Na^+/Na was $\text{O}'3(1)$. With further Na^+ extraction, a gradual transition occurred, leading to a biphasic region. Unlike most $\text{O}3$ or $\text{O}'3$ structures, which undergo complete transition after some biphasic region or solid-solution reaction, NMTO maintained the coexistence of both phases throughout the charging/discharging process. To provide a more intuitive comparison of the phase fractions and volume variations, the corresponding curves are displayed in **Figures 7b** and **c**. Since $\text{O}''3(1)$ is a Na-deficient derivative of $\text{O}'3(1)$ with the same monoclinic structure, they share identical reflections in **Figure 7a**. The $\text{O}'3(2)$ phase matches the reported $\text{Na}_{5/8}\text{MnO}_2$ phase. Although $\text{O}'3(2)$ also has a $C2/m$ structure, the Bragg positions differ significantly.

In previous studies on NMO, it has been observed that structures similar to $\text{O}'3(2)$ only exist within a state of charge (SOC) range of (5–40) %, after which further structural transformations occur.^{27,30} For NMTO, based on the first-cycle specific charge capacity of 150 mAh/g ($q_{\text{th}} = 245 \text{ mAh/g}$), the SOC was about 61 %. However, NMTO did not undergo further structural transformations after transitioning toward $\text{O}'3(2)$. A possible reason is that the introduction of Ti^{4+} effectively suppresses the Na-1/2 and Na-1/3 ordering, as well as the associated manganese valence ordering typically present in NMO. Instead, it seems to activate new sodium and/or manganese ordering, as also indicated by the additional features observed in **Figure S3** (Supporting Information).²⁷ At the same time, the complete phase transition can be impeded, resulting in the coexistence of the $\text{O}''3(1)$ and $\text{O}'3(2)$ phases throughout electrochemical cycling. From the XRD patterns in **Figure 7a**, it can be seen that NMTO did not revert to the initial $\text{O}'3(1)$ phase. The blue-shaded area highlights the reversible charge/discharge region, which was also maintained in the second charging process (**Figure S7**, Supporting Information) and followed a similar trend. These findings indicate that after the initial cycle, NMTO consistently alternates between the $\text{O}''3(1)$ and $\text{O}'3(2)$ phases, with the phase evolution following the trend shown in **Figure 7b**.

Taken together, the introduction of Ti^{4+} successfully prevents the formation of the $\text{O}1$ phase at high potentials. Consequently, the reduced volume changes (**Figure 7c**) lead to fewer particle fracture (**Figure 6f**) during battery operation, thereby significantly enhancing the cycling stability.

3. Results

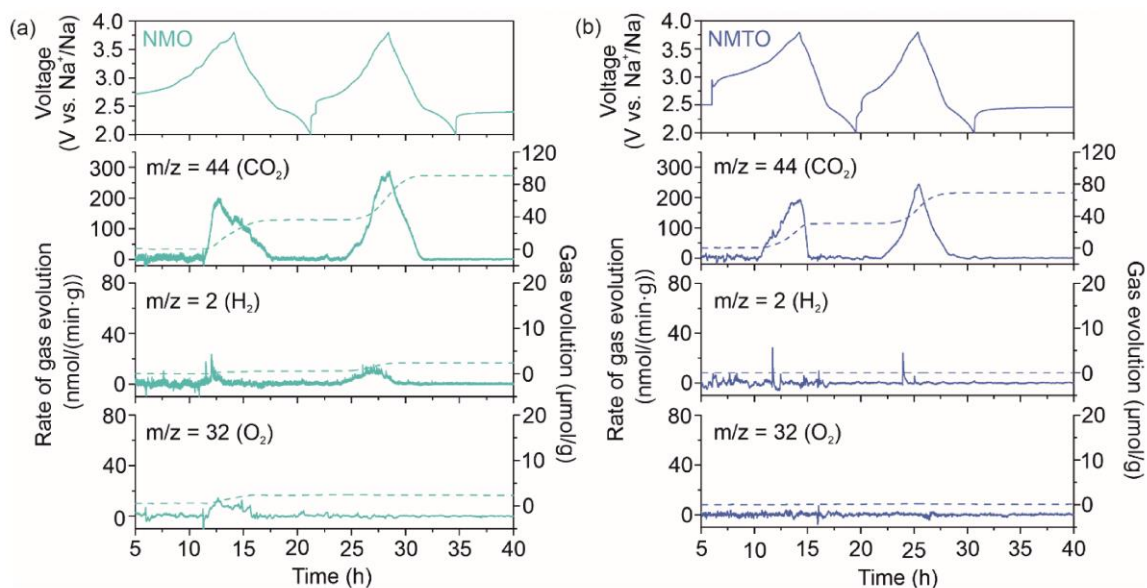


Figure 8. Voltage profiles of half-cells using either (a) NaMnO_2 (NMO) or (b) $\text{NaMn}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NMTO) at C/10 rate and corresponding time-resolved evolution rates (left y-axis) and cumulative amounts (right y-axis) of CO_2 , H_2 , and O_2 measured by DEMS.

Despite extensive research on various aspects of NMO, including electrochemical properties and structural evolution, studies on its gas evolution behavior are lacking.^{2,27,30} Here, to our knowledge, the first *in situ* gas analysis was conducted on NMO via DEMS. Furthermore, the same analysis was done with NMTO to unravel the effect of Ti^{4+} substitution on outgassing of NMO.

Both the NMO and NMTO cathodes were cycled at a rate of C/10 for two consecutive cycles in a customized battery configuration.^{46,47} **Figures 8a and b** present the voltage profiles, gas evolution rates, and total amounts for the gases that evolved most, namely oxygen (O_2 , $m/z = 32$), hydrogen (H_2 , $m/z = 2$), and carbon dioxide (CO_2 , $m/z = 44$). Due to the limited studies available on gas evolution in SIBs and their similarities with LIBs, the gassing mechanism can be inferred from LIBs.⁴⁸ Generally, CO_2 originates from the electrochemical and/or chemical decomposition of surface carbonates,^{49,50} the chemical oxidation of the electrolyte by lattice oxygen, or the electrochemical decomposition of the electrolyte at high potentials (> 4.7 V vs. Li^+/Li).⁵¹ H_2 is typically generated from residual water or alcohol species, or from protic species formed at high potentials at the cathode side, which subsequently migrate to the anode.⁵² The formation of O_2 usually results from the loss of lattice oxygen. However, due to its high reactivity, O_2 often cannot be directly detected and instead is present in the form of CO_2 .^{53,54}

The gassing behavior of NMO and NMTO is illustrated in **Figures 8a and b**, respectively. NMO exhibited a significant release of CO_2 ($36 \mu\text{mol/g}$) in the initial cycle, along with some H_2 and O_2 . Since CO_2 evolution already started at a relatively low potential, electrolyte oxidation as a reason for its generation can be largely ruled out.

A small amount of O₂ (2.3 μmol/g) evolved in the same potential window, thus hinting at irreversible anion redox. Notably, gas evolution started at 3.25 V vs. Na⁺/Na, coinciding with the phase transition of NMO to the O1 phase, where the generation of O₂ may be related to manganese migration.^{27,30} The similar evolution profiles observed for O₂ and CO₂ further corroborate that CO₂ is likely produced via chemical electrolyte oxidation by lattice oxygen. Aside from that, some of the CO₂ release in the initial cycle can also be attributed to the electrochemical oxidation of surface carbonate species. Specifically, the Fourier-transform infrared spectroscopy (FTIR) data in **Figure S8** (Supporting Information) confirm the presence of residual carbonates, while the ICP-OES results (**Table S3**, Supporting Information) indicate sodium excess. The minor release of H₂ is likely due to residual water being present in the sample or the cell parts or the formation of alcohol species during electrochemical cycling.

Unlike NMO, NMTO did not exhibit noticeable H₂ or O₂ signals but still showed a significant amount of CO₂ evolution (31 μmol/g). Both **Figure S8** and **Table S3** (Supporting Information) indicate that NMTO contains a higher amount of residual carbonates than NMO, suggesting that a higher share of the CO₂ evolution likely originates from their decomposition, while the remaining CO₂ may result from electrolyte oxidation. Studies on LIBs have shown that the oxidation of lithium carbonate on the LiNi_xCo_yMn_zO₂ (NCM) surface can also trigger the release of lattice oxygen, implying a similar mechanism may be at play here.⁵⁵ Additionally, the contribution of electrochemical electrolyte oxidation at high potentials cannot be entirely ruled out. Therefore, all of the aforementioned factors may contribute to the observed CO₂ evolution in the initial cycle.

In the second cycle, the peak CO₂ release rates increased, reaching 286 and 243 nmol/min/g for NMO and NMTO, respectively. This may be related to electrode breathing. Polycrystalline NMO likely exposes more reactive (fresh) surfaces than the quasi single-crystalline NMTO in the initial cycle, allowing, among others, previously encapsulated species to undergo oxidation. A similar trend has been observed in studies on poly- and single-crystalline LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathodes in LIBs.⁵⁶ Notably, previous DFT studies on Na_{2/3}Mg_{1/3}Ti_{1/6}Mn_{1/2}O₂ have shown that in the Ti⁴⁺–O bonding case (*d*⁰ configuration), electrons are more localized around the oxygen compared to Mn⁴⁺–O bonding, which may positively affect the reversibility of anion redox.⁵⁷ Therefore, Ti⁴⁺ in NMTO may play a similar role in mitigating irreversible lattice oxygen loss (chemical electrolyte oxidation), ultimately leading to lower CO₂ evolution.

Conclusions

In summary, Ti⁴⁺ as a structural stabilizer was successfully introduced into NMO. Electrochemical testing identified 10 mol.% Ti⁴⁺ as the optimal degree of substitution. Laboratory and synchrotron XRD revealed that titanium incorporation not only increases the interslab distance but also prevents unfavorable transition to the O1 phase at high potentials. Additionally, it facilitates the morphological evolution of polycrystalline NMO toward single-crystal cathode material. Overall, NMTO is found to

clearly outperform NMO in terms of cyclability and stability. Its quasi single-crystalline morphology mitigates crack formation, while the presence of titanium helps suppress irreversible oxygen redox during cycling operation.

Experimental Section

Synthesis. $\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$ ($0 \leq x \leq 0.3$) cathode materials were synthesized via a one-step solid-state reaction approach. To this end, Mn_3O_4 ($d_{50} \approx 14 \mu\text{m}$, BASF Shanshan Battery Materials Co. Ltd.), nanosized TiO_2 , and Na_2CO_3 (99.9%, Sigma-Aldrich) were accurately weighed in a molar ratio of $(1-x):x:1.05$, and then homogenized for 10 min under an argon atmosphere using a high-speed laboratory blender (Kinematica) to ensure uniform mixing. The resulting precursor mixture was transferred to an alumina crucible and calcined at 800°C for 12 h in a tubular furnace (Nabertherm RHTC80/230/16) under a constant flow (7 L/h) of air. The heating rate was maintained at 5 K/min. Upon completion of the calcination cycle, the samples were quenched to ambient temperature.

Battery Testing. Electrode fabrication was carried out by casting a slurry composed of 80 wt.% cathode material, 10 wt.% Super C65 conductive carbon, and 10 wt.% polyvinylidene difluoride (PVDF, Solef 5130, Solvay) binder dispersed in N-methyl-2-pyrrolidone (NMP). The slurry was homogenized using a planetary centrifugal mixer (Thinky ARE-250) at sequential speeds of 2000 and 400 rpm for a total of 6 min. Subsequently, the slurry was coated onto aluminum foil (30 μm thickness) serving as current collector and using a film applicator (Erichsen Coatmaster 510) at a coating speed of 5 mm/s. The cathode sheets were dried under a dynamic vacuum at 120°C , followed by calendaring at a line pressure of 14 N/mm (Sumet Messtechnik) to increase density. Circular electrodes with a diameter of 13 mm and areal mass loading of $(6 \pm 1) \text{ mg/cm}^2$ were punched and used for cell assembly. CR2032-type coin cells were assembled in an argon glovebox using sodium metal as counter/reference electrode, GF/D glass fiber as separator, and 95 μL of electrolyte. The electrolyte consisted of 1 M NaClO_4 in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and propylene carbonate (PC) in a volumetric ratio of 1:1:1, with 5 vol.% fluoroethylene carbonate (FEC) additive. A battery cycler from MACCOR Inc. was used for electrochemical testing via galvanostatic cycling in a potential window of 2.0–3.8 V vs. Na^+/Na , with a constant voltage step at 3.8 V maintained either for 30 min or until the current decreased below C/100 and with 1C being defined as 200 mA/g.

Laboratory X-ray Diffraction. Powder XRD measurements were performed in Debye-Scherrer geometry using a STOE STADI-P diffractometer (STOE & Cie GmbH) equipped with a molybdenum anode ($\lambda = 0.70926 \text{ \AA}$, operated at 50 kV and 40 mA) and a DECTRIS MYTHEN 1K strip detector. For data acquisition, the samples were sealed in 0.5 mm diameter borosilicate glass capillaries (Hilgenberg) of wall thickness 0.01 mm. Instrumental broadening (for line profile analysis) was assessed by collecting diffraction data from a LaB_6 standard reference material (NIST SRM 660c).

In Situ Synchrotron X-ray Diffraction. Synchrotron X-ray diffraction experiments were performed at the Powder Diffraction and Total Scattering beamline P02.1 of PETRA III, DESY (Hamburg, Germany)⁵⁸ using customized electrochemical cells featuring Kapton film windows and mounted in a dedicated sample holder, as described by Herklotz *et al.*⁵⁹ The wavelength of the incident beam was calibrated to 0.20726 Å through refinement of diffraction data collected from a LaB₆ standard reference material (NIST SRM 660c). Electrochemical cycling commenced only after acquisition of the initial diffraction pattern to accurately capture the pristine state of the cathode materials. The cells were cycled galvanostatically at a rate of C/10, and diffraction patterns were recorded using a VAREX 4343CT area detector (150 × 150 μm² pixel size, 2880 × 2880 pixel area, CsI scintillator directly deposited on amorphous Si photodiodes) with an exposure time of 130 s per scan. Detector calibration was accomplished using the LaB₆ standard reference material sealed in a coin cell. 2D images were integrated using the pyFAI software package,⁶⁰ and subsequent structural analysis was performed via Rietveld refinement employing the FullProf Suite.

Scanning Electron Microscopy. SEM images were acquired on a LEO-1530 field emission microscope (Carl Zeiss AG) operated at an accelerating voltage of 10 kV. For cross-sectional analysis, specimens were prepared using an ion beam cross-section polisher (JEOL IB-19510CP) equipped with an argon ion source.

Transmission Electron Microscopy. TEM measurements were performed on an image-corrected Titan Themis (Thermo Fisher Scientific) at an accelerating voltage of 300 kV. Chemical composition mapping was carried out using a SuperX EDS detector in STEM mode. Cross-sectional TEM specimens were prepared by FIB milling using a SARATA (FEI) dual beam with a gallium ion source. The samples were exposed to ambient conditions for about 5 min during FIB preparation. The FIB lamella was milled at 30 kV initially, followed by final polishing with 2 kV to minimize surface damage. Additionally, cathode material was dispersed onto holey C-Cu grids inside an argon glovebox and then transferred for investigation.

Inductively Coupled Plasma-Optical Emission Spectroscopy. The elemental composition was determined by ICP-OES using an ICAP 7600 DUO instrument (Thermo Fisher Scientific). About 10 mg of cathode material was digested in a graphite furnace using a mixture of hydrochloric acid and nitric acid at 353 K for 4 h. The resulting solutions were diluted and analyzed against four external calibration standards, with scandium serving as an internal standard. For each sample, measurements were repeated three times. The oxygen content was determined by carrier gas hot extraction using a TC600 oxygen/nitrogen analyzer (LECO Corp.), with calibration performed against the certified reference material KED-1025.

High-energy-resolution Fluorescence Detected X-ray Absorption Near-edge Structure Spectroscopy. HERFD-XANES spectroscopy was performed at beamline ID26 of the European Synchrotron Radiation Facility (Grenoble, France), a high-brilliance undulator beamline optimized for advanced X-ray spectroscopic studies. Both pristine and cycled cathodes (20 cycles at C/10) were sealed using Kapton tape to minimize air exposure and measured under ambient conditions. To mitigate potential

beam-induced damage, multiple spectra were recorded for each material. Energy calibration was performed by aligning the first inflection point in the first derivative of $\mu(E)$ from a titanium reference foil. Spectral normalization and averaging (over 15 individual scans) were performed using the PyMca software package (version 5.9.2).⁶¹

Differential Electrochemical Mass Spectrometry. DEMS measurements were conducted on customized half-cells with cathodes of 30 mm diameter and an areal mass loading of about 10 mg/cm² using 700 μ L of the aforementioned electrolyte. Electrochemical cycling was performed at a rate of C/10. A continuous flow of helium (purity grade 6.0, 2.5 mL/min) as carrier gas was maintained through the cells. The evolved gases were extracted in real-time and analyzed using a mass spectrometer (OmniStar GSD 320, Pfeiffer Vacuum GmbH).^{46,47}

Fourier-transform Infrared Spectroscopy. FTIR spectroscopy was performed under an inert atmosphere within an argon glovebox (to prevent sample degradation upon exposure to air/moisture) using an ALPHA FT-IR spectrometer (Bruker) fitted with a germanium crystal.

Associated Content

Supporting Information

SEM image and XRD pattern of Mn₃O₄ precursor, additional electrochemical data, XANES spectra, STEM mapping, *in situ* XRD patterns, FTIR spectra, and tables summarizing structural parameters and phase fractions from Rietveld analyses, as well as ICP-OES results.

Notes

The authors declare no competing financial interest.

Acknowledgments

This study was supported by BASF SE. The authors thank Dr. Thomas Bergfeldt (KIT), Dr. Yang Hu (HIU), and Jing Lin (KIT) and teams for helping collect the ICP-OES and XANES data, respectively. We acknowledge the ESRF for provision of synchrotron radiation facilities under proposal no. MA-6219 (DOI: 10.15151/ESRF-ES-1550923205). We also thank Dr. Sami Juhani Vasala for assistance and support in using beamlines ID26. We acknowledge DESY, a member of the Helmholtz Association (HGF), for the provision of experimental facilities. Parts of this research were carried out at PETRA III, and we thank Dr. Volodymyr Baran for assistance in using beamline P02.1. Beamtime was allocated for proposal I-20230867. The lead authors are grateful to the Federal Ministry of Education and Research (BMBF) for funding within the project ENTISE (03XP0579K).

References

- [1] N. Yabuuchi, K. Kubota, D. Mouad, S. Komaba, Research Development on Sodium-Ion Batteries, *Chem. Rev.* 114 (2014) 11636–11682. <https://doi.org/10.1021/cr500192f>.
- [2] X. Ma, H. Chen, G. Ceder, Electrochemical Properties of Monoclinic NaMnO₂, *J. Electrochem. Soc.* 158 (2011) A1307–A1312. <https://doi.org/10.1149/2.035112jes>.
- [3] A. Manthiram, A reflection on lithium-ion battery cathode chemistry, *Nat. Commun.* 11 (2020) 1550. <https://doi.org/10.1038/s41467-020-15355-0>.
- [4] U. Chang, J.T. Lee, J.-M. Yun, B. Lee, S.W. Lee, H.-I. Joh, K. Eom, T.F. Fuller, *In Situ* Self-Formed Nanosheet MoS₃/Reduced Graphene Oxide Material Showing Superior Performance as a Lithium-Ion Battery Cathode, *ACS Nano* 13 (2019) 1490–1498. <https://doi.org/10.1021/acsnano.8b07191>.
- [5] T. Yuan, S. Li, Y. Sun, J.-H. Wang, A.-J. Chen, Q. Zheng, Y. Zhang, L. Chen, G. Nam, H. Che, J. Yang, S. Zheng, Z.-F. Ma, M. Liu, A high-rate, durable cathode for sodium-ion batteries: Sb-doped O3-type Ni/Mn-based layered oxides, *ACS Nano* 16 (2022) 18058–18070. <https://doi.org/10.1021/acsnano.2c04702>.
- [6] K. Chayambuka, G. Mulder, D.L. Danilov, P.H.L. Notten, Sodium-Ion Battery Materials and Electrochemical Properties Reviewed, *Adv. Energy Mater.* 8 (2018) 1800079. <https://doi.org/10.1002/aenm.201800079>.
- [7] S. Li, Y. Sun, Y. Pang, S. Xia, T. Chen, H. Sun, S. Zheng, T. Yuan, Recent developments of layered transition metal oxide cathodes for sodium-ion batteries toward desired high performance, *Asia-Pac. J. Chem. Eng.* 17 (2022) e2762. <https://doi.org/10.1002/apj.2762>.
- [8] R.-M. Gao, Z.-J. Zheng, P.-F. Wang, C.-Y. Wang, H. Ye, F.-F. Cao, Recent advances and prospects of layered transition metal oxide cathodes for sodium-ion batteries, *Energy Storage Mater.* 30 (2020) 9–26. <https://doi.org/10.1016/j.ensm.2020.04.040>.
- [9] Y. You, S. Xin, H.Y. Asl, W. Li, P.-F. Wang, Y.-G. Guo, A. Manthiram, Insights into the Improved High-Voltage Performance of Li-Incorporated Layered Oxide Cathodes for Sodium-Ion Batteries, *Chem* 4 (2018) 2124–2139. <https://doi.org/10.1016/j.chempr.2018.05.018>.
- [10] K. Kubota, M. Dahbi, T. Hosaka, S. Kumakura, S. Komaba, Towards K-Ion and Na-Ion Batteries as “Beyond Li-Ion,” *Chem. Rec.* 18 (2018) 459–479. <https://doi.org/10.1002/tcr.201700057>.
- [11] R.C. Massé, E. Uchaker, G. Cao, Beyond Li-ion: electrode materials for sodium- and magnesium-ion batteries, *Sci. China Mater.* 58 (2015) 715–766. <https://doi.org/10.1007/s40843-015-0084-8>.
- [12] G.A. Elia, K. V. Kravchyk, M. V. Kovalenko, J. Chacón, A. Holland, R.G.A. Wills, An overview and prospective on Al and Al-ion battery technologies, *J. Power*

- Sources 481 (2021) 228870. <https://doi.org/10.1016/j.jpowsour.2020.228870>.
- [13] M.H. Han, E. Gonzalo, G. Singh, T. Rojo, A comprehensive review of sodium layered oxides: Powerful cathodes for Na-ion batteries, *Energy Environ. Sci.* 8 (2015) 81. <https://doi.org/10.1039/c4ee03192j>.
- [14] P.-F. Wang, Y. You, Y.-X. Yin, Y.-S. Wang, L.-J. Wan, L. Gu, Y.-G. Guo, Suppressing the P2-O2 Phase Transition of $\text{Na}_{0.67}\text{Mn}_{0.67}\text{Ni}_{0.33}\text{O}_2$ by Magnesium Substitution for Improved Sodium-Ion Batteries, *Angew. Chem., Int. Ed.* 128 (2016) 7571–7575. <https://doi.org/10.1002/ange.201602202>.
- [15] S. Guo, H. Yu, P. Liu, Y. Ren, T. Zhang, M. Chen, M. Ishida, H. Zhou, High-performance symmetric sodium-ion batteries using a new, bipolar O3-type material, $\text{Na}_{0.8}\text{Ni}_{0.4}\text{Ti}_{0.6}\text{O}_2$, *Energy Environ. Sci.* 8 (2015) 1237. <https://doi.org/10.1039/c4ee03361b>.
- [16] P.-F. Wang, H.-R. Yao, X.-Y. Liu, J.-N. Zhang, L. Gu, X.-Q. Yu, Y.-X. Yin, Y.-G. Guo, Ti-Substituted $\text{NaNi}_{0.5}\text{Mn}_{0.5-x}\text{Ti}_x\text{O}_2$ Cathodes with Reversible O3–P3 Phase Transition for High-Performance Sodium-Ion Batteries, *Adv. Mater.* 29 (2017) 1700210. <https://doi.org/10.1002/adma.201700210>.
- [17] C. Delmas, C. Fouassier, P. Hagenmuller, Structural classification and properties of the layered oxides, *Physica b+c* 99 (1980) 81–85. [https://doi.org/10.1016/0378-4363\(80\)90214-4](https://doi.org/10.1016/0378-4363(80)90214-4).
- [18] Y. Xie, E. Gabriel, L. Fan, I. Hwang, X. Li, H. Zhu, Y. Ren, C. Sun, J. Pipkin, M. Dustin, M. Li, Z. Chen, E. Lee, H. Xiong, Role of Lithium Doping in P2- $\text{Na}_{0.67}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$ for Sodium-Ion Batteries, *Chem. Mater.* 33 (2021) 4445–4455. <https://doi.org/10.1021/acs.chemmater.1c00569>.
- [19] C. Delmas, J.-J. Braconnier, C. Fouassier, P. Hagenmuller, Electrochemical intercalation of sodium in Na_xCoO_2 bronzes, *Solid State Ion.* 3–4 (1981) 165–169. [https://doi.org/10.1016/0167-2738\(81\)90076-X](https://doi.org/10.1016/0167-2738(81)90076-X).
- [20] S. Guo, P. Liu, H. Yu, Y. Zhu, M. Chen, M. Ishida, H. Zhou, A layered P2- and O3-type composite as a high-energy cathode for rechargeable sodium-ion batteries, *Angew. Chem., Int. Ed.* 54 (2015) 5894–5899. <https://doi.org/10.1002/anie.201411788>.
- [21] F. Wei, Q. Zhang, P. Zhang, W. Tian, K. Dai, L. Zhang, J. Mao, G. Shao, Review—Research Progress on Layered Transition Metal Oxide Cathode Materials for Sodium Ion Batteries, *J. Electrochem. Soc.* 168 (2021) 050524. <https://doi.org/10.1149/1945-7111/abf9bf>.
- [22] Z. Guo, X. Li, Y. Lyu, S. Xu, Improved electrochemical performance of B doped O'3- NaMnO_2 for Na-ion battery, *Electrochim. Acta* 430 (2022) 141079. <https://doi.org/10.1016/j.electacta.2022.141079>.
- [23] S. Kumakura, Y. Tahara, K. Kubota, K. Chihara, S. Komaba, Sodium and Manganese Stoichiometry of P2-Type $\text{Na}_{2/3}\text{MnO}_2$, *Angew. Chem., Int. Ed.* 55 (2016) 12760–12763. <https://doi.org/10.1002/anie.201606415>.

- [24] N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada, S. Komaba, P2-type $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ made from earth-abundant elements for rechargeable Na batteries, *Nat. Mater.* 11 (2012) 512–517. <https://doi.org/10.1038/nmat3309>.
- [25] M. Sathiya, J. Thomas, D. Batuk, V. Pimenta, R. Gopalan, J.M. Tarascon, Dual Stabilization and Sacrificial Effect of Na_2CO_3 for Increasing Capacities of Na-Ion Cells Based on P2- Na_xMO_2 Electrodes, *Chem. Mater.* 29 (2017) 5948–5956. <https://doi.org/10.1021/acs.chemmater.7b01542>.
- [26] M. Matsuzaki, R. Tatara, K. Kubota, K. Kuroki, T. Hosaka, K. Umetsu, N. Okada, S. Komaba, Application of Na_2CO_3 as a Sacrificial Electrode Additive in Na-ion Batteries to Compensate for the Sodium Deficiency in $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$, *Batter. Supercaps* 7 (2024) e202400009. <https://doi.org/10.1002/batt.202400009>.
- [27] X. Chen, Y. Wang, K. Wiaderek, X. Sang, O. Borkiewicz, K. Chapman, J. LeBeau, J. Lynn, X. Li, Super Charge Separation and High Voltage Phase in Na_xMnO_2 , *Adv. Funct. Mater.* 28 (2018) 1805105. <https://doi.org/10.1002/adfm.201805105>.
- [28] J. Manzi, A. Paolone, O. Palumbo, D. Corona, A. Massaro, R. Cavaliere, A.B. Muñoz-García, F. Trequattrini, M. Pavone, S. Brutti, Monoclinic and orthorhombic NaMnO_2 for secondary batteries: A comparative study, *Energies* 14 (2021) 1230. <https://doi.org/10.3390/en14051230>.
- [29] M. Shishkin, S. Kumakura, S. Sato, K. Kubota, S. Komaba, H. Sato, Unraveling the Role of Doping in Selective Stabilization of NaMnO_2 Polymorphs: Combined Theoretical and Experimental Study, *Chem. Mater.* 30 (2018) 1257–1264. <https://doi.org/10.1021/acs.chemmater.7b04394>.
- [30] K. Kubota, M. Miyazaki, E.J. Kim, H. Yoshida, P. Barpanda, S. Komaba, Structural change induced by electrochemical sodium extraction from layered $\text{O}'3\text{-NaMnO}_2$, *J. Mater. Chem. A* 9 (2021) 26810–26819. <https://doi.org/10.1039/d1ta05390f>.
- [31] H. Yu, S. Guo, Y. Zhu, M. Ishida, H. Zhou, Novel titanium-based O3-type $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ as a cathode material for sodium ion batteries, *Chem. Commun.* 50 (2014) 457–459. <https://doi.org/10.1039/C3CC47351A>.
- [32] S. Maletti, A. Sarapulova, A. Schökel, D. Mikhailova, Operando Studies on the $\text{NaNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ Cathode for Na-Ion Batteries: Elucidating Titanium as a Structure Stabilizer, *ACS Appl. Mater. Interfaces* 11 (2019) 33923–33930. <https://doi.org/10.1021/acsami.9b10352>.
- [33] S. An, L. Karger, S.L. Dreyer, Y. Hu, E. Barbosa, R. Zhang, J. Lin, M. Fichtner, A. Kondrakov, J. Janek, T. Brezesinski, Improving cycling performance of the NaNiO_2 cathode in sodium-ion batteries by titanium substitution, *Mater. Futures* 3 (2024) 035103. <https://doi.org/10.1088/2752-5724/ad5faa>.
- [34] T. Sato, K. Yoshikawa, W. Zhao, T. Kobayashi, H.B. Rajendra, M. Yonemura, N. Yabuuchi, Efficient Stabilization of Na Storage Reversibility by Ti Integration into

- O'3-Type NaMnO_2 , *Energy Mater. Adv.* 2021 (2021) 9857563. <https://doi.org/10.34133/2021/9857563>.
- [35] P. Vassilaras, X. Ma, X. Li, G. Ceder, Electrochemical Properties of Monoclinic NaNiO_2 , *J. Electrochem. Soc.* 160 (2013) A207–A211. <https://doi.org/10.1149/2.023302jes>.
- [36] I.-H. Jo, H.-S. Ryu, D.-G. Gu, J.-S. Park, I.-S. Ahn, H.-J. Ahn, T.-H. Nam, K.-W. Kim, The effect of electrolyte on the electrochemical properties of $\text{Na}/\alpha\text{-NaMnO}_2$ batteries, *Mater. Res. Bull.* 58 (2014) 74–77. <https://doi.org/10.1016/j.materresbull.2014.02.024>.
- [37] H.-H. Ryu, K.-J. Park, D.R. Yoon, A. Aishova, C.S. Yoon, Y.-K. Sun, $\text{Li}[\text{Ni}_{0.9}\text{Co}_{0.09}\text{W}_{0.01}]\text{O}_2$: A New Type of Layered Oxide Cathode with High Cycling Stability, *Adv. Energy Mater.* 9 (2019) 1902698. <https://doi.org/10.1002/aenm.201902698>.
- [38] Q. Ma, R. Li, R. Zheng, Y. Liu, H. Huo, C. Dai, Improving rate capability and decelerating voltage decay of Li-rich layered oxide cathodes via selenium doping to stabilize oxygen, *J. Power Sources* 331 (2016) 112–121. <https://doi.org/10.1016/j.jpowsour.2016.08.137>.
- [39] C.-C. Wang, A. Manthiram, Influence of cationic substitutions on the first charge and reversible capacities of lithium-rich layered oxide cathodes, *J. Mater. Chem. A* 1 (2013) 10209–10217. <https://doi.org/10.1039/c3ta11703k>.
- [40] S. Guo, H. Yu, D. Liu, W. Tian, X. Liu, N. Hanada, M. Ishid, H. Zhou, A novel tunnel $\text{Na}_{0.61}\text{Ti}_{0.48}\text{Mn}_{0.52}\text{O}_2$ cathode material for sodium-ion batteries, *Chem. Commun.* 50 (2014) 7998–8001. <https://doi.org/10.1039/c4cc02362e>.
- [41] T.-Y. Yu, H.-H. Ryu, G. Han, Y.-K. Sun, Understanding the Capacity Fading Mechanisms of O3-Type $\text{Na}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ Cathode for Sodium-Ion Batteries, *Adv. Energy Mater.* 10 (2020) 2001609. <https://doi.org/10.1002/aenm.202001609>.
- [42] J.-J. Braconnier, C. Delmas, C. Fouassier, P. Hagenmuller, Comportement electrochimique des phases Na_xCoO_2 , *Mater. Res. Bull.* 15 (1980) 1797–1804. [https://doi.org/10.1016/0025-5408\(80\)90199-3](https://doi.org/10.1016/0025-5408(80)90199-3).
- [43] K. Kubota, I. Ikeuchi, T. Nakayama, C. Takei, N. Yabuuchi, H. Shiiba, M. Nakayama, S. Komaba, New insight into structural evolution in layered NaCrO_2 during electrochemical sodium extraction, *J. Phys. Chem. C* 119 (2015) 166–175. <https://doi.org/10.1021/jp5105888>.
- [44] Q. Huang, J. Liu, L. Zhang, S. Xu, L. Chen, P. Wang, D.G. Ivey, W. Wei, Tailoring alternating heteroepitaxial nanostructures in Na-ion layered oxide cathodes via an *in-situ* composition modulation route, *Nano Energy* 44 (2018) 336–344. <https://doi.org/10.1016/j.nanoen.2017.12.014>.
- [45] T. Ma, G.-L. Xu, Y. Li, B. Song, X. Zeng, C.-C. Su, W.L. Mattis, F. Guo, Y. Ren, R. Kou, C. Sun, S.M. Heald, H.-H. Wang, R. Shahbazian-Yassar, J. Jorne, Z.

- Chen, K. Amine, Insights into the Performance Degradation of Oxygen-Type Manganese-Rich Layered Oxide Cathodes for High-Voltage Sodium-Ion Batteries, *ACS Appl. Energy Mater.* 1 (2018) 5735–5745. <https://doi.org/10.1021/acsaem.8b01325>.
- [46] B.B. Berkes, A. Jozwiuk, M. Vračar, H. Sommer, T. Brezesinski, J. Janek, Online Continuous Flow Differential Electrochemical Mass Spectrometry with a Realistic Battery Setup for High-Precision, Long-Term Cycling Tests, *Anal. Chem.* 87 (2015) 5878–5883. <https://doi.org/10.1021/acs.analchem.5b01237>.
- [47] B.B. Berkes, A. Jozwiuk, H. Sommer, T. Brezesinski, J. Janek, Simultaneous acquisition of differential electrochemical mass spectrometry and infrared spectroscopy data for *in situ* characterization of gas evolution reactions in lithium-ion batteries, *Electrochem. Commun.* 60 (2015) 64–69. <https://doi.org/10.1016/j.elecom.2015.08.002>.
- [48] L. Zhang, C. Tsolakidou, S. Mariyappan, J.-M. Tarascon, S. Trabesinger, Unraveling gas evolution in sodium batteries by online electrochemical mass spectrometry, *Energy Storage Mater.* 42 (2021) 12–21. <https://doi.org/10.1016/j.ensm.2021.07.005>.
- [49] N. Mahne, S.E. Renfrew, B.D. McCloskey, S.A. Freunberger, Electrochemical Oxidation of Lithium Carbonate Generates Singlet Oxygen, *Angew. Chem., Int. Ed.* 57 (2018) 5529–5533. <https://doi.org/10.1002/anie.201802277>.
- [50] A.T.S. Freiberg, J. Sicklinger, S. Solchenbach, H.A. Gasteiger, Li_2CO_3 decomposition in Li-ion batteries induced by the electrochemical oxidation of the electrolyte and of electrolyte impurities, *Electrochim. Acta* 346 (2020) 136271. <https://doi.org/10.1016/j.electacta.2020.136271>.
- [51] R. Jung, M. Metzger, F. Maglia, C. Stinner, H.A. Gasteiger, Chemical versus electrochemical electrolyte oxidation on NMC111, NMC622, NMC811, LNMO, and conductive carbon, *J. Phys. Chem. Lett.* 8 (2017) 4820–4825. <https://doi.org/10.1021/acs.jpclett.7b01927>.
- [52] M. Metzger, B. Strehle, S. Solchenbach, H.A. Gasteiger, Origin of H_2 Evolution in LIBs: H_2O Reduction vs. Electrolyte Oxidation, *J. Electrochem. Soc.* 163 (2016) A798–A809. <https://doi.org/10.1149/2.1151605jes>.
- [53] R. Jung, M. Metzger, F. Maglia, C. Stinner, H.A. Gasteiger, Oxygen Release and Its Effect on the Cycling Stability of $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) Cathode Materials for Li-Ion Batteries, *J. Electrochem. Soc.* 164 (2017) A1361–A1377. <https://doi.org/10.1149/2.0021707jes>.
- [54] J. Wandt, A.T.S. Freiberg, A. Ogrodnik, H.A. Gasteiger, Singlet oxygen evolution from layered transition metal oxide cathode materials and its implications for lithium-ion batteries, *Mater. Today* 21 (2018) 825–833. <https://doi.org/10.1016/j.mattod.2018.03.037>.
- [55] L.A. Kaufman, B.D. McCloskey, Surface Lithium Carbonate Influences

Electrolyte Degradation via Reactive Oxygen Attack in Lithium-Excess Cathode Materials, *Chem. Mater.* **33** (2021) 4170–4176. <https://doi.org/10.1021/acs.chemmater.1c00935>.

- [56] S. Oswald, M. Bock, H.A. Gasteiger, Elucidating the Implications of Morphology on Fundamental Characteristics of Nickel-Rich NCMs: Cracking, Gassing, Rate Capability, and Thermal Stability of Poly- and Single-Crystalline NCM622, *J. Electrochem. Soc.* **169** (2022) 050501. <https://doi.org/10.1149/1945-7111/ac5f7f>.
- [57] C. Zhao, Z. Yao, J. Wang, Y. Lu, X. Bai, A. Aspuru-Guzik, L. Chen, Y.-S. Hu, Ti Substitution Facilitating Oxygen Oxidation in $\text{Na}_{2/3}\text{Mg}_{1/3}\text{Ti}_{1/6}\text{Mn}_{1/2}\text{O}_2$ Cathode, *Chem* **5** (2019) 2913–2925. <https://doi.org/10.1016/j.chempr.2019.08.003>.
- [58] A.-C. Dippel, H.-P. Liermann, J.T. Delitz, P. Walter, H. Schulte-Schrepping, O.H. Seeck, H. Franz, Beamline P02.1 at PETRA III for high-resolution and high-energy powder diffraction, *J. Synchrotron Rad.* **22** (2015) 675–687. <https://doi.org/10.1107/S1600577515002222>.
- [59] M. Herklotz, J. Weiß, E. Ahrens, M. Yavuz, L. Mereacre, N. Kiziltas-Yavuz, C. Dräger, H. Ehrenberg, J. Eckert, F. Fauth, L. Giebeler, M. Knapp, A novel high-throughput setup for in situ powder diffraction on coin cell batteries, *J. Appl. Cryst.* **49** (2016) 340–345. <https://doi.org/10.1107/S1600576715022165>.
- [60] G. Ashiotis, A. Deschildre, Z. Nawaz, J.P. Wright, D. Karkoulis, F.E. Picca, J. Kieffer, The fast azimuthal integration Python library: PyFAI, *J. Appl. Cryst.* **48** (2015) 510–519. <https://doi.org/10.1107/S1600576715004306>.
- [61] V.A. Solé, E. Papillon, M. Cotte, P. Walter, J. Susini, A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra, *Spectrochim. Acta Part B, At. Spectrosc.* **62** (2007) 63–68. <https://doi.org/10.1016/j.sab.2006.12.002>.

4. Conclusions and Outlook

Ni- and Mn-rich O3-type layered oxides are considered promising next-generation energy-storage materials due to their high theoretical specific capacities. However, the prototype materials, NNO and NMO, exhibit unsatisfactory electrochemical performance. In the case of NNO, multiple degradation mechanisms contribute to this issue. First, the presence of the JT effect and the extraction of large-sized Na^+ ions can together lead to complex phase transitions. Additionally, at high potentials (>4.0 V vs. Na^+/Na), interlayer gliding and structural distortions prevent the fully discharged NNO from reverting to its original (pristine) phase. Furthermore, nickel migration and extensive side reactions with the electrolyte are also major contributors to its poor performance. For NMO, the situation is even more complex. NMO undergoes up to eight distinct phase transitions and suffers from severe manganese migration at high potentials (>3.8 V vs. Na^+/Na), resulting in irreversible structural changes. Notably, the latter is accompanied by lattice oxygen loss and manganese dissolution, leading to structural instability and decreasing crystallinity. Moreover, the migrated ions may occupy octahedral sites in the NaO_2 layers, further impeding sodium transport.

For Ni-based materials, the aforementioned issues have been extensively investigated. Although several studies have successfully improved the structural stability upon cycling, the reversible capacity remains relatively low. This limitation hinders further development and practical application of these materials. In contrast, research on Mn-based materials has largely focused on P2-type structures, as they exhibit higher ionic conductivities and are more favorable for synthesizing Mn-rich compositions. Mn-rich O3-type materials, however, have received less attention due to synthetic difficulties, often accompanied by the formation of P2- and β -phases, as well as their more complex phase-transition behavior. To address these challenges, this study presents practical and effective optimization strategies for both NNO and NMO cathodes.

The objective of publication I was to enhance the reversible capacity of NNO through TM-site substitution. Electrochemically inactive Ti^{4+} was introduced to partially replace Ni^{3+} , aiming at suppressing JT distortion. To ensure effective incorporation of Ti^{4+} into the NNO lattice, the focus was first placed on optimizing the solid-state synthesis conditions, including calcination temperature, cooling rate, and oxygen flow rate.

As the most critical parameter for the synthesis of layered materials, the temperature was first thoroughly investigated. To explore the phase evolution of precursors during heating, temperature-dependent *in situ* XRD was employed. The results showed that the target phase can be obtained within the range of (630-870) °C. Lower temperatures (<630 °C) can lead to incomplete reactions and poor crystallinity, whereas higher temperatures (>870 °C) cause decomposition of the target phase. Further studies on the cooling rate revealed that quenching introduces native strain, which in turn negatively affects performance. The material also exhibited high sensitivity to the oxygen flow rate. Insufficient oxygen flow often leads to incomplete oxidation of Ni^{2+} in the precursor, resulting in lower product purity. Furthermore, either a Na/TM ratio above 1 or reduced oxygen flow may also promote the formation of larger primary

4. Conclusions and Outlook

particles. In addition to optimizing the calcination conditions, both the Na/TM and Ni/Ti ratios were also tailored. Slightly Na-deficient NNTO samples exhibited better electrochemical performance due to the presence of sodium vacancies, facilitating ion transport. Meanwhile, optimization of the Ni/Ti ratio indicated that 10 mol.% Ti^{4+} substitution yields the best phase purity, crystallinity, and electrochemical performance under the optimized calcination conditions.

Through systematic optimization, a high-quality NNTO sample was successfully produced, achieving a phase purity of 98.5 % and reversible specific capacities as high as 190 mAh/g. Nevertheless, the long-term cycling performance and rate capability of NNTO remained unsatisfactory. *In situ* XRD revealed that, although the phase transitions in NNTO are reversible in nature, the formation of a Na-deficient O1 phase at high potentials (>4.0 V vs. Na^+/Na) causes structural collapse, leading to a 30 % volume shrinkage. Subsequent *post-mortem* SEM and AE measurements revealed severe mechanical degradation, including prominent crack formation and signs of plastic deformation. Further insights from DEMS pointed toward outgassing, where small amounts of O_2 and large amounts of CO_2 were detected. This suggests the occurrence of irreversible lattice oxygen loss and surface reconstruction, which compromise the interfacial stability between the cathode and the electrolyte.

In publication II, to further enhance the performance of NNTO, a pillaring ion strategy was proposed for mitigating the aforementioned issues of electro-chemo-mechanical degradation. While various pillaring ions have been studied in previous reports, as summarized in section 2.4.3, Ca^{2+} was identified as a particularly promising candidate. This is due to its ionic radius being the closest to that of Na^+ , increasing the likelihood of successful incorporation into the Na-site. Moreover, Ca^{2+} is expected to offer greater performance improvements compared to other pillaring ions.

To determine the optimal Ca^{2+} fraction, ten different concentrations were introduced into NNTO. XRD results revealed that a Ca^{2+} fraction of 2.5 mol.% coincides with the solubility limit and yields the largest unit-cell volume and interslab distance. This indicates the formation of wider sodium diffusion pathways. Subsequent electrochemical testing confirmed that the 2.5 mol.% Ca^{2+} -substituted sample exhibits the best capacity retention and rate capability. Further investigation clarified the underlying mechanisms. *In situ* XRD showed that CaNNTO does not form the Na-deficient O1 phase and experiences fewer phase transitions, with only 3 % absolute volume change during cycling. This suggests that Ca^{2+} located in the NaO_2 layers effectively inhibits interlayer gliding and prevents structural collapse caused by sodium depletion. *Post-mortem* SEM and AE analyses revealed fewer cracking and weaker plastic deformation, further supporting the enhanced mechanical stability. In addition, hard and soft XAS demonstrated that the introduction of Ca^{2+} improves the reversibility of redox reactions involving $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$. DEMS measurements further revealed negligible O_2 release and significantly reduced CO_2 evolution for CaNNTO, indicating improved reversibility of oxygen redox and enhanced interfacial stability as a result of Ca^{2+} incorporation.

4. Conclusions and Outlook

In publication III, the focus was placed on addressing the intrinsic challenges associated with NMO. In this study, precipitated Mn_3O_4 was employed, to our knowledge for the first time, as a precursor to synthesize NMO. XRD and electrochemical characterizations of the resulting samples confirmed that the structure and performance are consistent with previously reported NMO materials.

To enable successful synthesis of Mn-rich O3-type materials, the study built upon the work of Komaba and colleagues by further investigating the influence of Ti^{4+} substitution on the structure, morphology, and electrochemical properties of NMO. Systematic XRD and electrochemical measurements on samples with varying Ti^{4+} fractions revealed that a 10 mol.% substitution level provides the optimal balance among phase purity, suppression of JT distortion, and electrochemical performance. Furthermore, the incorporation of Ti^{4+} was found to alter the surface formation energy during sintering, promoting transformation from polycrystalline to quasi-single-crystalline particle morphology. *In situ* XRD further demonstrated that Ti^{4+} incorporation helps suppress the formation of manganese migration-induced phases. Additionally, this study conducted the first DEMS analysis on NMO. A comparison of the gas evolution behavior between pristine NMO and NMTO revealed that redox reactions involving lattice oxygen are partially suppressed in the latter case.

In summary, this study successfully enhanced the performance of NNO through sequential substitution with Ti^{4+} and Ca^{2+} , effectively unlocking the redox potential of nickel. Although the electrochemical performance of CaNNTO represents a substantial improvement over pristine NNO, it still falls short of the requirements for practical application. Further improvements, such as surface coating, additional doping, or morphological engineering (single-crystal design etc.), will be necessary to bridge this gap. For NMO, the successful incorporation of Ti^{4+} not only stabilized the O3 (α) phase and suppressed the formation of manganese migration-related phases, but also altered the material's morphology. Nevertheless, NMTO still requires further optimization to meet practical demands. Overall, the mechanistic insights provided by this work offer valuable guidance for the future design of advanced O3-type layered oxide cathodes.

5. Bibliography

- [1] F. Wei, Q. Zhang, P. Zhang, W. Tian, K. Dai, L. Zhang, J. Mao, G. Shao, *J. Electrochem. Soc.* **2021**, *168*, 050524.
- [2] Y. Xiao, N. M. Abbasi, Y.-F. Zhu, S. Li, S.-J. Tan, W. Ling, L. Peng, T. Yang, L. Wang, X.-D. Guo, Y.-X. Yin, H. Zhang, Y.-G. Guo, *Adv. Funct. Mater.* **2020**, *30*, 2001334.
- [3] R. J. Clément, P. G. Bruce, C. P. Grey, *J. Electrochem. Soc.* **2015**, *162*, A2589.
- [4] J. B. Goodenough, Y. Kim, *Chem. Mater.* **2010**, *22*, 587-603.
- [5] H. Su, S. Jaffer, H. Yu, *Energy Storage Mater.* **2016**, *5*, 116-131.
- [6] B. Scrosati, J. Hassoun, Y.-K. Sun, *Energy Environ. Sci.* **2011**, *4*, 3287-3295.
- [7] A. Manthiram, *Nat. Commun.* **2020**, *11*, 1550.
- [8] T. Yuan, S. Li, Y. Sun, J.-H. Wang, A.-J. Chen, Q. Zheng, Y. Zhang, L. Chen, G. Nam, H. Che, J. Yang, S. Zheng, Z.-F. Ma, M. Liu, *ACS Nano* **2022**, *16*, 18058-18070.
- [9] T.-Y. Yu, J. Kim, J.-Y. Hwang, H. Kim, G. Han, H.-G. Jung, Y.-K. Sun, *J. Mater. Chem. A* **2020**, *8*, 13776-13786.
- [10] S. An, L. Karger, P. Müller, J. Lin, S. Vasala, V. Baran, S. L. Dreyer, R. Zhang, F. Ulusoy, A. Kondrakov, J. Janek, T. Brezesinski, *Chem. Eng. J.* **2025**, *509*, 160939.
- [11] U. Chang, J. T. Lee, J.-M. Yun, B. Lee, S. W. Lee, H.-I. Joh, K. Eom, T. F. Fuller, *ACS Nano* **2019**, *13*, 1490-1498.
- [12] S. An, L. Karger, S. L. Dreyer, Y. Hu, E. Barbosa, R. Zhang, J. Lin, M. Fichtner, A. Kondrakov, J. Janek, T. Brezesinski, *Mater. Futures* **2024**, *3*, 035103.
- [13] M. Bianchini, M. Roca-Ayats, P. Hartmann, T. Brezesinski, J. Janek, *Angew. Chem., Int. Ed.* **2019**, *58*, 10434-10458.
- [14] K. Mizushima, P. C. Jones, P. J. Wiseman, J. B. Goodenough, *Mater. Res. Bull.* **1980**, *15*, 783-789.
- [15] S. Oswald, M. Bock, H. A. Gasteiger, *J. Electrochem. Soc.* **2022**, *169*, 050501.
- [16] N. Nitta, F. Wu, J. T. Lee, G. Yushin, *Mater. Today* **2015**, *18*, 252-264.
- [17] S.-T. Myung, F. Maglia, K.-J. Park, C. S. Yoon, P. Lamp, S.-J. Kim, Y.-K. Sun, *ACS Energy Lett.* **2017**, *2*, 196-223.
- [18] D. Andre, S.-J. Kim, P. Lamp, S. F. Lux, F. Maglia, O. Paschos, B. Stiaszny, *J. Mater. Chem. A* **2015**, *3*, 6709-6732.
- [19] P. G. Bruce, A. Lisowska-Oleksiak, M. Y. Saidi, C. A. Vincent, *Solid State Ionics* **1992**, *57*, 353-358.

5. Bibliography

- [20] T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, H. Komori, *Electrochim. Acta* **1993**, 38, 1159-1167.
- [21] K. Chayambuka, G. Mulder, D. L. Danilov, P. H. L. Notten, *Adv. Energy Mater.* **2018**, 8, 1800079.
- [22] R.-M. Gao, Z.-J. Zheng, P.-F. Wang, C.-Y. Wang, H. Ye, F.-F. Cao, *Energy Storage Mater.* **2020**, 30, 9-26.
- [23] S. Li, Y. Sun, Y. Pang, S. Xia, T. Chen, H. Sun, S. Zheng, T. Yuan, *Asia-Pac. J. Chem. Eng.* **2022**, 17, e2762.
- [24] I. Hasa, D. Buchholz, S. Passerini, J. Hassoun, *ACS Appl. Mater. Interfaces* **2015**, 7, 5206-5212.
- [25] J.-Y. Hwang, S.-T. Myung, Y.-K. Sun, *Chem. Soc. Rev.* **2017**, 46, 3529-3614.
- [26] S. Guo, H. Yu, P. Liu, Y. Ren, T. Zhang, M. Chen, M. Ishida, H. Zhou, *Energy Environ. Sci.* **2015**, 8, 1237-1244.
- [27] P.-F. Wang, Y. You, Y.-X. Yin, Y.-S. Wang, L.-J. Wan, L. Gu, Y.-G. Guo, *Angew. Chem., Int. Ed.* **2016**, 128, 7571-7575.
- [28] M. H. Han, E. Gonzalo, G. Singh, T. Rojo, *Energy Environ. Sci.* **2015**, 8, 81-102.
- [29] X. Li, Y. Wang, D. Wu, L. Liu, S.-H. Bo, G. Ceder, *Chem. Mater.* **2016**, 28, 6575-6583.
- [30] S. Kim, X. Ma, S. P. Ong, G. Ceder, *Phys. Chem. Chem. Phys.* **2012**, 14, 15571-15578.
- [31] F. Li, Z. Wei, A. Manthiram, Y. Feng, J. Ma, L. Mai, *J. Mater. Chem. A* **2019**, 7, 9406-9431.
- [32] X. Zheng, C. Bommier, W. Luo, L. Jiang, Y. Hao, Y. Huang, *Energy Storage Mater.* **2019**, 16, 6-23.
- [33] S. Schweidler, M. Bianchini, P. Hartmann, T. Brezesinski, J. Janek, *Batteries Supercaps* **2020**, 3, 1021-1027.
- [34] L. Sun, Y. Xie, X.-Z. Liao, H. Wang, G. Tan, Z. Chen, Y. Ren, J. Gim, W. Tang, Y.-S. He, K. Amine, Z.-F. Ma, *Small* **2018**, 14, 1704523.
- [35] J. Zhou, Y. Zhang, W. Xu, X. Li, W. Zhou, W. Zhang, N. Wang, M. Liu, K. Dai, *J. Electroanal. Chem.* **2024**, 969, 118541.
- [36] L. Zhang, J. Deshmukh, H. Hijazi, Z. Ye, M. B. Johnson, A. George, J. R. Dahn, M. Metzger, *J. Electrochem. Soc.* **2023**, 170, 070514.
- [37] Y. Mao, Y. Chen, J. Qin, C. Shi, E. Liu, N. Zhao, *Nano Energy* **2019**, 58, 192-201.
- [38] Z. Wu, J. Xie, Z. J. Xu, S. Zhang, Q. Zhang, *J. Mater. Chem. A* **2019**, 7, 4259-

- 4290.
- [39] P. Ge, S. Li, H. Shuai, W. Xu, Y. Tian, L. Yang, G. Zou, H. Hou, X. Ji, *Adv. Mater.* **2019**, *31*, 1806092.
 - [40] Y. He, S. L. Dreyer, T. Akçay, T. Diemant, R. Mönig, Y. Ma, Y. Tang, H. Wang, J. Lin, S. Schweidler, M. Fichtner, H. Hahn, T. Brezesinski, B. Breitung, Y. Ma, *ACS Nano* **2024**, *18*, 24441-24457.
 - [41] R. V. Panin, O. A. Drozhzhin, S. S. Fedotov, N. R. Khasanova, E. V. Antipov, *Electrochim. Acta* **2018**, *289*, 168-174.
 - [42] P. Feng, W. Wang, J. Hou, K. Wang, S. Cheng, K. Jiang, *Chem. Eng. J.* **2018**, *353*, 25-33.
 - [43] Y. Ni, G. He, *Electrochim. Acta* **2018**, *292*, 47-54.
 - [44] Q. Tao, H. Ding, H. Zhao, J. Huang, B. Dai, J. Li, *J. Alloys Compd.* **2024**, *976*, 172977.
 - [45] Y.-X. Chang, L. Yu, X. Xing, Y.-J. Guo, Z.-Y. Xie, S. Xu, *Chem. Rec.* **2022**, *22*, e202200122.
 - [46] P. Vassilaras, X. Ma, X. Li, G. Ceder, *J. Electrochem. Soc.* **2013**, *160*, A207.
 - [47] M. H. Han, E. Gonzalo, M. Casas-cabanas, T. Rojo, *J. Power Sources* **2014**, *258*, 266-271.
 - [48] L. Wang, J. Wang, X. Zhang, Y. Ren, P. Zuo, G. Yin, J. Wang, *Nano Energy* **2017**, *34*, 215-223.
 - [49] M. Shishkin, S. Kumakura, S. Sato, K. Kubota, S. Komaba, H. Sato, *Chem. Mater.* **2018**, *30*, 1257-1264.
 - [50] J. Manzi, A. Paolone, O. Palumbo, D. Corona, A. Massaro, R. Cavaliere, A. B. Muñoz-García, F. Trequattrini, M. Pavone, S. Brutti, *Energies* **2021**, *14*, 1230.
 - [51] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, *Chem. Rev.* **2014**, *114*, 11636-11682.
 - [52] C. Delmas, C. Fouassier, P. Hagenmuller, *Physica B+C* **1980**, *99*, 81-85.
 - [53] S.-B. Wei, Y.-J. He, Y. Tang, H.-W. Fu, J. Zhou, S.-Q. Liang, X.-X. Cao, *Rare Met.* **2024**, *43*, 5701-5711.
 - [54] L. Karger, D. Weber, D. Goonetilleke, A. Mazilkin, H. Li, R. Zhang, Y. Ma, S. Indris, A. Kondrakov, J. Janek, T. Brezesinski, *Chem. Mater.* **2023**, *35*, 648-657.
 - [55] A. Konarov, H. J. Kim, N. Voronina, Z. Bakenov, S.-T. Myung, *ACS Appl. Mater. Interfaces* **2019**, *11*, 28928-28933.
 - [56] S. Kumakura, Y. Tahara, K. Kubota, K. Chihara, S. Komaba, *Angew. Chem., Int. Ed.* **2016**, *55*, 12760-12763.

5. Bibliography

- [57] F.-X. Ding, X.-H. Rong, H.-B. Wang, Y. Yang, Z.-L. Hu, R.-B. Dang, Y.-X. Lu, Y.-S. Hu, *Acta Phys. Sin.* **2022**, *71*, 108801.
- [58] Y. Yu, D. Ning, Q. Li, A. Franz, L. Zheng, N. Zhang, G. Ren, G. Schumacher, X. Liu, *Energy Storage Mater.* **2021**, *38*, 130-140.
- [59] Z. Guo, X. Li, Y. Lyu, S. Xu, *Electrochim. Acta* **2022**, *430*, 141079.
- [60] M. Matsui, F. Mizukoshi, H. Hasegawa, N. Imanishi, *J. Power Sources* **2021**, *485*, 229346.
- [61] M. Sathiya, J. Thomas, D. Batuk, V. Pimenta, R. Gopalan, J.-M. Tarascon, *Chem. Mater.* **2017**, *29*, 5948-5956.
- [62] M. Matsuzaki, R. Tatara, K. Kubota, K. Kuroki, T. Hosaka, K. Umetsu, N. Okada, S. Komaba, *Batter. Supercaps* **2024**, *7*, e202400009.
- [63] K. Wang, H. Zhuo, J. Wang, F. Poon, X. Sun, B. Xiao, *Adv. Funct. Mater.* **2023**, *33*, 2212607.
- [64] Y. Wang, J. Liu, B. Lee, R. Qiao, Z. Yang, S. Xu, X. Yu, L. Gu, Y.-S. Hu, W. Yang, K. Kang, H. Li, X.-Q. Yang, L. Chen, X. Huang, *Nat. Commun.* **2015**, *6*, 6401.
- [65] K. Kubota, M. Miyazaki, E. J. Kim, H. Yoshida, P. Barpanda, S. Komaba, *J. Mater. Chem. A* **2021**, *9*, 26810-26819.
- [66] X. Chen, Y. Wang, K. Wiaderek, X. Sang, O. Borkiewicz, K. Chapman, J. LeBeau, J. Lynn, X. Li, *Adv. Funct. Mater.* **2018**, *28*, 1805105.
- [67] C. Delmas, D. Carlier, M. Guignard, *Adv. Energy Mater.* **2021**, *11*, 2001201.
- [68] D. Wu, X. Li, B. Xu, N. Twu, L. Liu, G. Ceder, *Energy Environ. Sci.* **2015**, *8*, 195-202.
- [69] H. Wang, Y. Xiao, C. Sun, C. Lai, X. Ai, *RSC Adv.* **2015**, *5*, 106519-106522.
- [70] S. Maletti, A. Sarapulova, A. Schökel, D. Mikhailova, *ACS Appl. Mater. Interfaces* **2019**, *11*, 33923-33930.
- [71] H. Yu, S. Guo, Y. Zhu, M. Ishida, H. Zhou, *Chem. Commun.* **2014**, *50*, 457-459.
- [72] K. Kubota, N. Fujitani, Y. Yoda, K. Kuroki, Y. Tokita, S. Komaba, *J. Mater. Chem. A* **2021**, *9*, 12830-12844.
- [73] P.-F. Wang, H.-R. Yao, X.-Y. Liu, J.-N. Zhang, L. Gu, X.-Q. Yu, Y.-X. Yin, Y.-G. Guo, *Adv. Mater.* **2017**, *29*, 1700210.
- [74] S. Komaba, C. Takei, T. Nakayama, A. Ogata, N. Yabuuchi, *Electrochem. commun.* **2010**, *12*, 355-358.
- [75] D. Hamani, M. Ati, J.-M. Tarascon, P. Rozier, *Electrochem. commun.* **2011**, *13*, 938-941.
- [76] P.-F. Wang, Y. You, Y.-X. Yin, Y.-G. Guo, *Adv. Energy Mater.* **2018**, *8*, 1701912.

5. Bibliography

- [77] J.-J. Braconnier, C. Delmas, C. Fouassier, P. Hagenmuller, *Mater. Res. Bull.* **1980**, *15*, 1797-1804.
- [78] C. Delmas, J.-J. Braconnier, C. Fouassier, P. Hagenmuller, *Solid State Ionics* **1981**, *3–4*, 165-169.
- [79] N. Yabuuchi, S. Komaba, *Sci. Technol. Adv. Mater.* **2014**, *15*, 043501.
- [80] Y. Takeda, J. Akagi, A. Edagawa, M. Inagaki, S. Naka, *Mater. Res. Bull.* **1980**, *15*, 1167-1172.
- [81] N. Yabuuchi, H. Yoshida, S. Komaba, *Electrochemistry* **2012**, *80*, 716-719.
- [82] X. Ma, H. Chen, G. Ceder, *J. Electrochem. Soc.* **2011**, *158*, A1307-A1312.
- [83] A. Mendiboure, C. Delmas, P. Hagenmuller, *J. Solid State Chem.* **1985**, *57*, 323-331.
- [84] L. A. V. Nagle-Cocco, A. R. Genreith-Schriever, J. M. A. Steele, C. Tacconis, J. D. Bocarsly, O. Mathon, J. C. Neuefeind, J. Liu, C. A. O'Keefe, A. L. Goodwin, C. P. Grey, J. S. O. Evans, S. E. Dutton, *J. Am. Chem. Soc.* **2024**, *146*, 29560-29574.
- [85] E. Chappel, M. D. Núñez-Regueiro, G. Chouteau, O. Isnard, C. Darie, *Eur. Phys. J. B* **2000**, *17*, 615-622.
- [86] K. Sada, S. Kmiec, A. Manthiram, *Angew. Chemie* **2024**, *136*, e202403865.
- [87] L. D. Dyer, B. S. Borie Jr., G. P. Smith, *J. Am. Chem. Soc.* **1954**, *76*, 1499-1503.
- [88] J.-J. Braconnier, C. Delmas, P. Hagenmuller, *Mater. Res. Bull.* **1982**, *17*, 993-1000.
- [89] J.-P. Parant, R. Olazcuaga, M. Devalette, C. Fouassier, P. Hagenmuller, *J. Solid State Chem.* **1971**, *3*, 1-11.
- [90] J. Billaud, R. J. Clément, A. R. Armstrong, J. Canales-Vázquez, P. Rozier, C. P. Grey, P. G. Bruce, *J. Am. Chem. Soc.* **2014**, *136*, 17243-17248.
- [91] I.-H. Jo, H.-S. Ryu, D.-G. Gu, J.-S. Park, I.-S. Ahn, H.-J. Ahn, T.-H. Nam, K.-W. Kim, *Mater. Res. Bull.* **2014**, *58*, 74-77.
- [92] T. Sato, K. Yoshikawa, W. Zhao, T. Kobayashi, H. B. Rajendra, M. Yonemura, N. Yabuuchi, *Energy Mater. Adv.* **2021**, *2021*, 9857563.
- [93] S. L. Dreyer, K. R. Kretschmer, Đ. Tripković, A. Mazilkin, R. Chukwu, R. Azmi, P. Hartmann, M. Bianchini, T. Brezesinski, J. Janek, *Adv. Mater. Interfaces* **2022**, *9*, 2101100.
- [94] T. Ma, G.-L. Xu, Y. Li, B. Song, X. Zeng, C.-C. Su, W. L. Mattis, F. Guo, Y. Ren, R. Kou, C. Sun, S. M. Heald, H.-H. Wang, R. Shahbazian-Yassar, J. Jorne, Z. Chen, K. Amine, *ACS Appl. Energy Mater.* **2018**, *1*, 5735-5745.

5. Bibliography

- [95] K. Kubota, I. Ikeuchi, T. Nakayama, C. Takei, N. Yabuuchi, H. Shiiba, M. Nakayama, S. Komaba, *J. Phys. Chem. C* **2015**, *119*, 166-175.
- [96] T.-Y. Yu, H.-H. Ryu, G. Han, Y.-K. Sun, *Adv. Energy Mater.* **2020**, *10*, 2001609.
- [97] N. Voronina, N. Yaqoob, H. J. Kim, K.-S. Lee, H.-D. Lim, H.-G. Jung, O. Guillon, P. Kaghazchi, S.-T. Myung, *Adv. Energy Mater.* **2021**, *11*, 2100901.
- [98] H. Kim, H. Kim, Z. Ding, M. H. Lee, K. Lim, G. Yoon, K. Kang, *Adv. Energy Mater.* **2016**, *6*, 1600943.
- [99] Q. Liu, Z. Hu, M. Chen, C. Zou, H. Jin, S. Wang, S.-L. Chou, Y. Liu, S.-X. Dou, *Adv. Funct. Mater.* **2020**, *30*, 1909530.
- [100] K. Wang, P. Yan, M. Sui, *Nano Energy* **2018**, *54*, 148-155.
- [101] Y. Yang, Y. Feng, Z. Chen, Y. Feng, Q. Huang, C. Ma, Q. Xia, C. Liang, L. Zhou, M. S. Islam, P. Wang, L. Zhou, L. Mai, W. Wei, *Nano Energy* **2020**, *76*, 105061.
- [102] Y. Li, G. Liu, J. Che, L. Chen, X. Wang, G. Wang, L. Lei, J. Hou, S. Li, J. Wang, Y. Xu, Y. Zhao, *Interdiscip. Mater.* **2025**, *4*, 24-51.
- [103] T. Zhang, M. Ren, Y. Huang, F. Li, W. Hua, S. Indris, F. Li, *Angew. Chemie* **2024**, *136*, e202316949.
- [104] S. Gao, Z. Zhu, H. Fang, K. Feng, J. Zhong, M. Hou, Y. Guo, F. Li, W. Zhang, Z. Ma, F. Li, *Adv. Mater.* **2024**, *36*, 2311523.
- [105] M. D. Radin, S. Hy, M. Sina, C. Fang, H. Liu, J. Vinckeviciute, M. Zhang, M. S. Whittingham, Y. S. Meng, A. Van der Ven, *Adv. Energy Mater.* **2017**, *7*, 1602888.
- [106] H. Y. Asl, A. Manthiram, *Science* **2020**, *369*, 140-141.
- [107] M. D. Radin, A. Van der Ven, *Chem. Mater.* **2018**, *30*, 607-618.
- [108] H. Y. Asl, A. Manthiram, *J. Am. Chem. Soc.* **2020**, *142*, 21122-21130.
- [109] T. Liu, A. Dai, J. Lu, Y. Yuan, Y. Xiao, L. Yu, M. Li, J. Gim, L. Ma, J. Liu, C. Zhan, L. Li, J. Zheng, Y. Ren, T. Wu, R. Shahbazian-Yassar, J. Wen, F. Pan, K. Amine, *Nat. Commun.* **2019**, *10*, 4721.
- [110] Z. Zhu, H. Peelaers, C. G. Van de Walle, *Chem. Mater.* **2019**, *31*, 5224-5228.
- [111] L. Mu, X. Feng, R. Kou, Y. Zhang, H. Guo, C. Tian, C.-J. Sun, X.-W. Du, D. Nordlund, H. L. Xin, F. Lin, *Adv. Energy Mater.* **2018**, *8*, 1801975.
- [112] L. Xing, O. Borodin, *Phys. Chem. Chem. Phys.* **2012**, *14*, 12838-12843.
- [113] A. Wuersig, W. Scheifele, P. Novák, *J. Electrochem. Soc.* **2007**, *154*, A449-A454.
- [114] C. Zhan, T. Wu, J. Lu, K. Amine, *Energy Environ. Sci.* **2018**, *11*, 243-257.
- [115] S. Sun, J. Li, C. Xu, T. Zhai, H. Xia, *J. Mater. Chem. A* **2022**, *10*, 19231-19253.
- [116] G.-L. Xu, Y. Qin, Y. Ren, L. Cai, K. An, K. Amine, Z. Chen, *J. Mater. Chem. A*

- 2015**, 3, 13031-13038.
- [117] Y. Kan, Y. Hu, C.-K. Lin, Y. Ren, Y.-K. Sun, K. Amine, Z. Chen, *Phys. Chem. Chem. Phys.* **2014**, 16, 20697-20702.
- [118] Z.-X. Huang, Z.-Y. Gu, Y.-L. Heng, E. H. Ang, H.-B. Geng, X.-L. Wu, *Chem. Eng. J.* **2023**, 452, 139438.
- [119] W. Zuo, Z. Xiao, M. Zarrabeitia, X. Xue, Y. Yang, S. Passerini, *ACS Mater. Lett.* **2022**, 4, 1074-1086.
- [120] Y.-F. Liu, K. Han, D.-N. Peng, L.-Y. Kong, Y. Su, H.-W. Li, H.-Y. Hu, J.-Y. Li, H.-R. Wang, Z.-Q. Fu, Q. Ma, Y.-F. Zhu, R.-R. Tang, S.-L. Chou, Y. Xiao, X.-W. Wu, *InfoMat* **2023**, 5, e12422.
- [121] Y. Su, L. Li, G. Chen, L. Chen, N. Li, Y. Lu, L. Bao, S. Chen, F. Wu, *Chin. J. Chem.* **2021**, 39, 189-198.
- [122] H.-R. Yao, L. Zheng, S. Xin, Y.-G. Guo, *Sci. China Chem.* **2022**, 65, 1076-1087.
- [123] Y. Zhang, R. Zhang, Y. Huang, *Front. Chem.* **2019**, 7, 335.
- [124] W. M. Seong, Y. Kim, A. Manthiram, *Chem. Mater.* **2020**, 32, 9479-9489.
- [125] K. Kubota, S. Komaba, *J. Electrochem. Soc.* **2015**, 162, A2538-A2550.
- [126] S. L. Dreyer, A. Kondrakov, J. Janek, T. Brezesinski, *J. Mater. Res.* **2022**, 37, 3146-3168.
- [127] L. A. Kaufman, B. D. McCloskey, *Chem. Mater.* **2021**, 33, 4170-4176.
- [128] L. Zhang, C. Tsolakidou, S. Mariyappan, J.-M. Tarascon, S. Trabesinger, *Energy Storage Mater.* **2021**, 42, 12-21.
- [129] A. T. S. Freiberg, J. Sicklinger, S. Solchenbach, H. A. Gasteiger, *Electrochim. Acta* **2020**, 346, 136271.
- [130] R. Jung, M. Metzger, F. Maglia, C. Stinner, H. A. Gasteiger, *J. Phys. Chem. Lett.* **2017**, 8, 4820-4825.
- [131] A. T. S. Freiberg, M. K. Roos, J. Wandt, R. de Vivie-Riedle, H. A. Gasteiger, *J. Phys. Chem. A* **2018**, 122, 8828-8839.
- [132] N. Mahne, S. E. Renfrew, B. D. McCloskey, S. A. Freunberger, *Angew. Chem., Int. Ed.* **2018**, 57, 5529-5533.
- [133] J. Wang, S. L. Dreyer, K. Wang, Z. Ding, T. Diemant, G. Karkera, Y. Ma, A. Sarkar, B. Zhou, M. V. Gorbunov, A. Omar, D. Mikhailova, V. Presser, M. Fichtner, H. Hahn, T. Brezesinski, B. Breitung, Q. Wang, *Mater. Futures* **2022**, 1, 035104.
- [134] B. Zhou, S. An, D. Kitsche, S. L. Dreyer, K. Wang, X. Huang, J. Thanner, M. Bianchini, T. Brezesinski, B. Breitung, H. Hahn, Q. Wang, *Small Struct.* **2024**, 5,

2400005.

- [135] R. Jung, M. Metzger, F. Maglia, C. Stinner, H. A. Gasteiger, *J. Electrochem. Soc.* **2017**, *164*, A1361-A1377.
- [136] J. Wandt, A. T. S. Freiberg, A. Ogrodnik, H. A. Gasteiger, *Mater. Today* **2018**, *21*, 825-833.
- [137] J. K. Papp, N. Li, L. A. Kaufman, A. J. Naylor, R. Younesi, W. Tong, B. D. McCloskey, *Electrochim. Acta* **2021**, *368*, 137505.
- [138] M. Metzger, B. Strehle, S. Solchenbach, H. A. Gasteiger, *J. Electrochem. Soc.* **2016**, *163*, A798-A809.
- [139] D. R. Gallus, R. Schmitz, R. Wagner, B. Hoffmann, S. Nowak, I. Cekic-Laskovic, R. W. Schmitz, M. Winter, *Electrochim. Acta* **2014**, *134*, 393-398.
- [140] Y. Lv, S. Huang, Y. Zhao, S. Roy, X. Lu, Y. Hou, J. Zhang, *Appl. Energy* **2022**, *305*, 117849.
- [141] T. Ma, G.-L. Xu, X. Zeng, Y. Li, Y. Ren, C. Sun, S. M. Heald, J. Jorne, K. Amine, Z. Chen, *J. Power Sources* **2017**, *341*, 114-121.
- [142] Q. Ma, F. Peng, R. Li, S. Yin, C. Dai, *Mater. Sci. Eng. B* **2016**, *213*, 123-130.
- [143] L. M. Nguyen, V. H. Nguyen, D. M. N. Nguyen, M. K. Le, V. M. Tran, M. L. P. Le, *ChemEngineering* **2023**, *7*, 33.
- [144] N. Yabuuchi, R. Hara, K. Kubota, J. Paulsen, S. Kumakura, S. Komaba, *J. Mater. Chem. A* **2014**, *2*, 16851-16855.
- [145] R. Stoyanova, D. Carlier, M. Sendova-Vassileva, M. Yoncheva, E. Zhecheva, D. Nihtianova, C. Delmas, *J. Solid State Chem.* **2010**, *183*, 1372-1379.
- [146] J. M. Paulsen, J. R. Dahn, *Solid State Ionics* **1999**, *126*, 3-24.
- [147] X. Liu, G. Zhong, Z. Xiao, B. Zheng, W. Zuo, K. Zhou, H. Liu, Z. Liang, Y. Xiang, Z. Chen, G. F. Ortiz, R. Fu, Y. Yang, *Nano Energy* **2020**, *76*, 104997.
- [148] G.-L. Xu, X. Liu, X. Zhou, C. Zhao, I. Hwang, A. Daali, Z. Yang, Y. Ren, C.-J. Sun, Z. Chen, Y. Liu, K. Amine, *Nat. Commun.* **2022**, *13*, 436.
- [149] X. Li, Y. Fan, B. Johannessen, X. Xu, K. W. See, W. K. Pang, *Batter. Supercaps* **2024**, *7*, e202300618.
- [150] D. Zhou, W. Huang, F. Zhao, X. Lv, *J. Mater. Sci.* **2019**, *54*, 7156-7164.
- [151] J. Lamb, A. Manthiram, *Chem. Mater.* **2020**, *32*, 8431-8441.
- [152] V. P. Mhaske, S. Jilkar, M. D. Yadav, *Energy Fuels* **2023**, *37*, 16221-16244.
- [153] C. Hakim, N. Sabi, I. Saadoune, *J. Energy Chem.* **2021**, *61*, 47-60.
- [154] H. Dong, G. M. Koenig Jr., *CrystEngComm* **2020**, *22*, 1514-1530.

5. Bibliography

- [155] H. Xu, Q. Yan, W. Yao, C.-S. Lee, Y. Tang, *Small Struct.* **2022**, 3, 2100217.
- [156] X. Wang, G. Liu, T. Iwao, M. Okubo, A. Yamada, *J. Phys. Chem. C* **2014**, 118, 2970-2976.
- [157] J. M. Gonçalves, G. T. M. Silva, H. Zanin, *J. Mater. Chem. A* **2024**, 12, 17756-17770.
- [158] P. Vassilaras, D.-H. Kwon, S. T. Dacek, T. Shi, D.-H. Seo, G. Ceder, J. C. Kim, *J. Mater. Chem. A* **2017**, 5, 4596-4606.
- [159] H.-H. Sun, J.-Y. Hwang, C. S. Yoon, A. Heller, C. B. Mullins, *ACS Nano* **2018**, 12, 12912-12922.
- [160] C. Zhao, Z. Yao, J. Wang, Y. Lu, X. Bai, A. Aspuru-Guzik, L. Chen, Y.-S. Hu, *Chem* **2019**, 5, 2913-2925.
- [161] L.-A. Zhu, J. Tian, H. Miao, Y. Liu, *Mater. Today Commun.* **2024**, 40, 109552.
- [162] Y. Yoda, K. Kubota, K. Kuroki, S. Suzuki, K. Yamanaka, T. Yaji, S. Amagasa, Y. Yamada, T. Ohta, S. Komaba, *Small* **2020**, 16, 2006483.
- [163] Z. Zhang, Y. Liu, Z. Liu, H. Li, Y. Huang, W. Liu, D. Ruan, X. Cai, X. Yu, *J. Power Sources* **2023**, 567, 232930.
- [164] Y.-H. Feng, Z. Cheng, C.-L. Xu, L. Yu, D. Si, B. Yuan, M. Liu, B. Zhao, P.-F. Wang, X. Han, *ACS Appl. Mater. Interfaces* **2022**, 14, 23465-23473.
- [165] R. Fielden, M. N. Obrovac, *J. Electrochem. Soc.* **2015**, 162, A453-A459.
- [166] C. Zhao, Q. Wang, Z. Yao, J. Wang, B. Sánchez-Lengeling, F. Ding, X. Qi, Y. Lu, X. Bai, B. Li, H. Li, A. Aspuru-Guzik, X. Huang, C. Delmas, M. Wagemaker, L. Chen, Y.-S. Hu, *Science* **2020**, 370, 708-711.
- [167] W. Kang, Z. Zhang, P.-K. Lee, T.-W. Ng, W. Li, Y. Tang, W. Zhang, C.-S. Lee, D. Y. W. Yu, *J. Mater. Chem. A* **2015**, 3, 22846-22852.
- [168] J. Wang, H. Liu, Q. Yang, B. Hu, F. Geng, C. Zhao, Y. Lin, B. Hu, *ACS Appl. Mater. Interfaces* **2020**, 12, 34848-34857.
- [169] J. Darga, A. Manthiram, *ACS Appl. Mater. Interfaces* **2022**, 14, 52729-52737.
- [170] T. Yuan, Y. Sun, S. Li, H. Che, Q. Zheng, Y. Ni, Y. Zhang, J. Zou, X. Zang, S.-H. Wei, Y. Pang, S. Xia, S. Zheng, L. Chen, Z.-F. Ma, *Nano Res.* **2023**, 16, 6890-6902.
- [171] J.-Y. Hwang, C. S. Yoon, I. Belharouak, Y.-K. Sun, *J. Mater. Chem. A* **2016**, 4, 17952-17959.
- [172] J. Yu, H. Yu, L. Zhou, Q. Cheng, H. Jiang, *Appl. Surf. Sci.* **2024**, 649, 159121.
- [173] Y. Wang, Z. Feng, P. Cui, W. Zhu, Y. Gong, M.-A. Girard, G. Lajoie, J. Trottier, Q. Zhang, L. Gu, Y. Wang, W. Zuo, Y. Yang, J. B. Goodenough, K. Zaghib, *Nat.*

- Commun.* **2021**, *12*, 13.
- [174] Y. Huang, Z. Yan, W. Luo, Z. Hu, G. Liu, L. Zhang, X. Yang, M. Ou, W. Liu, L. Huang, H. Lin, C.-T. Chen, J. Luo, S. Li, J. Han, S. Chou, Y. Huang, *Energy Storage Mater.* **2020**, *29*, 182-189.
- [175] Q.-C. Wang, J.-K. Meng, X.-Y. Yue, Q.-Q. Qiu, Y. Song, X.-J. Wu, Z.-W. Fu, Y.-Y. Xia, Z. Shadike, J. Wu, X.-Q. Yang, Y.-N. Zhou, *J. Am. Chem. Soc.* **2019**, *141*, 840-848.
- [176] S. C. Han, H. Lim, J. Jeong, D. Ahn, W. B. Park, K.-S. Sohn, M. Pyo, *J. Power Sources* **2015**, *277*, 9-16.
- [177] H. Fu, Y.-P. Wang, G. Fan, S. Guo, X. Xie, X. Cao, B. Lu, M. Long, J. Zhou, S. Liang, *Chem. Sci.* **2022**, *13*, 726-736.
- [178] S. Wu, B. Su, K. Ni, F. Pan, C. Wang, K. Zhang, D. Y. W. Yu, Y. Zhu, W. Zhang, *Adv. Energy Mater.* **2021**, *11*, 2002737.
- [179] S. Komaba, T. Ishikawa, N. Yabuuchi, W. Murata, A. Ito, Y. Ohsawa, *ACS Appl. Mater. Interfaces* **2011**, *3*, 4165-4168.
- [180] Y. Liu, X. Fang, A. Zhang, C. Shen, Q. Liu, H. A. Enaya, C. Zhou, *Nano Energy* **2016**, *27*, 27-34.
- [181] J.-Y. Hwang, T.-Y. Yu, Y.-K. Sun, *J. Mater. Chem. A* **2018**, *6*, 16854-16862.
- [182] Y. Yang, R. Dang, K. Wu, Q. Li, N. Li, X. Xiao, Z. Hu, *J. Phys. Chem. C* **2020**, *124*, 1780-1787.
- [183] R. Dang, Q. Li, M. Chen, Z. Hu, X. Xiao, *Phys. Chem. Chem. Phys.* **2019**, *21*, 314-321.
- [184] Y. You, A. Dolocan, W. Li, A. Manthiram, *Nano Lett.* **2019**, *19*, 182-188.
- [185] J. H. Jo, J. U. Choi, A. Konarov, H. Yashiro, S. Yuan, L. Shi, Y.-K. Sun, S.-T. Myung, *Adv. Funct. Mater.* **2018**, *28*, 1705968.

6. Appendix

6.1. Supporting Information

6.1.1. Supporting Information of Publication I

Supporting Information

Improving Cycling Performance of the NaNiO₂ Cathode in Sodium-Ion Batteries by Titanium Substitution

Siyu An¹, Leonhard Karger¹, Sören L. Dreyer¹, Yang Hu², Eduardo Barbosa¹, Ruizhuo Zhang¹, Jing Lin¹, Maximilian Fichtner², Aleksandr Kondrakov^{1,3}, Jürgen Janek^{1,4*} and Torsten Brezesinski^{1*}

¹Battery and Electrochemistry Laboratory (BELLA), Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

²Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Helmholtzstr. 11, 89081 Ulm, Germany

³BASF SE, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany

⁴Institute of Physical Chemistry & Center for Materials Research (ZfM/LaMa), Justus-Liebig-University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

*Email: juergen.janek@kit.edu, torsten.brezesinski@kit.edu

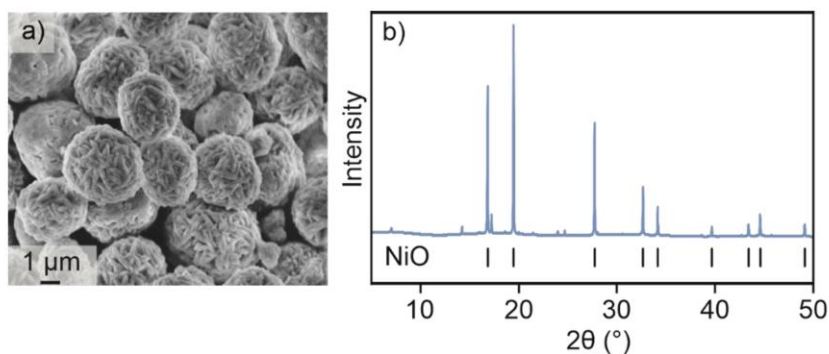


Figure S1. (a) SEM image of the $\text{Ni}(\text{OH})_2$ precursor. (b) XRD pattern of NNTO after pre-calcination at 300 °C.

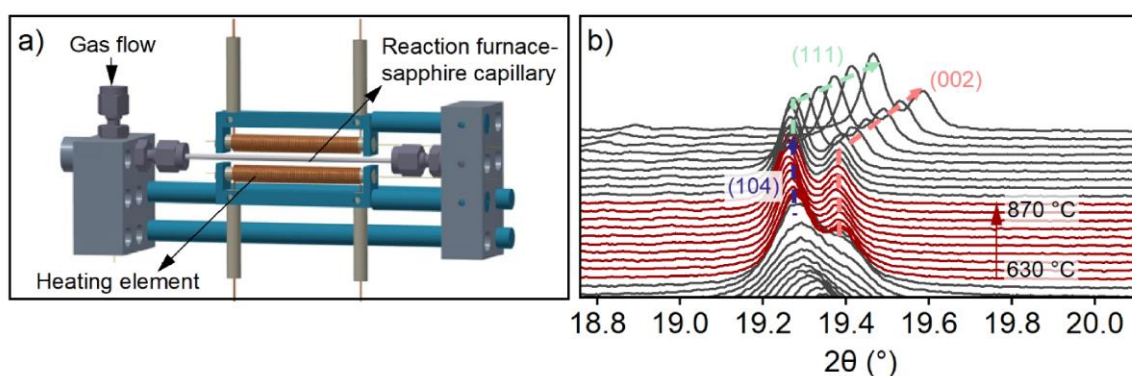


Figure S2. (a) Schematic of the *in situ* XRD setup. (b) Magnified view of the 2-theta region around the (104) reflection.

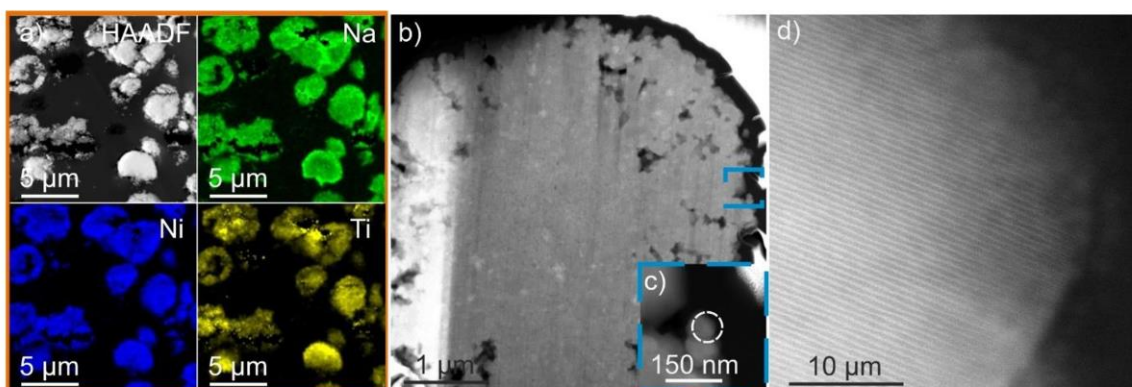


Figure S3. (a) STEM-EDS mapping of NNTO (700 °C). (b, c) Low- and high-magnification cross-sectional HAADF STEM images of a FIB-prepared NNTO (700 °C) particle. (d) High-resolution image of the area indicated by the white dashed circle in (c).

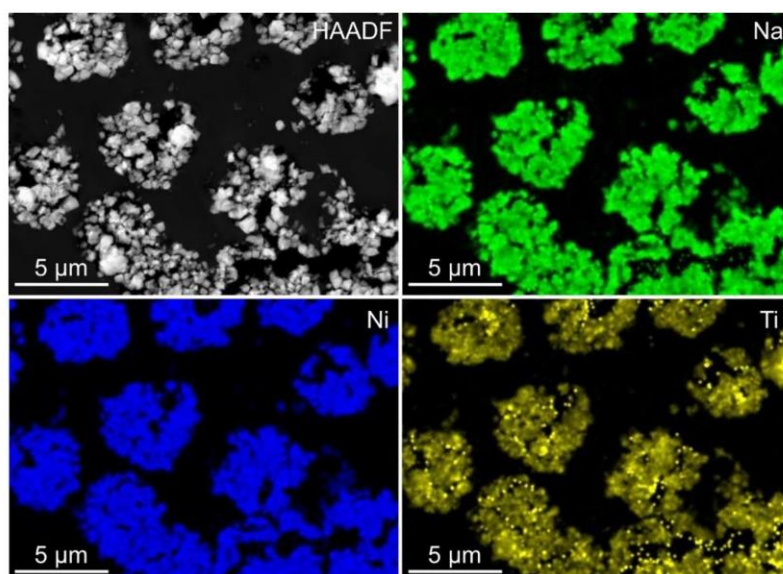


Figure S4. Low-magnification STEM-EDS mapping of NNTO (800 °C).

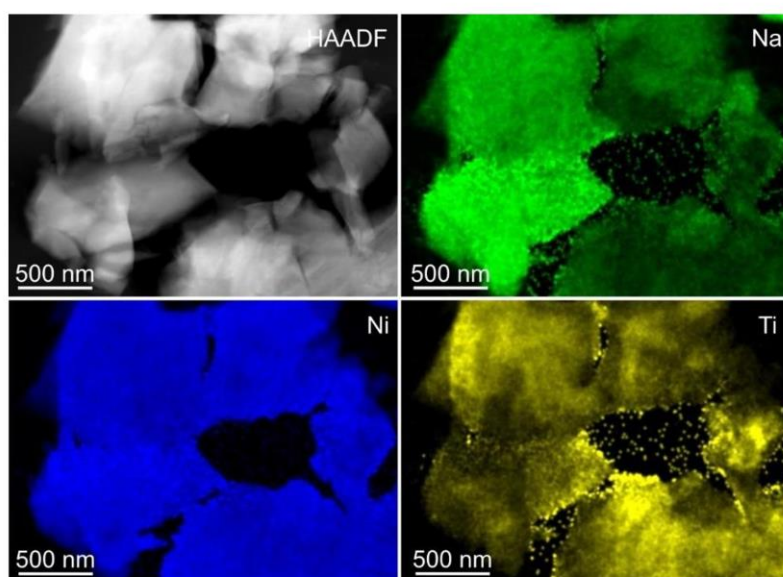


Figure S5. High-magnification STEM-EDS mapping of NNTO (800 °C).

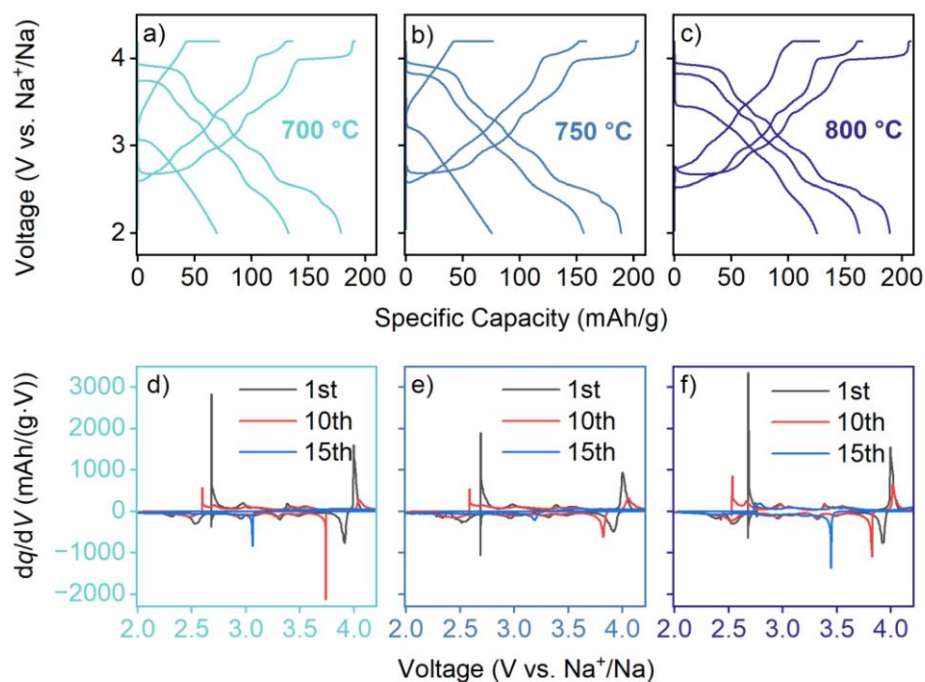


Figure S6. Voltage profiles (1st, 10th, and 15th cycle) and corresponding dq/dV curves of NNTO prepared at different temperatures of (a, d) 700 °C, (b, e) 750 °C, and (c, f) 800 °C.

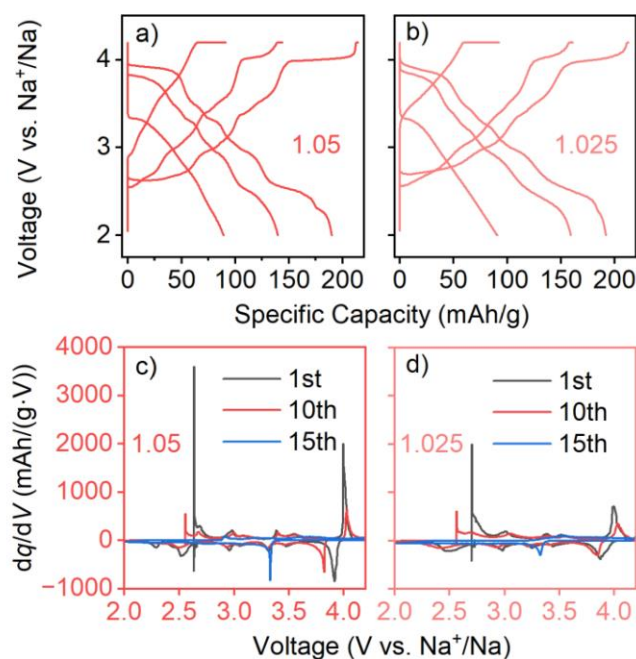


Figure S7. Voltage profiles (1st, 10th, and 15th cycle) and corresponding dq/dV curves of NNTO prepared with different molar Na/TM ratios of (a, c) 1.05 and (b, d) 1.025.

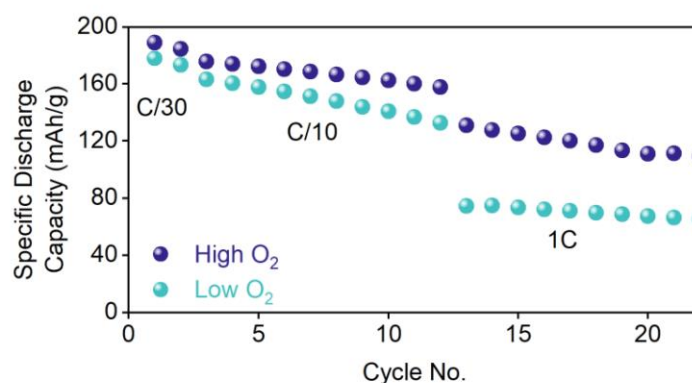


Figure S8. Cycling performance of NNTO prepared with different O₂ flow rates.

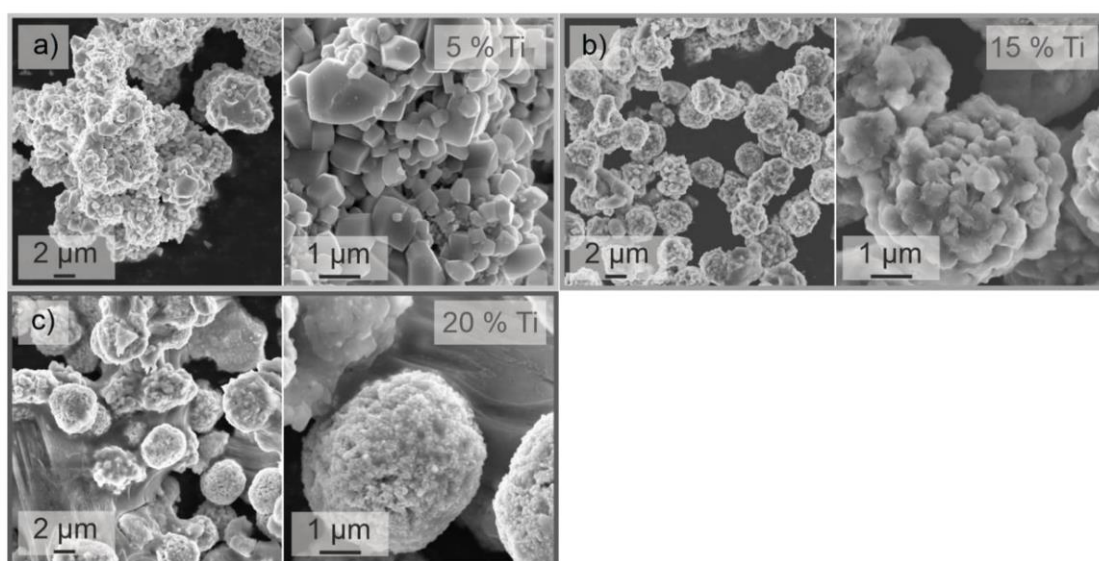


Figure S9. High- and low-magnification SEM images of NNTO prepared with different Ti fractions of (a) 5%, (b) 15%, and (c) 20%.

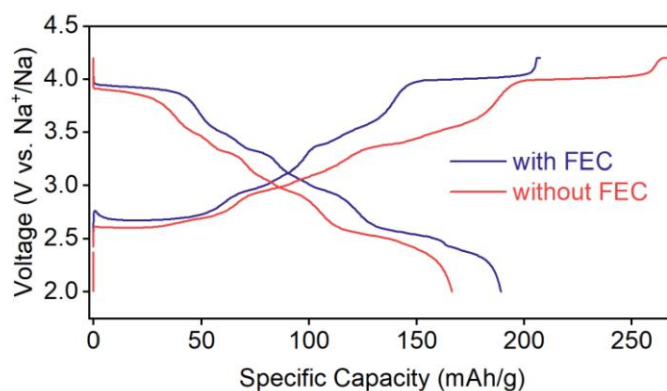


Figure S10. First-cycle voltage profiles of NNTO cathodes cycled with and without FEC electrolyte additive.

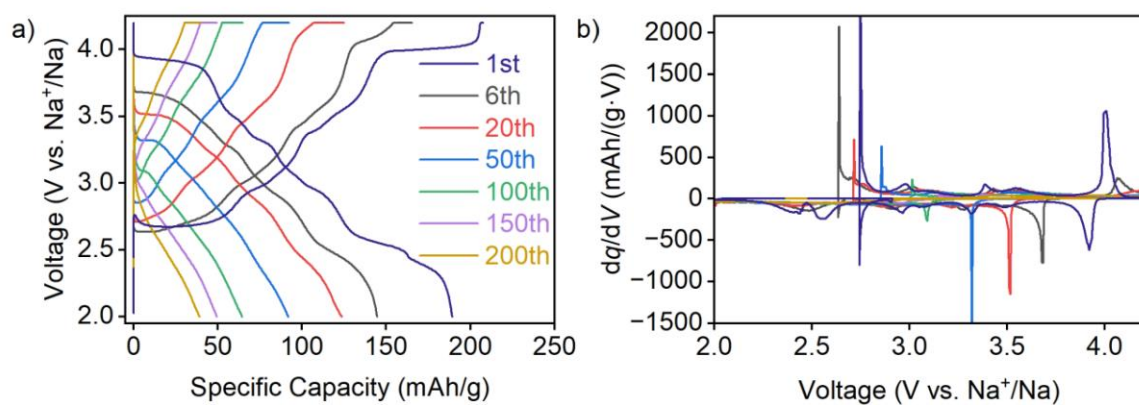


Figure S11. (a) Evolution of voltage profiles and (b) dq/dV curves of NNTO during long-term cycling.

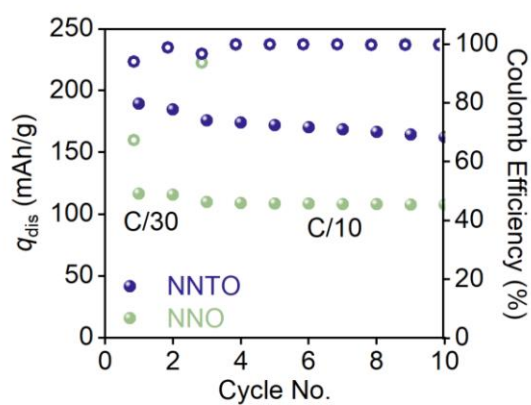


Figure S12. Cycling performance and Coulomb efficiency of NNTO and NNO cathodes used for XAS measurements.

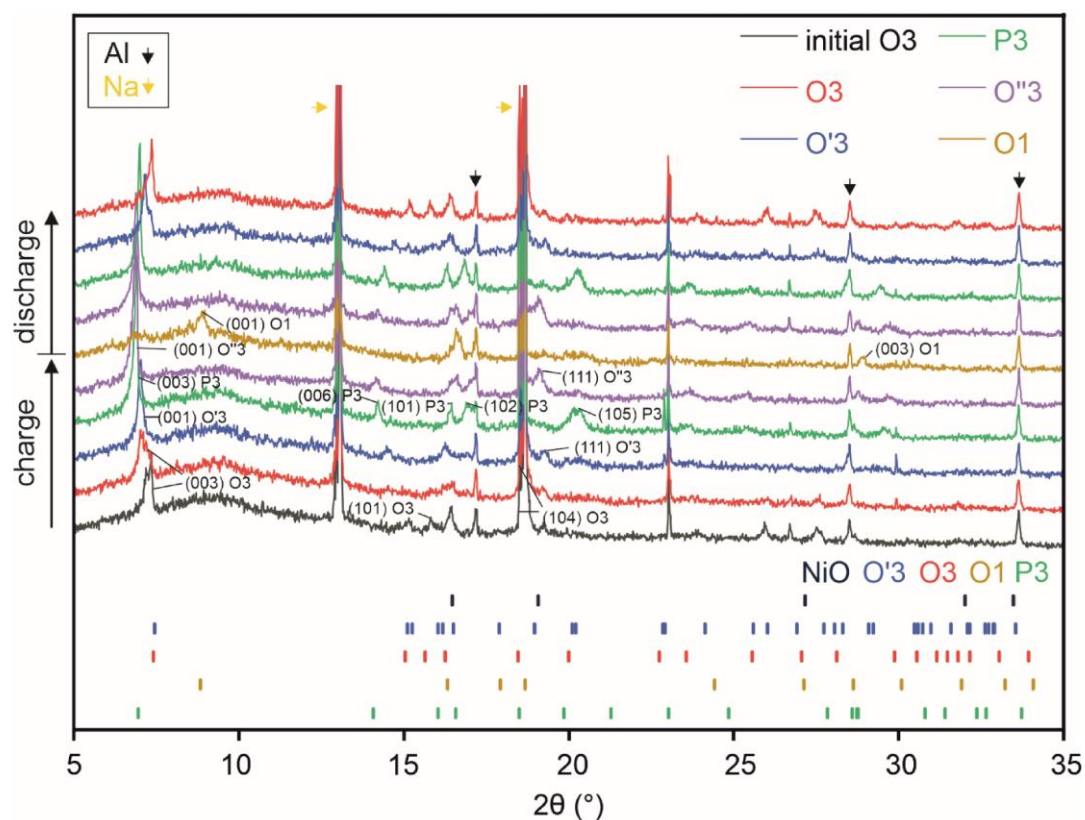


Figure S13. Individual XRD patterns collected during the initial cycle.

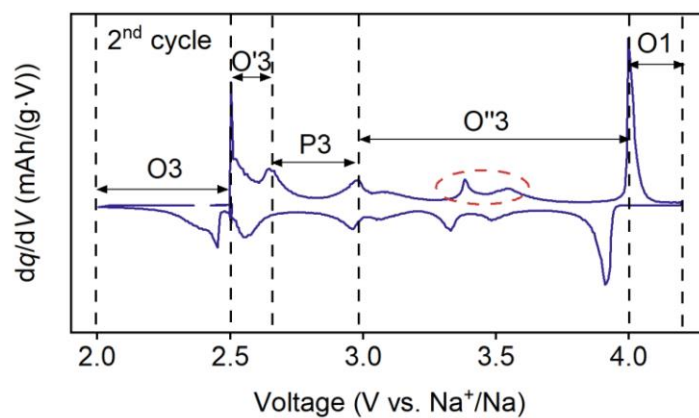


Figure S14. dq/dV curve indicating the different phase transitions of NNT0 occurring during the second cycle. Na^+ /vacancy ordering is denoted by a red dashed circle.

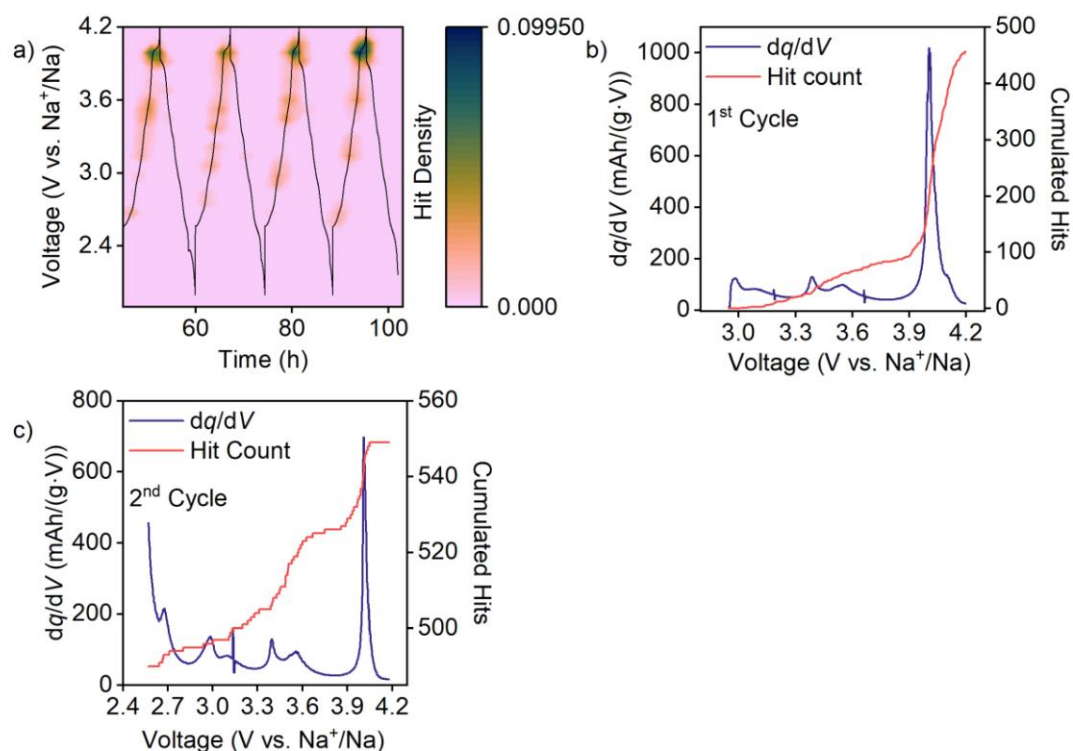


Figure S15. (a) Contour plot of acoustic activity (hit density) as a function of time and voltage for cycles 2–5. dq/dV curves of the (b) first and (c) second charge cycle and corresponding cumulated hits.

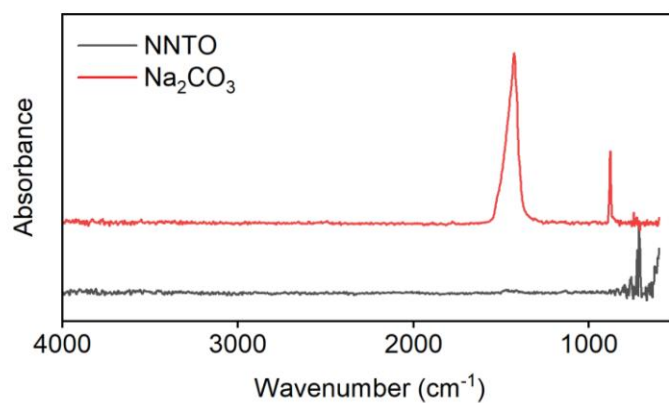


Figure S16. FT-IR spectra collected from the as-prepared NNTO and Na₂CO₃.

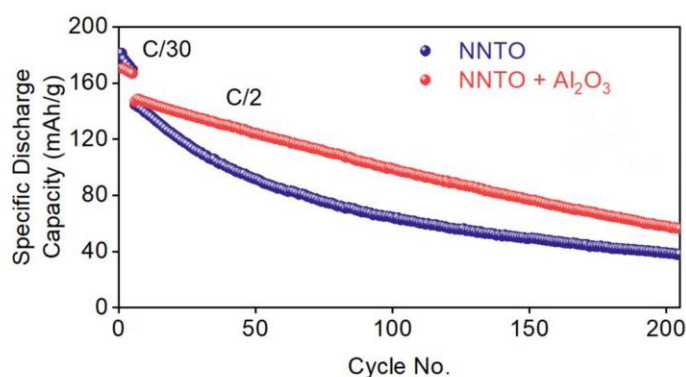


Figure S17. Long-term cycling performance of bare and Al₂O₃-coated NNTO cathodes.

Table S1. Phase fractions from Rietveld analysis of NNTO prepared at different temperatures.

Temperature (°C)	<i>R-3m</i> (wt.%)	<i>C2/m</i> (wt.%)	<i>Fm-3m</i> (wt.%)	<i>R_{wp}</i> (%)
900	4.3(0.2)	47.2(0.4)	48.5(0.3)	15.94
850	59.9(0.3)	24.2(0.3)	15.9(0.2)	13.87
800	98.5(0.1)	-	1.5(0.1)	12.48
750	93.8(0.2)	3.6(0.2)	2.6(0.1)	12.03
700	85.4(0.5)	11.3(0.5)	3.3(0.2)	15.48
600	79.5(0.4)	16.2(0.4)	4.3(0.2)	14.72

Table S2. Phase fractions from Rietveld analysis of NNTO prepared with different molar Na/TM ratios.

Na/TM	<i>R-3m</i> (wt.%)	<i>C2/m</i> (wt.%)	<i>Fm-3m</i> (wt.%)	<i>R_{wp}</i> (%)
1.05	97.9(0.2)	1.9(0.2)	0.2(0.1)	15.66
1.025	97.0(0.2)	1.9(0.2)	1.1(0.1)	18.58
1.0	98.5(0.1)	-	1.5(0.1)	12.48

Table S3. ICP-OES results for NNTO prepared with different molar Na/TM ratios.

Na/TM	Na (mol.%)	Ni (mol.%)	Ti (mol.%)	O (mol.%)
1.05	1.038(0.010)	0.9(0.004)	0.098(0)	2.30(0.030)
1.025	0.996(0.010)	0.9(0.006)	0.092(0)	2.30(0.008)
1.0	0.977(0.005)	0.9(0.002)	0.095(0)	2.05(0.060)

Table S4. Phase fractions from Rietveld analysis of NNTO prepared with different cooling rates.

Cooling rate	<i>R-3m</i> (wt.%)	<i>C2/m</i> (wt.%)	<i>Fm-3m</i> (wt.%)	<i>R_{wp}</i> (%)
0.5 K/min	96.1(0.2)	1.5(0.2)	2.4(0.1)	16.34
Quenching (O ₂)	97.0(0.1)	-	3.0(0.1)	14.39
2 K/min	98.5(0.1)	-	1.5(0.1)	12.48

Table S5. Phase fractions from Rietveld analysis of NNTO prepared with different O₂ flow rates.

Rate	<i>R-3m</i> (wt.%)	<i>C2/m</i> (wt.%)	<i>Fm-3m</i> (wt.%)	<i>R_{wp}</i> (%)
1.4 L/h	93.2(0.1)	1.1(0.2)	5.7(0.1)	14.22
7.0 L/h	98.5(0.1)	-	1.5(0.1)	12.48

Table S6. Phase fractions from Rietveld analysis for NNTO prepared with different Ni/Ti ratios.

Ni/Ti	<i>R-3m</i> (wt.%)	<i>C2/m</i> (wt.%)	<i>Fm-3m</i> (wt.%)	<i>R_{wp}</i> (%)
95:5	46.6(0.5)	49.4(0.5)	4.0(0.2)	20.49
85:15	82.4(0.3)	1.8(0.3)	15.8(0.2)	18.85
80:20	51.5(0.5)	-	48.5(0.5)	20.22

Table S7. Refined lattice parameters for pristine O3-NNTO.

Phase	Symmetry	Space group	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	<i>R_{wp}</i> (%)
α-NaFeO ₂	Rhombohedral	<i>R-3m</i>	2.9612 (0.0002)	15.7769 (0.0008)	119.812 (0.013)	12.48

6. Appendix

Table S8. Rietveld refinement results for the individual XRD patterns shown in Figure S13.

<i>E</i> (V)	Type	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)	<i>V</i> (cub, Å ³)	<i>R</i> _{Bragg} (%)	<i>R</i> _{wp} (%)	Gof
2.9	O3	<i>R</i> -3 <i>m</i>	2.94 (0.0003)	-	15.713 (0.004)	-	117.612 (0.035)	39.2	6.69	23.12	2.67
2.75	O'3	<i>C</i> 2/ <i>m</i>	5.286 (0.014)	2.842 (0.004)	5.906 (0.019)	113.6 (0.397)	81.259 (0.134)	40.6	1.76	22.49	2.57
3.3	P3	<i>R</i> 3 <i>m</i>	2.879 (0.0002)	-	16.559 (0.0016)	-	118.867 (0.021)	39.6	0.76	29.89	3.45
4.0	O''3	<i>C</i> 2/ <i>m</i>	5.188 (0.01)	2.832 (0.002)	6.033 (0.009)	113.8 (0.189)	81.864 (0.04)	40.9	1.65	21.6	2.42
4.0	O1	<i>P</i> -3 <i>m</i> 1	2.754 (0.0014)	-	4.348 (0.006)	-	28.58 (0.03)	28.6	0.76	15.32	1.56
3.6	O'3	<i>C</i> 2/ <i>m</i>	5.187(7)	2.843(6)	6.011(12)	112.5(4)	81.85(17)	40.9	1.66	28.29	3.23
2.8	P3	<i>R</i> 3 <i>m</i>	2.881(9)	-	16.540(10)	-	118.87(9)	39.6	4.32	22.73	2.35
2.5	O'3	<i>C</i> 2/ <i>m</i>	5.305(36)	2.839(6)	5.861(21)	114.0(4)	80.62(61)	40.3	1.28	23.51	2.45
2.1	O3	<i>R</i> -3 <i>m</i>	2.942(3)	-	15.679(24)	-	117.49 (18)	39.2	6.30	20.14	2.12

6.1.2. Supporting Information of Publication II

Supporting Information

Exploring Calcium Pillaring of O3-Type $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ Cathodes to Advance Na-Ion Battery Technology

Siyu An¹, Leonhard Karger¹, Philipp Müller², Jing Lin¹, Sami Vasala³, Volodymyr Baran⁴, Sören L. Dreyer¹, Ruizhuo Zhang¹, Fatih Ulusoy¹, Aleksandr Kondrakov^{1,2*}, Jürgen Janek^{1,5*} and Torsten Brezesinski^{1*}

¹Battery and Electrochemistry Laboratory (BELLA), Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

²BASF SE, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany

³European Synchrotron Radiation Facility (ESRF), avenue des Martyrs 71, 38000 Grenoble, France

⁴Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany

⁵Institute of Physical Chemistry & Center for Materials Research (ZfM/LaMa), Justus-Liebig-University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

*Corresponding authors: aleksandr.kondrakov@basf.com, juergen.janek@kit.edu, torsten.brezesinski@kit.edu

6. Appendix

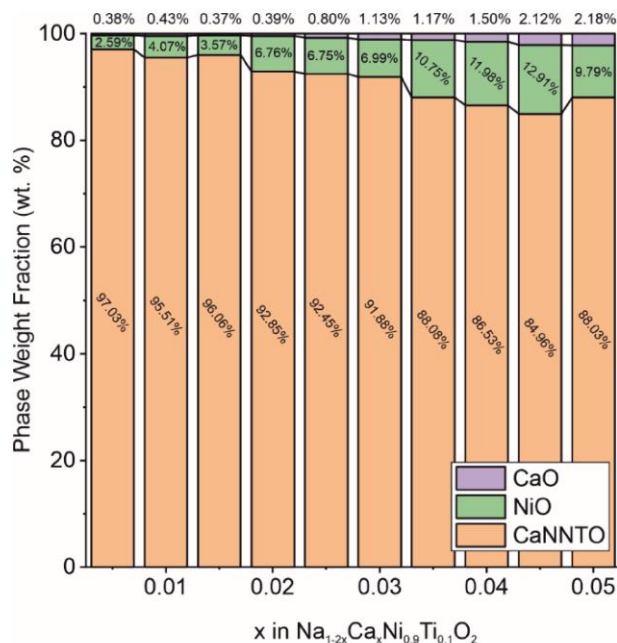


Figure S1. Phase fractions in $\text{Na}_{1-2x}\text{CaTi}_{0.9}\text{O}_2$, with $x = 0.005, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040, 0.045$, and 0.050 .

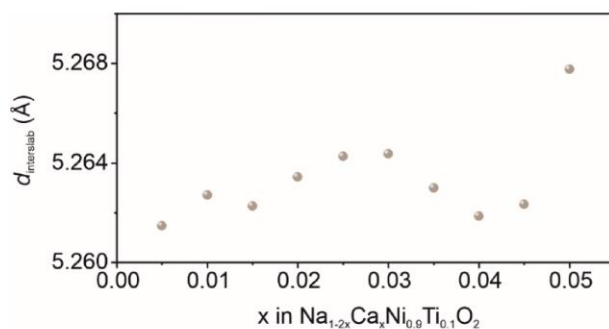


Figure S2. Interlayer distances in $\text{Na}_{1-2x}\text{CaTi}_{0.9}\text{O}_2$, with $x = 0.005, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040, 0.045$, and 0.050 .

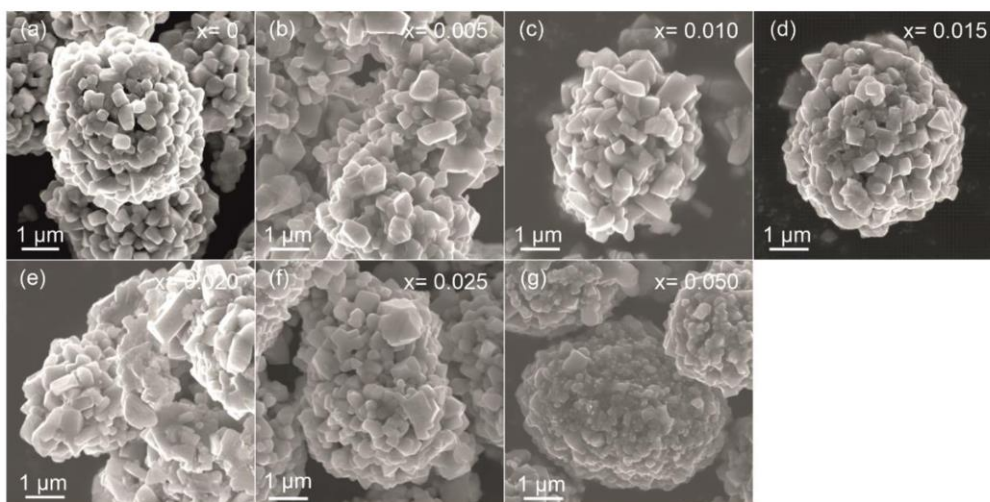


Figure S3. SEM images of $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$, with $x = 0.005, 0.010, 0.015, 0.020, 0.025$, and 0.050 , and NNTO.

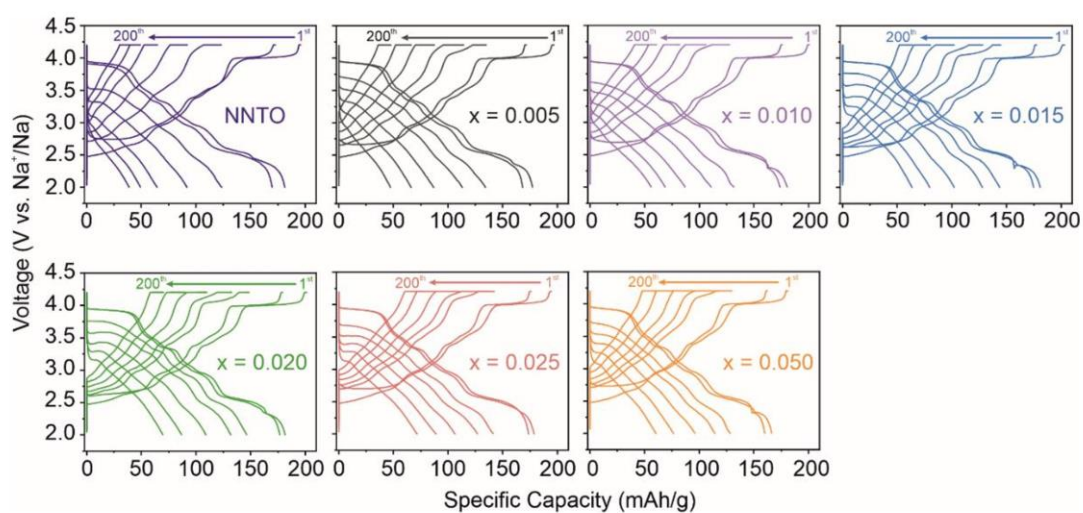


Figure S4. Voltage profiles of $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$, with $x = 0.005, 0.010, 0.015, 0.020, 0.025$, and 0.050 , and NNTO cells for the 1st, 5th, 20th, 50th, 100th, 150th, and 200th cycles.

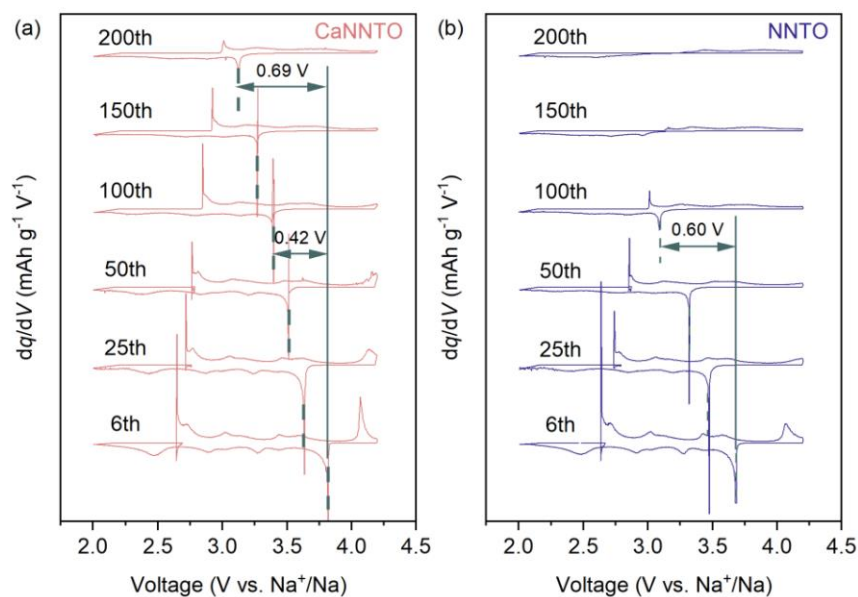


Figure S5. dq/dV curves of $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) and NNTO cells for the 6th, 25th, 50th, 100th, 150th, and 200th cycles at C/2 rate.

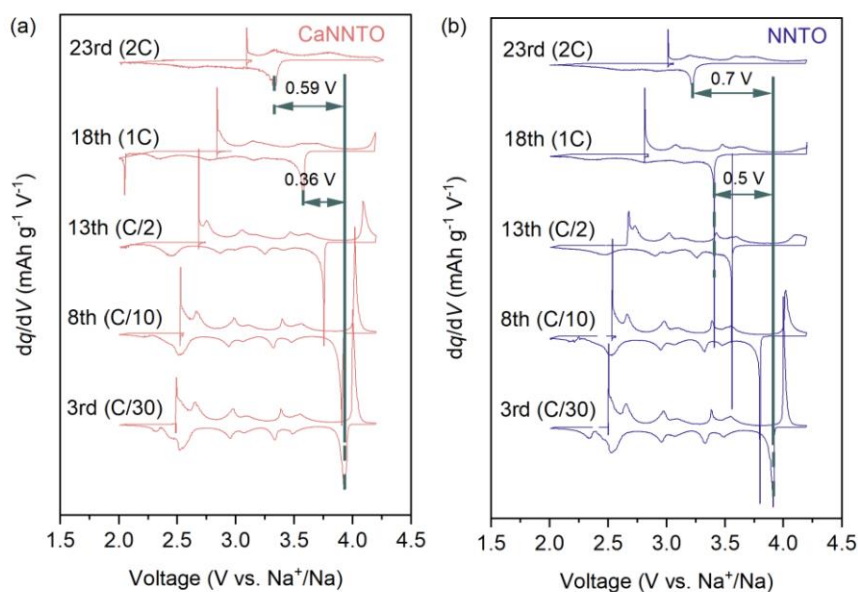


Figure S6. dq/dV curves of $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) and NNTO cells for the 3rd, 8th, 13th, 18th, and 23rd cycles during rate-performance testing.

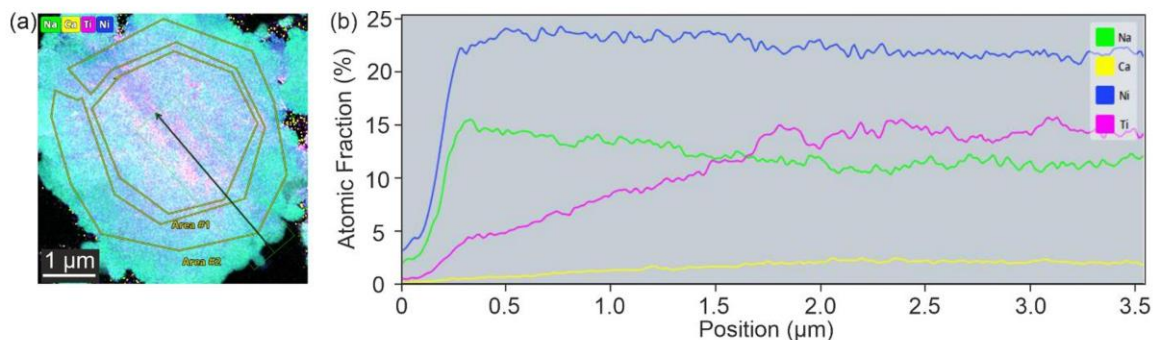


Figure S7. (a) EDS mapping and (b) corresponding line-scan analysis along the direction indicated by the black arrow in panel (a).

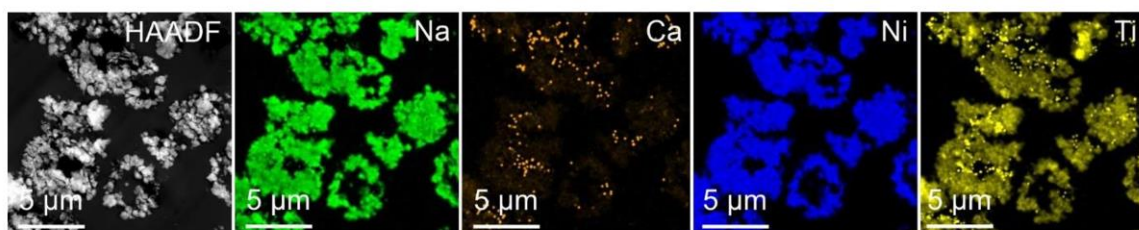


Figure S8. Low-magnification STEM-EDS mapping of Na_{0.95}Ca_{0.025}Ni_{0.9}Ti_{0.1}O₂ (CaNNTO). The random dots present in the Ca and Ti maps are artefacts.

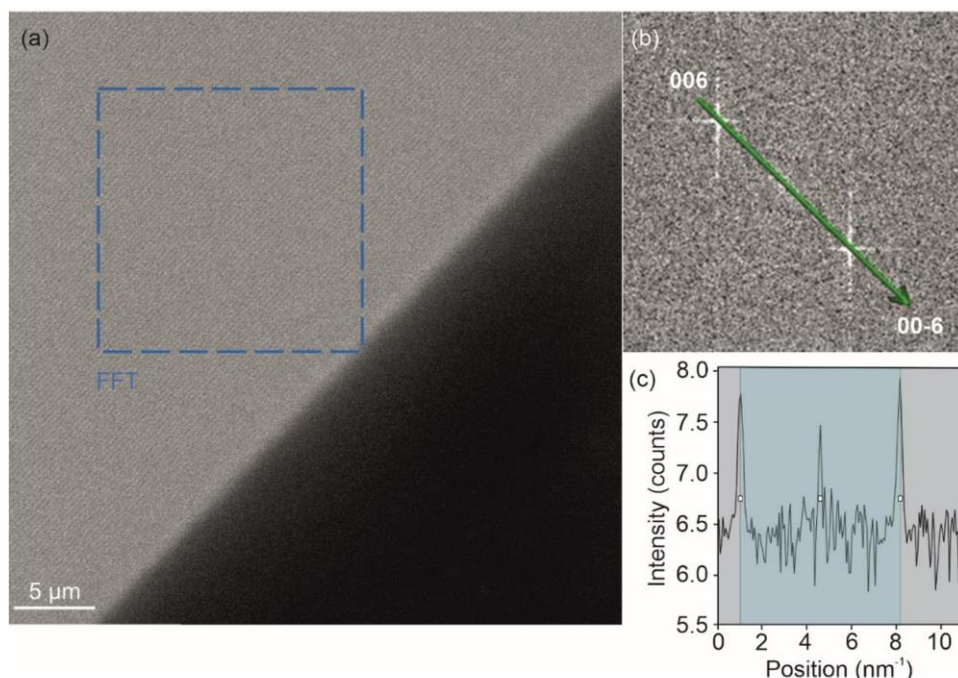


Figure S9. (a) Atomic-resolution HAADF-STEM image of Na_{0.95}Ca_{0.025}Ni_{0.9}Ti_{0.1}O₂ (CaNNTO). (b) FFT pattern from the region indicated by the dashed blue box in panel (a). (c) Intensity line scan along the direction indicated by the green arrow in panel (b). The distance of 0.26 nm corresponds to the {006} lattice planes of the layered phase.

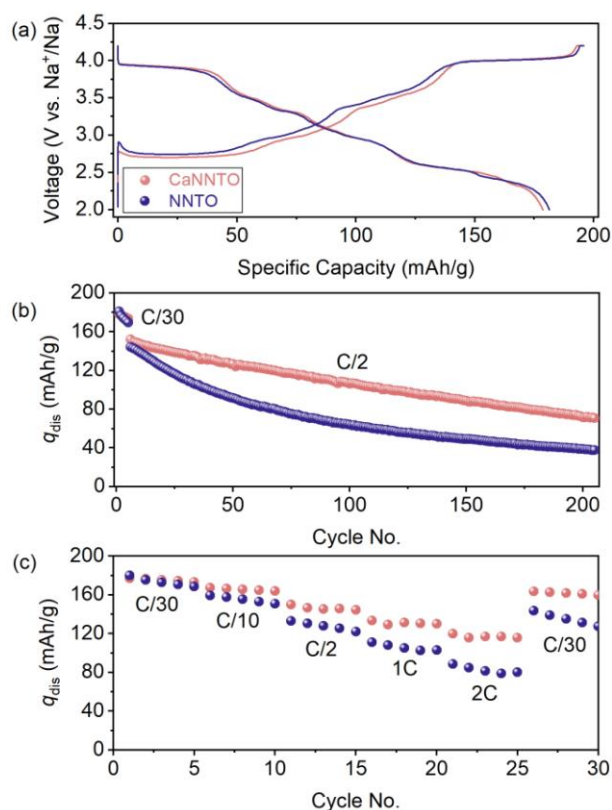


Figure S10. (a) Voltage profiles, (b) long-term cycling performance, and (c) rate capability of $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) and NNTO cells.

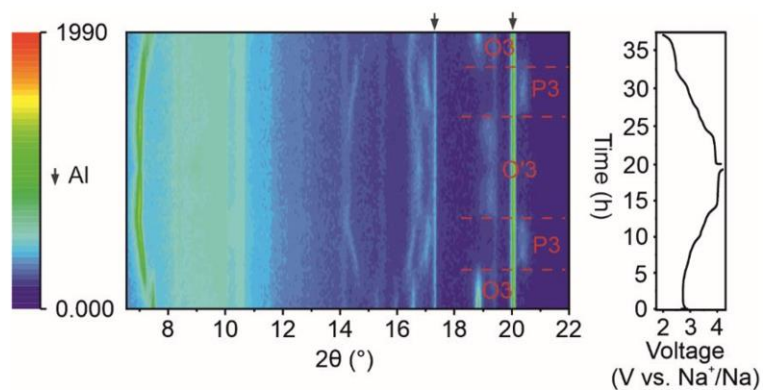


Figure S11. 2D contour plot of *operando* laboratory XRD data collected from $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) during the initial cycle at C/10 rate.

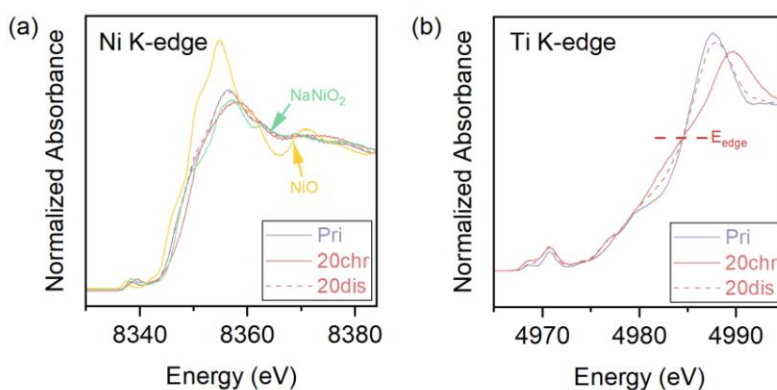


Figure S12. *Ex situ* XANES at the (a) Ni K-edge and (b) Ti K-edge of $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) in the pristine and charged/discharged states (after 20 cycles).

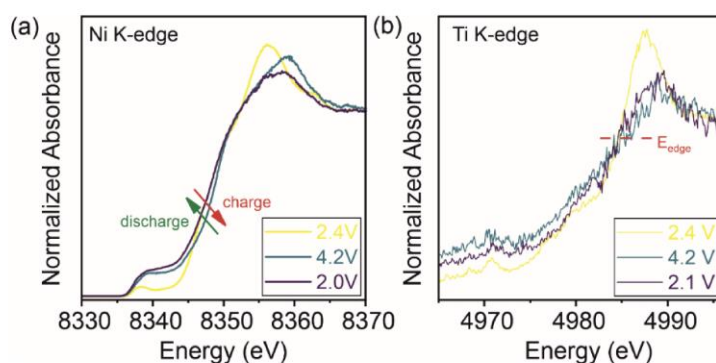


Figure S13. *In situ* XANES at the (a) Ni K-edge and (b) Ti K-edge of $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) under OCV conditions and in the fully charged and discharged states.

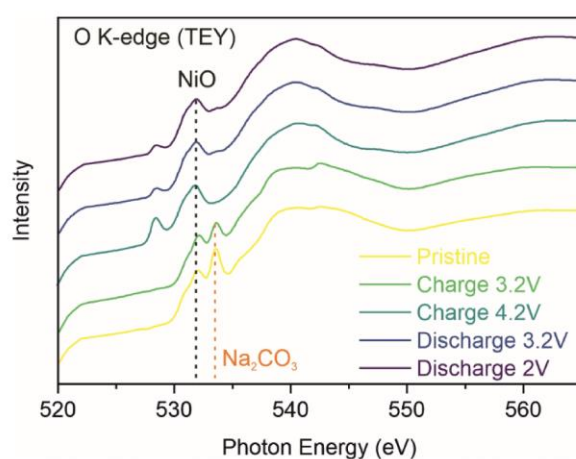


Figure S14. *Ex situ* O K-edge sXAS in TEY mode of $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) at different states of charge.

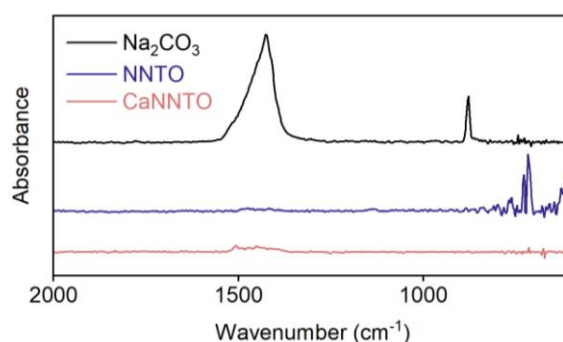


Figure S15. FT-IR spectra collected from the as-prepared $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO), NNTO, and Na_2CO_3 .

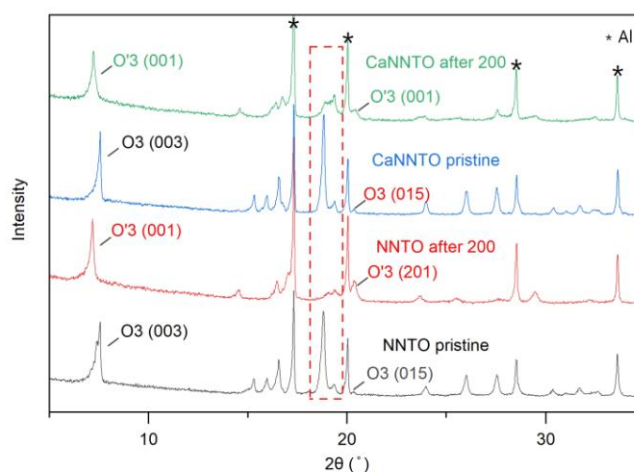


Figure S16. XRD patterns of pristine and cycled (discharged) $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) and NNTO.

Table S1. Phase fractions from Rietveld analysis of XRD data collected from $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$, with $x = 0.005, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040, 0.045$, and 0.050 .

Ca^{2+} nominal (mol.%)	CaNNTO (wt.%) <i>R-3m</i>	NiO (wt.%) <i>Fm-3m</i>	CaO (wt.%) <i>Fm-3m</i>	R_{wp} (%)
0.005	97.03 (1.78)	2.59 (0.22)	0.38 (0.02)	16.8
0.010	95.51 (1.84)	4.07 (0.26)	0.43 (0.01)	17.4
0.015	96.06 (1.72)	3.57 (0.23)	0.37 (0.01)	16.0
0.020	92.85 (1.77)	6.76 (0.30)	0.39 (0.01)	16.9
0.025	92.45 (1.66)	6.75 (0.32)	0.80 (0.22)	16.7
0.030	91.88 (1.62)	6.99 (0.33)	1.13 (0.29)	15.6

6. Appendix

0.035	88.08 (1.63)	10.75 (0.39)	1.17 (0.33)	16.4
0.040	86.53 (1.62)	11.98 (0.41)	1.50 (0.34)	16.6
0.045	84.96 (1.74)	12.91 (0.45)	2.12 (0.39)	16.1
0.050	88.03 (1.64)	9.79 (0.38)	2.18 (0.36)	15.3

Table S2. Structural parameters from Rietveld analysis of XRD data collected from $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$, with $x = 0.005, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040, 0.045$, and 0.050 .

Ca^{2+} nominal (mol.%)	a (Å)	c (Å)	V (Å ³)	$d_{\text{interslab}}$ (Å)	R_{wp} (%)
0.005	2.96282 (0.000271)	15.7844 (0.001139)	119.997 (0.018)	5.26147	16.8
0.010	2.96337 (0.000284)	15.7881 (0.001166)	120.069 (0.019)	5.26270	17.4
0.015	2.96347 (0.000269)	15.7868 (0.001104)	120.068 (0.018)	5.26227	16.0
0.020	2.96347 (0.000265)	15.7903 (0.001102)	120.094 (0.018)	5.26343	16.9
0.025	2.96449 (0.000350)	15.7928 (0.001516)	120.196 (0.024)	5.26427	16.7
0.030	2.96362 (0.000274)	15.7931 (0.001124)	120.128 (0.018)	5.26437	15.6
0.035	2.9635 (0.000276)	15.789 (0.001108)	120.087 (0.018)	5.26300	16.4
0.040	2.96344 (0.000291)	15.7856 (0.001223)	120.057 (0.019)	5.26187	16.6
0.045	2.96376 (0.000324)	15.787 (0.001387)	120.092 (0.022)	5.26233	16.1
0.050	2.96477 (0.000300)	15.8033 (0.001341)	120.298 (0.020)	5.26777	15.3

Table S3. ICP-OES results for $\text{Na}_{1-2x}\text{Ca}_x\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$, with $x = 0.005, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040, 0.045$, and 0.050 .

Ca^{2+} nominal (mol.%)	Na (mol.%)	Ca (mol.%)	Ni (mol.%)	Ti (mol.%)	O (mol.%)
0.005	0.9520 (0.0276)	0.0045 (0.00016)	0.9 (0.0171)	0.0903 (0.0023)	2.2150 (0.1838)
0.010	0.9714 (0.0282)	0.0098 (0.00034)	0.9 (0.0171)	0.0941 (0.0024)	2.3632 (0.1961)
0.015	0.9573 (0.0278)	0.0145 (0.00051)	0.9 (0.0171)	0.0922 (0.0023)	2.2746 (0.1888)

6. Appendix

0.020	0.9375 (0.0272)	0.0185 (0.00065)	0.9 (0.0171)	0.0918 (0.0023)	2.3886 (0.1983)
0.025	0.9296 (0.0270)	0.0238 (0.00083)	0.9 (0.0171)	0.0915 (0.0023)	2.2152 (0.1839)
0.050	0.8856 (0.0257)	0.0462 (0.00016)	0.9 (0.0171)	0.0921 (0.0023)	2.3160 (0.1922)

Table S4. Refined lattice parameters for $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) and NNTO.

	Space group	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	<i>d</i> _{interslab}	<i>d</i> _{104}	<i>d</i> _{006}	<i>R</i> _{wp} (%)
CaNNTO	<i>R</i> -3 <i>m</i>	2.96456 (0.00002)	15.80247 (0.0001)	120.273 (0.002)	5.2675	2.1527	2.6337	2.13
NNTO	<i>R</i> -3 <i>m</i>	2.9612 (0.0002)	15.7769 (0.0008)	119.812 (0.013)	5.2590	-	-	12.48

Table S5. Phase fractions from Rietveld analysis of XRD data collected from $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (CaNNTO) and NNTO.

	<i>R</i> -3 <i>m</i> (wt.%)	NiO (wt.%) <i>Fm</i> -3 <i>m</i>	CaO (wt.%) <i>Fm</i> -3 <i>m</i>	<i>R</i> _{wp} (%)
CaNNTO	92.3 (0.37)	6.64 (0.09)	1.06 (0.06)	2.13
NNTO	98.5 (0.1)	1.5 (0.1)	-	12.48

6.1.3. Supporting Information of Publication III

Supporting Information

Titanium Substitution to Advance the Prospect of NaMnO₂ Cathodes for Practical Application in Sodium-Ion Batteries

Siyu An¹, Rajib Sahu^{1,2}, Ruizhuo Zhang¹, Fatih Ulusoy¹, Christian Kübel^{2,3}, Aleksandr Kondrakov^{1,4*}, Jürgen Janek^{1,5} and Torsten Brezesinski^{1*}

¹Battery and Electrochemistry Laboratory (BELLA), Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

²Karlsruhe Nano Micro Facility (KNMFi), Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

³Institute of Materials Research, Technical University Darmstadt (TUDa), Peter-Grünberg-Str. 2, 64287 Darmstadt, Germany

⁴BASF SE, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany

⁵Institute of Physical Chemistry & Center for Materials Research (ZfM/LaMa), Justus-Liebig-University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

*Corresponding authors: aleksandr.kondrakov@basf.com,
torsten.brezesinski@kit.edu

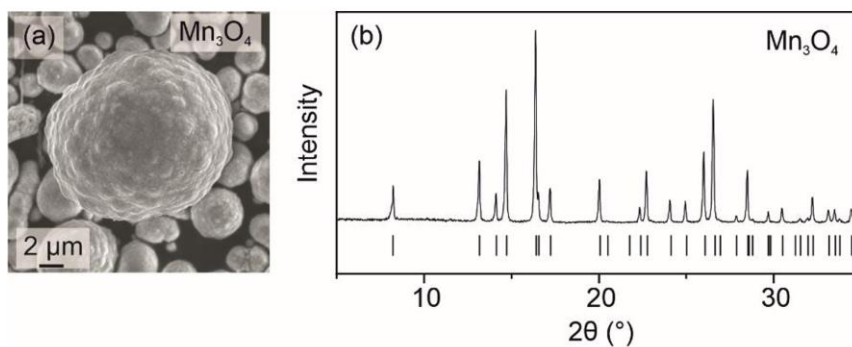


Figure S1. (a) SEM image and (b) XRD pattern of the Mn₃O₄ precursor used in the synthesis.

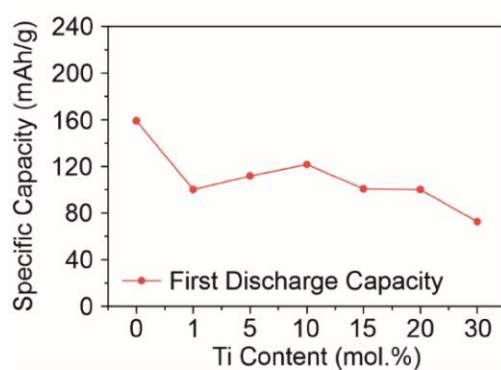


Figure S2. First-cycle specific discharge capacity of NaMnO₂ (NMO) or NaMn_{1-x}Ti_xO₂ cathodes, with $x = 0.01, 0.05, 0.10, 0.15, 0.20$, and 0.30 , at C/10 rate.

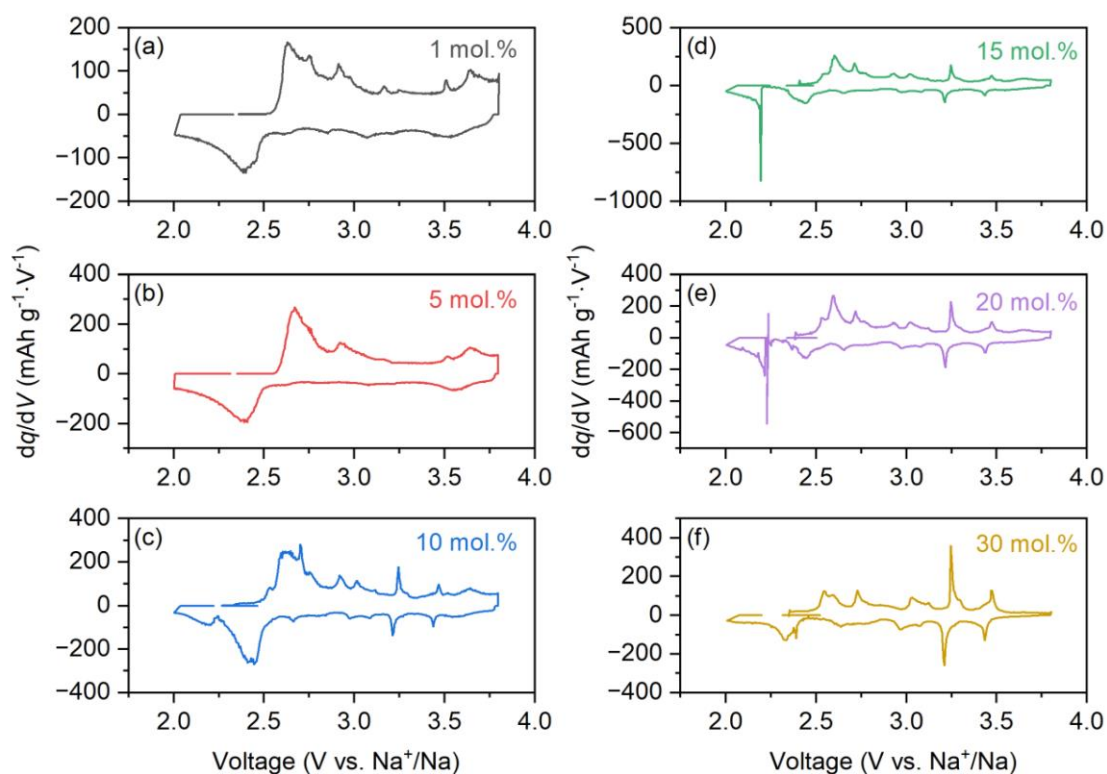


Figure S3. Differential capacity curves for the second cycle of $\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$ cathodes, with $x = 0.01, 0.05, 0.10, 0.15, 0.20$, and 0.30 .

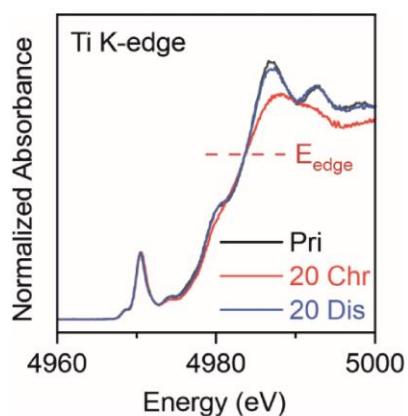


Figure S4. *Ex situ* XANES at the Ti K-edge of $\text{NaMn}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NMTO) in the pristine state and after charging and discharging in the 20th cycle.

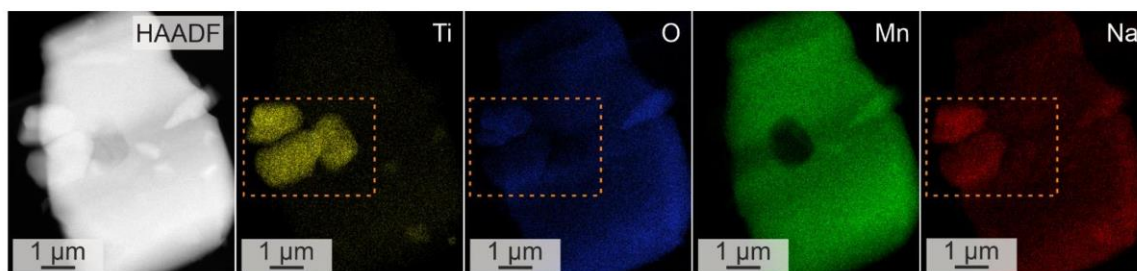


Figure S5. STEM mapping of $\text{NaMn}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NMTO) indicating non-uniform chemical composition.

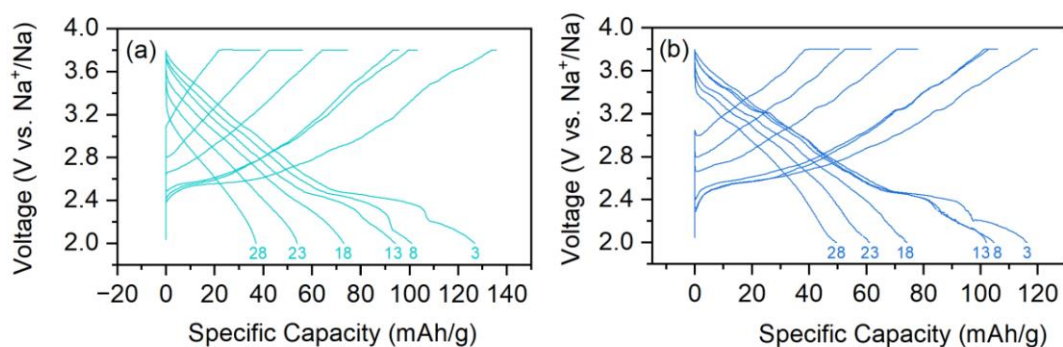


Figure S6. Voltage profiles for the 3rd, 8th, 13th, 18th, 23rd, and 28th cycles of NaMnO_2 (NMO) and $\text{NaMn}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NMTO) cathodes at C/10 rate.

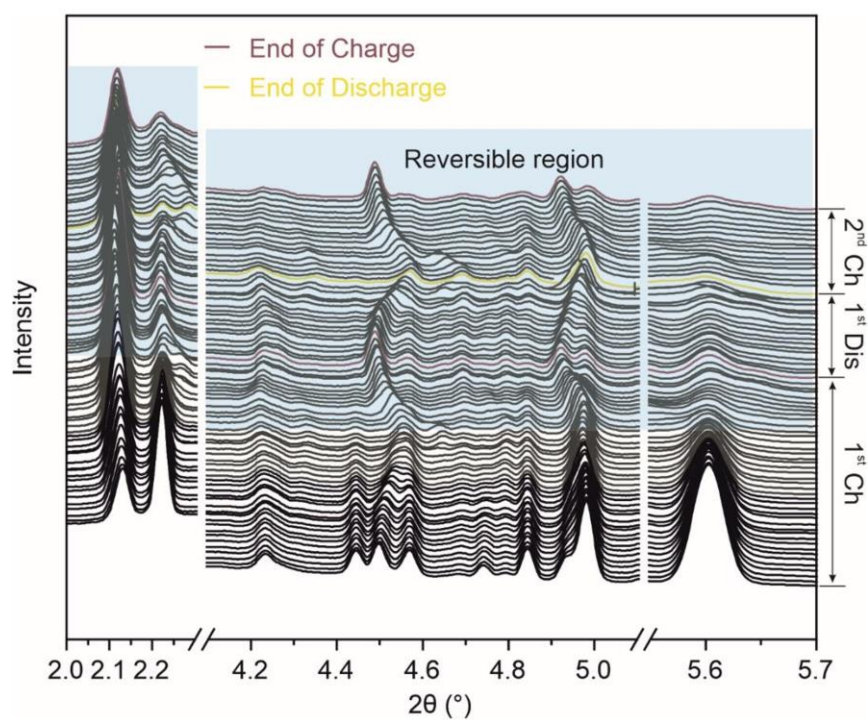


Figure S7. *In situ* XRD patterns of $\text{NaMn}_{0.9}\text{Ti}_{0.1}\text{O}_2$ (NMTO) shown in the form of a contour plot.

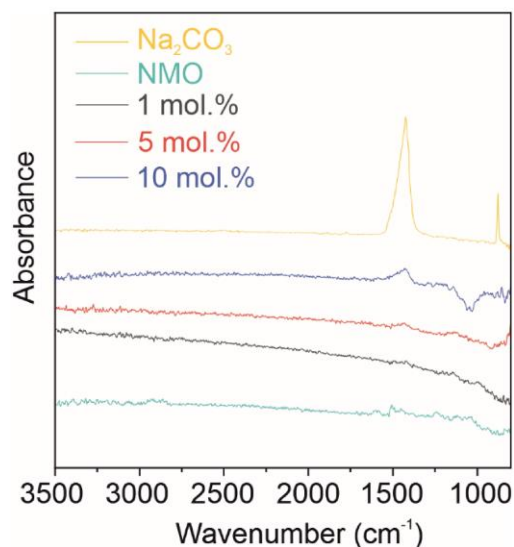


Figure S8. FTIR spectra of Na_2CO_3 , NaMnO_2 (NMO), and $\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$, with $x = 0.01$, 0.05, and 0.10.

Table S1. Structural parameters from Rietveld analysis of XRD data collected from NaMnO_2 (NMO) and $\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$, with $x = 0.01$, 0.05, 0.10, 0.15, 0.20, and 0.30.

Ti^{4+} nominal (mol.%)	a (Å)	b (Å)	c (Å)	β (°)	$d_{\text{interslab}}$ (Å)	R_{wp} (%)
0	5.66565 (0.001946)	2.86019 (0.000139)	5.80334 (0.002044)	113.174 (0.0045)	5.335	13.1
1	5.66021 (0.002546)	2.85789 (0.000176)	5.803484 (0.002672)	113.106 (0.0058)	5.338	16.5
5	5.65093 (0.002571)	2.8589 (0.000193)	5.802834 (0.002698)	113.023 (0.0059)	5.341	18.3
10	5.65044 (0.00020)	2.86111 (0.00020)	5.80894 (0.00023)	112.963 (0.00184)	5.349	13.8
15	5.61604 (0.00025)	2.84435 (0.00011)	5.77579 (0.00028)	112.94 (0.00250)	-	14.7
20	5.61607 (0.00031)	2.84427 (0.00014)	5.77704 (0.00034)	112.936 (0.00322)	-	16.0
30	5.61534 (0.00107)	2.84527 (0.00052)	5.77390 (0.00106)	112.923 (0.01354)	-	21.8

Table S2. Phase fractions from Rietveld analysis of XRD data collected from $\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$, with $x = 0.01, 0.05, 0.10, 0.15, 0.20$, and 0.30 .

Ti^{4+} nominal (mol.%)	NMO (wt.%) <i>C2/m</i>	$\text{Na}_4\text{Mn}_4\text{Ti}_5\text{O}_{18}$ (wt.%) <i>Pbam</i>	Na_xTiO_2 (wt.%) <i>R-3m</i>	R_{wp} (%)
1	100 (2.4)	-	-	16.5
5	97.58 (2.17)	1.5 (0.015)	0.92 (0.26)	18.3
10	93.14 (1.79)	4.06 (0.46)	2.80 (0.41)	13.8
15	60.18 (1.08)	31.71 (1.15)	8.11 (0.66)	14.7
20	45.89 (1.02)	44.13 (1.47)	9.98 (0.76)	16.0
30	10.39 (0.82)	79.12 (3.17)	10.49 (1.18)	21.8

Table S3. ICP-OES results for NaMnO_2 (NMO) and $\text{NaMn}_{1-x}\text{Ti}_x\text{O}_2$, with $x = 0.01, 0.05$, and 0.10 .

Ti^{4+} nominal (mol.%)	Na (mol.%)	Mn (mol.%)	Ti (mol.%)	O (mol.%)
0	1.030 (0.0294)	1.000 (0.0288)	-	2.231 (0.1481)
1	1.047 (0.0301)	0.990 (0.0294)	0.011 (0.0003)	2.245 (0.1371)
5	1.046 (0.0302)	0.950 (0.0274)	0.048 (0.0015)	2.192 (0.1302)
10	1.052 (0.0301)	0.900 (0.0252)	0.097 (0.0026)	2.212 (0.1297)

6.2. Scientific Contributions

6.2.1. List of Publications

S. An, L. Karger, P. Müller, J. Lin, S. Vasala, V. Baran, S. L. Dreyer, R. Zhang, F. Ulusoy, A. Kondrakov, J. Janek, T. Brezesinski, Exploring Calcium Pillaring of O3-type $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$ Cathodes to Advance Na-Ion Battery Technology. *Chemical Engineering Journal* **2025**, 509, 160939.

S. An, R. Sahu, R. Zhang, F. Ulusoy, C. Kübel, A. Kondrakov, J. Janek, T. Brezesinski, Titanium Substitution to Advance the Prospect of NaMnO_2 Cathodes for Practical Application in Sodium-Ion Batteries, *submitted*.

S. An, L. Karger, S. L. Dreyer, Y. Hu, E. Barbosa, R. Zhang, J. Lin, M. Fichtner, A. Kondrakov, J. Janek, T. Brezesinski, Improving Cycling Performance of the NaNiO_2 Cathode in Sodium-Ion Batteries by Titanium Substitution. *Materials Futures* **2024**, 3, 035103.

B. Zhou, S. An, D. Kitsche, S. L. Dreyer, K. Wang, X. Huang, J. Thanner, M. Bianchini, T. Brezesinski, B. Breitung, H. Hahn, Q. Wang, Improved Performance of High-Entropy Disordered Rocksalt Oxyfluoride Cathode by Atomic Layer Deposition Coating for Li-Ion Batteries, *Small Structures* **2024**, 5, 2400005.

S. An, Y. Ma, S. Payandeh, A. Mazilkin, R. Zhang, J. Janek, A. Kondrakov, T. Brezesinski, Comparative Analysis of Aqueous and Nonaqueous Polymer Binders for the Silicon Anode in All-Solid-State Batteries. *Advanced Energy and Sustainability Research* **2023**, 4, 2300092.

6.2.2. List of Patents

“Cathode Active Material and Its Use in Rechargeable Electrochemical Cells” (Transition Metal Doped Sodium Containing Layered Oxide Cathode Active Material for Sodium-Ion Battery)

Appl. no.: EP23174942.5; May **2023**

L. Karger, S. An, W. van den Bergh Saarbergh, T. Brezesinski, A. Kondrakov

7. Acknowledgements

The final part of this dissertation is dedicated to all those who supported and helped me throughout my PhD journey.

First and foremost, I would like to express my sincere gratitude to Prof. Dr. Jürgen Janek for accepting me as one of his students. His kindness, professionalism, and dedication have been truly inspiring. I am deeply thankful for his valuable guidance and insightful suggestions throughout my doctoral studies, as well as for his support during the revision and defense of my dissertation.

I would also like to thank Prof. Dr. Philipp Adelhelm for kindly agreeing to serve as the second reviewer of my thesis.

My heartfelt thanks go especially to Dr. Torsten Brezesinski. He is not only an outstanding scientist, but also a remarkable team leader. No matter the challenges I encountered, he was always ready to help with enthusiasm and resolve every issue perfectly. He supported many of my scientific decisions, including research directions, conference participation and more. From my Master's thesis to this doctoral dissertation, he has constantly provided me with selfless guidance. To me, he is not only a respected supervisor, but also a true friend.

I am also truly grateful to Dr. Aleksandr Kondrakov for offering valuable insights from an industrial perspective during my research, and for his selfless help during my Master's internship and job search. As the first member of BELLA to work on sodium-ion batteries, both Dr. Brezesinski and Dr. Kondrakov guided me through new research directions, engaged in fruitful discussions, and provided constructive feedback for which I am sincerely thankful.

I would like to thank Dr. Seyedhosein Payandeh, my direct supervisor during my Master's thesis, for patiently answering my questions and helping me understand the battery field when I was just getting started. Special thanks go to Ruizhuo Zhang, who supported me greatly during both my Master's thesis and paper writing, and later helped me extensively with SEM measurements. I am also very thankful to Dr. Sören L. Dreyer for entrusting me with the well-maintained DEMS system and for sharing his deep knowledge on DEMS testing, data processing, and analysis. My gratitude extends to Dr. Leonhard Karger, who introduced me to layered oxide materials and engaged in many insightful scientific discussions. Thanks to him, I was able to quickly gain a deep understanding of this new field. I would also like to thank Dr. Jing Lin, whose guidance gave me my first experience with synchrotron-based techniques. Her support not only helped me obtain high-quality data, but also greatly expanded my knowledge in this area.

I would also like to extend my sincere thanks to all members of the BELLA group. Their generous support during the early stages of my Master's thesis helped me quickly gain hands-on experience with various characterization techniques, and their continued assistance played a vital role in the smooth progress of my PhD research.

7. Acknowledgements

Finally, I am deeply thankful to my parents. Their unwavering encouragement and support gave me the strength and opportunity to come to Germany and pursue my academic goals. I could not have completed this journey without them.

A very special thank you goes to my little family. To my fiancée, Wenqing Kong, thank you for always being by my side and supporting both my academic work and my passion for bodybuilding. Your presence fills my life with light and motivation every single day. I am also grateful to my cat, Guodong, whose unique way of bringing joy and calm has helped me relax and stay positive. Together, they have made my life in Germany feel truly like home.

Once again, I would like to sincerely thank everyone mentioned above. It is only with your support, guidance, and encouragement that I have been able to achieve what I have today.