STRUCTURE-ELECTROCHEMICAL PROPERTY RELATIONSHIPS IN MONOPHASIC AND BIPHASIC LAYERED OXIDE CATHODES FOR Na-ION BATTERIES

Ph.D. Thesis

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DISCIPLINE OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE DECEMBER 2024

STRUCTURE-ELECTROCHEMICAL PROPERTY RELATIONSHIPS IN MONOPHASIC AND BIPHASIC LAYERED OXIDE CATHODES FOR Na-ION BATTERIES

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

by HARI NARAYANAN VASAVAN



DISCIPLINE OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE DECEMBER 2024



INDIAN INSTITUTE OF TECHNOLOGY INDORE

I hereby certify that the work which is being presented in the thesis entitled STRUCTURE-ELECTROCHEMICAL PROPERTY RELATIONSHIPS in MONOPHASIC and BIPHASIC LAYERED OXIDE CATHODES for Na-ION BATTERIES in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July,2022 to December, 2024 under the supervision of Dr. Sunil Kumar, Associate Professor, MEMS department, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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ACKNOWLEDGEMENTS

Foremost, I owe a great debt of gratitude to my thesis supervisor Dr. Sunil Kumar, for his continuous support, patience, motivation, and enthusiasm. His valuable advice, constructive criticism, extensive discussions, and immense knowledge helped me for a fundamental understanding of the subject and accomplish my thesis. The thesis would hardly have been completed without his encouragement and persistent guidance on a daily basis throughout my Ph.D. I also thank him for believing in my research skill and allowing me to work on this project.

I would also like to thank my PSPC members; **Dr. Eswara Prasad Korimilli** and **Dr. Ankur Miglani**, for giving their precious time for my assessment and evaluation of my work.

I am thankful to **Dr. Pradeep Kumar**, and **Ms. Sonia Deswal**, IIT Mandi for XPS measurements, **Dr. Velahga Srihari**, Syncrotron Utilisation section, RRCAT, Indore for *operando* XRD measurements, and **Professor Christian Masquelier** for his guidance during the Raman Charpak fellowship programe.

My sincere thanks also go to **Prof. Suhas S. Joshi (Director, IIT Indore)**. I am so grateful to Indian Institute of Technology Indore and Department of Metallurgical Engineering and Materials Science of IIT for providing me the financial support and research facilities for my Ph.D. degree.

I also want to thank my lab mates for all the handy help, technical support, invaluable discussion, and suggestions. It was a pleasant experience to work with them. Finally, I want to thank my parents for their encouragement, strong support, and patience.

Hari Narayanan Vasavan

SYNOPSIS

The field of energy storage has witnessed significant advancements, with a growing focus on sustainable and efficient battery materials. Amidst global resource constraints and the demand for renewable energy solutions, sodium-ion batteries (SIBs) are emerging as a promising alternative to lithium-ion batteries due to the abundance and low cost of sodium. However, achieving high energy density, structural stability, and energy efficiency in SIBs presents notable challenges, particularly concerning cathode materials [1]. Layered oxide materials, commonly composed of sodium-transition metal oxides like Na_xMeO₂, exhibit varying phase structures such as P2, P3, and O3. These phases refer to different atomic arrangements within the material, each influencing electrochemical properties like ion mobility and capacity retention. In terms of electrochemical properties, the P2 type frameworks show higher ionic conductivity and structural stability but suffer from low specific capacities. In contrast, O3 type materials exhibit relatively higher specific capacities but are known to undergo O3 to P3 phase transformations during desodiation, limiting their cyclability. P3 type compounds, on the other hand, have properties similar to P2 phases. These are known to have good Na⁺ transport properties and form at lower calcination temperatures, which makes it easier to synthesize [2].

To improve the electrochemical performance of layered oxide cathodes, researchers have widely investigated biphasic cathode materials with mixed O3 and P2-type phases. In O3/P2 biphasic cathodes, the coexistence of both phases creates a synergistic effect that improves structural stability and Na⁺ ion transport, leading to enhanced rate capability and cycling stability. Although less studied, P2/P3 biphasic cathodes show similar improvements, with the interlocking P2 and P3 structures offering better electrochemical performance than monophasic materials. Combining P3 and P2 phases leverages the high Na⁺ transport properties of both structures, while these materials can also be

synthesized at relatively lower calcination temperatures compared to those with P2/O3-type phases [3, 4].

Another strategy to enhance electrochemical performance in layered oxides involves the partial incorporation of electrochemically inactive ions, such as Mg^{2+} , Al^{3+} , or Zn^{2+} , into the transition metal layers. These ions act as "pillar" ions that stabilize the structure during cycling without contributing directly to electrochemical reactions. While less studied in SIB cathodes, Al^{3+} substitution has shown to improve rate performance and cycle stability in LIB cathodes, suggesting promising benefits for similar modifications in SIBs [5, 6].



Figure S1. (a) Pseudo-ternary diagram of Na_{3/4}(Mn-Al-Ni)O₂ system. (b) Rietveld refinement of XRD data showing deconvoluted P2 and P3 phases in the 2 θ range of 30-40° belonging to NNM1-750,780, and 850 samples ($\lambda = 1.54$ Å). (c) Zoomed views of Operando Synchrotron xray diffraction patterns of NMA1-750 obtained during the galvanostatic charge/discharge process at 0.1C in the vicinity of the 8-10° ($\lambda = 0.8312$ Å).

This study investigates cathode materials within the Na_{3/4}(Mn-Al-Ni)O₂ pseudo-ternary system (figure S1(a)), targeting structural and electrochemical optimization for SIBs. Beginning with Na_{0.75} Mn_{0.75}Ni_{0.25}O₂ (NMA1) and Na_{0.75}Mn_{0.75}Al_{0.25}O₂(NMA2), synthesized

in monophasic P3, biphasic P3/P2, and monophasic P2 configurations, the materials were subjected to controlled calcination to adjust phase proportions (figure S1(b)). Initial findings showed that P3-phase materials had the highest specific capacity, with biphasic P3/P2 compositions achieving better rate performance due to their finer particle size and an optimal phase fraction. Operando synchrotron XRD revealed that the biphasic Na_{0.75} Mn_{0.75}Ni_{0.25}O₂ cathodes prevented phase transitions (e.g., P3 \rightarrow O'3/O3) seen in monophasic P3 under cycling (figure S1(c)), while Na_{0.75}Mn_{0.75}Al_{0.25}O₂ retained the P3 phase throughout, likely due to the stabilizing influence of Al³⁺.

The study expanded to investigate trends in structural and electrochemical performance across compositions in the Na_{3/4}(Mn-Al-Ni)O₂ pseudo-ternary diagram, focusing on the variations in Jahn-Teller active Mn³⁺ and Mn⁴⁺ ions. Notably, P3-type cathodes with high Ni content (represented NMA3 and NMA5 in figure S1(a)) demonstrated impressive capacities of nearly 195 mAh g⁻¹ and 75 mAh g⁻¹ at 0.1C and 6C, respectively, within a voltage window of 1.5 to 4.0 V (figure S2). The concentration of Mn³⁺, alongside the material's biphasic nature, was found to significantly impact cycling performance. For example, the biphasic P3/P2-Na_{0.75}Mn_{0.50}Ni_{0.25}Al_{0.25}O₂ cathode, free from Mn³⁺, retained 70% of its original capacity over 300 cycles at 1C between 1.5-4.0 V which improved \sim 80% when the cell was cycled between 2.0-4.0 V (figure S2). Operando synchrotron XRD data revealed notable unit cell variation in the P3 and P2 phases during cycling below 2 V due to Mn³⁺/Mn⁴⁺ redox activity and confirmed that Al-substitution effectively prevented P3 to O3 phase transitions, thus enhancing cyclic stability.



Figure S2. Rate performance (a)-(b) and (c)-(d) cyclic stability curves of NMA3 and NMA5 series of cathodes cycled between 1.5 V and 4.0 V.
(e) Cyclic performance of NMA3-P3P2 and NMA5-P3P2 at 1C between 2.0 V and 4.0 V.

Following the identification of biphasic P3/P2-Na_{0.75}Mn_{0.50}Ni_{0.25}Al_{0.25}O₂ as an optimal cathode, additional Mn³⁺-free compositions explored along the "zero Mn³⁺ line" were $(Na_{\frac{3}{4}}Mn_{\frac{5-x}{8}}Al_{\frac{2x}{8}}Ni_{\frac{3-x}{8}}O_2$, with x ranging from 0 to 1, depicted as A0 -A4 in figure S3) in the pseudo ternary diagram. Phase diagrams, particularly in layered oxides, are essential for designing optimal cathode compositions by clarifying the complex relationships between metal cations in LO cathodes and their electrochemical properties. Unlike traditional phase diagrams, where elemental composition alone primarily determines phase properties, pseudo-ternary systems also depend heavily on the oxidation states of electrochemically active elements, influencing composition-structure-property behavior. In this study, the 'zero Mn³⁺ line' is introduced, confining Mn ions to a 4+ oxidation state by varying Mn, Ni, and Al concentrations. This innovative approach contrasts with traditional ternary diagrams, where at least one element's concentration remains fixed. In the Na_{3/4}(Mn-Al-Ni)O₂ pseudo-ternary system, the 'zero Mn³⁺ line' also delineates the boundary between a forbidden region (where Ni is restricted to a 2+ state) and an allowed region, offering new insights into phase stability and functionality.



Figure S3. Pseudo-ternary diagram of Na_{3/4}(Mn-Al-Ni)O₂ system depicting the 'zero Mn³ line'⁺.

Structural analysis of this series of cathode materials, performed using X-ray diffraction (XRD) and Extended X-ray Absorption Fine Structure (EXAFS), revealed that increasing Al³⁺ content (notated as Ax-1 for P3 structures and Ax-3 for P2 structures) increased Na⁺ conduction bottleneck area in both P3 and P2 structures. This enhanced the rate performance of Al-substituted samples. Furthermore, X-ray Absorption Near-Edge Structure (XANES) and X-ray Photoelectron Spectroscopy (XPS) analyses confirmed the absence of Mn³⁺ in the A0-A4 cathode materials series, showing only Mn⁴⁺ present (see Figure S4).



Figure S4. a) XANES spectra of A0-A4 samples taken at Mn Kedge with relevant standard compounds. (b) Mn 2p XPS plots of A0-2 to A4-2 compounds.

The electrochemical performance of the cathode samples was evaluated between 1.5-4.2V and 2.0-4.0 V voltage windows. The P3 type cathodes showed a high specific capacity of ~ 195 mAh g^{-1} , which decreased with increased P2 phase concentration. Compared to the Na_{0.75}Mn_{0.625}Ni_{0.375}O₂ cathode (A0), the Al-substituted samples exhibited significantly higher rate performance and cyclic stability. It was also observed that, within each composition, the biphasic cathode with ~ 50% P3 and ~ 50% P2 phase fractions outperformed their monophasic counterparts in almost all electrochemical performance parameters. The biphasic A2 sample with 0.125 A1 concentration, in particular, demonstrated excellent cyclic properties, retaining close to 78% of its initial specific capacity after 300 cycles at 1C between 1.5-4.2 V, which improved to 87% after 500 cycles when the cycling was limited in the 2.0-4.0 V voltage range. The material also exhibited about 88% energy efficiency after 500 cycles. Various properties of all biphasic cathode materials are summarized in Figure S5. Further, the full cell assembled with the biphasic A2 cathode showed only a 10% reduction in specific capacity compared to its half-cell and retained 90% capacity after 100 cycles at 0.2C. The remarkable electrochemical performance of the biphasic cathode was attributed to the synergistic effect of P3/P2 coexistence, which was found to suppress the volume expansion of both the P3 and P2 structures during cycling.



Figure S5. Spider charts comparing the various characteristics of biphasic A0 to A4 cathode materials. All biphasic cathodes of each composition are represented by Ax-2.

The stabilizing role of Al^{3+} also allowed for further structural innovation. By increasing the Na content in $Na_3^3Mn_{4.5}^{4.5}Al_1Ni_{2.5}O_2$ to $NaMn_{4.5}^{4.5}Al_1Ni_{2.5}O_2(Na1)$, a high Na-containing P3 and P2 cathodes were synthesised. Al^{3+} not only mitigated the formation of O3 phases but also bolstered the performance and cycle stability of these materials. A full cell with the monophasic P2-type cathode delivered a specific capacity of 123 mAh g⁻¹ at 0.1C and retained 90% capacity after 200 cycles at 0.2C (figure S6). The excellent stability of both monophasic P2 and biphasic P3/P2 materials was attributed to the suppression of structural transformations, as verified by operando synchrotron XRD. These findings underline the promise of Al-doped, Mn³⁺-free layered oxide cathodes for achieving durable, high-capacity sodium-ion batteries.



Figure S6. (a) GCD curves of Na1-P2 Full cells at various C rates. (b) Cyclic performance curves of Na1-P2 Full cell at 0.2C along with columbic efficiency after each cycle.

Finally, a new P2-type cathode material, Na_{0.7}Ni_{0.2}Cu_{0.15}Ti_{0.65}O₂ (NNCT), was investigated as an extension of previous work on Na_{0.77}Ni_{0.2}Cu_{0.15}Ti_xMn_(0.65-x)O₂-based cathodes. This study aimed to complete the series by examining NNCT, the end member where Ti⁴⁺ fully substitutes Mn⁴⁺. Impedance studies and chronoamperometric data revealed that NNCT exhibited a poor conductivity of ~ 1.37×10^{-7} S cm⁻¹ at room temperature, with the electronic conductivity contribution to the total electrical conduction to be only 0.4%. The sample exhibited specific capacities of 83 mAh g⁻¹, 54 mAh g⁻¹, and 42 mAh g⁻¹ at discharge rates of 0.1C, 0.5C, and 1C, respectively, with a remarkable

cyclic stability of 96% capacity retention after 700 cycles at 0.5C (figure S7) which makes NNCT an attractive cathode for Na-ion batteries in stationary storage applications. The ex-situ XRD analysis confirmed that NNCT maintains a single P2 phase during cycling between 2.0 V to 4.2 V. NNCT also exhibited moisture stability, thus enabling the use of a cost-effective water-based slurry for cathode layer fabrication.



Figure S7. (a) Galvanometric charge-discharge curves and (b) rate performance of NNCT cathode at different discharge rates. (c) Cyclic performance of NNCT at 0.5C for 700 cycles.

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Nomenclature

X-ray Diffraction	XRD
Field Emission Scanning Electron	FESEM
Microscopy	
Complex Impedence Spectrocsopy	CIS
X-ray Photoelectron Spectroscopy	XPS
Galvanometric Charge and Discharge	GCD
Cyclic Votammetry	CV
Inductively Coupled Plasma	ICP
Extended X-ray Absorption Fine	EXAFS
Structure	
Real part of Impedance	Z'
Imaginary part of Impedance	Ζ"
Conductivity	σ
Boltzman constant	k_B
Resistance	R
Capacitance	C
Constant phase Element	CPE
Na ion Transference Number	t _{Na+}
Na0.75Mn0.75Ni0.25O2	NNM/NMA1
Na0.75Mn0.75Al0.25O2	NMA/NMA2
Na0.75Mn0.5Ni0.25Al0.25O2	NMA3/A4
Na0.75Mn0.625Ni0.125Al0.25O2,	NMA4
Na0.75Mn0.625Ni0.25Al0.125O2	NMA5
Na0.75Mn0.75Ni0.125Al0.125O2	NMA6

$Na_{\frac{3}{4}}Mn_{\frac{5}{8}}Ni_{\frac{3}{8}}O_2$	A0
$Na_{\frac{3}{4}}Mn_{\frac{4.75}{8}}Al_{\frac{0.5}{8}}Ni_{\frac{2.75}{8}}O_{2}$	A1
$Na_{\frac{3}{4}}Mn_{\frac{4.5}{8}}Al_{\frac{1}{8}}Ni_{\frac{2.5}{8}}O_{2}$	A2
$Na_{\frac{3}{4}}Mn_{\frac{4.25}{8}}Al_{\frac{1.5}{8}}Ni_{\frac{2.25}{8}}O_{2}$	A3

Introduction

1.1. Energy Storage Systems

Energy storage systems are increasingly becoming the cornerstone of modern energy infrastructure and are pivotal in efficient power management. As global energy demand continues to rise, and as nations increasingly shift towards renewable energy sources such as wind and solar, the need for reliable and efficient energy storage solutions has never been more critical. They store excess energy generated during periods of low demand and compensate for the excess demand during times of peak consumption, thereby ensuring a consistent and reliable power supply. Furthermore, energy storage systems are vital for the seamless integration of intermittent renewable energy sources, such as wind and solar, which are inherently variable and unpredictable. They allow for the storage of surplus energy generated during periods of high renewable output and release it when production is low, making it possible to rely more heavily on clean energy and reduce dependence on fossil fuels. Beyond their role in grid stabilization and renewable integration, in the rapidly expanding electric vehicle market, energy storage systems are crucial for supporting the necessary charging infrastructure and ensuring that the grid can handle the additional load.

Energy storage systems exist in various forms (Figure 1.1). They include potential, mechanical, thermal, electrical, chemical, and electrochemical. Even though each type has its own distinct features, electrochemical energy storage systems are often regarded as the most versatile of all.



Figure 1.1. Types of energy storage systems.

1.2. Electrochemical energy storage

Electrochemical energy storage systems have revolutionized the way we store and utilize energy, offering unparalleled efficiency, scalability, and adaptability across a wide range of applications. These systems operate by converting electrical energy into chemical energy during charging and then reversing the process to convert chemical energy back into electrical energy during discharge. They are known for their high energy density, allowing them to store substantial amounts of energy in compact spaces, which is crucial for applications like portable electronics and electric vehicles. In addition, it also possesses rapid response capabilities, providing short-term energy bursts, which is invaluable for grid stabilization and emergency backup. Electrochemical energy storage systems can be primarily classified into 3 different types: batteries, supercapacitors, and fuel cells. Supercapacitors deliver rapid bursts of energy and quick charge/discharge cycles, ideal for applications needing fast power delivery. Fuel cells continuously generate electricity from fuel and oxidants with high efficiency and low emissions, while batteries store energy through chemical reactions for use in everything from portable electronics to grid-scale storage. Unlike supercapacitors, which are suited for short bursts of power, batteries can provide a sustained energy supply over a longer period. Compared to fuel cells, batteries are more widely established, with a broad range of available chemistries that don't require a continuous supply of fuel, making them more versatile and convenient. Figure 1.2 displays a Ragone plot that compares different types of electrical and electrochemical energy storage systems based on their specific energy (Wh kg⁻¹) and specific power (W kg⁻¹) outputs.



Figure 1.2. A typical Ragone plot comparing different energy storage systems. The dashed cyan lines indicate discharge times.

1.3. Batteries

Batteries, as compact and versatile energy storage systems, play a pivotal role in the energy storage market. They are divided into two types: primary and secondary batteries. Primary batteries are non-rechargeable and deliver power until the chemical components are exhausted. Secondary batteries, on the other hand, are rechargeable, store energy through reversible chemical reactions, and are widely employed in a variety of applications, from gadgets to electric vehicles. Popular examples of secondary batteries include ion storage batteries such as Li-ion and Na-ion batteries. The global secondary lithium-ion battery market was valued at approximately \$44 billion in 2020 and is expected to reach around \$193 billion by 2030, growing at an annual rate of around 18-20% during this period. This growth is primarily driven by the increasing adoption of electric vehicles (EVs) and the need for energy storage solutions to support renewable energy sources like solar and wind power.

1.4. The ion storage cell

Ion Storage cells that use Li ions or Na ions are primarily composed of 5 components: cathode, anode, electrolyte, current collector, and separator. Ion storage cells use a rocking chair mechanism where the ions cycle between the positive (cathode) and negative (anode) electrodes through the electrolyte during charging and discharging (Figure 1.3). Current collectors serve as the pathways for electrons to move between the electrodes and the external circuit, while separators in liquid electrolyte-based cells have electrical Insulation between the cathode and anode. When a cell is charged, ions move from the cathode to the anode through the electrolyte, and electrons flow through an external circuit to balance the charge. During discharge, the ions move back from the anode to the cathode, releasing energy that is used to power devices connected to the external circuit. Among the different components in ion storage cells, cathodes contribute 50% of the cost and 60% of the weight. This makes cathode-active materials a critical component in ion storage batteries. The choice of cathode material affects not just the performance and longevity of the battery but also its

applicability in different devices, from smartphones to electric vehicles. Hence, ongoing research and development in cathode materials are crucial for advancing battery technology and meeting the growing demands for energy storage solutions.



Figure 1.3. Schematic representation of an ion storage cell.

1.5. Choice of Ions storage batteries

Since their commercialization by Sony in 1991, Li ion batteries have dominated the market. The energy density of these batteries has also risen significantly from 90-100 Wh kg⁻¹ in the 1990s to 200-250 Wh kg⁻¹ today. The cathode materials used in Lion batteries have also diversified from LiCoO₂ (150-200 Wh kg⁻¹; ~3.7 V (nominal)) to LiFePO₄ (90-120 Wh kg⁻¹; ~3.2-3.3 V), Li(Ni_xMn_xCo_x)O₂, where *x* varies like in the case of NMC111, NMC622, NMC811 (150-220 Wh kg⁻¹ depending on the composition); ~3.7-3.8 V) and LiNi_xCo_xAl_xO₂ (200-250 Wh kg⁻¹; 3.6-3.7 V). The advances in manufacturing, economies of scale, and improvements in battery chemistry have resulted in a steady decrease in the cost of Li ion batteries over the last decade to around \$101 per kWh as of 2023 [1].

While lithium-ion (Li-ion) batteries are becoming cheaper each year, As the demand for batteries continues to rise across various sectors, having a diversified portfolio of battery technologies will be crucial. Na-ion batteries provide an alternative that can be used in specific scenarios where they offer advantages over Li-ion batteries, thereby reducing the pressure on lithium resources. Sodium is far more abundant and cheaper to source than lithium, leading to lower raw material costs and reducing the risk of supply chain disruptions as battery demand grows. As of recent data, lithium carbonate costs around \$30,000 to \$40,000 per ton. This high cost is driven by increasing demand, limited supply, and the concentration of lithium resources in specific geographic regions. In contrast, sodium precursors, such as sodium carbonate or sodium hydroxide, are significantly cheaper, with sodium carbonate costing around \$200 to \$300 per ton. The extraction and processing of sodium generally has a lower environmental impact compared to lithium. This makes Na-ion batteries a more environmentally friendly option, which is increasingly important as industries seek to reduce their carbon footprints. While Na-ion batteries may not completely replace Li-ion batteries, they are seen as a complementary technology, particularly for large-scale energy storage and applications where cost and resource availability are critical factors [2, 3].

1.6. Cathode materials for Na ion batteries

Various cathode materials have been explored for NIBs, including Layered oxides, NASICON-type, and Prussian blue analogs. NASICON (Na Super Ionic Conductor) type materials are known for their structural stability. NASICON-type cathode materials like Na₃V₂(PO₄)₃ and Na₄VMn(PO₄)₃ exhibit specific capacities close to 120 mAh g⁻¹ with nominal voltages greater than 3.4 V and are promising cathode materials. Similarly, Prussian blue analog cathodes offer open frameworks that facilitate rapid sodium ion diffusion, contributing to their high-rate capabilities. Despite these advantages, challenges such as limited capacity and stability issues under prolonged cycling still need to be addressed [2, 3].

Layered oxides (LOs) are known for their compositional flexibility, seamless synthesis, and superior electrochemical performance compared to the other cathodes, which makes them the most popular option for replacing Li-ion-based cathodes in commercial Na ion batteries. In addition, the current Li-ion battery technology also uses cathodes based on the layered oxide structure and shares many commonalities with Na-ion-based layered oxide cathodes. This would pave the way for their accelerated growth, as much of the data available on Liion-based cathodes can aid in advancing Na-based LOs, which is an added benefit.

1.7. Layered oxide cathodes

LOs typically have a basic formula of Na_xTMO₂; $0 \le x \le 1$; TM- transition metal cation or a mixture of multiple cations and are known to exist in a variety of phases like P2, P3, O3, O2, etc. This classification is based on the site configuration of Na-ions and the number of different O layers in the unit cell. O3-type LOs have $x \sim 1$, while P2 and P3 phases typically have x < 0.75 [2, 4]. With higher Na-ion concentrations, O3 phases usually show higher specific capacitates, while P2 and P3 type LOs fare better in rate and cyclic performance. This is due to the comparatively better open structure and resilience of P-type LOs to phase transition, which improves Na-ion conduction dynamics in the material. In P2 and P3-type materials, the Na-ion occupies a prismatic site as opposed to an octahedral site in the O3-type compounds. Further, in a P2-type framework, Na-ions occupy 2 different prismatic sites, which are either face-sharing (Na_f) or edge-sharing (Na_e) with the transition metal octahedron (TM-O₆). In P3, all prismatic sites are crystallographically equivalent Na_f sites (Figure 1.4) [5].



Figure 1.4. Diagram representing P2 and O3 type layered oxide structures

P3, P2, and O3 layered oxide structures are known to undergo phase transitions during the intercalation and deintercalation of sodium ions. These phase transitions are critical phenomena that affect the performance, stability, and longevity of sodium-ion (Na-ion) batteries. During cycling, as sodium ions are inserted, the P3 structure is reported to undergo transitions to an O3-type phase. P3-type structures also develop monoclinic distortion at lower Na⁺ concentrations (typically when x < 0.3) and transform into P'3-type structures. In P2-type materials, during the deintercalation of Na ions (particularly at low sodium concentrations), P2 structures can transition to O2, P'2, or OP4 phases. These transitions are typically associated with changes in the coordination environment of sodium ions and alterations in the stacking sequence of the layers. The P2-to-O2 transition, for example, involves a shift in the oxygen layers, which can be reversible but may still cause some structural strain [4, 6].

Chapter 1

1.8. Literature Survey

1.8.1. Layered oxide structures

The literature on various structures and electrochemical properties of P2 and O3type cathode materials is extensive [7-10]. Materials based on a P2-type framework possess notable features such as improved electrical conductivity and cyclic stability compared to the other structures because of their relatively open structure and resilience to resist phase transformations during Na-ions extraction [11-13]. O3-type materials typically exhibit higher specific capacities but suffer from poor rate performance and cyclic stability. In contrast, research on thermodynamically stable P3-type materials has only recently started to emerge [10, 14-17]. The studies on the P3 phase primarily revolve around those obtained electrochemically during the charging of O3-type cathodes, where the diffusion coefficient of the material shows a sharp rise [14, 18]. New reports on thermodynamically synthesized P3-type materials also suggest high diffusion coefficients comparable to P2-type materials [17, 19, 20]. However, rapid structural changes during cycling render this ineffective as other phases (O3, O'3, and P'3 that form at lower and higher voltages) do not support fast Na-ion kinetics, severely limiting the rate performance of these P3 phases [20-22].

1.8.2. Mono-metallic layered oxides

In layered oxide cathodes, the transition metal site can contain single or multiple redox-active transition metal elements. The presence of each of these transition metal elements brings its advantages and disadvantages. Monometallic oxides containing single transition metals such as Na_xMnO₂ [23, 24], Na_xCoO₂, and NaNiO₂ [25, 26] are known to show high specific capacities close to 200 mAh/g during the first charge-discharge cycle but suffer from rapid capacity degradation to about 50% of the original capacity in less than 100 cycles, even at a C/10 discharge rate. The charge/discharge curves of these materials also show multiple plateaus, which, in most cases, indicate various phase transitions during cycling.

These phase changes are caused by Na⁺ vacancy ordering and anisotropic volume changes induced by Jahn Teller active ions (such as Mn³⁺) during cycling, which affects cyclability. Interestingly, in Na_xMnO₂ and Na_xCoO₂, the P2 phase showed similar capacity degradations with each cycle and had a similar number of phase transitions as that of P3 and O3 type phases (synthesized by altering the concentration of Na⁺). In the case of iron-based LOs such as P2 and O3 type Na_xFeO₂, the Jahn Teller active Fe^{4+} ions and possible migration of Fe^{3+} ions from their octahedral site to neighboring tetrahedral interstitials due to the lower octahedral stabilization energy (OSSE) of Fe³⁺ ions. In most cases, this is irreversible and leads to phase transformations [6, 27]. OSSE is the difference in crystal field stabilization energy of octahedral and tetrahedral sites. It is an indicator of the relative stability of an ion in an octahedral coordination compared to a tetrahedral coordination. The OSSE of Fe^{3+} ions is equal to 0, meaning they possess the same energy in both sites. This increases the probability of their migration from their original octahedral site. Overall, among monometallic Fe-based LOs, O3-NaFeO2 reportedly showed a capacity of 120 mAh/g at a discharge rate of C/10 with a 50% reduction in initial capacity after 10 cycles [28].

Among lesser-known cathode materials based on Cr, Cu, and V, NaCrO₂ stands out. Even though the scarcity of Cr ores and its poisonous nature would limit the practical application of Cr-based cathodes of the O3 type, NaCrO₂ demonstrated excellent electrochemical performance [29, 30]. The cathode exhibits a nominal voltage of 3V and achieved a specific capacity of 120 mAh/g, with almost 90% of the initial capacity retained after 300 cycles at 1 C. Even at a discharge rate of 100C, this cathode maintained a capacity of 60 mAh/g, which is quite impressive [30]. The capacity fading mechanism in Cr-based cathode materials is also quite different from those already discussed. In the case of O3 type NaCrO₂, rock salt CrO₂ was formed during charging due to the instability of Cr⁴⁺ ions in the LO structure [31-33].

1.8.3. Multi-metallic layered oxides

In Cu-based monometallic cathodes, such as O3 type NaCuO₂, the dissociation of the compound into CuO and Na₂O at higher voltages causes severe capacity fading in just 10 cycles [34]. NaVO₂, with V^{3+} ions as the active TM, is challenging to synthesize, as it requires a reducing atmosphere to prevent V^{3+} ions from assuming a 5+ oxidation state. The material with a specific capacity of 110 mAh/g shows a nominal voltage of only 1.8 V and, hence, has a low energy density [35].

Each monometallic LOs discussed has decent specific capacities, but rapid phase transitions induced by Na-ion vacancy ordering pose various challenges that limit their cyclic stability. Like Li-based cathode materials, cationic substitutions in the TM layer can help circumvent many of these challenges. Cationic substitutions involving active materials use transition metals such as Ni²⁺, Cu²⁺, Co^{3+} , etc., that show their corresponding redox reactions. This helps reduce dependence on a single metal ion for charge compensation processes and can reduce some of its drawbacks. Additionally, the presence of multiple elements in the TM site in LOs has been reported to be instrumental in preventing Na-ion vacancy ordering during charging, which can help avoid multiple phase transitions that plague monometallic oxides. Typically, Na_xMnO_2 is preferred as the parent material for catatonic substitutions. This is mainly due to 2 reasons: a relative abundance of Mn ores, making Mn-based cathodes relatively cheaper, and the second being the ability of Mn to show a 3+ and 4+ oxidation state. This enables greater flexibility in the concentration of Na and allows for the inclusion of other cations with 2+ oxidation states, as Mn ions would readily assume a 4+ oxidation to compensate for the loss. For example, substituting Mn with Ni²⁺ ion is a well-studied combination where the Ni underdoes a 2-electron transfer reaction from a 2+ to 4+ oxidation state during charging and hence boosts the cathode's capacity. P2 type Na_{0.67}Mn_(0.66+x)Ni_(0.33-x)O₂ series of cathode materials have shown capacities close to 130 mAh/g [36-38]. The detrimental effect of phase transformations on cyclic stability can be imbibed from the operational

voltage dependent studies on $Na_{0.67}Mn_{0.66}Ni_{0.33}O_2$, where the sample was able to show excellent cyclic properties retaining 75% of initial capacity at a discharge rate of 5C when cycled between 2-4 V after 1200 cycles when compared to just 70% of initial capacity retention after 70 cycles at 0.1C between 1.5-4.5V. This is because the material has been shown to undergo phase transformations beyond initial voltage ranges. Mn⁴⁺ remains largely inactive in the cathode when Ni ~0.33. At lower Ni concentrations, the concentration of the Jahn Teller Mn^{3+} ions increases, which drastically affects cyclic properties. The recently reported P3 type Na_{0.67}Mn_{0.66}Ni_{0.33}O₂ shows similar capacities as the P2 type sample. Still, it has inferior cyclic and rate performance due to phase changes between P3, O3, and Z phases and lower Na-ion diffusion coefficients [10, 39]. Even with commendable electrochemical properties, Na_{0.67}Mn_{0.66}Ni_{0.33}O₂ cathode exhibits a nominal low voltage close to 3 V due to the low reduction potential of Ni^{4+/2+} redox couples. Na-ion vacancy ordering persists as a challenge in this cathode. Even its performance at higher voltages above 3.8 V leaves much to be desired. Surprisingly, Cu substitution for Ni in Na-Ni-Mn based system mitigated many of these challenges. The P2 type Na_xMn_{0.67}Ni_{0.33-x}Cu_xO₂ [13, 40-43] series of cathodes have shown an elevated nominal voltage of 3.4 V (mainly due to higher oxidation potentials of $Cu^{2+/3+}$ at 3.9V) with considerable reduction in Na-ion vacancy ordering during charging. P2 type Na_{0.67}Mn_{0.67}Ni_{0.18}Cu₁₅O₂ [41] and Na_{0.70}Mn_{0.65}Ni_{0.20}Cu_{0.15}O₂ [43] cathodes have shown a 115 mAh/g and have improved structural stability with phase transformations occurring only at 4.4V.

Even with the inclusion of Cu, the rate performance and cyclic properties remained unchanged, with 95% capacity retentions reported after 300 cycles at a 1C rate between 2.0-4.3 V. Similar enhancement in structural stability with the inclusion of Cu has also been seen in Na-Fe-Mn and Na-Fe-Ni-Mn based systems where structural stability of both cathodes improved with the inclusion of Cu ions. Even though the capacities of these cathodes reduced drastically from 180 mAh/g to 90 mAh/g, the cyclic stability showed exceptional improvements, with 85% capacity retained after 150 cycles at a discharge rate of 1C [44-46] compared to 60% retained after 30 cycles for the parent

compounds Na_{0.67}Fe_xMn_{1-x}O₂ [47] and Na_{0.67}Ni_{0.33-x}Fe_xMn_{0.67}O₂ [48-55]. In Febased systems, the migration of Fe to tetrahedral voids at voltages below 4 V was observed to have dwindled with Cu addition, which delays the formation of the OP4 phase during charging. Even in Na_{0.67}Cu_{0.14}Mn_{0.86}O₂ [42] compounds, drastic improvements in cyclic performance have been reported compared to Na_{0.67}MnO₂. Another popular substituent in Na-Mn systems is cobalt (Co), which shows impressive electrochemical properties in bimetallic and polymetallic LOs. Na_{0.67}Co_xMn_{1-x}O₂ [56-59] with Co substitution behaves similarly to Cu-substituted LOs. Although the former has shown higher specific capacities, the rate performance and cyclability improvements are comparable to the Na_{0.67}(Ni-Cu-Mn)O₂ series of cathodes already discussed.

Similar to the substitution of the multiple electrochemically active ions, the incorporation of electrochemically inactive ions, such as Al³⁺, Zn²⁺, Mg²⁺, Ti⁴⁺, etc., into the transition metal layers is a widely explored strategy to improve the electrochemical performance of layered oxide cathodes. These inactive ions function as structural supports during the insertion and extraction of Na ions and have been shown to enhance the cyclic stability of layered oxide compounds. As their name implies, these ions do not participate in electrochemical reactions but act as stabilizing pillars during cycling. For example, in the case of Ti⁴⁺. It was reported that the presence of a larger ion (such as Ti-ions) in place of Mn⁴⁺ ions in Na_{0.7}Ni_{0.2}Cu_{0.15}Mn_{0.65}O₂ [43, 60] led to the expansion of the unit cell and an increase in the area of the Na ion conduction bottlenecks. Consequently, the Na0.7Ni0.2Cu0.15Mn0.575Ti0.075O2 cathode also showed improvements in its particle morphology and electrical properties, which led to a remarkable improvement of 27% in the observed specific capacity of the parent compound. In another instance, Ti substituted P2 Na_{0.67}Ni_{0.33}Mn_{0.67}O₂, effectively suppressing P2 to O2/OP4 phase transitions and enhancing cyclic performance [61, 62]. Other inactive ions, such as Mg^{2+} and Zn^{2+} , have also been reported to have similar effects on the P2-type structure [63-65]. The 2+ oxidation state of these ions is particularly useful in Mn-based layered oxides, as it helps reduce Mn³⁺ concentrations. Although not extensively studied in NIB cathodes, Al³⁺

substitution in layered oxides is reported to enhance the rate performance and cyclic stability of LIB cathodes [1, 66-69].

1.8.4. Mixed phase layered oxides

Another approach that has recently garnered significant research interest for improving the electrochemical performance of layered oxide cathodes involves the use of hybrid P2/O3 cathodes with different fractions of O3 and P2 type phases [41, 70-74]. This method has demonstrated improvements in cyclic stability without sacrificing specific capacity. Additionally, biphasic P2/O3 cathode materials have successfully reduced structural distortions caused by the activation of $Mn^{3+/4+}$ in NaNi_xMn_{1-x}O₂. This allows a wider operational voltage window during cycling, substantially boosting the specific capacity [74, 75]. Further, in O3/P2 biphasic cathodes, the synergistic effect arising from the coexistence of P2 and O3 type phases has been reported to enhance structural stabilities and Na⁺ transport kinematics, leading to better rate and cyclic performance [8, 22, 76]. Although not as extensively studied, P2/P3 biphasic cathodes also show similar enhancement in electrochemical properties due to an interlocking of P3 and P2 structures [16, 17, 77, 78]. These materials have shown higher rate performance compared to their monophasic counterparts. Combining P3 and P2 type phases also leverages the superior Na⁺ transport properties of both phases; the biphasic P3 and P2 type compounds can be obtained at relatively lower calcination temperatures than the P2 and O3 type phases. The electrochemical properties of various cathode materials are compared in table 1.1

	Specific	Cyclability	
Composition	capacity	(%, C-rate,	Ref
	(mAh/g)	Cycles)	
$Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$	210 (1.5-4.4	80% after 50	[37]
	V)	cycles at 1 C	
Na _{0.67} Cu _{0.28} Mn _{0.72} O ₂	109 (2-4.5 V)	98% after 50	[79]
		cycles at 1 C	
NaNi1/3Mn1/3Fe1/3O2	130 (2-4 3 V)	75% after 200	[80]
	150 (2-4.5 V)	cycles at 1C	
NaNi _{0.25} Fe _{0.25} Mn _{0.5} O ₂	193 (1.5-	40% after 50	[81]
	4.3V)	cycles at 0.5C	
$Na_{0.67}Ni_{0.1}Cu_{0.2}Mn_{0.7}O_2$	114 (2-4.5V)	78% after 200	[42]
		cycles 1C	
Na _{0.67} Mn _{0.65} Ni _{0.2} Co _{0.15} O ₂	155 (1.5-	78% after 100	[82]
	4.2V)	cycles at 1 C	
$NaCu_{0.22}Fe_{0.30}Mn_{0.48}O_2$	100 (2-4.05	97% after 100	[83]
	V)	cycles at 0.1	
		С	
$Na_{0.75}Ni_{0.82}Co_{0.12}Mn_{0.06}O_2$	171 (2-4V)	65% after 400	[84]
		cycles at 1C	
$Na_{0.83}Cr_{1/3}Fe_{1/3}Mn_{1/6}Ti_{1/6}O_2$	161 (1.5-4.1	35% after 100	[85]
	V)	cycles at 0.2C	
Na _{0.8} Mn _{0.55} Ni _{0.25} Fe _{0.1} Ti _{0.1} O ₂	155 (1.5-4.3	80% after	[86]
	V)	100 cycles at	
		0.1C	
Na $_{0.47}$ Mn $_{0.47}$ Ni $_{0.22}$ Mn $_{0.1}$ O $_{2}$	120 (1.5-4.0	95% after 50	[87]
1 100.0/11110.0/1 10.25111g0.102	V)	cycles at 1C	[0/]

Table 1.1. Comparison of electrochemical properties between different layered oxide cathodes.

$Na_{0.6}Ni_{0.22}Al_{0.11}Mn_{0.66}O_2$	252 (1.5-4.6	80% after 50	[88]
	V)	cycles at 20	
		$mA \cdot g^{-1}$	
Na2/3Ni1/3 Mn5/9Al1/9O2	117 (1.6-4.0	77.5% after	[89]
	V)	100 cycles at	
		0.2 C	
$NaNi_{0.32}Mn_{1/3}Fe_{1/3}Zn_{0.01}O_2$	125(2-4.3)	82% after 200	[80]
		cycles at 1C	
NaCu _{0.22} Fe _{0.30} Mn _{0.43} Ti _{0.05} O ₂	90 (2.5-4.05	96% after 200	[90]
	V)	cycles at 2C	
NaNi _{0.4} Fe _{0.2} Mn _{0.2} Ti _{0.2} O ₂	145(2-4.2)	84% after 200	[91]
		cycles at 1C	
$Na_{0.70}Ni_{0.20}Cu_{0.15}Mn_{0.575}Ti_{0.075}O_2$	130 (2-4.25	95% after 300	[43]
	V)	cycles at 1C	
$NaNi_{0.45}Mn_{0.2}Ti_{0.3}Zr_{0.05}O_2$	141 (2-4 V)	70% after 200	[92]
		cycles at	
		0.05C	
$Na_{2/3}Mn_{0.7}Ni_{0.1}Fe_{0.1}Mg_{0.1}O_2$	122 (2-4.3 V)	80% after 250	[93]
		cycles at 0.2	
		С	
NaMn _{0.48} Ni _{0.2} Fe _{0.3} Mg _{0.02} O ₂	160 (1.5-4.2	99% after 100	[94]
	V)	cycles at 0.1	
		C.	
$Na_{0.9}Cu_{0.12}Ni_{0.10}Fe_{0.30}Mn_{0.43}Ti_{0.05}O_2$	105 (2.5-4.2	90% after 200	[90]
	V)	cycles at 0.2C	
$Na_{0.9}Ca_{0.05}Ni_{1/3}Fe_{1/3}Mn_{1/3}O_2$	127 (2-4 V)	92% after	[95]
		200 cycles at	
		0.2C	
P2/O3	146 (2.0-4.2	92% after 200	[96]
$Na_{0.80}Mn_{0.60}Ni_{0.30}Cu_{0.10}O_2$	V)	cycles at 1C	

P2/O3	130 (2.0–	73.1% after	[97]
Na _{0.736} N1 _{0.264} MIg _{0.1} MIn _{0.636} O ₂	4.3 V)	200 at TC 89.6% after	
P2/O3 Na _{0.80} Li _{0.13} Ni _{0.20} Fe _{0.10} Mn _{0.57} O ₂	181 (2.0–4.5 V)	100 cycles at 1C	[76]
$\begin{array}{c} P2/O3 \\ Na_{0.67}Li_{0.15}Ni_{0.18}Mg_{0.02}Mn_{0.8}O_2 \end{array}$	160 (1.5– 4.2 V)	70% after 100 cycles 0.1C	[98]
P2/O3 Na _{0.76} Ni _{0.33} Mn _{0.50} Fe _{0.10} Ti _{0.07} O ₂	160 (2.2– 4.3 V)	79.2% after 100 cycles at 1C	[99]
P2/O3 Na _{0.8} Li _{0.2} Ni _{0.33} Mn _{0.67} O ₂	132 (2.0–4.3 V)	80.1% after 120 cycles at 1C	[100]
P2/O3 Na _{0.85} Ni _{0.34} Mn _{0.33} Ti _{0.33} O ₂	126 (2.2–4.4 V)	80.6% after 200 cycles at 1C	[74]
P2/Tunnel/Z Na _{0.7} MnO _{2.5}	185 (2.0–4.3 V)	77% after 100 cycles at 0.5C	[101]

1.9. Motivation

India is the third largest consumer of energy in the world. About 42% of India's total installed energy capacity comes from renewable sources (Figure 1.5). India ranks fourth globally in installed wind power and fifth in solar power capacity. Over the last decade, India has witnessed a rapid jump in solar power generation form from 2.6 GW to 89.43 GW since 2014. Given India's ambitious renewable energy targets to reach 500 GW of renewable capacity by 2030 and increasing energy demand, there is a pressing need for cost-effective and scalable energy storage solutions [102].



Figure 1.5 Energy production in India by source.

Sodium-ion (Na-ion) batteries present a promising option for India due to their cost-effectiveness and reliance on locally abundant sodium precursors. Unlike lithium, which is scarce and requires imports, sodium is plentiful and inexpensive. This reduces the overall cost of battery production and aligns with India's Atmanirbhar Bharat initiative, which seeks to enhance domestic manufacturing and reduce import dependency. Additionally, the layered oxide cathode materials studied in this work incorporate widely available elements such as manganese and aluminum, abundantly found in India, a key global exporter of these materials (Figure 1.6). Hence, developing high-performance Na-ion batteries using locally abundant resources like sodium is a strategic move. This would lower costs, strengthen India's energy security, and boost its domestic manufacturing capabilities. Enhanced battery performance ensures competitiveness with lithium-ion technology while promoting sustainability and reducing the environmental impact of mining for rare materials.



Figure 1.6 Manganese and Bauxite (Al ore) production over the world.

1.10. Scope of the thesis work

The thesis primarily focuses on designing and optimizing the composition of monophasic/mixed phase layered oxide cathode materials (such as P2/O3 and P3/P2 phases) to improve their electrochemical performance. The objectives outlined for the study are as follows:

- 1. To synthesize and study the structural, electrical, and electrochemical properties of mixed phase layered oxides.
- 2. To explore the electrochemical properties of biphasic/triphasic systems involving P2, P3, and O3 phases in varying concentrations.
- 3. To undertake a systematic study of a system of cathode materials and map the effect of each of its constituent elements on functional properties.
- 4. To study the structural evolution of the different cathode materials and the various parameters that influence them during cycling.
- 5. To establish a fabrication protocol for the preparation of full cells using hard carbon anode.

1.11. References

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Materials and Methods

2.1. Sol-gel synthesis

A conventional sol-gel method was used to prepare the P2/P3 series of cathode materials. A homogeneous solution containing stoichiometric amounts of precursors such as manganese (II) acetate tetrahydrate (source of Mn ions), nickel acetate tetrahydrate (source of Ni ions), aluminum nitrate (source of Al ions), and sodium carbonate (source of Na ions) was prepared in DI water and stirred for 6 h, after which ethylene glycol and citric acid were added. After stirring for another 12 h, the solution was heated to produce a gel. The gel was then dried and subsequently ground to obtain a powder. The powder was heat treated at 550 °C in air for 12 h and further calcined at different temperatures (700 – 850 °C) to obtain the final product before being moved into a glovebox (Figure 2.1).



Figure 2.1. The steps involved in sol-gel synthesis.

2.2. Cell Fabrication

The slurry for the positive electrode was prepared by blending the active material, Ketjen black, and a PVDF binder in NMP, with a weight ratio of 75:10:15. This mixture was applied to an aluminum current collector, dried, and then cut into 16 mm discs. In a similar process, the negative electrode was formed by mixing commercially available hard carbon with Ketjen black and

PVDF binder in NMP, using the same 75:10:15 weight ratio. The resulting slurry was coated using a desktop coater (Figure 2.2) and dried at 100 °C for 8 h in a vacuum oven onto an aluminum current collector and punched into 16 mm discs. CR2032 half cells were fabricated for electrochemical tests of cathodes using the Na metal as the counter electrode, 1M NaClO₄ in Ethylene Carbonate - Propylene Carbonate (vol. ratio of 1:1) as the electrolyte, and a Whatman GF/D filter paper acting as the separator in a glovebox. The full cells, on the other hand, contain hard carbon anode discs instead of Na metal.



Figure 2.2. Desktop coating machine used in cathode preparation.

2.3. Structural characterization

2.3.1. X-ray diffraction

X-ray diffraction (XRD) is a powerful analytical technique used to determine the crystal structure, identify crystalline phases, analyze lattice parameters, and detect structural changes. The powder x-ray diffraction (XRD) patterns were obtained at room temperature using Malvern Panalytical, Empyrean, diffractometer (Cu-K α radiation source) between 10°- 70° 2 θ range (Figure 2.3). The crystallographic data for the samples were obtained through Rietveld refinement of the XRD data with the help of the *TOPAS Academic* (version 6) software package.



Figure 2.3 The Malvern Panalytical diffractometer.

2.3.2 Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscopy (FESEM) is an advanced imaging technique used to capture highly detailed images of a material's surface at the nanoscale. FESEM uses a field emission gun to produce a focused beam of electrons, which interacts with the sample, generating high-resolution images with minimal beam damage. The microstructure of the samples was analyzed using a Joel field emission scanning electron microscope (model JEOL-7610) equipped with energy-dispersive x-ray spectroscopy (EDS) for elemental mapping (Figure 2.4).

Chapter 2



Figure 2.4. The JEOL-7610 Field Emission Scanning Electron Microscope.

2.3.3. X-ray Photoelectron Spectroscopy

XPS spectra were acquired to determine the valence states of their constituent elements in each sample. In XPS, a sample is irradiated with X-rays, which causes the emission of photoelectrons from the material's surface. By measuring the kinetic energy and number of emitted electrons, researchers can identify the elements present and analyze their chemical bonding and oxidation states. X-ray photoelectron spectra (XPS) were obtained using a Thermofisher Scientific - Naxsa base with an Al K α X-ray source (1486.6 eV).

2.3.4. Inductively Coupled Plasma

Inductively Coupled Plasma (ICP) is an analytical technique used to detect and quantify trace elements in various materials. In ICP, a sample is ionized by exposing it to a high-temperature plasma (typically generated using argon gas), which excites the atoms and ions. These excited species emit light at characteristic wavelengths. The intensity of the emitted light correlates with the concentration of each element, allowing for precise elemental analysis. Inductively coupled plasma atomic emission spectrometry (ICP-AES) (SPECTRO Analytical Instruments GmbH, Germany, Model: ARCOS, Simultaneous ICP Spectrometer) was used to determine the specific chemical compositions of the cathode materials.

2.3.5. Extended X-ray absorption fine structure (EXAFS)

The Mn and Ni K-edge extended x-ray absorption fine structure (EXAFS) spectra were obtained from the scanning EXAFS beamline (BL-9) at Indus-2 synchrotron source (2.5 GeV, 150 mA) at Raja Ramanna Centre for Advanced Technology (RRCAT) Indore, India, and were analyzed using ATHENA and ARTEMIS software packages. EXAFS is a technique used to study the local atomic environment around specific elements within a material. EXAFS is part of X-ray absorption spectroscopy (XAS), focusing on the oscillations that occur in the X-ray absorption spectrum just beyond the absorption edge of an element. These oscillations arise due to interference between outgoing photoelectrons (ejected by X-ray absorption) and the surrounding atoms. By analyzing these oscillations, EXAFS provides detailed information about the distances, coordination numbers, and types of neighboring atoms, as well as the disorder around the absorbing atom.

2.4. Electrochemical Characterization

2.4.1. Cyclic Voltammetry

Cyclic voltammetry (CV) is an electrochemical technique used to study the redox behavior of materials and reaction mechanisms. The redox peaks in CV curves indicate the voltages at which the cathode material undergoes oxidation and reduction, revealing the active redox couples. The cyclic voltammetry (CV) tests were performed at a scan rate of 0.1 mV/s with the help of a Keithley Model 2450-EC Source Meter.

2.4.2 Galvanostatic Charge/Discharge and Galvanometric Intermittent Titration Technique

Galvanometric charge-discharge (GCD) tests and the galvanometric intermittent titration technique (GITT) were carried out using a Neware battery tester (CT-4008T). The rate performance of the samples was evaluated at different currents, and the cyclic performance was tested for 200-500 cycles. The mass loading for the samples was around 2-3 mg/cm² (unless otherwise specified), and C-rates were calculated assuming a nominal capacity of 150 mAh/g (assuming a Na⁺ extraction of ~0.6).

2.4.3. Electrochemical impedance spectroscopy

Impedance measurements were performed using a computer-controlled LCR meter (model: ZM 2376, NF Corp.) equipped with an internal DC bias up to 5 V over a 1 mHz – 1 MHz frequency range. The impedance data was analyzed using equivalent circuit modelling. The impedance was fitted to equivalent circuit models to extract parameters such as electrolyte resistance, charge transfer resistance, and interfacial layers resistance from the overall cell resistance.

2.4.4. Operando Synchrotron XRD

Operando X-ray Diffraction (operando XRD) combines X-ray diffraction with real-time monitoring of materials under operating conditions during electrochemical reactions in batteries. This method allows observing structural changes in materials while they are functioning, providing valuable insights into their behavior and performance. *Operando* Synchrotron XRD studies were carried out using extreme conditions angle dispersive/energy dispersive synchrotron X-ray diffraction (BL11) at the Indus-2 beamline (RRCAT) with different beam wavelengths and beam energy of 2.5 GeV in transmission mode. The CR2032 coin cells for the *operando* studies were prepared by drilling 3 mm



holes in the cathode and anode casings, which were sealed using Kapton films (schematically shown in Figure 2.5).

Figure 2.5. Schematic of the *operando* Synchrotron XRD setup.

Chapter 2

Unveiling the Potential of P3 Phase in Enhancing the Electrochemical Performance of a Layered Oxide Cathode

In this chapter, a series of P3/P2 biphasic Na_{0.75}Mn_{0.75}Ni_{0.25}O₂ (NNM) cathode with varying P2/P3 phase fractions were synthesized, and the impact of a varying P3 phase on the electrochemical properties between 1.5 V and 4.2 V is reported. The variable concentration of the P3 phase, ranging from 0-100%, was achieved by appropriately tuning the calcination temperature. The P3 phase typically forms a lower temperature compared to the P2 and O3 phases. This was found to have profound implications on the morphology and electrochemical properties of the cathode material, with P3 dominant biphasic cathodes showing substantially superior rate performance and cyclic stability compared to monophasic P2 and P3 cathodes. Apart from morphological changes, the manifestation of the synergetic effect between the two phases mitigated the severe structural distortions during cycling, resulting in a better cyclability of biphasic cathodes.

3.1 Structural Characteristics

The Na_{0.75}Mn_{0.75}Ni_{0.25}O₂ (NNM-x; x represents the calcination temperatures) series of materials were synthesized through the sol-gel route with calcination temperatures ranging between 700 to 850 °C. Powder XRD was used to analyze the crystal structure of these samples. The room temperature XRD pattern of each sample and their corresponding Rietveld refinement profiles are depicted in Figure 3.1(a) & (c) and Figure 3.2. Initial analysis of Figure 3.1(a) shows drastic variations in the peaks' positions and intensities, confirming the changes in the crystal structure of the material due to the change in calcination temperature. The Rietveld refinement of the XRD data for the NNM-700 and 750 samples confirms the existence of a single P3 ($R\bar{3}m$ space group) phase, with minor impurities (< 10 wt.%) observed in the former sample. With further increase in synthesis temperature, the P3 (006), (101), (102), (104), and (015) peaks show a gradual decline in intensity in comparison to P2 (002), (100), (102), (103), (104) diffraction indicating the emergence of a biphasic P2/P3 system with P2 phase becoming dominant with the increase in calcination temperate from 750 °C - 850 °C. The deconvoluted XRD patterns of P2 and P3 phases for NNM-750, 780, and 850 between the 20 range of 30° - 40° are shown in Figure 3.1(c).

The XRD data confirm a continuous conversion of the P3 phase into a P2-type phase with an increase in the calcination temperature and complies with the recent reports in the literature where the P3 phase is regarded as an ordered phase of P2 with lower calcination temperatures [1, 2]. In this investigation, we have synthesized hitherto unknown pure P3 phase in extensively studied Na_{0.75}Mn_{0.75}Ni_{0.25}O₂. More importantly, these XRD results demonstrated that the phase fraction of the P2/P3 biphasic system could be tailored from 0% to 100% simply by controlling the calcination temperature. The crystallographic parameters obtained from Rietveld refinement (Table 3.1) also show that unit cell volume for P2 (number of formula unit cells in one crystallographic unit cell, Z = 2) and P3 (Z = 3) phases formed at different synthesis temperatures remained essentially unchanged and was found to be around ~80.4 Å³ and ~121.2 Å³, respectively, with similar areas of around 9.51 Å² for the prismatic faces that form the primary Na⁺ migration bottlenecks. The P2 and P3 crystal structures generated using VESTA [3] and output parameters of Rietveld refinement are depicted in Figure 3.1(b).



Figure 3.1. (a) Phase evolution of Na_{0.75}Mn_{0.75}Ni_{0.25}O₂ with calcination temperature. (b) 2D visualization of P2 and P3 structures generated using VESTA software. (c) Rietveld refinement of XRD data belonging to NNM-750,780, and 850 samples, along with the deconvoluted P2 and P3 phases in the 2θ range of 30-40°.

Another noticeable feature of NNM samples investigated in the present study is the considerable influence of *Na content* on the phase fractions obtained at various calcination temperatures. Figure 3.3 displays the room temperature XRD patterns of NNM-700, 750 & 800 prepared by adding 5% extra Na. The peaks marked by a * correspond to an O3 phase. This establishes 0.75 as a critical point of Na concentration for obtaining a P2/P3 biphasic system in Na_{0.75}Mn_{0.75}Ni_{0.25}O₂, above which a tri-phasic system involving P2/P3/O3 starts to form. Interestingly, the

temperature at which O3 peaks appeared matched that of the P3 phase formation temperature at ~ 700 °C. With an increase in synthesis temperature, however, the conversion of the P3 phases in the P2 phase continued even in the 5% extra Na samples. At the same time, the relative intensity of the O3 peaks remained the same even after the entire P3 phase had transformed into a P2 phase at 850 °C. Since the main aim of this study was to investigate the structural, electrical, and electrochemical properties of the biphasic P2/P3 system, further characterizations of the 5% additional Na samples were not carried out.



Figure 3.2. Rietveld refinement profiles of XRD data of NNM-765 and 800 samples.

The local structure around the transition metal ions in P3 type NNM-750 and P2 type NNM-850 were probed using fitting of EXAFS data at Mn and Ni K-edge. Figure 3.4(a-d) represents the Fourier transforms of Mn and Ni K-edge in NNM-750 and NNM-850 samples. The peaks representing (Mn/Ni)-O and (Mn/Ni)-TM coordination are also marked in the figures. The (Mn/Ni)-O bond lengths obtained from the fit for P2 and P3 type phases matched those obtained from the Rietveld refinement of XRD data and put the bond lengths at ~2 Å. The distance between the transition metal ions obtained from the fit in both P2 and P3 type structures was estimated to be around 2.88 Å.



Figure 3.3. Room temperature XRD patterns of NNM-750, 765, and 850 synthesized with 5% extra Na₂CO₃.



Figure 3.4 (a-b) Mn-K edge and (c-d) Ni K edge EXAFS spectra of NNM-750 and NNM-850 samples.

Sample	Phase (Fraction)	a (Å)	c (Å)	V (Å ³)	Reliability Factors
NNM-	P3 (100%)	2.8866	16.792	121.18	R _{exp} : 2.00
750		±0.0001	± 0.002	± 0.01	R _{wp} : 2.72
	P2 (0%)	-	-	-	R _p : 2.12
					GOF: 1.14
NNM-	P3	2.8879	16.636	121.07	R _{exp} : 2.00
765	(76.7%)	±	± 0.002	± 0.02	R _{wp} : 2.72
		0.0001			R _p : 2.12
	P2	2.8864	11.144	80.41	GOF: 1.14
	(23.3%)	±	± 0.002	± 0.01	
		0.0001			
NNM-	P3	2.8895	16.771	121.26	R _{exp} : 2.35
780	(48.3%)	±	± 0.002	± 0.03	R _{wp} : 2.68
		0.0003			R _p : 2.12
	P2 (52.7)	2.8874	11.154	80.54	GOF:
		±	± 0.001	± 0.01	1.14
		0.0001			
NNM-	P3	2.8887	16.744	121.01	R _{exp} : 2.11
800	(28.4%)	±	± 0.002	± 0.03	R _{wp} : 2.72
		0.0003			R_p : 2.06
	P2	2.8880	11.1493	80.53	GOF: 1.28
	(81.6%)	±	±	± 0.09	
		0.0001	0.0006		
	P3 (0%)	-	-	-	R _{exp} : 2.85

Table 3.1. Lattice parameters of NNM-x samples obtained from the Rietveld refinement of room temperature XRD data.

NNM-	P2 (100%)	2.9041	11.1485	80.33	Rwp: 2.15
850		±	±	± 0.01	R_p : 2.19
		0.0007	0.0004		GOF: 1.32

The morphology and microstructure of the NNM-*x* samples were studied using FESEM. The representative SEM micrographs of NNM-750, 780, and 850 are displayed in Figure 3.5(a-c), and those of NNM-765 and 800 are presented in Figure 3.6. The figures show agglomerated and fused particles for samples calcined at 800 °C and 850 °C. In contrast, the samples calcinated at temperatures below 800 °C have smaller particles with better-defined contours and facets. The elemental map of NNM-780 portrayed in Figure 3.5(b1-b4) shows the homogeneous distribution of all the constituent elements.



Figure 3.5. SEM micrographs of (a) NNM-750, (b) NNM-780, and (c) NNM-850, along with (b1-b4) elemental maps depicting the distribution of the Na, Mn, Ni, and O in NNM-780.



Figure 3.6. SEM images of (a) NNM-765 and (b) NNM-800.

The microstructure of a cathode material is a significant factor in determining its GCD rate performance. Samples with smaller and lesser agglomerated particles usually show higher specific capacities (especially at higher discharge rates) than those with larger and fused particles. This is because liquid electrolytes typically have much higher ionic conductivities than cathode materials; hence, a porous cathode layer with smaller particles effectively provides a shorter diffusion path for Na-ions than a cathode with larger and highly agglomerated particles [4, 5]. The effect of particle sizes is not so apparent at low discharge rates (~ 0.1C) but becomes a deterministic factor in boosting specific capacity at higher discharge rates. Hence, even though the available literature on layered oxides suggests a higher value of Na⁺ diffusion coefficient for P2-type materials compared to P3-types, the higher concentration of fused particles observed in the P2-dominated NNM-800 and NNM-850 samples could lower their specific capacities at high discharge rates (inferior rate performance) compared to the P3 dominated samples NNM-750 and 780 samples.



Figure 3.7. XPS spectra of NNM-750 and NNM-850.

The XPS spectra of the NNM-750 and 850 samples were acquired to determine the valence states of their constituent elements, shown in Figure 3.7, along with the fitted data. The Ni 2p spectra shows 2 coupled peaks at 854.26 and 871.75 eV, which suggests the presence of Ni²⁺ ions [6-8]. The O 1s spectra show the presence of adsorbed CO₂ along with bonded oxygen in the LO. The Mn 2p XPS spectra can be deconvoluted into 4 peaks: at 641.8 & 653.2 eV belonging to Mn^{3+} , 643.2 & 654.7 eV corresponding to Mn^{4+} , indicating a mixed valence state of Mn-ions in 3+ and 4+ oxidation states in these samples [6-8].

The X-ray absorption near edge structure spectra (XANES) of NNM-750 and 850 at Mn and Ni K-edge, depicted in Figure 3.8, also show similar energy levels for Mn and Ni ions for both samples. The XANES and XPS spectra of both samples are almost identical, suggesting that Na volatilization during the NNM-*x* series synthesis was negligible. This also indicates that the phase transformation of NNM from a P3-

type to a P2-type upon increasing the calcination temperature from 750 °C to 850 °C is not guided by the starvation of Na-ion within the structure (due to Na volatilization) and both the P3 and P2 type cathodes contained a similar concentration on Na-ions.



Figure 3.8. Normalized XANES spectra of NNM-750 and 850 at Mn and Ni K edges.

3.2. Electrochemical Characteristics

The electrochemical characterization of NNM-x samples was evaluated in a coin cell configuration, cycled between 1.5 and 4.2 V. Figure 3.9 shows the cyclic voltammograms of NNM-750, 780, and 850 and the same for NNM-765 and NNM-800 are displayed in Figure 3.10. The redox peaks observed below 3 V in the cyclic voltammograms are attributed to the $Mn^{3+/4+}$ redox process [9, 10]. In comparison, the peaks in 3.0 V – 3.5 V and 3.5 V - 4.0 V ranges indicate the activity of Ni^{2+/3+} and Ni^{3+/4+} couples, respectively [11, 12]. Interestingly, in the NNM-750 sample, containing a pure P3 phase, the CV curve shows only 3 pairs of distinct peaks at 2.35/1.79 V, 3.50/3.00 V, and 3.92/3.35 V. An increased number of peaks are observed in the CV curves for P2 dominated NNM-800, 850 samples, possibly due to Na⁺ vacancy ordering in P2-type materials as reported in the literature [9, 13]. The relatively lower concentration of Na-ion vacancy ordering peaks in the other P3 dominant samples points to an innate ability of the P3-type phase to suppress Naion vacancy ordering. This could reflect higher rate performance and cyclic stability in the P3 dominant samples, as ordering of Na-ion vacancies is known to induce severe structural transitions that degrade electrochemical performance.



Figure 3.9. Cyclic voltammograms of NNM-750, 780, and 850 samples.



Figure 3.10. Cyclic voltammograms of NNM-765 and 800.

The galvanostatic charge-discharge curves of NNM-*x* half cells obtained at different C rates are displayed in Figure 3.11(a). As expected, the GCD curves for all the samples show multiple plateaus relating to different redox couples at voltage ranges identified in their respective cyclic voltammograms. To further analyze the charge/discharge performance of the cathodes, the dQ/dV vs. voltage (V) plots were obtained for all samples at 0.1C. The dQ/dV vs. V plots (Figure 3.11(b)) reveal an interesting trend: ΔV between corresponding oxidation and reduction peaks decreases from ~ 0.2 V for NNM-750 (with a single P3 phase) sample to ~ 0.05 V for NNM-780 (with a biphasic P2/P3 structure). This could be due to the multiple phase transformations occurring in the cathode, which lowers the diffusion coefficient of Na-ions and increases the polarisation voltage. With the introduction of the P2 phase in the NNM-760 and NNM-780 samples, ΔV reduces considerably, suggesting better stabilisation of the structure in the biphasic cathodes. In contrast, a higher ΔV of almost 0.15 V in P2 phase dominant NNM-800 and NNM-850

samples may result from their particle morphologies (fused and agglomerated particles, as reported in the microstructural section).



Figure 3.11. (a) GCD curves of NNM-*x* series of cathode materials at different C rates. (b) dQ/dV vs. voltage (V) plots of NNM-*x* cathodes at a discharge rate of 0.1C. (c) Rate performance and (d) cyclic stability of NNM-*x* cathodes at a discharge rate of 1C.

Another striking feature of GCD curves (Figure 3.11(a)) is the decrease in the specific capacity of the NNM-*x* cathodes with an increase in P2 concentration at a charge/discharge rate of 0.1C. The specific capacity decreases from 190 mAh g⁻¹ in the NNM-750 to 180 mAh g⁻¹ in NNM-765, 172 mAh g⁻¹ in NNM-780, and further to 155 mAh g⁻¹ for the NNM-850. This corresponds to the extraction/insertion of about 0.8 Na-ions in the monophasic P3 sample, which drops to 0.65 Na-ions in the NNM-850 cathode. The higher amount of Na-ions required during cycling of the P3 type cathode is obtained from the Na metal anode during the discharge process. It is important to keep in mind that the as-synthesized NNM-750 contains only 0.75 Na-ions per formula unit cell, assuming a final concentration of Na_{0.15}Mn_{0.75}Ni_{0.25}O₂ at the end of charging, a deficiency of 0.25 Na ions need to be compensated to obtain a capacity of 190 mAh/g. Hence, in a full-cell configuration, the P3-type cathode cannot deliver the same specific capacity. Accordingly, other synthesis techniques

should be explored to stabilize Na-rich P3-type structures. The decreasing trend in specific capacity with the increase in P2 concentration is also expected. It confirms often theorized speculations in the literature about a thermodynamically synthesized P3-type phase being able to accommodate higher amounts of Na ions within its structure than its P2 counterpart. With the increase in C rate (Figure 3.11(c)), the P3 dominant samples start to underperform, losing about 60% of their capacity at 0.1C to reach about 74 mAh g⁻¹ at 1C, which then lowers to only \sim 5 mAh g⁻¹ at 6C. In contrast, NNM-765 and 780 cathodes show incredible rate performance, with their specific capacities reaching 122 mAh g⁻¹ and 130 mAh g⁻¹ at 1C, representing a fading of only about 32% and 23% of their capacities at 0.1C. Even with a charge/discharge rate of 6C, these cathodes exhibited a capacity of about 82 mAh g⁻ ¹ and 97 mAh g⁻¹, respectively. Such high-rate performance makes these samples attractive for stationary and portable storage applications. The lower rate performance of the P3 represents a poor Na-ion diffusion coefficient of the material, possibly due to rapid phase conversions that do not support a fast transport of Naions. Incorporating a P2 phase may have opened up better Na⁺ conducting pathways within the material and prevented unwanted phase transitions, resulting in greater extraction of Na⁺ even at high C rates in the NNM-765&780 cathodes. On the other hand, the lower rate performance observed for NNM-800 and NNM-850 samples (where specific capacities drop from around 155 mAh g⁻¹ at 0.1C to about 74 mAh g⁻¹ and 64 mAh g⁻¹ at 1C, respectively) could be resulting from agglomerated & fused particle morphologies caused by higher calcination temperatures that increase the overall diffusion path for Na-ions in cathode layer.

Figure 3.11(d) illustrates the cyclic performance of the NNM-*x* cathodes at a charge/discharge rate of 1C between 1.5 V and 4.2 V. The cyclic data indicates the monophasic P3 cathode to have the highest capacity retention of ~ 90% after 200 cycles. On the other hand, the high-performing NNM-765 and 780 show a specific capacity of 97 mAh g⁻¹ and 104 mAh g⁻¹, respectively, after 200 cycles, which is close to 83% and 80% of their initial capacity at 1C. The poor cyclic performance of the NNM-800 & NNM-850 cathodes (only 65 % capacity retention after 200 cycles) was expected as the detrimental effects of activating $Mn^{3+/4+}$ on the P2 structure in the Na-Mn-Ni system are well reported in the literature due to the presence of Jahn-Teller active Mn^{3+} below 2 V [14, 15]. Early signs of structural

instability in these compounds with the introduction of Mn^{3+} can be inferred from their GCD curves (Figure 3.11(a)), where a notch-like feature caused by the sudden change in slope is visible at 1.7 V. Moreover, the biphasic cathodes also exhibit lower polarization potentials, which enabled them to achieve energy efficiencies of ~85% compared to ~75% in the P3-type cathodes. This is depicted in the GCD curves of the NNM-750 (Figure 3.12), with the portion shaded in red representing energy loss.



Figure 3.12. GCD curves of NNM-750, 765, 780, and 850 depicting energy loss and energy recovered during discharge.

The Nyquist plots of NNM-750, 780, and 850 cells illustrated in Figure 3.13 also concur with the cyclic data where after 200 charge/discharge cycles, the NNM-850 cell showed an increased resistance of 1150 Ω , which is almost twice that of the 550 Ω in NNM-780. Compared to the P2 phase, the P3 structure seems resilient to the structural distortions induced by the Mn³⁺. The resilience of the P3-type structure in maintaining its structural integrity even after undergoing multiple phase transitions may have also been aided by its smaller particle size and lower degrees of agglomeration, allowing each particle to expand and contract freely without generating a high degree of stress. Further, the widely reported synergistic effects found in biphasic layered oxides prevent each other from undergoing structural

transformations during cycling and may have also contributed to the higher cyclic stability of NNM-780 [2, 16-18].



Figure 3.13. Nyquist plots of half-cells with NNM-750, 780, and 850 cathodes (a) before and (b) after cycling. The impedance data in Figure 3.13 was fitted using the equivalent circuit shown in the figure inset.

The Na-ion diffusion kinetics for the NNM-*x* samples were investigated using the galvanostatic intermittent titration technique (GITT) between 1.5 and 4.2 V. The technique involves applying a constant current pulse for 10 minutes, followed by a dwell time, during which the cell is allowed to reach a quasi-equilibrium state. This process is repeated till the cut-off voltages are reached. Figure 3.14 shows the GITT charge-discharge curves for the NNM-*x* samples. The Na⁺ diffusion inside the cathode material is assumed to obey Fick's first law, and the Na⁺ diffusion coefficient (D_{Na^+}) can be calculated using the following Eq. 3.1.

$$D_{Na^{+}} = \frac{4}{\pi\tau} \left(\frac{m_{B}V_{m}}{M_{B}S}\right)^{2} \left(\frac{\Delta E_{S}}{\Delta E_{\tau}}\right)^{2}$$
(3.1)

Here, M_B and V_m represent the molar mass and molar volume of the cathode material, m_B is the mass of active material, τ is the time of a single constant current pulse, and S denotes the active surface area of the electrode. ΔE_S and ΔE_{τ} represent the change of the steady-state voltage and the voltage change during the constant current pulse, respectively. Figure 3.15 shows the variation of D_{Na}^+ of NNM-*x* with voltage. Unsurprisingly, NNM-765 and 780 cathodes showed the highest diffusion



coefficient of 4×10^{-10} and 7.6×10^{-10} cm²s⁻¹, respectively, while the NNM 750 & 850 showed the lowest diffusion coefficients close to 1×10^{-10} cm² s⁻¹.

Figure 3.14. GITT curves of NNM-x series of cathodes.

All NNM-*x* cathodes show slow diffusion kinetics at the start of a charge and discharge process. The lower diffusion coefficients at the outset of the charging are due to a larger concentration of Na-ions within the structure, causing starvation of Na-ion vacancies. In contrast, a higher number of Na-ion vacancies may have led to sluggish Na-ion diffusion kinetics at the initial phase of the discharge process. The Na-ion diffusion coefficient also shows lower variations in the P2 type structure, which points to its excellent structure stability throughout the charge-discharge process, while larger variations in the P3 containing cathodes, especially at voltages where a peak is observed in their corresponding dQ/dV vs. V plots, may be due to structural variations within the P3 type structure. Nevertheless, the decline in the

intensity of these variations and higher diffusion coefficients in NNM-765 and NNM-780 cathodes aligns with the observations from the GCD rate performance curves on the importance of the P2 phase enhancing Na⁺ diffusion through the material.



Figure 3.15. Variation of diffusion coefficients of NNM-*x* cathodes during charging and discharging.

3.3. Operando Synchrotron XRD studies

Many of the speculations regarding the varied electrochemical performance of the P3-type NNM-750 and other biphasic cathodes can be confirmed through the *operando* synchrotron XRD studies of NNM-750 (Figure 3.16) and NNM-780 (Figure 3.17) cathodes. The *operando* SXRD patterns of NNM-750 portray the structural evolution of the P3 phase during a charge/discharge cycle. Apart from the apparent shifting of the P3 (003) peak (Figure 3.16(b)) towards higher angles during discharge and the appearance of an O3 phase at lower voltages (~ below 2.5 V), the emergence of a new but subtle O'3 phase in P3-type NNM-750 at voltages below 3.6 V (Figure 3.16(b1)) is an important development [11, 12, 18]. This phase appears at about ~3.6 V during the discharge cycle and persists throughout the discharge process, even after the entire P3 is converted into an O3 phase (at about 2 V, as shown in Figure 3.16(b1 & c). However, the O'3 peaks coalesce with the existing P3

peaks during the charging cycle. The emergence of the O'3 phase at 3.6 V during discharge and its coalescence with the P3 phase at 3.2 V would explain the increase in polarisation potential observed from the dQ/dV vs. V plots, especially at higher voltages, where $Ni^{2+/3+}$ and $Ni^{3+/4+}$ redox couples are active. During the charging cycle, the Na ions are extracted from a pure P3 phase at the characteristic oxidation potential of Ni^{2+} to 3+ & 4+ oxidation states, which will be vastly different from the potential required to reduce the Ni^{4+} to 2+ oxidation state in the P3/O'3 biphasic system developed during the discharge process, widening the potential gap between the two redox processes. The existence of the O'3 phase alongside the P3 and O3 phases for extended voltage windows could also explain the poor rate performance exhibited by NNM-750, as the distorted monoclinic O'3 phase shows slower Na ion transport properties.



Figure 3.16. (a) *Operando* Synchrotron x-ray diffraction patterns of NNM-750 obtained during the galvanostatic charge/discharge process at 0.1C with (b-d) displaying zoomed views in the vicinity of the marked regions.

In comparison, the number of structural transformations in the biphasic NNM-780 sample appears to be limited. The *operando* SXRD patterns do not show any changes to the P2-type structure throughout the discharge process. At the same time, only a partial conversion of the P3 to O3 phase conversion is observed, possibly due to the synergetic effect of the P2/P3 system [2, 16-18]. No evidence of the P2 \rightarrow OP4 phase transformation (often reported in the literature) during charging (in the 2.0 to 4.2 V range) or the P3 \rightarrow O'3 transformation is observed in the SXRD plots, suggesting high structural stability of the material. The endurance of its structure

towards phase transformations and the coexistence of highly conducting P2 & P3 phases throughout most of its charge-discharge process has resulted in the superior cyclic stability and rate performance exhibited by NNM-780.



Figure 3.17. (a) *Operando* SXRD patterns of NNM-780 with (a1) depicting the zoomed portion between a 2θ range of 8° to 9° .

3.4. References

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Impact of P3/P2 Mixed Phase on the Structural and Electrochemical Performance of Na0.75Mn0.75Al0.25O2 Cathode

This chapter reports a novel method to suppress the structural modifications brought about by the activation of Mn^{3+/4+} redox reactions by preparing a P3/P2 biphasic Na_{0.75}Mn_{0.75}Al_{0.25}O₂ (NMA) where 25% of the Mn ions were substituted with Al³⁺ ions. An inactive Al³⁺ was chosen to act as a pillar ion during the charge/discharge process. It has a similar ionic radius as Mn⁴⁺ in an octahedral configuration that prevents transition metal ordering. Along with introducing Al³⁺, a biphasic P2/P3 type cathode configuration was adopted to stabilise the cathode structure during cycling further. Similar to the Na_{0.75}Mn_{0.75}Ni_{0.25}O₂ cathode reported in Chapter 3, the phase fraction of the P2 and P3 phases in the P2/P3 biphasic cathode was found to be dependent on the calcination temperature. Moreover, the lower calcination temperature required for P3-type materials was instrumental in obtaining the desired P2/P3 phase fractions at lower calcination temperatures. This was found to have profound implications on the morphology and electrochemical properties of the cathode material, with P3 dominant biphasic cathodes showing substantially superior rate performance and cyclic stability compared to monophasic P2 cathodes that formed at higher temperatures. Further, the manifestation of the synergetic effect between the two phases mitigated the severe structural distortions induced during cycling, resulting in a better cyclability of the biphasic cathodes.

4.1 Structural Characteristics

Various Na_{0.75}Mn_{0.75}Al_{0.25}O₂ samples were prepared by varying the calcination temperature between 600 °C and 800 °C. Figure 4.1(a) shows the room temperature XRD patterns of Na_{0.75}Mn_{0.75}Al_{0.25}O₂ (NMA-*x: x* denotes the calcination temperature in °C) samples calcinated at different temperatures along with the Bragg positions of P3 (JCPDS No. 04-020-1860) and P2 (JCPDS No.27-0751) type phases. The figure shows an unreacted phase at 600 °C and a P2/P3 mixed phase forming at around 650 °C with diffraction peaks corresponding to the P2 phase gradually increasing in intensity with increased calcination temperature. At a calcination temperature of 800 °C, a monophasic P2-type structure is obtained with no peaks corresponding to the P3 phase discernible in the XRD pattern. This is confirmed by the Rietveld refinement of the XRD data (Figure 4.1(b)), which shows the P2:P3 phase ratio around ~ 52:48 for the sample calcined at 650 °C. The fraction of the P2

phase increased to \sim 72.5% in the sample calcined at 750 °C, and a pure P2-type material was obtained at 800 °C.

The crystallographic parameters of the NMA-x series of materials obtained after refinement are presented in Table 1. The refinement results show that the crystallographic volume for P2 and P3 type phases remained largely invariant, ~78.4 Å³ and ~117.4 Å³, respectively, in all samples. The unit cell volume of P3 is about 1.5 times the P2 phase, which is expected as the number of formula unit cells in one crystallographic unit cell (Z) for P2 is 2, while for P3, Z is 3. The area of rectangular faces of the triangular prisms in P2 and P3 type structures, which forms a major bottleneck to Na ion conduction, was around 11.11 Å². This points to similar interlayer spacings (in both the TM-O and Na-O layers) in the P2 and P3 phases. Although P3 is often regarded as an ordered P2 phase where Na ions reside in a single crystallographically equivalent lattice site as opposed to the 2 different sites in the latter, the structural information obtained through Rietveld refinement for NMA-x series materials suggests similar Na^+ conduction dynamics in both the phases. The detailed structural parameters of the P2 and P3 type NMA obtained from the Rietveld refinement of XRD patterns are given in Tables S1 and S2, respectively.



Figure 4.1. (a) Phase evolution of Na_{0.75}Mn_{0.75}Al_{0.25}O₂ samples at various calcination temperatures along with brag positions of P3 (JCPDS: 04-020-1860) and P2 (JCPDS: 27-0751) type structures. (b) Rietveld refinement of room temperature XRD data belonging to NMA-650, 750, and 850 samples, along with the deconvoluted P2 and P3 phases in the 2θ range of 30-40°.

l.	Phase		- (°)	TZ (Å 3)	Reliability
Sample	(Fraction)	<i>a</i> (A)	<i>c</i> (A)	$V(\mathbf{A}^3)$	Factors
	D3 (17 7%)	2.8500	16.678	117.47	<i>R</i> _{exp} : 1.73
NMA 650	15(47.7%)	± 0.0003	± 0.003	± 0.03	R_{wp} : 2.30
11/1/A-030	DO (50 20/)	2.8580	11.126	78.81	$R_p: 1.79$
	P2 (52.3%)	± 0.0003	± 0.001	± 0.02	GOF: 1.33
	P3 (27.5%)	2.8453	16.716	117.41	<i>R</i> _{exp} : 2.12
NMA_750		± 0.0003	± 0.003	± 0.03	R_{wp} : 2.51
11111A-750	P2 (72.5%)	2.8491	11.137	78.81	$R_p: 1.98$
		± 0.0002	± 0.001	± 0.01	GOF: 1.18
					<i>R</i> _{exp} : 1.97
NMA_800	P2(100%)	2.8577	11.1474	78.839	$R_{wp}: 2.34$
MMA-800	F2 (100%)	± 0.0009	± 0.0008	± 0.008	$R_p: 1.84$
					GOF: 1.18

Table 4.1. Lattice parameters of NMA-x samples obtained after the Rietveld

 refinement of room temperature XRD data.

Table 4.2. Crystallographic parameters of P2-type NMA obtained from the Rietveld

 refinement of room temperature XRD data.

P2 Type NMA (P63/mmc space group)						
Atom	х	У	Z	Occupancy	Site	
Na1	2/3	1/3	1/4	0.45	2d	
Na2	0	0	1/4	0.30	2b	
Mn/Al	0	0	0	0.75/0.25	2a	
0	2/3	1/3	0.090	1	4f	

P3 Type NMA (R3m space group)						
Atom	Х	У	Z	Occupancy	Site	
Na	0	0	0.17	0.75	3a	
Mn/Al	0	0	0	0.75/0.25	3a	
01	0	0	0.394	0.75/0.25	3a	
02	0	0	0.607	1	3a	

Table 4.3. Crystallographic parameters of P3-type NMA obtained from Rietveld

 refinement of room temperature XRD data.

Further, the crystallographic parameters obtained from Rietveld refinement were used to simulate the Na ion migration pathways and calculate the migration energy barrier in the P3 and P2 type structures of NMA using the bond-valence site energy (BVSE) calculation. The calculated migration energy for Na⁺ in P2 and P3 type NMA was 0.181 eV and 0.237 eV, respectively (Figure 4.2(a & b). The reaction pathway diagram of P2 and P3 type structures generated using VESTA [1] is shown in Figure 4.2(c & d). Besides the higher activation energy, another drawback of using P3-type cathodes in Na-ion batteries is related to the multiple structural transformations P3 undergoes during cycling. These transformations lead to a lower Na⁺ conductivity and degrade the cathode's electrochemical performance. In addition to enhancing the overall conduction in the material, the P2 phase in the biphasic cathodes is expected to stabilise the P3 phase and prevent unwanted phase transitions during the charge/discharge process [2, 3].



Figure 4.2. Na⁺ migration energy barrier of (a) P3 and (b) P2 type structures obtained after BVSE analysis. Schematic of diffusion pathways (depicted in cyan) in (c) P3 and (d) P2 type structures. The I1 in (a) stands for interstitial site 1.

The SEM micrographs on NMA-650, 750, and 800 displayed in Figure 4.3 depict hexagonally shaped grains consistent with layered oxides. The elemental map of NMA-750 is portrayed in Figure 4.3(b1-b4). In NMA-650, the particles with welldefined contours and facets with a relatively low agglomeration are observed. In contrast, the microstructure in NMA-750 and 800 display a higher degree of agglomeration, with particles fusing to form lumps in NMA-800. Particle morphology is an important parameter that affects electrochemical properties such as the rate performance of cathodes. Ideally, nano-size particles with a low degree of agglomeration are preferred in cathodes as they increase the total surface area of each particle (in contact with the liquid electrolyte) compared to its volume. As liquid electrolytes have higher ionic conductivities than cathode materials, nanosized particles could reduce the Na⁺ conduction path through the crystalline material, Na⁺ extraction/insertion enhancing during cycling, especially at high charge/discharge rates [4, 5]. Hence, NMA-650 is expected to show a better rate performance than the other samples.



Figure 4.3. SEM micrographs of (a) NMA-650, (b) 750, and (g) 800, along with (b1-4) elemental maps depicting the distribution of Na, Mn, Al, and O in NMA-750.

The Mn 2p and Al 2s XPS spectra (Figure 4.4) for NMA-650 and 800 samples were obtained to confirm the valence states of the Mn and Al ions in each compound. The peak at 85 eV in the Al 2p spectra suggests the presence of Al^{3+} ions in all the samples [6-8]. In contrast, the Mn 2p XPS spectra can be deconvoluted into 4 peaks; the 2 coupled peaks at 641.8 & 653.2 eV belong to Mn³⁺, while those at 643.2 & 654.7 eV correspond to Mn⁴⁺ [6, 7, 9]. The similarity of Mn 2p XPS spectra of both samples indicates their similar Na⁺ contents. Lower Na⁺ content in either sample would alter the sample's peak intensity ratio of Mn³⁺ and Mn⁴⁺ ions. Hence, the P3 to P2 phase transformation observed in the NMA-*x* samples can only be driven by the better stability of P2 over the P3 at higher temperatures rather than due to the change in Na-ions concentration in the sample.



Figure 4.4. XPS spectra of NMA-650 and NMA-800.

4.2 Electrochemical Characteristics

The electrochemical properties of the NMA-x cathodes were analysed between 1.5 V and 4.2 V using a coin cell with Na metal acting as the reference & counter electrode. The cyclic voltammograms in Figure 4.5 show peaks indicating the redox activity of Mn ions below 3V in all the cathode materials [10, 11]. While the CV curves of NMA-650 show only a single redox peak, multiple peaks attributing the $Mn^{3+/4+}$ redox reaction can be observed for NMA-750 and 800 samples. Multiple peaks attributed to the same redox reaction in the latter samples could indicate structural changes in the cathode materials caused by either Na-ion vacancy ordering or Jahn-Teller active Mn³⁺. Structural variations induced by the activity of Mn³⁺ are usually reported as the primary reason behind capacity fading in P2-type layered oxides where Mn is active [9, 10, 12-14]. In the P2 dominant NMA-750 and 800 samples, a higher amount of the P2 phase seems to be initiating a similar reduction in specific capacity with cycling as the peak intensities of the oxidation and reduction peak appear to be fading with each cycle along with the area under the curve. In contrast, the cyclic voltammogram of NMA-650 with $\sim 52\%$ P3 phase shows almost no reductions in peak intensities or area under the curves, suggesting better structural durability. As a result, a biphasic cathode could show better cyclic performance.



Figure 4.5. Cyclic voltammograms of NMA-600, 750, and 800 samples.

The galvanostatic charge-discharge curves of NMA-650, 750, and 800, presented in Figure 4.6, concur with the CV curves. The GCD curves show rapid voltage drops between 4.2 V and 3 V, with plateaus emerging only below 3V. This is also reflected in the dQ/dV vs. voltage curves (Figure 4.7), as peaks (indicating the changes in slopes of the GCD curve) between 1.5 V and 3 V. Overall, the NMA-650 exhibited the highest specific capacity, 150 mAh g⁻¹ at a discharge rate of 0.1C. With an increase in the P2 phase fraction, the specific capacity dropped to 139 mAh g⁻¹ in NMA-750 and 113 mAh g⁻¹ in NMA-800, which marks about a 32% decline in capacity from NMA-650.



Figure 4.6. GCD curves of NMA-*x* cathode materials at different C rates.

P3-type cathodes are generally reported to have higher specific capacities than P2type materials, as these can accommodate more Na ions by undergoing a reversible transformation to O3-type structures) [2, 3, 15, 16]. Hence, a lower specific capacity in the cathodes with a dominant P2 phase is expected. In terms of the amount of Na⁺ extracted, 150 mAh g⁻¹ (in NMA-650) corresponds to about 0.55. while a specific capacity of 113 mAh g⁻¹ in NMA-800 corresponds to only about 0.40. Even with a higher Na⁺ extraction, the NMA-650 still exhibits a higher energy efficiency of ~ 83%, compared to 76% for the monophasic NMA-800 cathode (Figure 4.8). This is an interesting observation, as in the NMA layered oxide cathodes, a higher specific capacity also means a higher concentration of Mn^{3+} at the end of the discharge cycle, which would induce higher stresses in the material that could trigger structural transformations that hinder energy efficiency. The higher capacity while maintaining an impressive energy efficiency points to the resilience of the NMA-650 biphasic cathode and could be attributed to the widely reported synergetic often found in multiphasic cathodes [2, 3, 16, 17].



Figure 4.7. dQ/dV vs. voltage (V) plots of NNM-x cathodes at a discharge rate of

0.1C.



Figure 4.8. GCD curves of NMA-*x* samples. The portions colored in green depict energy recovered during discharge.

As the discharge rate increases from 0.1C to 4C, the specific capacities of all the cathodes deteriorate drastically (Figure 4.6 and Figure 4.9). NMA-650 shows a specific capacity of 80 mAh g⁻¹ and 73 mAh g⁻¹ at 1C and 4C, respectively. Even though 80 mAh g⁻¹ denotes a 42% reduction in capacity compared to the material's original capacity at 0.1C, it is still 30% higher than the P2-type cathode. While the presence of the P2 phase might have been beneficial in opening better Na⁺ conducting pathways within the material, the drastic reduction in specific capacity in NMA-650 suggests a decrease in diffusion coefficient with an increase in the C-rate. On the other hand, the unexpected drop in rate performance of the P2 dominant NMA-750 and 800 cathodes might be due to their agglomerated & fused particle morphologies that lowered the extraction of Na⁺ at high C rates by increasing the overall diffusion path for Na-ions in the cathode layer.



Figure 4.9. Rate performance of NMA-*x* cathodes with C.E representing columbic efficiency.

Figure 4.10 illustrates the cyclic performance of the cathodes at 1C when cycled between 1.5 V and 4.2 V. The data indicate that the specific capacity of the NMA-650 cathode dropped from 86 mAh g⁻¹ to 67 mAh g⁻¹, exhibiting an ~ 80% capacity retention after 200 cycles. In contrast, the other cathodes, NMA-750 and 800, showed a substantial reduction in specific capacity by being able to retain only about 67% and 56% of their original capacity at 1C.



Figure 4.10. Cyclic stability of NMA-x cathodes at a discharge rate of 1C.

Figure 4.11 shows the Nyquist plots of NMA-650 and 800 cells before and after 200 charge/discharge cycles. The figure shows a drastic increase in the total resistance of the NMA-800 cell (from 480 Ω to 970 Ω), while the NMA-650 cell exhibits only a 50% increase in resistance after 200 charge/discharge cycles. Further, analysis of the Nyquist plot using equivalent circuit modeling revealed a 130% increase in charge transfer resistance in the cell with NMA-800 cathode. In comparison, the increase in resistance was ~ 60% in the cell with NMA-650 cathode (R1, R2, and R3 in the equivalent circuit in Figure 4.11 inset denote the electrolyte resistance, SEI layer resistance, and charge transfer resistance, respectively [18-20]). The higher charge transfer resistance in NMA-800 could be due to structural degradation of the active material, side reactions, etc., causing the material to exhibit lower capacity retention than NMA-650 at the end of 200 charge-discharge cycles.

The excellent structural resilience of the NMA-650 cathode material predicted from the CV curves enabled it to harness the capacity obtained by activating Mn^{3+/4+} redox couple, which is usually avoided in Mn-based layered oxides due to its detrimental effects on cyclic performance. The improved cyclic stability of the NMA-650 over the other cathodes suggests that the adoption of a biphasic composition of the same material with nearly equal shares of P2 and P3 phases could be ideal for enhancing capacity retention in other layered oxide-based cathodes in literature where severe structural deformations have been identified as the primary cause of capacity degradation.



Figure 4.11. Nyquist plots of half-cells with NMA-650 and 800 cathodes (a) before and (b) after cycling. The impedance data was fitted using the equivalent circuit shown in Figure 4.11(a) inset.

Figure 4.12 shows the variation of Na⁺ diffusion coefficients in the NMA-*x* samples obtained from the galvanostatic intermittent titration technique (GITT). The technique, performed between a voltage range of 1.5 V – 4.2 V, involves the application of a constant current pulse for 10 minutes, followed by a dwell time of 30 minutes, during which the cell is allowed to reach a quasi-equilibrium state. This process is repeated till the cut-off voltages are reached. The diffusion kinematics of Na ion through the materials are assumed to obey Fick's first law, and the Na⁺ diffusion coefficient (D_{Na^+}) can be calculated using the following Eq. 3.1.

As expected, the diffusion coefficient of NMA-650 showed the highest diffusion coefficient of 2.5×10^{-10} while the diffusion coefficients of NMA-750 & 800 were ~ 50% lower. The lower diffusion coefficients at the onset of the charge/discharge process are due to a larger/smaller concentration of Na-ions within the structure, causing starvation of vacancies/ Na-ions.



Figure 4.12. Variation of diffusion coefficients of NMA-*x* cathodes during charging and discharging.

4.3 Operando Synchrotron XRD studies

The structural evolution of the material during the charge/discharge cycle could confirm many of the speculations regarding the electrochemical properties of NMAx cathodes. Figure 4.13 and Figure 4.14 illustrate the operando synchrotron XRD (SXRD) patterns NMA-650 and NNM-750 during the second cycle. The SXRD pattern of the NNM-650 sample obtained during the formation cycle (cycle 1) is displayed in Figure 4.15. The data analysis for both the cathode materials reveals an interesting detail, where a continued existence of the P3 phase is observed throughout the entire charge-discharge process. The P3 phase is usually reported to appear at higher voltages when the concentration of Na in the compound is below \sim 0.75 [3, 15, 16, 21]. At lower voltages, a P3 \rightarrow O3 phase transformation is expected. However, in both NMA-650 and 750, the P3 \rightarrow O3 phase conversion is not observed. The continued existence of the P3 phase also explains the improved cyclability and rate performance of the biphasic compounds, as the P3 phase is known to have a higher diffusion coefficient than the O3 phase. The continued existence of P3 phase transformations in layered oxides is rarely reported and could result from a relatively high Al content in the compound. Even at a low voltage of 1.5 V, where Na concentration in the unit cell exceeds ~ 0.8 in NMA-650, the P3 structure appears stable across the voltage window. During the first discharge cycle, the P3 phase contracts along the c axis, where c reaches a value of ~ 16.59 Å at the end of discharge. In the subsequent charge-discharge cycle, the *c* axis expands to only about 16.66 Å at the fully charged state as opposed to its initial value of 16.69 Å at the pristine state, as evidenced by the presence of 2 peaks between 7-8° in Figure 4.13 as opposed to a single broad & asymmetric peak at the start of the first charging cycle (Figure 4.15).



Figure 4.13. *Operando* Synchrotron x-ray diffraction patterns of NMA-650 obtained during the second galvanostatic charge/discharge cycle at 0.1C.



Figure 4.14. (a) *Operando* SXRD patterns of NMA-750 obtained during the second charge/discharge cycle at 0.1C.

Regarding volume expansion, the NMA-650 only shows an increase of only about 0.5%, which is marginal compared to the 1.5 % in NMA-750, where c increased from 16.74 Å to 17.01 Å. The P2 phase shows almost no volume changes and

behaves like a pillar within the material. During charging/discharging, the P2 layers remain nearly invariant; hence, stress develops at the phase boundary in a direction opposite to the gliding direction of TMO₂ layers in the adjacent P3 phase (usually, the gliding motion of the TM-O₂ layers is initiated when the change in *c* parameter of the unit cell reaches a critical value and is responsible for the P3-O3 phase transitions), which restrains the transition metal layers from gliding. This synergetic interaction between the two phases interlocks the TM-O₂ layers of adjacent P2 and P3 layers, which ensures better stability to the P3 structure [2, 3, 16, 17].

In both the compounds, most of the change in the *c* parameters occurs below 2 V during the discharge cycle (indicated by a more significant degree of shift in (003) peak towards higher angles in Figure 4.12, which is consistent with the results from the electrochemical tests where the $Mn^{4+/3+}$ reduction peaks were obtained below 2 V.



Figure 4.15. (a) *Operando* SXRD patterns of NMA-650 obtained during the first galvanostatic charge/discharge cycle at 0.1C.

4.4. References

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Rational Design of an Optimal Al-substituted Layered Oxide Cathode for Naion Batteries

Chapter 5 explores trends in the structural and electrochemical performance of various compositions in the Na_{3/4}(Mn-Al-Ni)O₂ pseudo-ternary system (Figure 5.1) to identify optimal cathodes. All the compositions were synthesized in 3 different phase configurations: monophasic P3, biphasic P3/P2, and monophasic P2. $Na_{0.75}Mn_{0.75}Ni_{0.25}O_2$ and $Na_{0.75}Mn_{0.75}Al_{0.25}O_2$ (marked as NMA1 and NMA2 in Figure 5.1) reported earlier were the parent materials chosen for the study. Phase diagrams, especially in layered oxides, help to rationally design optimal cathode compositions by revealing the complex relationship between metal cations in LO cathodes and different electrochemical properties [1, 2]. It is important to point out that, unlike a traditional phase diagram, where the elemental compositions alone largely determine the functional properties of various phases, in a pseudo-ternary system, the oxidation states of the electrochemically active elements involved also play a major role in deciding composition-structure-property behaviour. The concentration of the Jahn-Teller active Mn³⁺ and commonly preferred Mn⁴⁺ ions vary across all the compositions, which may significantly affect the electrochemical properties of the cathode materials. The Al-substituted compounds synthesized for the study, Na0.75Mn0.5Ni0.25Al0.25O2, Na0.75Mn0.625Ni0.125Al0.25O2, Na_{0.75}Mn_{0.625}Ni_{0.25}Al_{0.125}O₂, and Na_{0.75}Mn_{0.75}Ni_{0.125}Al_{0.125}O₂ are a part of the Na_{3/4}(Mn-Al-Ni)O₂ pseudo ternary diagram and will hereafter be referred to as NMA3, NMA4, NMA5 and NMA6, respectively.



Figure 5.1. The positions of compositions under investigation in this study in the pseudo-ternary Na_{3/4}(Mn-Al-Ni)O₂ system.

5.1. Structural Characteristics

The NMA*x* series of cathode materials were synthesized through the sol-gel route. Each cathode material is synthesized in 3 different phase configurations, namely P3, P2, and P3/P2 mixed phase with equal proportions. This was achieved by calcining the samples at optimum temperatures (by a hit-and-trial method). Table 5.1 summarizes the ICP-AES data of the P2-type NMA*x* series of cathode materials. The results from ICP concurred with the expected compositions of each cathode.

Table 5.1. The chemical compositions of the as-prepared samples were measured

 by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Sample	Nominal composition	Calculated composition	
Sumpre	Na/ Mn/ Ni/ Al	Na/ Mn/ Ni/ Al	
NMA3-P2	0.75/0.50/0.25/0.25	0.735/0.501 /0.252/0.247	

NMA4-P2	0.75/0.625/0.125/0.25	0.744/0.628/0.123/0.245
NMA5-P2	0.75/0.625/0.25/0.125	0.742/0.621/0.247/0.127
NMA6-P2	0.75/0.75/0.125/0.125	0.745/0.739/0.128/0.123

Figure 5.2 displays the room temperature XRD patterns of NMAx cathodes calcined at different temperatures. The figure shows peaks consistent with a P3-type structure at 650 °C, transforming into a P2-type structure at higher calcination temperatures. Similar phase evolution in Na_{0.75}Mn_{0.75}Ni_{0.25}O₂ (NMA*I*) and Na_{0.75}Mn_{0.75}Ni_{0.25}O₂ (NMA2) compounds was reported earlier. Additionally, 0.75 Na was identified as the critical concentration of sodium at which an O3-type phase can be avoided during synthesis. The detailed analysis of the crystal structure and quantification of phase concentrations in the monophasic and P3/P2 mixed-phase samples was performed using the Rietveld refinement of XRD data (Figure 5.3 and Figure 5.4). The crystallographic information for each of the NMA3-NMA6 materials is given in Tables 5.2-5.5. The refinement confirmed the biphasic nature of the NMA*x*-P3P2 series of cathodes with close to 50% P3 and P2 phases. It also established the presence of only monophasic P3 (*R*3*m* space group) and P2-type (*P*6₃/*mmc* space group) phases at the lower (< 750 °C) and high calcination temperatures, respectively, in all compositions.



materials with calcination temperature.



Figure 5.3. Rietveld refinement of XRD data for NMA3-P3P2, NMA4-P3P2, NMA5-P3P2, and NMA6-P3P2 samples with their respective along with the deconvoluted P2 and P3 phases in the 2θ range of 30-40°.



Figure 5.4. Rietveld refinement of XRD data for NMA*x*-P3 and NMA*x*-P2 samples.

Sample	Phase (Fraction)	a (Å)	c (Å)	$V(\text{\AA}^3)$	Reliability Factors
NMA3-P3	P3 (100%)	2.8838 (1)	16.7924 (2)	120.97 (1)	R _{exp} : 2.23 R _{wp} : 2.51 R _p : 1.99 GOF: 1.12
NMA3- P3P2	P3 (47.3%)	2.8864 (1)	16.773 (1)	121.00 (2)	<i>R_{exp}</i> : 2.29 <i>R_{wp}</i> : 3.41
	P2 (52.7%)	2.8842 (2)	11.164 (1)	80.42 (1)	<i>R_p</i> : 2.59 <i>GOF</i> : 1.48
NMA3-P2	P2(100%)	2.8834 (2)	11.1669 (4)	80.404 (5)	R _{exp} : 1.98 R _{wp} : 3.41 R _p : 2.49 GOF: 1.71

Table 5.2. Lattice parameters of NMA3 samples obtained from the Rietveld

 refinement of room temperature XRD data.

Table 5.3. Lattice parameters of NMA4 samples obtained from the Rietveld

 refinement of room temperature XRD data.

Samula	Phase	$a(\mathbf{\hat{\lambda}})$	a (Å)	$\mathbf{V}(\mathbf{\hat{x}}3)$	Reliability
Sample	(Fraction)	<i>u</i> (A)	<i>c</i> (A)	$\mathbf{V}(\mathbf{A}^{*})$	Factors
					R _{exp:} 2.49
	D2(1000/)	2.8762 (2)	16.7789	119.87	Rwp: 3.08
INIVIA4-F3	F3 (100%)		(4)	(2)	R _p : 2.39
					GOF: 1.23
	D2(500/)	2.8876 (2)	16.761	120.05	<i>R</i> _{exp} : 2.11
NMA4- P3P2	P3 (50%)		(2)	(2)	<i>R</i> _{wp} : 2.75
		2.8820 (1)	11.133	80.18	$R_p: 2.12$
	P2 (50%)		(2)	(1)	GOF: 1.30

					R _{exp} : 2.29
	P2(100%)	2.8751 (3)	11.176	80.01	Rwp: 2.75
19191747-1 2			(2)	(1)	R _p : 2.14
					GOF: 1.19

Table 5.4. Lattice parameters of NMA5 samples obtained from the Rietveld

 refinement of room temperature XRD data.

Sample	Phase	Thase $a(\text{\AA}) c(\text{\AA})$		$V(\text{\AA}^3)$	Reliability
	(Fraction)				Factors
		2.8862	16.775	120.02	Rexp: 2.11
NIMA5 D2	D2(1000%)	(1)	(2)	(1)	Rwp: 2.57
NIVIAJ-I J	F3 (100%)	(1)	(2)	(1)	R _p : 1.98
					GOF: 1.21
	P3	2.8875	16.778	120.50	<i>R</i> _{exp} : 2.09
NMA5-	(53.25%)	(2)	(2)	(2)	$R_{wp}: 2.68$
D3D 7					$R_p: 1.91$
1512	P2	2.8840	11.147	80.20(1)	GOF: 1.28
	(46.75%)	(3)	(1)	80.29 (1)	
					R _{exp} : 2.67
NINTAS DO	D2(1000/)	2.8800	11.165	<u>90 25 (1)</u>	R _{wp} : 3.38
1 111/1/1/13-1⁻ 2	F2(100%)	(1)	(1)	00.23 (1)	R _p : 2.66
					GOF: 1.26

Table 5.5. Lattice parameters of NMA6 samples obtained from the Rietveld

 refinement of room temperature XRD data.

Sample	Phase (Fraction)	a (Å)	c (Å)	V (Å ³)	Reliability Factors
					R _{exp} : 2.01
NMA6-	D2(1000/)	2.8848	16.7749	120.89	Rwp: 2.45
P3	P3 (100%)	(1)	(1)	(1)	R _p :1.92
					GOF: 1.21

NMA6- P3P2	P3 (48.5%) P2 (51.5%)	2.8751 (1) 2.8746 (1)	16.775 (1) 11.160 (5)	120.23 (1) 79.80 (1)	R_{exp} : 1.90 R_{wp} : 2.21 R_p : 1.16 GOF: 1.79
NMA6- P2	P2(100%)	2.876 (2)	11.164 (4)	80.02 (2)	R _{exp} : 1.95 R _{wp} : 3.49 R _p : 2.49 GOF: 1.78

The varying concentrations of Mn^{3+} in the NMAx series have been identified by analyzing their Mn 2p X-ray photoelectron spectra (Figure 5.5). The Mn 2p XPS spectra of NMA4 to NMA6 are deconvoluted into 4 peaks at 641.8 & 653.2 eV and 643.2 & 654.7 eV belonging to Mn³⁺ and Mn⁴⁺, respectively [3-5]. The increasing intensity of the deconvoluted Mn³⁺ peaks from NMA4 to NMA5 and NMA6 points to a rising concentration of Mn³⁺ in these compounds. Unlike the other samples, the Mn 2p spectra of NMA3 are fitted with only 2 peaks at 643.2 and 654.7 eV belonging to Mn^{4+} , indicating the absence of Mn^{3+} . The nominal concentration of Mn³⁺ and Mn⁴⁺ in the NMA series of cathodes is summarised in Table S6, and analysis of XPS data fitting indicates that the Mn³⁺ and Mn⁴⁺ fractions match closely with expected values within the acceptable error margins. Additionally, the Mn 2p spectra of P3-type samples in the NMAx series resemble their corresponding P2type counterparts. This suggests a negligible Na loss during the calcination of P2type samples, as a loss of Na during calcination would have increased the Mn⁴⁺ concentration in these materials, leading to alterations in the peaks in the Mn 2p spectrum. The Ni 2p XPS spectra of the NMAx samples displayed in Figure 5.6 show similar peak energies, indicating the presence of only Ni²⁺ in all samples [3-5].



Figure 5.5. Mn 2p XPS plots of NMAx-P3 and NMAx-P2 type compounds.



Figure 5.6. Ni 2p XPS plots of NMAx-P3 and NMAx-P2 type samples.

Table 5.6.	The nominal	concentration	of Mn ³⁺	and Mn ⁴⁺	in the I	NMA <i>x</i> se	eries of
compounds.							

Composition	Mn ³⁺ concentration	Mn ⁴⁺ concentration
Na _{0.75} Mn _{0.50} Ni _{0.25} Al _{0.25} O ₂ (NMA3)	0	0.5
Na _{0.75} Mn _{0.625} Ni _{0.125} Al _{0.25} O ₂ (NMA4)	0.25	0.375
Na _{0.75} Mn _{0.625} Ni _{0.25} Al _{0.125} O ₂ (NMA5)	0.125	0.5
Na0.75Mn0.75Ni0.125Al0.125O2(NMA6)	0.375	0.375

The microstructural and morphological characteristics of the cathode materials were observed using FESEM, and the micrographs are displayed in Figure 5.7 and Figure 5.8. The SEM images of the P3 and P3/P2 mixed-phase samples show spheroidal and hexagonally shaped particles with a relatively lower degree of agglomeration. With increased calcination temperature, agglomeration increases, resulting in large particle clusters in the P2-type samples. Typically, materials with smaller particle sizes are preferred in cathode materials as these enhance the rate performance and cyclic stability of the electrode materials [6, 7]. Accordingly, it is expected that P3 and P3/P2 mixed-phase cathodes would exhibit better electrochemical performance than their P2 counterparts. The elemental maps of NMA*5*-P3P2 displayed in Figure 5.7 show a homogeneous distribution of all its constituent elements.



Figure 5.7. SEM micrographs of (a1-a3) NMA5-P3, NMA5-P3P2, and NMA5-P2 with (a4-a8) depicting the elemental maps of the NMA5-P3P2 sample.



Figure 5.8. SEM micrographs of (a1-a3) NMA*3*-P3, P3P2, and P2, respectively. (b1-b3) NMA4-P3, P3P2, and P2, respectively. (c1-c3) NMA6-P3, P3P2, and P2, respectively.

5.2. Electrochemical Characteristics

The galvanostatic charge-discharge (GCD) curves of NMAx samples cycled at different C rates between 1.5 V and 4.0 V are depicted in Figures 5.9 and 5.10. The cathodes were cycled in a half-cell configuration with Na metal as the counter electrode. The initial columbic efficiency of all the cathodes is higher than 100% because of the increasing reduction of Mn^{4+} ions when the concentration of Na⁺ exceeds 0.75 in these samples during the discharge process.



NMA3-P2 (b1) NMA5-P3, (b2) NMA5-P3P2, (b3) NMA5-P2 series of cathodes at

different C rates.



different C rates.

Among different cathodes in the NMAx series, the NMA3-P3 and NMA5-P3 stand out in their specific capacities. At a charge-discharge rate of 0.1C, both the cathodes show specific capacities close to 195 mAh g⁻¹ due to the higher Ni concentrations (Figure 5.9(a1) and (b1)). This is validated by multiple peaks appearing in their respective dQ/dV vs V plots above 3 V (Figure 5.11) that correspond to Ni^{2+/4+} redox couples [5, 8-10]. In contrast, the lower concentration of Ni²⁺ in NMA4 and NMA6 cathodes limited their specific capacity to 170 mAh g⁻¹ at 0.1C. Moreover, unlike NMA3-P3 and NMA5-P3, more than 50% of the specific capacity in NMA4-P3 and NMA6-P3 is due to the activation of Mn^{3+/4+} redox couples, which could lead to lower cyclic performance in the latter.



cathodes cycled at 0.1C.

With an increase in the P2 phase concentration, the specific capacities of all the cathode materials show a decreasing trend. In NMA3-P3P2 and NMA5-P3P2, the specific capacities drop to ~ 175 mAh g⁻¹, further decreasing to ~ 150 mAh g⁻¹ in NMA3-P2 and NMA5-P2. We had earlier reported such reductions in specific capacities with an increase in P2 phase concentration in both NMA1 and NMA2 compounds, which was attributed to the ability of the P3 phase to accommodate more Na ions by transforming to an O3 type phase, as in the case of NMA1-P3.

Regarding other electrochemical performance parameters, such as rate performance, unlike NMA*1* and NMA*2*, the monophasic P3 type cathodes of the NMA*x* compounds showed marginally better rate performance than their corresponding P3/P2 mixed-phase counterparts (Figure 5.12(a-b) and Figure 5.13(a-b)). At a discharge rate of 1C, NMA*3*-P3 and NMA*5*-P3 exhibited a specific capacity of 126

mAh g⁻¹ and 115 mAh g⁻¹, respectively. At a higher discharge rate of 6 C, NMA*3*-P3 and NMA*5*-P3 and their P3/P2 mix phase compounds could sustain a specific capacity of ~ 77 mAh g⁻¹. Meanwhile, in the NMA*4* and NMA*6* type cathodes, their P3 and P3/P2 mix phased compounds showed much lower capacities, close to 95 mAh g-1 at 0.1 C and 60 mAh g⁻¹ at 6C. Another notable feature of the rate performance curves is the consistently poor capacities exhibited by the P2-type cathodes. In all compositions, P2-type phases showed higher drops in specific capacities with an increase in discharge current, which could be attributed to large particle agglomerations in the P2 materials.



Figure 5.12. Rate performance (a)-(b) and (c)-(d) cyclic stability curves of NMA3 and NMA5 series of cathodes cycled between 1.5 V and 4.0 V. (e) Cyclic performance of NMA3-P3P2 and NMA5-P3P2 at 1C between 2.0 V and 4.0 V.


and NMA6 series of cathodes cycled between 1.5 V - 4.0 V.

Even though the P3-type cathodes showed a relatively high specific capacity and rate performance, their cyclic stability was surprisingly underwhelming. Figures 5.12(c-d) and 5.13(c-d) depict the cyclic performance of the NMAx series of cathode materials at 1C between 1.5 V and 4.0 V. The biphasic P3/P2 type cathodes consistently retain higher capacity than their P3 and P2 counterparts in all the compounds. For instance, in NMA3 and NMA5 cathodes, NMA3-P3/P2 and NMA5-P3/P2 showed ~ 70% capacity retention after 300 cycles, while their P3 and P2 type cathodes retained less than 60% of their initial specific capacities, at 1C. Cyclic performance drops even in the case of NMA4-P3P2 and NMA6-P3P2, where capacity retention is only about 60% of the initial capacity after 300 cycles. This could be due to the increased activity of $Mn^{3+/4+}$ redox couples in NMA4 and NMA6, which is known to cause large variations in unit cell volume during cycling. The interlocking between the P3 and P2 phases may aid in minimizing this large variation in unit cell volume at low voltages in the mixed-phase samples, allowing these to achieve higher cyclic stabilities.

To limit the activation of $Mn^{3+/4+}$ redox couples, NMA3-P3P2 and NMA5-P3P2 were tested further in a narrower voltage window between 2.0 V and 4.0 V (Figure

5.12(e)). NMA3-P3P2 and NMA5-P3P2 exhibited about 82% and 75% capacity retention after 300 cycles at 1C in this voltage window. Although the superior cyclic performance of the NMA3-P3P2 compared to NMA5-P3P2 could be attributed to the presence of Jahn-Teller active Mn³⁺ in the latter, the enhancement of cyclic stabilities of the cathode materials in the narrower voltage range is evidence of the detrimental impact (on cyclic stability) of utilizing Mn^{3+/4+} redox couples in layered oxide cathodes.

Nyquist plots of half-cells with NMA3-P3P2 and NMA5-P3P2 samples as cathodes illustrated in Figure 5.14 concur with the cyclic data. The Nyquist plot was analyzed through an equivalent circuit model shown in Figure 5.14 inset. The circuit consists of 3 resistors, R1, R2, and R3, which represent the DC resistances of the electrolyte, SEI layers, and charge transfer, respectively. NMA3-P3P2 and NMA5-P3P2 cells show higher overall resistance after cycling between 1.5-4.0 V when compared to the resistance of the cells cycled in the 2.0-4.0 V range. In NMA3-P3P2, there was a drastic increase in the charge transfer resistance (R2) (60 to 350 Ω) after cycling between 1.5-4.0 V compared to 2.0-4.0 V (60 to 150 Ω) NMA5-P3P2 also exhibited similar trends in charge transfer resistance which is consistent with a higher degree of structural degradation in the cathodes cycled between 1.5-4.0 V.



Figure 5.14. Nyquist plots of NMA3-P3P2 and NMA5-P3P2 cathodes before and after cycling. Figure inset shows the equivalent circuit used to fit the impedance data.

5.3. Operando Synchrotron XRD

Operando Synchrotron XRD (SXRD) was used to probe variations in lattice parameters during cycling and investigate the structural variations in the cathode materials during cycling. Figure 5.15(a-b) illustrates the operando *SXRD* pattern of NMA3-P3P2 and NMA5-P3P2 samples obtained at different states of charge. As expected, the figure shows large changes in the *c* lattice parameter of the P3 and P2 type unit cells below 2 V in both the cathodes, indicated by the significant shift in the (003) and (002) peaks of the P3 and P2 type phases. As discussed earlier, the change in the *c* lattice parameter is due to the presence of Jahn-Teller active Mn³⁺, which causes large distortions in the hexagonal lattice, leading to poor cyclic stability in the monophasic cathodes.

Interestingly, as reported in NMA2, the presence of Al³⁺ in the NMA3 and NMA5 cathodes has also impeded the transformation of P3 phases into an O3-type structure at lower voltages. Even when the specific capacity of the cathodes reached as high as 190 mAh g⁻¹, no peaks corresponding to the O3 phase were observed in both mixed-phase cathodes. P3 to O3 phase transformations have long been observed in P3 and O3-type materials. The slab glide mechanism leading to this transformation is often believed to cause rapid capacity degradation in these materials. Such transformations were also observed in NMA*1*-P3 and NMA*1*-P3P2 materials, which limited their cyclic performances. The absence of P3 to O3 transformations in both the Al-substituted compounds is an important finding and could open new avenues for research into O3 and P3-type layered oxides. The absence of phase transitions and the synergistic effect due to the biphasic nature of the NMA*3*-P3P2 and NMA*5*-P3P2 cathodes enhanced their structural stability, allowing them to achieve excellent cyclic properties.



Figure 5.15. *Operando* Synchrotron XRD patterns (a) NMA3-P3P2 (collected with a beam of a wavelength of 0.6645 Å) and (b) NMA5-P3P2 (collected with a beam of a wavelength of 0.74 Å) half cells obtained during the first charge/discharge cycle at 0.1C.

Figure 5.16 classifies the compositions in the NMAx series along different Mn^{3+} concentration lines in the Na_{3/4}(Mn-Al-Ni)O₂ pseudo-ternary diagram and reveals some interesting trends. Along the constant Al content (= 0.25) from NMA2 to NMA3, both the specific capacity and rate performance increased. This was expected; as the Ni²⁺ concentration in these cathode materials increased from 0 (for NMA2) to 0.25 (NMA3), the amount of Na⁺ that could be extracted also increased. This is further evidenced by similar specific capacities observed in NMA1, NMA5, and NMA3 cathodes having the same Ni content. The rate performance, on the other hand, improved along this line from NMA1 to NMA3. This is attributed to the increase in the Na⁺ conduction bottleneck area with an increase in Al content from NMA1 to NMA3. Further, NMA3 and NMA5 compositions that exhibit the best rate performance and highest cyclic stability lie along the 0-Mn³⁺ and 0.125-Mn³⁺ lines, respectively. In a limited voltage window between 2.0 to 4.0 V, where the Mn^{3+/4+} redox couple is largely inactive, NMA3-P3P2 showed better cyclic performance. Hence, the various Mn³⁺ concentration lines displayed in Figure 5.16 could serve as a guide to identify an optimal cathode material in the Na_{3/4}(Mn-Al-Ni)O₂ pseudoternary diagram.



Figure 5.16. Pseudo-ternary diagram of Na_{3/4}(Mn-Al-Ni)O₂ system showing constant Mn³⁺ concentration lines. The solid blue arrow indicates the increasing specific capacity, cyclability, and rate performance in compositions with constant Al³⁺ content. The dotted arrow depicts the compositions (constant Ni²⁺ content) along which the rate performance improves.

It should be noted that while Mn is +4 oxidation state in as-synthesized NMA3, during discharging to lower voltages in a half-cell configuration, sodiation could activate the $Mn^{4+/3+}$ redox due to additional Na-ions supplied by the Na metal anode. In the wider 1.5 V – 4.0 V window, NMA3-P3P2 and NMA5-P3P2 cathodes exhibited a 30% higher specific capacity than the 2.0 V – 4.0 V window while retaining 70% of their initial specific capacity after 300 cycles. This cyclic performance points to excellent structural stabilities of NMA3-P3P2 and NMA5-P3P2 enabled by the presence of Al³⁺ and their biphasic nature, which mitigate the effects of the structural distortions caused by the presence of Mn³⁺. Therefore, it stands to reason that an optimal cathode composition in the Na_{3/4}(Mn-Al-Ni)O₂ pseudo-ternary diagram may be found along the lower Mn³⁺ concentration line; however, the activation of Mn^{3+/4+} redox couple could still be utilized to improve the electrochemical behaviour while maintaining the structural stability of these cathodes.

5.5. References

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Identification of Optimal Composition with Superior Electrochemical Properties Along the Zero Mn³⁺ Line in Na_{0.75}(Mn-Al-Ni)O₂ Pseudo Ternary System

This chapter explores the structural and electrochemical properties of P3/P2 biphasic cathode materials that lie on the so-called 'zero Mn^{3+} line' (Figure 6.1) in the Na_{3/4}(Mn-Al-Ni)O₂ pseudo-ternary phase diagram. The compounds identified have a general formula $Na_{\frac{3}{4}}Mn_{\frac{5-x}{8}}Al_{\frac{2x}{8}}Ni_{\frac{3-x}{8}}O_2$ (x = 0, 0.25, 0.50, 0.75, and 1). The 'zero Mn^{3+} line' identified in this study confines the Mn ions to a 4+ oxidation state by varying the concentration of Mn, Ni, and Al ions. This novel approach differs from the conventional method of analyzing ternary diagrams in which the concentration of at least one of the elements remains constant. Moreover, in the Na_{3/4}(Mn-Al-Ni)O₂ pseudo-ternary system, the 'zero Mn^{3+} line' is also the boundary between the forbidden region (assuming Ni is only allowed to maintain a 2+ oxidation state) and the allowed region. As the presence of Jahn-Teller active Mn³⁺ is considered detrimental to cyclic performance, structural and electrochemical analysis in monophasic and biphasic P2/P3 samples along the 'zero Mn^{3+} line' is crucial in identifying compositions with desired electrochemical properties in the Na_{3/4}(Mn-Al-Ni) O_2 system. This approach can be extended to other composition phase diagrams involving Jahn-Teller active cations in selecting electrode materials with superior performance. The Al substituted series of compounds $Na_{\frac{3}{4}}Mn_{\frac{5}{8}}Ni_{\frac{3}{8}}O_2$, $Na_{\frac{3}{4}}Mn_{\frac{4.75}{8}}Al_{\frac{0.5}{8}}Ni_{\frac{2.75}{8}}O_{2} \ , \ Na_{\frac{3}{4}}Mn_{\frac{4.5}{8}}Al_{\frac{1}{8}}Ni_{\frac{2.5}{8}}O_{2} \ , \ Na_{\frac{3}{4}}Mn_{\frac{4.25}{8}}Al_{\frac{1.5}{8}}Ni_{\frac{2.25}{8}}O_{2} \ , \ and$ $Na_{\frac{3}{4}}Mn_{\frac{1}{2}}Al_{\frac{1}{4}}Ni_{\frac{1}{4}}O_2, \text{ (general composition } Na_{\frac{3}{4}}Mn_{\frac{5-x}{8}}Al_{\frac{2x}{8}}Ni_{\frac{3-x}{8}}O_2, \text{ where } x = 0, 0.25,$ 0.50, 0.75, and 1) synthesized for the study will henceforth be abbreviated as A0, A1, A2, A3, and A4, respectively (also see Table 1 for details).

Composition	Phase type	Label
$Na_{\frac{3}{4}}Mn_{\frac{5}{8}}Ni_{\frac{3}{8}}O_{2}$	Р3	A0- 1
_	P3+P2	A0- 2
_	P2	A0- 3
$Na_{\frac{3}{4}}Mn_{\frac{4.75}{8}}Al_{\frac{0.5}{8}}Ni_{\frac{2.75}{8}}O_{2}$	Р3	A1- 1
—	P3+P2	A1- 2
-	P2	A1- 3
$Na_{\frac{3}{4}}Mn_{\frac{4.5}{8}}Al_{\frac{1}{8}}Ni_{\frac{2.5}{8}}O_{2}$	Р3	A2- 1
_	P3+P2	A2- 2
_	P2	A2- 3
$Na_{\frac{3}{4}}Mn_{\frac{4.25}{8}}Al_{\frac{1.5}{8}}Ni_{\frac{2.25}{8}}O_{2}$	Р3	A3- 1
_	P3+P2	A3- 2
—	P2	A3- 3
$Na_{\frac{3}{4}}Mn_{\frac{1}{2}}Al_{\frac{1}{4}}Ni_{\frac{1}{4}}O_{2}$	Р3	A4- 1
_	P3+P2	A4- 2
_	P2	A4- 3

Table 6.1. Details of the composition and phase type for various samples prepared in the study.

6.1. Structural characteristics

A series of Al-substituted $Na_{\frac{3}{4}}Mn_{\frac{5-x}{8}}Al_{\frac{2x}{8}}Ni_{\frac{3-x}{8}}O_2$ (x = 0, 0.25, 0.50, 0.75, and 1) were synthesized through the sol-gel route. All these compositions (A0-A4) lie on the 'zero Mn^{3+} line' in the Mn-Ni-Al pseudo-ternary diagram where the concentration of Mn³⁺ is 0, as illustrated in Figure 6.1. All compositions were synthesized with three intended phase structures: monophasic P3 (denoted as -1), monophasic P2 (denoted as -2), and biphasic P3/P2 (denoted as -3). For example, the P3 and P2 phases of A0 are denoted as A0-1 and A0-3, respectively, and the P3/P2 biphasic A0 will be denoted as A0-2.



Figure 6.1. Pseudo-ternary diagram of Na_{3/4}(Mn-Al-Ni)O₂ system.

Figure 6.2 illustrates the phase evolution of the A0 to A4 series of compounds with calcination temperature. The figure shows that the P3 phase in all 5 compositions formed at 650 °C, and as the calcination temperature increased, peaks consistent with a P2-phase started to emerge, while the intensity of those corresponding to the P3 phase decreased.



Figure 6.2. (a-e) Structural evolution of A0-A4 cathode materials with calcination temperature.

Another noticeable feature of Figure 6.2 is that the complete transformation of all the materials to a P2-type phase occurs at different temperatures. For A4 (which has the highest, i.e., 0.25, A1 content), a monophasic P2 phase (A4-3) is obtained at 900 °C. In contrast, in other compositions with lower levels of A1³⁺, like in the case of A2 and A0, a pure P2 phase was obtained at relatively lower temperatures of 850 °C and 825 °C, respectively. Accordingly, the calcination temperatures for biphasic A2-

2 and A0-2 were also lower than A4-2. The changes to crystallographic parameters in the P3 and P2 phases in the A0-A4 series of compounds were analyzed using Rietveld refinement of room temperature XRD data (Figures 6.3-6.7). The refinement confirmed the existence of a single P3 phase (*R3m* space group) in all samples at 650 °C. With an increase in temperature, the intensities of (101), (102), and (105) peaks belonging to the P3 phase decline while (100), (102), and (103) peaks belonging to the P2 phase (*P6*₃/*mmc* space group) become prominent. Table 6.2-6.6 displays the crystallographic parameters of the A0-A4 series of compounds obtained after Rietveld refinement of XRD data. Interestingly, the P3 and P2 unit cell volumes were ~ 121 Å³ and 80.5 Å³ across all compositions. On the other hand, TM-O₆ octahedral volume in P3 and P2 type structures decreased from ~ 10.92 Å³ and 10.90 Å³ in A0 to ~ 9.67 Å³ and 10.05 Å³ in A4 while the volume of Na-O₆ prism increased from 11.98 Å³ and 11.91 Å³ in the former to 12.90 Å³ and 12.59 Å³ in latter. As a result, Na ion conduction bottlenecks (area of the rectangular face of Na-O₆ prism) are also bigger in A4.

The contraction of the TM-O₂ layers with an increase in Al concentration was further confirmed by the fitting of EXAFS data obtained at the Mn K-edge (Figure 6.8). The Fourier transform fits of Mn K-edge in P3 and P2 type A0-A4 samples show decreasing Mn-O bond lengths from 2.01 Å (for P2 and P3) in A0 to 1.94 Å (P3) and 1.96 Å (P2) in A4. The decrease in effective TM-O bond length could be due to a higher bond strength of Al-O bonds (511 kJ mol⁻¹) compared to Ni-O (382 kJ mol⁻¹) and Mn-O (401 kJ mol⁻¹) bonds, which lowers the effective TM-O bond lengths in P3 and P2 layered oxide compounds, allowing the TM-O₆ octahedra to shrink with an increase in Al content [1]. Such alterations to TM-O₂ layers in layered oxide materials have also been reported in the Na-Mn-O system of cathode materials, where similar reductions in TM-O₆ octahedral volume were reported with Al substitution [2]. The higher bottleneck area in A4 compared to A0 could also lower the Na⁺ migration energy with the material, which would help enhance its rate performance.



Figure 6.3. Rietveld refinement of XRD data for A2-1, A2-2, and A2-3 samples, along with their deconvoluted P2 and P3 phases.



Figure 6.4. Rietveld refined XRD data for A0-1, A0-2, and A0-3 samples.



Figure 6.5. Rietveld refinement of XRD data for A1-1, A1-2, and A1-3 samples.



Figure 6.6. Rietveld refinement of XRD data for A3-1, A3-2, and A3-3 samples.



Figure 6.7. Rietveld refinement of XRD data for A4-1, A4-2, and A4-3 samples.



Figure 6.8. Mn K edge EXAFS spectra of A2-1, A2-3, A0-1, and A0-3 samples.

Sample	Phase	a (Å)	c (Å)	$V(Å^3)$	Reliability
	(Fraction)				Factors
					Rexp: 2.92
40.1	P3 (100%)	2.8875	16.765	120.92	R _{wp} : 4.72
		± 0.0001	± 0.001	± 0.01	R _p : 3.34
					GOF: 1.61
		2.8879	16.774	121.15	R_{exp} : 2.89
AQ 2	P3 (48.3%)	± 0.0002	± 0.002	± 0.02	<i>R_{wp}</i> : 4.41
110 2		2.8885	11.15	80.57	<i>R</i> _{<i>p</i>} : 3.06
	P2 (51.7%)	± 0.0001	± 0.002	± 0.01	GOF: 1.52
					R _{exp} : 2.99
A0-3	P2(100%)	2.8885	11.1457	80.53	Rwp: 4.70
		± 0.0001	± 0.0005	± 0.01	R _p : 3.79
					GOF: 1.57

Table 6.2. Lattice parameters of A0 samples obtained from the Rietveld refinementof room temperature XRD data.

Sample	Phase	a (Å)	c (Å)	$V(Å^3)$	Reliability
	(Fraction)				Factors
					Rexp: 2.71
A 1-1	P2(100%)	2.8885	16.7745	121.21	R _{wp} : 4.02
		±0.0001	± 0.001	± 0.01	R _p : 2.86
					GOF: 1.47
	P3 (52.9%)	2.8874	16.757	120.99	<i>R</i> _{exp} : 3.04
A 1 2		± 0.0002	± 0.002	± 0.02	R_{wp} : 4.51
111 2		2.8874	11.134	80.391	$R_p: 3.17$
	P2 (47.1%)	± 0.0001	± 0.002	± 0.01	GOF: 1.48
					R _{exp} : 2.69
A1-3	P2(100%)	2.8878	11.143	80.47	R _{wp} : 4.31
		± 0.0001	± 0.001	± 0.01	R _p : 3.05
					GOF: 1.59

Table 6.3. Lattice parameters of A1 samples obtained from the Rietveld refinement

 of room temperature XRD data.

Sample	Phase	a (Å)	c (Å)	$V(Å^3)$	Reliability
	(Fraction)				Factors
					Rexp: 2.72
A2-1	P3 (100%)	2.8864	16.758	120.92	R _{wp} : 3.54
		±0.0001	± 0.001	± 0.01	R _p : 2.75
					GOF: 1.3
		2.8858	16.781	121.04	<i>R_{exp}</i> : 2.82
A2-2	P3 (52.6%)	± 0.0002	± 0.002	± 0.02	<i>R_{wp}</i> : 3.43
		2.8878	11.143	80.47	<i>R</i> _p : 2.65
	P2 (47.4%)	± 0.0001	± 0.002	± 0.01	GOF: 1.36
					R _{exp} : 2.76
A2-3	P2(97%)	2.8881	11.137	80.45	Rwp: 3.30
		± 0.0001	± 0.001	± 0.01	R _p : 2.57
					GOF: 1.19

Table 6.4. Lattice parameters of A2 samples obtained from the Rietveld refinementof room temperature XRD data.

Sample	Phase	a (Å)	c (Å)	$V(Å^3)$	Reliability
	(Fraction)				Factors
					Rexp: 2.67
A 3-1	P3(100%)	2.8841	16.779	120.87	R _{wp} : 3.24
	10 (10070)	±0.0001	± 0.001	± 0.01	R _p : 2.54
					GOF: 1.21
	P3 (54.3%)	2.8863	16.7620	120.93	$R_{exp}: 2.73$
					cup
		± 0.0001	± 0.002	± 0.02	R_{wp} : 3.44
A3-2		0.0054	11.1(2	00.40	D 2 72
	D2(45,70/)	2.8854	11.163	80.49	$K_p: 2.72$
	P2 (43.7%)	± 0.0001	± 0.001	± 0.01	GOF: 1.25
					R _{exp} : 1.98
A3-3	P2(100%)	2.8834	11.1669	80.404	R _{wp} : 3.41
		± 0.0002	± 0.0004	± 0.005	R _p : 2.49
					GOF: 1.71

Table 6.5. Lattice parameters of A3 samples obtained from the Rietveld refinementof room temperature XRD data.

Sample	Phase	a (Å)	c (Å)	$V(Å^3)$	Reliability
	(Fraction)				Factors
					Rexp: 2.23
A 4 1	P3 (100%)	2.8838	16.7924	120.97	R _{wp} : 2.51
		± 0.0001	± 0.002	± 0.01	R _p : 1.99
					GOF: 1.12
		2.8864	16.773	121.00	<i>R_{exp}</i> : 2.29
A 4 2	P3 (47.5%)	± 0.0001	± 0.001	± 0.02	R_{wp} : 3.41
		2.8842	11.164	80.42	$R_p: 2.59$
	P2 (52.5%)	± 0.0002	± 0.001	± 0.01	<i>GOF</i> : 1.48
					R _{exp} : 1.98
A4-3	P2(100%)	2.8834	11.1669	80.404	Rwp: 3.41
		± 0.0002	± 0.0004	± 0.005	R _p : 2.49
					GOF: 1.71

Table 6.6. Lattice parameters of A4 samples obtained from the Rietveld refinementof room temperature XRD data.

The morphological and microstructural studies of the A0-A4 series were carried out using FESEM. Figure 6.9(a-c) portrays the SEM micrographs of A2-1,2,3, while the SEM images of A0, A1, A3, and A4 series of compounds are displayed in Figure 6.10. The SEM micrographs reveal an increase in particle agglomeration with increased calcination temperature. The monophasic P3-type samples of all compounds show smaller particles with spheroid shape. In comparison, the biphasic P3/P2 type materials can be observed to have bigger particles with a slightly higher degree of agglomeration. Samples with smaller particles and a relatively lower degree of agglomeration are preferred in cathode materials as they usually show better rate performance and cyclic stabilities [3, 4]. In this regard, the P2-type compounds that exhibit highly agglomerated particle clusters may show degradations in specific capacities at higher C rates. The elemental mapping of A2-2 displayed in Figure 6.9(b1-b5) confirms a homogeneous distribution of all the constituent elements.



Figure 6.9. SEM micrographs of (a) A2-1, (b) A2-2, and (c) A2-3 samples with (b1-5) representing the elemental maps of different elements in A2-2.



Figure 6.10. SEM micrographs of (a1) A0-1, (a2) A0-2, (a3) A0-3, (b1) A1-1, (b2) A1-2, (b3) A1-3, (c1) A3-1, (c2) A3-2, (c3) A3-3, (d1) A4-1, (d2) A4-2, and (d3) A4-3 samples.

A combination of X-ray absorption near-edge spectra (XANES) obtained at the Mn K-edge and Mn 2p X-ray photoelectron spectra (XPS) was used to analyze the oxidation state of Mn ions in the as-synthesized A0-A4 series of materials. In Mn K-edge XANES spectra (Figure 6.11(a)), the peak energies of all the compositions coincide at ~ 6561 eV, which indicates a 4+ oxidation state of Mn ions in these samples [5-8]. Similar conclusions are drawn from the Mn 2p spectra (Figure 6.11(b)), which can be deconvoluted into 2 peaks at 643.2 and 654.7 eV, suggesting

the presence of only Mn⁴⁺ in these samples [9-11]. The oxidation state of Ni ions was identified by analyzing Ni 2p XPS spectra (Figure 6.12), where the peaks at 854.26 and 871.75 eV confirmed a 2+ oxidation state of Ni ions in all samples [9-11]. The 4+ oxidation state of Mn ions is a highly desirable feature in layered oxide cathodes that boosts their cyclic stability. Confirming the absence of Jahn-Teller active Mn³⁺ has tremendous implications on the structural stability of the cathode materials during cycling, ensuring better cyclic performance.



Figure 6.11. (a) XANES spectra of A0-A4 samples taken at Mn Kedge with relevant standard compounds. (b) Mn 2p XPS plots of A0-2 to A4-2 compounds.



Figure 6.12. Ni 2p XPS plots of A0-2 to A4-2 samples.

6.2. Electrochemical characteristics

The impacts of Al content and different P3/P2 phase fractions on electrochemical characteristics were analyzed by varying the charge-discharge rate between 0.1C and 6C in a 1.5-4.2 V range. Figure 6.13 portrays the charge-discharge curves of A2-1, A2-2, and A2-3 along with their corresponding dQ/dV vs. Voltage plots at 0.1C, while the same for A0, A1, A3, and A4 series of samples are displayed in Figure 6.14-6.17. Interestingly, despite the decrease in the concentration of Ni²⁺ active ions from A0 to A4, P3-type cathodes in all compositions (i.e., A0-1, A1-1, A2-1, A3-1, and A4-1) showed similar capacities close to 200 mAh g⁻¹ at 0.1C, which is equivalent to the extraction of ~ 0.8 Na⁺ from each formula unit cell. Concurrently, all the biphasic P3/P2 and monophasic P2 type cathodes also exhibited similar specific capacities close to 175 mAh g⁻¹ and 155 mAh g⁻¹, respectively. This suggests an increase in the activity of Mn⁴⁺ from A0-A4, as evidenced by the increase in the broadness of redox peaks below 2.5 V in the dQ/dV vs. Voltage (V) plots from A0 to A4, compensating for the decrease in Ni content (the redox peaks above 3 V in dQ/dV vs. Voltage plots are attributed to Ni^{3+/4+} redox couples).



Figure 6.13. (a-c) GCD curves of A2-1, A2-2, and A2-3 cathode materials at different C rates with (a1-c1) showing their respective dQ/dV vs. voltage (V) plots at 0.1C.



Figure 6.14. GCD curves of (a) A0-1, (b) A0-2, and (c) A0-3 cathode materials at different C rates with (a1-c1) showing their respective dQ/dV vs. voltage (V) plots at 0.1C.



Figure 6.15. GCD curves of (a) A1-1, (b) A1-2, and (c) A1-3 cathode materials at different C rates with (a1-c1) showing their respective dQ/dV vs. voltage (V) plots at 0.1C.



Figure 6.16. GCD curves of (a) A3-1, (b) A3-2, and (c) A3-3 cathode materials at different C rates with (a1-c1) showing their respective dQ/dV vs. voltage (V) plots at 0.1C.



Figure 6.17. GCD curves of (a) A4-1, (b) A4-2, and (c) A4-3 cathode materials at different C rates with (a1-c1) showing their respective dQ/dV vs. voltage (V) at plots at 0.1C.

Further, the activity of Mn^{3+/4+} redox couples also points to an increase in Na content in the cathode materials beyond 0.75. Hence, the specific capacities obtained at 0.1C between 1.5-4.2 V may not be realistic in a full-cell configuration. A possible solution to this problem would be to explore layered oxide cathodes with high Na or to limit the voltage window to 2.0-4.2 V, where Mn activity can be constrained. Limiting the voltage window to 2 V would cause an obvious reduction in specific capacity (up to 40% in A3 and A4 samples). Nevertheless, A3 and A4 cathodes possess larger Na⁺ conduction bottleneck areas that facilitate superior rate performance and cyclic stability and can be employed in batteries for stationary storage applications. The decrease in specific capacity observed with an increase in P2 phase fraction is also widely reported in the literature. This is due to the inability of the P2 phase to accommodate a higher number of Na-ions [12-14]. In contrast, P3 phases can circumvent this problem by readily transforming into an O3 phase, typically when the concentration of Na⁺ exceeds 0.75. Similar differences in specific capacities between P2 and P3 phases and superior performance of the P2/P3 mixed phase at high C rates in Mn/Ni-based layered oxide cathodes have also been reported previously.

To study the rate performance behaviour, GCD tests were conducted at different Crates. Figures 6.18(a), 6.18(b), and 6.18(c) represent the specific capacities of P3, biphasic P2/P3, and P2 samples for all compositions, respectively. The biphasic samples for all compositions (except A4) show better specific capacity at higher Crates than their monophasic counterparts. In P3-type cathodes, A4-1 shows the highest rate performance, with discharge capacities close to 125 mAh g⁻¹ and 77 mAh g⁻¹ at 1C and 6C, respectively. This was closely followed by the A3-1, which exhibited specific capacities close to 120 mAh g⁻¹ and 66 mAh g⁻¹ at 1C and 6C, respectively. The superior rate performance of A4-1 and A3-1 concurs with the conclusions drawn from XRD data, where a higher Na⁺ conduction bottleneck area was observed with increased Al content. In contrast, Al-substituted P2-type cathodes (A1-A4) show higher degradation in specific capacities during cycling. This could be attributed to the higher agglomeration of particles observed in the P2-type materials reported earlier.

Contrary to the trend observed in P3 type cathodes, the rate performed of the P3/P2 biphasic cathode materials (Figure 6.18(b)) initially improved with an increase in Al content till A1-2 and then decreased till A4-2. The P3/P2 biphasic A2-2 cathodes exhibited exceptional rate performance, delivering a specific capacity of 125 mAh g⁻¹ and 91 mAh g⁻¹ at 1C and 6C, respectively. At the same time, the initial enhancement in rate performance with an increase in Al content can be attributed to the increasing area of Na⁺ conduction bottlenecks, with further increase in Al content, drastic reduction in electronic conduction due to the presence of a high concentration of inactive Al³⁺. This inevitably became the bottleneck limiting Na⁺ extraction from the cathode materials, leading to inferior rate performance in A3-2 and A4-2. Since such a reduction in rate performances was not observed in the P3-type cathodes, the size of the cathode particles may have played a pivotal role in boosting their electronic conductivities. The Ketjen black additive mixed with the cathode slurry (to boost electronic conduction) is more effective in enhancing the

electronic conductivity of the cathode layer containing smaller P3 phase particles (compensating for the decrease in electronic conductivity of P3 cathodes with high Al content) than in the larger and much more agglomerated P3/P2 cathodes.



Figure 6.18. Rate performance of (a) A0-1 to A4-1, (b) A0-2 to A4-2, and (c) A0-3 to A4-3 series of cathodes cycled between 1.5-4.2 V.

To evaluate the effect of $Mn^{3+/4+}$ redox couples on the cyclic performance of the cathodes, the cells were cycled between two different voltage windows: 1.5-4.2 V and 2.0-4.0 V ($Mn^{3+/4+}$ redox couples are largely active below 2.0 V). In the 1.5-4.2 V voltage window (Figure 6.19(a1-a3)), the cyclic stability of the biphasic cathode materials in all five compositions is higher than their respective monophasic P3 and

P2 counterparts. The superior cyclic performance of the biphasic cathode materials is attributed to the synergistic effect (manifested due to the coexistence of two phases) that stabilizes both the P3 and P2 type structures, preventing phase transitions and large volume changes during cycling [15, 16].

With an increase in the Al content, the cyclic stability shows rapid improvement initially, with A1-2 and A2-2 exhibiting about 68% and 78% capacity retention after 300 cycles compared to just 50% in A0-2. However, with a further increase in Al content beyond A2-2, capacity retention drops back to 68% in A4-2. The poor cyclic stability could be attributed to the increasing activity of Mn^{3+/4+} redox couples (known to degrade structural stability) in the A4 and A3 compositions. Additionally, in the unsubstituted cathode samples (A0), the cyclic performance curves show a rapid decay in specific capacity after only a few cycles of steady performance, consistent with rapid structural degradation with cycling. This appears to have been remedied in the Al-substituted samples, where the capacity degradation appears gradual, suggesting improved structural stability with the substitution of Al^{3+} for Mn⁴⁺ and Ni²⁺. After limiting the voltage window to 2.0-4.0 V (Figure 6.19(b1-b3)), A2-2 still delivered an impressive capacity of 99 mAh g⁻¹ at 1C and retained 87% of the initial capacity after 500 cycles. This is a substantial improvement over the unsubstituted biphasic A0-2, which exhibits a capacity retention of only 55% after 500 cycles. The monophasic P2 and P3 type A2 cathodes (Figure 6.19(b2)) also showed higher cyclic performance, retaining up to 78% of their original capacity after 500 cycles. In higher Al substituted samples, A4-2 showed capacity retention of 78%, dropping from 87 mAh g⁻¹ to 66 mAh g⁻¹ after 500 cycles. Liming the lower cutoff voltage to 2 V limited the activity of the $Mn^{3+/4+}$ redox couple, which improved the cyclic performance of all the cathode materials.



Figure 6.19. Cyclic performance of A0-A4 series of cathodes at a discharge rate of 1C (a1-a3) between 1.5-4.2 V and (b1-b3) between 2.0-4.0 V.

The A2-2 cell was also able to achieve a 94% energy efficiency during the initial cycles at 1C and still maintained an energy efficiency as high as 88% after 500 cycles (Figure 6.20). Energy efficiency is vital to battery performance, often unreported in the literature. It determines the practical applicability of high-energy electrode materials and can also be used to diagnose various structural instabilities/variations (especially in interaction-type electrode materials) [17]. In the GCD curves plotted in Figure 6.20, the overpotential seems to increase when the voltage drops below 3.0 V, indicating large-scale structural variations/transformations. Even at a high discharge rate of 1C, the high energy efficiency makes A2-2 a strong contender for commercialization in Na ion batteries.



Figure 6.20. GCD curves of A2-2 depicting energy loss and energy recovered during charge-discharge at 1C.

In the Nyquist plots in Figure 6.21(a), A2-2 half cells show the lowest overall resistance ~ 300 Ω and 410 Ω after 500 cycles (cycled between 2.0 to 4.0 V) and 300 cycles (cycled between 1.5 to 4.2 V), respectively. The analysis of EIS data using an equivalent circuit model revealed an increase in charge transfer resistance from ~170 Ω in the fresh cells to 387 Ω after 500 cycles (in the 2.0-4.0 V range) and to 587 Ω after 300 cycles (in the 1.5-4.2 V range) for cell with A4-2 as the cathode. The charge transfer resistance increased to 260 Ω (after 500 cycles) and 354 Ω (after 300 cycles) in the half-cell with A2-2 cathode. The increase in charge transfer resistance of both the cells also indicates a higher degree of structural degradation in the materials when cycled in a wider voltage window. The lower charger transfer resistance in A2-2 also indicates the high structural durability of the cathode material.

The galvanostatic intermittent titration technique (GITT) was used to probe Na-ion kinematics in the A4, A2, and A0 series of compounds, and their resulting curves depicting the variation in Na⁺ diffusion coefficients at different states of charge are displayed in Figure 6.21(b), Figure 6.22, and Figure 6.23. As expected, in all the compounds, monophasic P3 and the biphasic P2/P3 biphasic cathodes show the lowest dispersion in diffusion coefficients at different states of charge compared to the P2-type cathode. In A2, the highest diffusion coefficient is observed in A2-2 (4.0 × 10⁻¹⁰ cm² s⁻¹) type cathode, while in A1, the highest diffusion coefficient is observed in A4-1 (4.0×10^{-10} cm² s⁻¹) which concurs with the rate performance results.



Figure 6.21. (a) Nyquist plots of A0-2, A2-2, and A4-2 cathodes before and after cycling. Figure inset shows the equivalent circuit used to fit the impedance data.(b) Variation of diffusion coefficients of A0-2, A2-2, and A4-3 cathodes during a charge/discharge cycle.


Figure 6.22. Variation of diffusion coefficients in A0-1, A2-1, and A4-1 cathodes during a charge/discharge cycle.



Figure 6.23. Variation of diffusion coefficients in A0-3, A2-3, and A4-3 cathodes during a charge/discharge cycle.

The remarkable electrochemical performance of the A2-2 cathode prompted me to test the material further in a full-cell configuration with a hard carbon anode. The hard carbon was pre-sodiated before being assembled into the full cell; the charge-discharge cycle of hard carbon is shown in Figure 6.24. During electrochemical tests, the A2-2 full cell exhibited a specific capacity of 104 mAh g⁻¹ (~ 90% capacity of A2-2 half cell) between 2.0-4.0 V at a charge/discharge rate of 0.2C and retained 90% of its initial specific capacity after 100 cycles (Figure 6.25).



Figure 6.24. GCD curves of hard carbon half-cell cycled at 0.05C.



Figure 6.25. GCD curves of A2-2 full cells cycled at 0.2C.

6.3. Operando Synchrotron XRD studies

The improved structural stability of the Al-substituted cathodes and the adverse effects of $Mn^{3+/4+}$ redox couples on the layered oxide structure were confirmed using *operando* Synchrotron XRD of cathode materials. The Synchrotron XRD patterns were obtained for the A2 and A4 series of cells while cycling at a charge/discharge rate of 0.1C between 1.5-4.2 V. Figure 6.26(a-c) depicts the XRD patterns of A2-1, A2-2, and A2-3 cathode materials, and the same for A4-1, A4-2, and A4-3 are presented in Figure 6.27. Initial analysis of the XRD patterns of both A2-1 and A4-1 confirmed our speculations about large variations in lattice parameters associated with the activation of $Mn^{3+/4+}$ in layered oxide structures, as evidenced by the shift in the (003) peak to higher angles (signifying a shrinkage of unit cell along the *c* axis due to a decreased repulsion between O^{2-} with an increasing amount of Na⁺ in the unit cell) during the discharge cycle when the cell voltage falls below 2 V.



Figure 6.26. *Operando* Synchrotron XRD patterns of half-cells employing (a) A2-1, (b) A2-2, and (c) A2-3 samples as cathodes collected during the first charge/discharge cycle.



Figure 6.27. *Operando* synchrotron XRD patterns of half-cells employing (a) A4-1, (b) A4-2, and (c) A4-3 samples as cathodes collected during the first charge/discharge cycle.

Further analysis using Le-Bail fitting (Figure 6.28(a-c) and Figure 6.29(a-c)) also revealed a peculiar feature in the XRD patterns of Al substituted P3 type samples where a complete absence of the O3 phase was observed even when the voltage reached 1.5 V. Even in the A4-1, where the $Mn^{3+/4+}$ redox couples were largely active, Le-Bail fitting could find any peaks related to an O3 phase. As discussed in the previous section, the activation of $Mn^{3+/4+}$ redox couples in the A1-A4 series of

materials indicated an increase in Na content above 0.75, which would ideally trigger the P3-O3 phase transformations as reported in the literature, especially in A4-1 where Mn^{3+/4+} redox couples contributed close to 40% of its specific capacity [18-23]. Yet the complete absence of an O3 phase points to the ability of Al-ions to suppress the P3-O3 phase transformations in these samples. As Na⁺ kinetics in the O3 phases is quite poor compared to the P3 and P2 type structures, the absence of the O3 phase also explains the comparatively high-rate performance of the A4-1 cathode.

In the P2 type structures, the activation of Mn^{3+/4+} redox couple not only causes large variations in the c parameter of the $P6_3/mmc$ unit cell but also initiates phase transformation as evidenced by the presence of an extra peak next to the P2 (002) at $\sim 7.5^{\circ}$ in Figure 6.26(c) and Figure 6.27(c). This was confirmed to be the (004) peak of a P'2 phase (C2/c space group) through Le-bail fitting of XRD patterns (Figure 6.28(c) and Figure 6.29(c)). P2 to P'2 phase transformation has been reported in Na-Mn-Ni-based systems at low voltages [24, 25]. It is often described as an intermediatory phase that forms before the P2-type structure completely transforms into an OP4 phase. Contrary to the drastic structural variations and phase transformations observed in the P3 and P2-type cathodes, the operando-XRD patterns of the biphasic A2-2 and A4-2 cathode materials exhibit smoother structural variations throughout the entire charge/discharge cycle. The synergistic effects, widely reported in biphasic cathodes, appear to have stabilized both the P3 and P2 type structures in the material, preventing any unwanted phase transformations even at voltages, which may very well have led to their impressive electrochemical performance [15, 16, 26]. As prominent structural changes observed in Figures 6.26 and 6.27 occur when the cell is discharged below 2.0 V, restricting the chargedischarge voltage window to 2.0-4.0 V improves the cycling performance of all the samples quite significantly, as expected.



Figure 6.28. Lebail fitted *operando* Synchrotron XRD patterns of (a) A2-1, (b)
A2-2, and (c) A2-3 cathodes obtained at fully charged (4.2 V) and fully discharged (1.5 V) states with (a1-c1) depicting their respective variations in P2 and P3 unit cell volumes during cycling.



Figure 6.29. Lebail fitted *operando* synchrotron XRD patterns of (a) A4-1, (b) A4-2, and (c) A4-3 cathodes obtained at fully charged (4.2 V) and fully discharged (1.5 V) states with (a1-c1) depicting their respective variations in unit cell volume of P2 and P3 phases during cycling.

To study the effect of Al substitution and the role of a biphasic cathode in structural stabilization, the variation in volume and lattice parameters of the hexagonal unit cells were quantified. The variation in volume of the A2 and A4 series of materials (Figure 6.28(a1-c1) and Figure 6.29(a1-c1)), on the other hand, shows a decrease in unit cell volume upon charging and expands during discharging. The variations in the *c* parameter of all A2 and A4 cathodes (Figure 6.30) follow a trend well documented in layered oxides where the unit cell expands and contracts along the *c* axis during charging and discharging [2, 24, 27]. Table 6.7 summarises the maximum percentage change in cell volume of P2 and P3 type phases in A4 and A2 monophasic and biphasic cathodes. As expected, the P3 and P2 phases in the A2-2

and A4-2 cathodes exhibited much lower variation in cell volume than their monophasic counterparts. In fact, the P3 and P2 structures in the A2-2 only expanded to about 0.9% and 0.8% of the minimum volumes, which makes it on par with some of the 'zero strain' cathodes reported in the literature. Overall, biphasic P3/P2 cathode materials were found to have superior electrochemical performance compared to their monophasic P3 and P2 counterparts. Figure 6.31 and Table 6.8 compare the various properties of all biphasic cathode materials. During electrochemical testing, A2-2 exhibited several outstanding electrochemical properties, such as high specific capacity, cyclability, and energy efficiency, characteristics that are highly sought after in cathodes for commercial applications.



Figure 6.30. Variation in the *c* parameter of P2 and P3 phases in (a) A2-1, (b) A2-2, (c) A2-3, (d) A4-1, (e) A4-2, and (f)A4-3 cathodes during cycling.

Table 6.7. Percentage changes in unit cell volume of A2 and A4 series of cathodes.

		Maximum percent	age change in unit
Sample		cell volume	
		P2	P3
A4	A4-1	-	1.50%
	A4-2	1.3%	1.0%
	A4-3	3.6%	-
A2	A2-1	-	1.3%
	A2-2	0.8%	0.9%
	A2-3	3.3%	-

	Specific		
Material	capacity at	Rate performance	Cyclic
	C/10		Performance
$Na_{\frac{3}{4}}Mn_{\frac{5}{8}}Ni_{\frac{3}{8}}O_{2}$ (A0-2) $Na_{\frac{3}{4}}Mn_{\frac{4.75}{8}}Al_{\frac{0.5}{8}}Ni_{\frac{2.75}{8}}O_{2}$ (A1-2)	166 mAh g ⁻¹ 173 mAh g ⁻¹	112 mAh g ⁻¹ at 1C 70 mAh g ⁻¹ at 6C 125 mAh g ⁻¹ at 1C 84 mAh g ⁻¹ at 6C	51 % capacity retention after 300 cycles at 1C 69 % capacity retention
(A1-2)			after 200 cycles at 1C 79% capacity
$\frac{Nu_{3}Mn_{4.5}Au_{1}Nu_{2.5}O_{2}}{(A2-2)}$	175 mAh g ⁻¹	127 mAh g ⁻¹ at 1C 92 mAh g ⁻¹ at 6C	retention after 300 cycles at 1C
$Na_{\frac{3}{4}}Mn_{\frac{4.25}{8}}Al_{\frac{1.5}{8}}Ni_{\frac{2.25}{8}}O_{2}$ (A3-2)	171 mAh g ⁻¹	122 mAh g ⁻¹ at 1C 72 mAh g ⁻¹ at 6C	73 % capacity retention after 300 cycles at 1C
$\frac{Na_{\frac{3}{4}}Mn_{\frac{4}{8}}Al_{\frac{2}{8}}Ni_{\frac{2}{8}}O_{2}}{(A4-2)}$	173 mAh g ⁻¹	110 mAh g ⁻¹ at 1C 73 mAh g ⁻¹ at 6C	69 % capacity retention after 300 cycles at 1C

Table 6.8. Electrochemical properties of A0-2 to A4-2 cathodes.



Figure 6.31. Spider charts comparing the various characteristics of A0-2 to A4-2 cathode materials.

6.4. References

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Elevating the Concentration of Na ions to 1 in P2 Type Layered Oxide Cathodes

As discussed in the previous chapters, in an effort to identify the optimal cathode material in the Na_{3/4}(Mn-Al-Ni)O₂ pseudo-ternary diagram, the biphasic P2/P3-type Na₃/4 Mn_{4.5}Al₁Ni_{2.5}O₂ material was identified as the optimal cathode, showcasing impressive rate performance and cyclic stability. Additionally, the studies revealed that the presence of Al³⁺ in the P3 type structure helped prevent P3 to O3 type transitions, which were observed in non-Al-containing materials in the pseudo-ternary system, such as the P3 type Na₃/4 Mn₃Ni₁O₂. It was concluded that Al³⁺ could stabilize the P3-type structure during the discharge cycle even when Na concentrations reached values beyond 0.8. In this chapter, this property of Al³⁺ has been leveraged to prepare high Na-containing P3 and P2-type cathodes by increasing the concentration of Na in Na₃/4 Mn₄·5 Al₁Ni_{2.5}O₂ to NaMn_{4.5}Al₁Ni_{2.5}O₂. It is demonstrated that the presence of Al³⁺ can also prevent the formation of O3-type phases in high Na-containing P3 and P2-type NaMn_{4.5}Al₁Ni_{2.5}O₂ exhibited impressive rate performance and cyclic stability.

7.1. Structural characteristics

NaMn $\frac{4.5}{8}$ Al $\frac{1}{8}$ Ni $\frac{2.5}{8}$ O₂ was prepared in 3 configurations: monophasic P3 (Na1-P3), monophasic P2 (with a minor O3 phase, henceforth referred to as Na1-P2), and biphasic P3/P2 (Na1-P3P2) with almost equal proportions of P3 and P2. This was achieved by calcinating the samples at different temperatures. This yielded a P3 phase at lower temperatures (650 °C) with increasing P2 phase fractions as the calcination temperature increased. The composition of Na1-P3, Na1-P2, and Na1-P3P2 was analyzed using ICP-AES (Table 7.1), which confirmed the concentration of Na to be close to 1.0 in all three materials. The crystal structure and phase configurations of the three materials were studied using Rietveld refinement of XRD data displayed in Figure 7.1. The diffraction peaks in Na1-P3 calcined at 650 °C were indexed with the *R3m* space group, while that of Na1-P2 calcinated at 850 °C was indexed using the *P63/mmc* space group. The analysis also confirmed the equal proportions of the P3 and P2 phases in the Na1-P3P2 sample, which was calcined at 800 °C for 8 h. Additionally, the presence of a minor O3 phase was also identified in both Na1-P3P2 and Na1-P2. This was expected as P2-type phases are rarely reported to contain Na concentrations beyond 0.8.

Sample	Calculated composition		
Sample	Na/ Mn/ Ni/ Al		
Na1-P3	0.997/0.562/0.312/0.123		
Na1-P3P2	0.993/0.562/0.312/0.122		
Na1-P2	0.99/0.562/0.311/0.123		

Table 7.1. The chemical compositions of the as-prepared samples were measured

 by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Ordinarily, an O3-type phase is expected in high Na-containing layered oxide materials. Instead, in Na1, a P3 phase formed at a lower calcination temperature and converted into a P2-type phase at higher calcination temperatures, with O3 crystalizing only as a minor phase. This could be due to the presence of Al³⁺ in the material, which may favor the formation of P-type phases. This was also noticed in our previous works involving the Na_{3/4}(Mn-Al-Ni)O₂ pseudo ternary system where operando synchrotron XRD on the P3 type materials showed that the P3 to O3 type transformations observed in a non-Al containing material was found to be absent in all Al substituted samples even after being discharged up to 1.5 V (where Na concentrations reach close to 1.0). The conclusion drawn from that study was that the presence of Al³⁺ in layered oxide compounds can stabilize the P3 crystal structure enough to prevent the 'slab gliding' mechanism that transforms it into an O3-type phase when Na ions are inserted into the structure electrochemically during cycling. The fact that the P-type phases contributed to most of the phase composition in the Na1 cathode material during synthesis proves that the Al³⁺ favors the formations of the P-type materials.

The crystallographic parameters of all these materials obtained after Rietveld refinement are summarised in Table 7.2. Interestingly, the P2 unit cell volume was found to be 80.17 Å³, which was lower than the previously reported volume of the

P2 type $Na_{\frac{3}{4}}Mn_{\frac{4.5}{8}}Al_{\frac{1}{8}}Ni_{\frac{2.5}{8}}O_2$ due to the former's lower *c* parameter. This resulted from shrinking Na-O₆ prisms in the Na1-P2 type structure, which could hinder the diffusion of Na-ions through the material initially during charging. However, unit cell parameters of the P3 structure remained unaffected by the increase in Na-ion concentration and were found to be similar to that of the P3 type $Na_{\frac{3}{4}}Mn_{\frac{4.5}{8}}Al_{\frac{1}{8}}Ni_{\frac{2.5}{8}}O_2$.



Figure 7.1. Rietveld refinement of XRD data for Na1-P3, Na1-P3P2, and Na1-P2 materials with enlarged views of their respective deconvoluted P2, P3, and O3 phases in the vicinity of 30-40° 2θ range.

Sample	Phase (Fraction)	a (Å)	c (Å)	$V(\text{\AA}^3)$	Reliability Factors	
Na1-P3	P3 (100%)	2.8857 (5)	16.7656 (2)	121.05 (4)	R _{exp} : 2.93 R _{wp} : 4.51 GOF: 1.54	
Na1-P3P2	P3 (48%)	2.8869 (3)	16.7745 (2)	120.86 (2)	$P \rightarrow 2.40$	
	P2 (48%)	2.8891 (4)	11.1125 (1)	80.34 (2)	<i>R_{wp}</i> : 2.99 <i>GOF</i> : 1.20	
	O3 (4%)	2.9404 (3)	16.10 (1)	120.58 (3)		
Na1-P2	P2 (91%)	2.8834 (2)	11.1669 (4)	80.404 (5)	R _{exp} : 2.01 R _{wp} : 2.41 GOF: 1.28	
	O3 (9%)	2.9409 (3)	16.097 (2)	120.05 (5)		

Table 7.2. Lattice parameters of Na1-x samples obtained from the Rietveld refinement of room temperature XRD data.

The microstructure of the Na1 samples was studied using a field emission secondary electron microscope (FESEM). The SEM micrographs of the materials in Figure 7.2 show an increasing degree of particle agglomeration in samples synthesized at higher calcination temperatures. Smaller particle sizes and relatively lower degree of agglomeration of particles are preferred in cathode materials as they usually support better ionic conduction [1, 2]. Hence, Na1-P2, with its high degree of particle agglomeration, may not fare well in terms of rate performance. The elemental maps of the Na1-P3P2, shown in Figures 7.2(b1-b5), show a uniform distribution of its constituent elements within the sample.



Figure 7.2. SEM micrographs of (a) Na1-P3, (b) Na1-P3P2, and (c) Na1-P2 samples with (b1-5) representing the maps of different elements in Na1-P3P2.

The oxidation states of the constituent elements in the monophasic P3 and P2 type samples were identified by analyzing their respective Mn 2p and Ni 2p XPS spectra (Figure 7.3). The Mn 2p XPS spectra could be deconvoluted into 4 peaks at 641.8 & 653.2 eV and 643.2 & 654.7 eV, suggesting a combination of 3+ and 4+ oxidation states for Mn ions in both materials [3-5]. In the Ni 2p XPS spectra, the peaks at 854.26 eV and 871.75 eV indicated that Ni ions existed primarily in a 2+ oxidation state [3-5].



Figure 7.3. Mn 2p and Ni 2p XPS plots of Na1-P3 and Na1-P2 samples.

7.2. Electrochemical characteristics

The electrochemical properties of the three cathode materials were tested in half cells in a voltage range between 1.5 V and 4.0 V. This was to ensure the activation of both $Mn^{3+/4+}$ and $Ni^{2+/4+}$ redox couples, which are active between 1.5-2.5 V and 3.0-4.0 V, respectively [6-9]. Figure 7.4 and Figure 7.5 depict the galvanostatic charge-discharge (GCD) curves of Na1-P3, Na1-P2, and Na1-P3P2 at various C rates, along with their respective dQ/dV vs. voltage plots at 0.1C. The curves show that the P3-type material exhibited the highest specific capacity of 196 mAh g⁻¹ at 0.1C, which decreased progressively in the materials with a higher P2 phase. The dQ/dV vs. voltage plots of all 3 materials also confirm the activity of $Mn^{3+/4+}$ and $Ni^{2+/4+}$ redox couples. Compared to its P2-type $Na_{\frac{3}{4}}Mn_{\frac{4.5}{8}}Al_{\frac{1}{8}}Nl_{\frac{2.5}{8}}O_2$, Na1-P2 showed significant improvement in rate performance, exhibiting specific capacities reaching up to 121 mAh g⁻¹ and 87 mAh g⁻¹ at 1C and 6C, respectively (Figure 7.6(a)). Surprisingly, the Na1-P3 showed a significant decline in rate performance compared to the P3 type $Na_{\frac{3}{4}}Mn_{\frac{4.5}{8}}Al_{\frac{1}{8}}Nl_{\frac{2.5}{8}}O_2$, and this could be due to multiple phase transitions from P3 to P3' and P3" during cycling [10, 11].



Figure 7.4. (a-b) GCD curves of Na1-P3P2 and Na1-P2 cathode materials at different C rates with (c-d) showing their respective dQ/dV vs. voltage plots at 0.1C.



its dQ/dV vs. voltage plots at 0.1C.

In contrast, Na1-P3P2 demonstrated significantly enhanced rate performance compared to its single-phase counterparts, achieving specific capacities close to 102 mAh g⁻¹ at 6C. This remarkable enhancement in rate performance for the biphasic cathode material can be attributed to the continued existence of high Na-ion conducting P-type phases. Furthermore, the high specific capacities demonstrated by the Na1 series of materials are also achievable in a full cell configuration, as each started from a Na1 configuration and did not require the insertion of any additional sodium ions from the Na metal anode during cycling.

Following the rate performance tests, the cyclic stability of the cathode materials was evaluated within a voltage range of 1.5-4.0 V at 1C over 300 cycles (Figure 7.6(b)). The results indicated that Na1-P2 exhibited the highest cyclic performance with approximately 80% capacity retention, followed by Na1-P3P2 with 73% capacity retention after 300 cycles. Despite having a significantly lower specific capacity at 1C (80 mAh g⁻¹), the monophasic P3-type cathode only retained about 66% of its capacity. Additionally, the cyclic curve for the P3-type material showed a marked increase in slope after about 200 cycles. This indicates a rapid capacity decline with each subsequent cycle, which may have been caused by a severe structural degradation in the cathode material. Although subtle, a similar increase in slope was also observed in the biphasic Na1-P3P2 after 250 cycles. This provides two key insights: first, the capacity decline in the biphasic material may also be caused by structural degradation of its P3 phase; second, the presence of the P2 phase in the biphasic cathode is beneficial in both delaying the onset of severe structural degradation in the P3 type structure and reducing its intensity in each subsequent cycle. Furthermore, contrary to what was observed in the other materials in the Na_{3/4}(Mn-Al-Ni)O₂ pseudo-ternary system, the biphasic Na1-P3P2, for the first time, has shown inferior cyclic properties compared to its monophasic P2, counterpart. This points to the excellent structural stability of the high Na-containing P2 structure.



Figure 7.6. (a) Rate performance of Na1 series of cathodes at various C rates and their (b) cyclic performance curves at 1 C.

After conducting cyclic performance tests on the Na1-P2 half cells, the electrochemical performance of the Na1-P2 cathodes was evaluated in a full-cell configuration. In this setup, a pre-sodiated hard carbon was used as the anode (the GCD curve of HC half cells is displayed in Figure 7.7). Figure 7.8(a) presents the GCD curves of the Na1-P2 full cells between 1.5 to 4.0 V at various C rates. At a discharge rate of 0.1C, the Na1.0-P2 full cell exhibited a specific capacity of 123 mAh g⁻¹. The lower capacity observed in the full cell, compared to the Na1-P2 half-cell, is attributed to the limited activity of the $Mn^{3+/4+}$ redox couples in the cathode, which may only be active at further lower voltages in the full-cell configuration. The Na1-P2 full cells demonstrated excellent cyclic performance, retaining approximately 90% of their initial capacity after 200 cycles at a charge-discharge



rate of 0.2 C (Figure 7.8(b)). This impressive cycle stability might also be due to the limited activity of $Mn^{3+/4+}$ redox couples within the cycled voltage window.

Figure 7.7. GCD curve of a hard carbon half-cell at 0.1 C.



Figure 7.8. (a) GCD curves of Na1-P2 full cells at various C rates. (b) Cyclic performance of Na1-P2 Full cell at 0.2C along with columbic efficiency for each cycle.

7.3 Operando Synchrotron XRD studies

Most electrochemical properties of cathode materials stem from structural changes or transformations during cycling. To explore the structural evolution of the cathode materials, operando synchrotron XRD measurements were carried out while the cells were being cycled at a constant 0.1C current. Figure 7.9 and Figure 7.10 show the operando SXRD patterns of Na1-P3P2 and Na1-P2 half cells at various states of charge. The XRD patterns show no visible transformations of the P3 and P2 type structures in both the cathode materials. From the onset of charging, the (002) and (003) peaks of P2 and P3 type structures in Na1-P3P2 and (002) of P2 in Na1-P2 shift to lower angles, indicating the expansion of the unit cells along the *c*-axis [12-14]. In contrast, the P2-type Na₃Mn_{4.5}Al₁Ni_{2.5}N₂ had shown a P2 to P2' phase transition when discharged to lower voltages below 2.0 V when Mn^{4+/3+} redox couples became active, and Na concentrations increased above 0.75 in the structure. This was prevented in the biphasic P3/P2 type cathode of the same material. Increasing the Na content in the same P2-type cathode material to 1.0 also prevented phase transitions in the P2-type structure, especially at low voltages.



Figure 7.9. Operando Synchrotron XRD patterns of Na1-P3P2 obtained at 0.1C.



0.1C.

Le-bail fitting was employed to analyze the operando XRD patterns of both cathodes (Figure 7.11-7.12). The analysis confirmed the absence of any phase transformations in P3 and P2 type structures in both materials. Figure 7.13 and Figure 7.14 display the variation in the c parameter and unit cell volume obtained from the Le-bail fitting of XRD data of both samples. The changes in the c parameter follow an expected trend. The maximum c parameter is obtained at the end of charging, and the minimum is observed at the end of the discharge. In contrast, the changes in unit cell volume follow the opposite trend due to the contraction of the unit cells along the a and b axis during charging and expansion on discharging. The fluctuation in cell volume in P2 type structures in Na1-P3P2 and Na1-P2 structures was calculated to be about 0.86% and 0.78%, respectively. The relatively low variation in unit cell volume and the absence of transformations in both the cathode materials led to their high-rate performance and excellent cyclic stability.



Figure 7.11. Le-bail fitted *operando* synchrotron XRD patterns of Na1-P3P2 cathode obtained at fully charged (4.0 V) and fully discharged (1.5 V) states.



Figure 7.12. Le-bail fitted *operando* synchrotron XRD patterns of Na1-P2 cathode obtained at fully charged (4.0 V) and fully discharged (1.5 V) states.



Figure 7.13. Variation in the c and unit cell volume parameter of P2 and P3 phases



Figure 7.14. Variation in the *c* and unit cell volume parameter of P2 in Na1-P2 cathode during cycling.

7.4. References

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Excellent Structural Stability Driven Cyclability in P2-type Ti-based Cathode for Na-ion Batteries

The structural, electrical, and electrochemical properties of Na_{0.7}Ni_{0.2}Cu_{0.15}Ti_{0.65}O₂ (NNCT), which occupies the end member of the Na_{0.7}Ni_{0.2}Cu_{0.15}Mn_(0.65-x)Ti_xO₂ series [1, 2] where Ti⁴⁺ ions fully replace Mn⁴⁺ ions are detailed in this chapter. In this compound Ni²⁺ and Cu²⁺ are both stable in the divalent state, which helps to stabilize Mn in the 4+ oxidation state. This is beneficial as Mn⁴⁺ is Jahn–Teller inactive, reducing structural distortion during cycling. Furthermore, the Ni²⁺/Ni⁴⁺ redox couple involves a two-electron transfer, which helps compensate for the capacity loss associated with the elimination of the Mn³⁺/Mn⁴⁺ redox activity in this composition. Cu²⁺ also contributes significantly to the stabilization of the P2-type layered structure, particularly at higher voltages, which enhances both cyclic performance and structural robustness. Additionally, Cu incorporation improves the ambient stability of the material, making it more suitable for practical applications.

The oxidation potentials of Ni²⁺–Ni⁴⁺ (~ 3.2 V vs. Na/Na⁺) and Cu²⁺/Cu³⁺ (~ 4 V vs. Na/Na⁺) are higher than that of the Mn³⁺/Mn⁴⁺ redox couple which contributes to an improvement in energy density. The results obtained have been extensively compared with the parent material Na_{0.7}Ni_{0.2}Cu_{0.15}Mn_{0.65}O (NNCM) and Na_{0.7}Ni_{0.2}Cu_{0.15}Mn_{0.575}Ti_{0.075}O₂ (NNCMT) [2] which have been reported in the literature, to establish a trend of structural and electrochemical properties arising from Ti substitution.

8.1. Structural characteristics

Figure 8.1(a) displays the XRD patterns of NNCT at different calcination temperatures between 700 °C – 950 °C. The figure shows the emergence of O3 and P3 type phases (along with impurity peaks related to other unreacted phases) at 850 °C and 900 °C which is concurrent with the findings in NNCMT samples where a minor O3 phase (JCPDS:09- 0063) was detected upon Ti substitution. The total phase fraction of both these phases was estimated to be less than 10% of the total sample. Upon increasing the calcination temperature to about 950 °C, the O3 and P3 phases disappeared, and a single P2 phase (JCPDS:27- 0751) was obtained. This was confirmed by Rietveld refinement of the room temperature XRD data of the sample calcinated at 950 °C, which shows the existence of a single P2 phase in a

 $P6_3/mmc$ space group (Figure 8.1(b)). The hexagonal unit cell was found to have a volume of 85.142 ± 0.004 Å³ with lattice parameters $a = 2.96573 \pm 0.00005$ Å, $c = 11.1772 \pm 0.0002$ Å. The crystallographic parameters used in Rietveld refinement are displayed in Table 8.1. The disappearance of the O3 and P3 phases with temperature could be related to the volatilization of Na and the conversion of the P3-type structure to a P2-type structure at higher synthesis temperatures. For the sample synthesized at 950 °C, a minor impurity phase (a small peak at $2\theta \sim 36^{\circ}$ in Figure 8.1(a), possibly a CuO phase) was observed along with the dominant P2 phase. As the fraction of this impurity phase was < 1 wt.%, it was ignored in further discussion.



Figure 8.1. (a) XRD patterns illustrating the phase evolution of NNCT with calcination temperature recorded at room temperature. (b) Rietveld refinement profile of room temperature XRD data for the NNCT powder sample calcinated at 950 °C.

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Atom	X	У	Z	Occupancy	Site
Na1	2/3	1/3	1/4	0.45	2d
Na2	0	0	1/4	0.25	2b
Ti/ Ni/	0	0	0	0 65/0 20/0 15	
Cu	0	Ũ	Ū	0.00/ 0.20/ 0.15	
0	2/3	1/3	0.09	1	4f
U	215	1/5	0.07	1	71

Table. 8.1. Crystallographic parameters of P2-NNCT sample calcinated at 950 °C.

Compared to NNCT, NNCM and NNCMT LOs showed lower cell volumes and unit cell parameters [1, 2]. This is expected as Ti^{4+} ions (0.605 Å in 6 coordination) have a higher ionic radius compared to the Mn^{4+} ions (0.530 Å in 6 coordination), which would expand the unit cell, increasing its volume and is reported in the literature [3-5]. The Vesta software package [6] was used to generate the 3D image visualization of the NNCT unit cell using the refined parameters, and the image is displayed in Figure 8.2. The volume of the TM–O₆ octahedron and Na–O₆ prism in the layered oxide structure were calculated to be around 10.44 Å³ and 13.45 Å³, respectively. In NNMC and NNMCT, however, the TM–O₆ octahedra showed a lower volume (8.53 $Å^3$ and ~ 8.45 Å³, respectively), while Na–O₆ prism had a higher volume (13.83 Å³ and 14.09 Å³, respectively). Consequently, the area of the rectangular face of Na- $O_6(10.47 \text{ Å}^2)$ in NNCT was about 10-11% lower than the other samples. This face forms one of the primary bottlenecks for the Na-ion conduction through LOs. The lower area of this plane in NNCT indicates the possibility of lower Na-ion conduction that could limit its rate performance. Also, contrary to NNCM, the absence of superlattice peaks in NNCT at ~ 27.2° and 28.3° in the XRD patterns caused by Na-ion vacancy ordering shows a highly disordered Na-ion structure. Naion vacancy ordering is a known phenomenon that induces various structural transformations of the cathode during cycling, severely limiting its cyclability [7-9]. The absence of Na-ion vacancy ordering in NNCT could enhance the structural stability of the NNCT unit cell during cycling, leading to better cyclic stability and Na-ion conduction through the material.



Figure 8.2. Crystal structure visualization of P2-type NNCT.

Figure 8.3(a) shows the cross-sectional SEM image of the NNCT fractured pellet. The SEM micrograph of the powered sample (calcinated at 950 °C) is presented in Figure 8.3(b). The image of the powder sample shows particles with irregularly shaped polyhedra, possibly formed due to the agglomeration of individual particles. This is in sharp contrast to the hexagonal plates observed in NNMC and NNMCT samples, where an increase in the area of the ($\overline{1}00$) ($0\overline{1}0$), ($0\overline{1}0$) ($\overline{1}00$) was observed with an increase in Ti concentration, which was instrumental in improving the rate performance of the parent NNMC cathode sample. However, the elemental maps of the sample (Figure 8.3(b1- b5)) do not show any segregation of the constituent elements in the material. The SEM micrograph showing the cross-sectional of the sintered pellet indicates tightly packed and randomly oriented particles. The relative density of the pellet was estimated to be around 90 ± 2 %.


Figure 8.3. SEM micrographs of the NNCT (a) fractured pellet sintered at 950 °C(b) powder sample. (b1) - (b5) Elemental maps of NNCT showing the distribution of its constituent elements.

XPS was used to ascertain the oxidation states of the transition metal elements in the sample, and the spectra obtained for Cu 2p, Ni 2p, and Ti 2p are depicted in Figure 8.4. The Ni2p spectrum shows four peaks that belong to Ni $2p_{3/2}$ (~ 855 eV) and Ni $2p_{1/2}$ (~ 872 eV) and their respective satellites, confirming the presence of Ni²⁺ [10-12]. The Cu 2p spectrum shows 2 peaks at ~ 933 eV (characteristic of Cu $2p_{3/2}$) and ~ 953 eV (attributed to Cu $2p_{1/2}$), indicating Cu²⁺ in the materials [10-12]. The characteristic peaks at 458 and 464 eV in the Ti 2p spectrum are attributed to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ and confirming that Ti maintains a 4+ oxidation state in the material [11, 12].



Figure 8.4. XPS spectra of as-prepared Na_{0.7}Ni_{0.20}Cu_{0.15}Ti_{0.65}O₂ sample.

8.2. Electrical characteristics

To investigate the transport phenomenon through the material, Complex Impedance Spectroscopy was performed on the pelletized sample sintered at 950 °C for 12 h. Figure 8.5(a) shows the Nyquist plots depicting the impedance data at different temperatures. A temperature-independent tail component observed at low frequencies in the Nyquist plot suggests ion-blocking by the silver electrodes and indicates substantial ionic conduction through the material. A decreasing trend of the overall resistance of the sample with an increase in temperature is also evident in the figure. Equivalent circuit modelling (Figure 8.5(a) insert) was used to analyze the Nyquist plot and estimate the conductivity of the sample. The room temperature conductivity of the NNCT sample was estimated to be about 1.37×10^{-7} S cm⁻¹. In comparison, NNCM showed a room temperature conductivity of ~ 4.03 × 10⁻⁶ S cm⁻¹ , and it increased to 3.07×10^{-5} S cm⁻¹ in the Ti substituted NNCMT sample, both of which are considerably higher than that of the NNCT. Linear fitting of temperature-dependent conductivity values using the Arrhenius equation (equation 7.1) was used to estimate the activation energy (E_A) of the overall sample (Figure 8.5 (b)).

$$\sigma(T) = \sigma_o \, e^{-(\frac{E_A}{kT})} \tag{7.1}$$

Here σ_0 is the pre-exponential factor, *k* is Boltzmann's constant, and *T* is the absolute temperature. The activation energy of the sample was calculated to be about 0.41 ± 0.02 eV, which is about twice the value reported for the manganese analog Na_{0.7}Ni_{0.2}Cu_{0.1}Mn_{0.65}O₂ sample [1]. This suggests poor ion conduction dynamics of the NNCT cathode, resulting from the lower area of the conduction bottlenecks and the irregular particle morphology observed earlier. The diffusion coefficient of the NNCT sample calculated using the Nernst Einstein relation at 310 K (equation 7.2) was around 1.94×10^{-16} m² s⁻¹.

$$\mathbf{D} = \frac{kT}{Nq^2} \ \sigma_{DC} \tag{7.2}$$

N is the number density of charge carriers per unit volume of the unit cell, and *q* is the elementary charge. Even though the diffusion coefficient for NNCT is lower than that of NNCM and NNCMT cathodes, it is comparable to other cathodes such as Na_{0.67}Mn_{0.65}Ni_{0.2}Co_{0.15}O₂, Na_{0.67}Mn_{0.55}Ni_{0.25}Li_{0.2}O₂, Na_{2/3}Ni_{1/3}Mn_{5/9}Al_{1/9}O₂, etc. reported in the literature [13-15]. However, the chronoamperometry data (Figure 8.5(c)) of the NNCT put the electron transference number (*t_e*) of the sample at 0.004 and Na⁺ transference number (*t_{Na}*) at 0.996, which suggests significantly low electronic conduction through the material. This is typically observed in materials containing d⁰ ions, such as Ti⁴⁺, as the ion is relatively stable in the current configuration and does not donate its electrons to the conduction band, drastically bringing down the electronic conduction. Poor electronic conduction coupled with lower ionic conductivity would adversely affect the rate performance of the NNCT cathode during cycling.



Figure 8.5. Electrical properties of NNCT. (a) Nyquist plots at different temperatures and their fitted curves modeled using the equivalent circuit shown as an inset. (b) Arrhenius plot showing temperature dependence of electrical conductivity. (c) Chronoamperometry curve of NNCT under an applied potential of 1 V.

8.3. Electrochemical characteristics

Figure 8.6(a) depicts the cyclic voltammetry curves of the NNCT cathode between 2 V and 4.2 V at a scan rate of 0.1 mV s⁻¹. The curve portrays a broad peak at 3.7 V, attributed to the Ni^{2+/4+} and Cu^{2+/3+} redox couples.[3, 16] On the other hand, the NNCT and NNCMT samples showed 2 distinct peaks for Ni^{2+/4+} and Cu^{2+/3+} reactions between 3.3 V and 4.0 V, along with some vacancy ordering peaks, particularly in NNCM. This could be due to a comparatively higher disordering in the NNCT structure that inhibits Na-vacancy ordering. Ti maintains a 4+ oxidation state within the voltage range and acts like pillar ions supporting the structure during the extraction/ intercalation of Na-ions. The dQ/dV vs. voltage graphs are presented





Figure 8.6. (a) Cyclic voltammogram of NNCT at a scan rate of 0.1 mV s⁻¹ (b)dQ/dV vs voltage plots of NNCT at different C rates.

Figure 8.7(a) shows the galvanostatic charge/discharge curves of NNCT at different C rates between 2 V and 4.2 V. The curve depicts a higher slope between 2 - 3 V compared to 3 - 4.2 V. This is due to the unavailability of the redox process in the lower voltage regions compared to the higher voltage ranges where Ni^{2+/4+} and Cu^{2+/3+} redox processes become active. At a comparatively lower discharge rate of 0.1C, the NNCT cathode shows a specific capacity of 83 mAh g⁻¹, which drops to 54 mAh g⁻¹ and 42 mAh g⁻¹ at 0.5C and 1C, respectively. The rate performance of the cathode at different discharge rates between 0.1C and 2C is displayed in Figure 8.7(b). In contrast, the NNMC cathode showed a specific capacity of 99 mAhg⁻¹ and 64 mAh g⁻¹ at 0.1C and 1C discharge rates, which was increased to 127 mAh g⁻¹ and 96 mAh g⁻¹ upon Ti substitution in the NNMCT sample. Even at a discharge rate of 2C, a specific capacity of 87 mAh g⁻¹ could be obtained from the latter. The comparatively high reduction in specific capacity with an increase in discharge rate

in the NNCT cathode sample can be attributed to the unfavorable structural properties, lower electrical conductivity, and t_e values discussed in the electrical properties section. In terms of cyclability, however, the cathode shows much better performance, with 96% of the initial capacity retained after 700 cycles at a charge/discharge rate of 0.5C with a median discharge voltage ~ 3.2 V. (Figure 8.7(c)). This points to a remarkable resilience of the NNTC unit cell to distortions induced by repeated extraction/intercalation of Na ions during each cycle.



Figure 8.7. (a) Galvanometric charge-discharge curves. (b) Rate performance of NNCT cathode at different discharge rates. (c) Cyclic performance of NNCT at 0.5C for 700 cycles.

To investigate the changes in structural parameters during cycling, ex-situ XRD was performed on the cathodes at different states-of-charge (Figure 8.8(a)). The data show an expansion of the unit cell with charging as illustrated by the shifting of the (002) and (004) peaks towards lower diffraction angles (Figure 8.8(a1, a2)) [17-19]. This trend was also observed in the NNCM and NNCMT cathodes due to the increased repulsion between oxygen layers in the LO structure after Na ions are extracted. These peaks return to their original positions upon discharging, implying the reversibility of the structural changes occurring during GCD cycling. The moisture sensitivity of the sample was tested by storing the cathode powder in DI water for 1 week. The XRD patterns of the dried water-treated samples showed no changes compared to that of the untreated sample (Figure 8.8(b)). This has allowed the use of CMC as the binder and DI water as the solvent. In addition, the excellent

moisture stability of the cathode also meant that the as-synthesized sample could be stored in ambient conditions. Both these factors would considerably reduce the fabrication cost of cells.

Although the NNCT cathode shows excellent cycle stability, a property highly sought after in cathodes, its specific capacity at 0.1C is only about 56% of its theoretical capacity (146 mAh g⁻¹). This could be due to its unfavorable structural and electrical properties discussed above, and this material could show considerably higher specific capacities at lower discharge rates (0.05C and lower). However, keeping the real-world applications in mind, the specific capacity of NNCT should be further improved at relevant C-rates (0.2C to 2C). As lower electronic and ionic conductivities seem to be the limiting factor for observed specific capacities, techniques such as in-situ carbon coating, tailoring the particle morphology of NNCT particles, etc., could be explored to address these issues. Nevertheless, excellent cycle stability makes NNCT an attractive candidate for Na-ion batteries in stationary storage applications.





8.4. References

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9.1. Conclusions

This investigation into the Na_{3/4}(Mn-Al-Ni)O₂ pseudo-ternary system makes a significant contribution to the development of high-performance sodium-ion battery (SIB) cathodes by integrating structural and electrochemical optimization strategies. The study systematically examined the interplay between phase composition, oxidation states, and structural properties, offering novel insights into their impact on battery performance and presenting innovative approaches to cathode design.

A key finding is the superior performance of biphasic P3/P2 cathodes, which outperformed monophasic counterparts in cyclic stability, rate capability, and energy efficiency. For instance, the biphasic composition $Na_{\frac{3}{4}}Mn_{\frac{4.5}{8}}Al_{\frac{1}{8}}Ni_{\frac{2.5}{8}}O_2$ retained 87% of its initial capacity after 500 cycles at 1C within a 2.0–4.0 V voltage window while maintaining 88% energy efficiency. This biphasic configuration effectively mitigated structural stress and volume expansion during cycling, demonstrating the advantages of phase coexistence.

The "zero Mn³⁺ line" concept emerged as a pivotal innovation, confining Mn to the Mn⁴⁺ oxidation state while varying Mn, Al, and Ni concentrations to enhance cathode stability and performance. This approach expands the utility of pseudo-ternary phase diagrams by incorporating oxidation state control, allowing for precise tuning of cathode properties. Al³⁺ substitution played a critical role in stabilizing P3 and P2 phases, suppressing detrimental P3 \rightarrow O3 transitions, and improving rate performance by enlarging the Na⁺ conduction bottleneck area. For example, the biphasic P3/P2 Na_{0.75}Mn_{0.75}Al_{0.25}O₂ cathode retained 70% of its initial capacity over 300 cycles at 1C in the 1.5–4.0 V range, which improved to ~80% when cycled in the 2.0–4.0 V range, highlighting the dual benefits of Al³⁺ doping in capacity retention and cycle longevity.

The study also extended its focus to high-Na-content cathodes, such as $NaMn_{\frac{4.5}{8}}Al_{\frac{1}{8}}Ni_{\frac{2.5}{8}}O_2$, which demonstrated stable performance while avoiding O3 phase formation. A monophasic P2 cathode derived from this composition delivered 123 mAh g⁻¹ at 0.1C and retained 90% of its capacity after 200 cycles at 0.2C, showcasing its scalability for commercial applications.

The investigation into Na_{0.7}Ni_{0.2}Cu_{0.15}Ti_{0.65}O₂ (NNCT) revealed its potential for stationary energy storage. Despite moderate specific capacities (e.g., 83 mAh g⁻¹ at 0.1C), NNCT achieved 96% capacity retention after 700 cycles at 0.5C. Its resistance to moisture facilitates cost-effective, water-based manufacturing, addressing critical challenges in SIB commercialization.

Advanced characterization techniques, such as operando synchrotron XRD, XPS, and EXAFS, provided deep insights into structural and electrochemical mechanisms. These analyses clarified the suppression of phase transitions, the role of Mn³⁺/Mn⁴⁺ redox activity, and the absence of Mn³⁺ in Al-doped compositions, establishing a comprehensive framework for understanding and optimizing cathode materials. The introduction of the "zero Mn³⁺ line" further exemplifies a shift from traditional phase diagram methodologies to a more sophisticated design approach that integrates composition and oxidation state control.

This work establishes a robust foundation for future studies focused on achieving an optimal balance between capacity, stability, and cost-efficiency in SIB cathodes. Developing moisture-stable materials like NNCT also supports sustainable and economically viable manufacturing practices. Overall, this research advances the understanding of SIB cathodes and offers actionable strategies for their practical application. The findings highlight the transformative potential of Al-doped, Mn³⁺ free layered oxides to drive sodium-ion battery innovation, offering competitive and environmentally friendly solutions for both portable and stationary energy storage needs.

9.2. Future scope of work

- Future studies can extend the biphasic approach to other layered oxide systems beyond the Na_{3/4}(Mn-Al-Ni)O₂ pseudo-ternary diagram. This can involve integrating additional transition metals like Cu, Fe, or Ti to explore their synergistic effects on structural stability, energy density, and rate performance. Investigating the role of phase composition beyond the P3/P2 combination, such as incorporating O3-type phases, could further optimize performance metrics.
- The "zero Mn³⁺ line" concept can be extended to design phase diagrams for other sodium-ion cathode systems, emphasizing the controlled oxidation

state of electrochemically active elements. Incorporating this framework into other pseudo-ternary systems (e.g., Mn-Co-Ni or Mn-Fe-Co) can facilitate the development of new compositions with optimized electrochemical and structural properties.

- While this study highlighted the advantages of biphasic P3/P2 cathodes, further operando studies are needed to delve deeper into the mechanisms behind phase interaction during cycling. Advanced techniques such as neutron diffraction and in situ TEM could provide atomic-level insights into the interplay between coexisting phases and their influence on volume changes, stress distribution, and Na⁺ migration pathways.
- Developing moisture-stable cathodes like NNCT highlights the need to adapt water-based manufacturing processes for other cathode materials. Future work should optimize slurry formulations, binder selection, and coating techniques to ensure scalability and cost-effectiveness while maintaining performance.
- Finally, the research should progress from fabricating coin cells to developing pouch cells with higher active cathode material loading, a crucial step toward demonstrating the feasibility and scalability required for commercial applications.