P2-TYPE LAYERED OXIDE CATHODE MATERIALS FOR SODIUM-ION BATTERY

M.Tech. Thesis

By

AKASH KANKANE

DEPARTMENT OF METALLURGY ENGINEERING AND MATERIALS SCIENCE

INDIAN INSTITUTE OF TECHNOLOGY INDORE

JUNE 2022

P2-TYPE LAYERED OXIDE CATHODE MATERIALS FOR SODIUM-ION BATTERY

A THESIS

Submitted in partial fulfillment of the

requirements for the award of the degree

of

Master of Technology

by

AKASH KANKANE

DEPARTMENT OF METALLURGY ENGINEERING AND MATERIALS SCIENCE

INDIAN INSTITUTE OF TECHNOLOGY INDORE

JUNE 2022

INDIAN INSTITUTE OF TECHNOLOGY
INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"P2-type Layered Oxide Cathode Materials for Sodium Ion Battery"** in the partial fulfilment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DEPARTMENT OF METALLURGY ENGINEERING AND MATERIAL SCIENCE, Indian Institute of Technology Indore,** is an authentic record of my own work carried out during the time period from August 2020 to June 2022 under the supervision of **Professor Parasharam M. Shirage,** Department of MEMS, Indian Institute of Technology 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.

23/5/22
Signature of the student with date

(AKASH KANKANE)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

03/06/2022
Signature of the Supervisor of
M.Tech. thesis (with date)

(Prof. Parasharam M. Shirage)

AKASH KANKANE has successfully given his M.Tech. Oral Examination held on 03/06/22.

Signature(s) of Supervisor(s) of M.Tech. thesis

Date: 03/06/2022

Signature of PSPC Member #1

Date: 07-06-2022

Signature of Convener, DPGC

Date:

Signature of PSPC Member #2

Date: 08/6/2022

ACKNOWLEDGEMENTS

First of all, I would like to convey my sincere appreciation to my thesis advisor **Prof. Parasharam M. Shirage** for the constant assistance in my M.Tech. project for offering all facilities and providing me the opportunity to work in a pleasant environment, for his motivation, patience, and vast expertise.

I would take the opportunity to convey my thankfulness to my PSPC members **Dr. Dudekula Altaf Basha** and **Dr. Kiran Bala** for their important suggestions.

I am specifically thankful for the assistance provided by Ms. Sheetal Gupta and Ms. Archana Kanwade and for their useful and positive suggestions throughout the preparation and progress of this research work. I would like to convey my very great gratitude to Mr. Subhash Yadav and Dr. B Venkata Reddy for their enthusiasm to give their time so generously and for assisting me with everything.

I would also like to add my thanks to all AFMRG lab colleagues. I am thankful to all members of AFMRG lab for their continuous motivation and entertaining conversations. A special note of thanks to Abhishek Shrivastava, Manish Tiwari, and Bhaskar Singh Chouhan for their love and support during project work.

In the end, I must convey my very sincere thankfulness to my parents for offering me unfailing assistance and constant inspiration during my years of study and through the process of researching and writing this thesis.

Dedicated to my Family,

Friends, and

all my teachers

Abstract

Sodium-ion batteries (SIBs) have collected major interest recently and are believed a possible replacement for lithium-ion batteries (LIBs). SIBs have a price-benefit over LIBs for two major causes. Sodium, not like Lithium, does not make alloy with Aluminium in the region of anodic potential. Therefore, anodic current collector copper is utilized as the in LIBs, can be changed with the less expensive Aluminium for SIBs. Another reason is that reserves of sodium are more extensive and plentiful than Li-based raw materials. One of the encouraging groups for cathode materials is layered metal oxides, Na_xTMO_2 (TM = transition metal). In this group, there are various dominant subclasses, which are specified based on the coordination of the sodium ions between the layers of TM and oxygen. Following the terminology proposed by Delmas et al., in P-phase materials, sodium ions (Na^+) is coordinated by oxygen in prismatic way, however in O-phase materials, the coordination is octahedral manner. Variations in filling, i.e., layers shifting comprised of edge-sharing MO6-octahedra opposed to one another, are shown by digits. In a P2-structure, two layers of MO6-octahedra need to be represented in the unit cell to precisely explain the structure. The earliest experiments on insertion procedures into these layered oxides have been performed in the 1980s. Newly, especially P2-phase materials have obtained significant attention since their good capacity and cycling stability. Transition metal oxides are examined in terms of their opportunity as cathode materials for SIBs. The most recent advancement in research in the several structures of the layered oxide cathode material in SIBs are charted. Furthermore, their cost, concerns and electrochemical performance estimated in detail along with a brief viewpoint on prospects. P2 phase $Na_{0.67}Ni_{0.15}Fe_{0.15}Mn_{0.7}O_2$ layered oxide synthesized by sol gel methods and have shown well grown morphology at 850 ^{o}C and phase have been confirmed by X-ray diffraction. Electrochemical performance of the as prepared material has been measured by Autolab instrument in three electrode system and have shown specific capacity of 353.5 mAh/g at 0.002 V/s scan rate and 52.17 mAh/g at 0.1 V/s from cyclic voltammetry. From GCD it shows 289.95 mAh/g at 1 mA current and 139.13 mAh/g at 3 mA current in 1.38 V voltage range. The aluminium doped layered oxide material have performed well in electrochemical analysis by three electrode system. The different phase of layered transition-metal oxides ($Na_x\mathit{TM}O_2$; *TM*= Mn, Ti, Co, Ni, Fe, Al, V, Cr, and a grouping of various elements) show good capacity, structural stability, Na^+ ion conductivity, and cyclic number, which make them a first choice for the cathode materials of SIBs. In this work, the structural evolution, and recent improvement and certain challenges of $Na_x\mathit{TM}O_2$ cathodes for SIBs are summarized. This work proposes to give a reference for the evolution of many layered transition-metal oxide (LTMOs) cathode materials for SIBs, mainly for their promising commercialization.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS **i**

ABSTRACT **iii-iv**

TABLE OF CONTENT **v-vi**

LIST OF PUBLICATIONS **vii-viii**

LIST OF FIGURES **ix-x**

LIST OF TABLES **xi**

ABBREVIATIONS **xii**

Chapter 1: A brief introduction **1-13**

1.1 Energy storage devices

1.2 Why do we need batteries?

1.3 Working of battery

1.4 Sodium-Ion Battery: A replacement to Lithium-Ion Battery

1.5 Working of SIBs

Chapter 2: Review of past work and problem formulation **14-25**

2.1 Literature Survey

2.2 Transition metal layered oxide

2.3 Motivation of the work

2.4 Objectives

Chapter 3: Experimental Techniques **26-33**

3.1. Synthesis of cathode material
3.2 Preparation of electrode
3.3 Physicochemical characterization
3.4 Electrochemical performance analysis

Chapter 4: Results and Discussion **34-41**

4.1 XRD Analysis for structural characterization
4.2 FESEM Analysis for morphological characterization
4.4 Electrochemical analysis

Chapter 5: Summary and Scope of Future Work **42-43**

REFERENCES

LIST OF PUBLICATIONS

1. Journal: RSC Sustainable energy and fuels

Title: "Phosphate based cathode materials to boost the electrochemical performance of sodium-ion battery"

Authors: Kanwade, Archana; Gupta, Sheetal; Kankane, Akash; Srivastava, Abhishek; Shirage, Parasharam

Manuscript Status: Published https://doi.org/10.1039/D2SE00475E

2. Journal: Batteries and supercapacitors

Title: "Pseudocapacitive performance of P2 type $Na_{0.67}Fe_{0.15}Cu_{0.15}Mn_{0.7}O_2$ layered oxide material"

Authors: Kankane, Akash; Gupta, Sheetal; Kanwade, Archana; Shirage, Parasharam

Manuscript Status: Submitted

3. Journal: Electroanalytical Chemistry

Title: "A review on O3 and P2 type layered oxide materials for flourishing sodium-ion battery"

Authors: Gupta, Sheetal; Kankane, Akash; Kanwade, Archana; Tiwari, Manish Kumar; Srivastava, Abhishek; Yadav, Subhash Chand; Shirage, Parasharam

Manuscript Status: Submitted

4. Journal: Journal of Materials Chemistry A

Title: "Synthesis Evolution and Characterization of Transition Metal oxides for Indispensable Na-ion Batteries"

Authors: Kankane, Akash; Gupta, Sheetal; Kanwade, Archana; Yadav, Subhash Chand; Shirage, Parasharam

Manuscript Status: Submitted

LIST OF FIGURES

Figure 1.1 Estimated number of devices and related energy demand for 2016–2050.

Figure 1.2 Schematic showing the working principle of the Sodium-ion battery.

Figure 1.3 Charge storage and transfer mechanism in (a) Battery (b) Pseudocapacitor (c) EDLC.

Figure 1.4 Earth crust elements abundance comparison.

Figure 1.5 Comparison for energy density of the various battery prototype.

Figure 1.6 Schematic showing sodium ion battery cathode, anode, and electrolyte.

Figure 2.1 A comparison of different cathode materials for SIBs.

Figure 2.2 Categorization of Na−M−O layered materials with sheets of edge-shared MO6 octahedral and phase transition processes generated by sodium removal.

Figure 2.3 Representation of typical structural growth throughout charge/discharge of O3-phase and P2-phase layered oxides.

Figure 2.4 The number of scientific publications on Na-ion battery and layered cathodes in each year from 2000 to 2021. (Data are encapsulated from Scopus).

Figure 2.5 Total and Annual lithium utilization in 2015–2050 under the belief that only the requirement from electric vehicles will grow, although other uses stay constant.

Figure 3.1 Experimental method used to synthesize P2 type layered oxide cathode material for sodium ion battery.

Figure 3.2 Electrode slurry preparation process.

Figure 3.3 Schematic of X-ray diffraction instrumentation.

Figure 3.4 Working principal X-ray Diffraction (Braggs Law).

Figure 3.5 Schematic showing working of Scanning Electron Microscopy.

Figure 3.6 A Computer-controlled potentiostat/galvanostat with a standard three-electrode system connected to an electrochemical cell.

Figure 4.1 Refined X-ray diffraction of the $Na_{0.67}Ni_{0.15}Fe_{0.15}Mn_{0.7}O_2$ at 850 °C.

Figure 4.2 FESEM images of $Na_{0.67}Ni_{0.15}Fe_{0.15}Mn_{0.7}O_2$ Synthesized at different temperatures.

Figure 4.3 Cyclic voltammetry plot of P2-NFM at different scan rates in 2 M KOH solution with 1 mg active mass loading in voltage range 1.38 V.

Figure 4.4 Specific capacity vs scan rate plot for NFM.

Figure 4.5 GCD plot of NFM at different current densities from -1V to 0.38.

Figure 4.6 Specific capacity vs current density plot for NFM.

Figure 4.7 Nyquist graph of NFM and inset displays the enlarged image of the low-frequency zone.

LIST OF TABLES

Table 1.1: Different energy storage technology and their respective implementation methods.

Table 2.1: Benefits and drawbacks of different types of cathode materials used in sodium-ion batteries.

Table 2.2. A conclusion of the basic characteristics, Na content, and benefits/drawbacks of layered oxide materials in sodium-ion batteries.

Table 2.3. Electrochemical performance of various P2 and O3 phase layered TMOs.

ABBREVIATION

ESSs	Energy storage systems
EVs	Electrical vehicles
LIBs	Lithium-Ion Batteries
SIBs	Sodium-Ion Batteries
GCD	Galvanometric charge-discharge
CV	Cyclic voltammetry
EIS	Electrochemical impedance spectroscopy
EDLC	Electrode double-layer capacitor
ICE	Internal combustion engine
TMOs	Transition metal oxides
XRD	X-ray Diffraction
FESEM	Field emission scanning electron microscopy
PBAs	Prussian Blue Analogs

Chapter 1

A brief introduction

1.1 Energy storage devices

Overlooking the problem from a rapid increment in global energy expenditure throughout the last two decades, it is required to develop energy storage technology with superior performance and sustainability[1]. As energy appears in various forms like heat, radiation, electricity, chemistry, and gravity, energy storage methods that involve transforming energy from forms that are challenging to collect are indispensable for the economic usage of energy. Due to the global crisis and the adverse awareness of nuclear energy production, energy storage systems (ESSs) and electric vehicles (EVs) have developed as potential ecologically friendly choices and extended the area of utilization of rechargeable batteries from minor devices to grid-size apparatus[2]. Though, huge services need a bulky source of power capable of managing MWh or hundreds of kWh of energy.

Thermal storage (latent heat storage, chemical heat storage, sensible heat storage *etc*.), petroleum derivatives/fossil fuel (oil, coal, natural gases, and so on), mechanical storage (flywheel energy storage, hydropower siphon stockpiling, and so on), electromagnetic/electrical capacity (electrical twofold layer capacitor, dielectric capacitor, superconducting capacity gadgets), electrochemical energy storage (batteries, super-capacitors, chemical storage (hydrated salts, biofuels, hydrogen stockpiling, and so on)[3].

Table 1.1: Different energy storage technology and their respective implementation methods.

Energy storage technology	**Method/medium of implementation**

Biological storage	Starch, Glycogen.
Chemical storage	Hydrogen storage, Hydrated salts, Biofuels, Power to gas.
Fossil fuels	Oil, Coal, Natural gas
Electromagnetic/Electrical storage	Electrical double layer capacitor, Dielectric capacitor, Superconducting magnetic energy storage,
Mechanical storage	Fly wheel energy storage, hydraulic accumulator, compressed air energy storage, pumped storage of hydropower
Electrochemical energy storage	Faradaic super-capacitor, Flow battery, rechargeable battery, primary battery
Thermal storage	Latent and sensible heat storage, Chemical heat storage.

1.2 Why we need batteries?

Over the past five decades, the implementation of small-sized sealed batteries in the domestic (consumer batteries) have phenomenally expanded because of the broad range of energy production from nanowatt-hour to megawatt-hour, batteries have obtained a wide application in many industries[4]. Figure 1.1 shows the energy demand for estimated number of devices working on different sizes of batteries in the upcoming years.

Nowadays, batteries are available in various sizes. The scale extends from tiny button cells of energy all the way to load leveling batteries of very high energy content. For transportation and portable applications especially, a fuel cell or battery should be able to deliver (and store) the maximum energy at the desired power level (rate) from a device that has the smallest achievable volume and weight[5].

Nowadays, rechargeable, or small primary batteries are used in an immense number of applications. Some examples are as follows,

1. Household: Clock-radios, telephones, security alarms, portable fluorescent lamps, smoke detectors, torches and lanterns, car central-locking activators and door-chimes.
2. Entertainment: Keyboards, portable radios, televisions, tape recorders, compact disc players, remote controllers for televisions, electronic games and toys, compact disc players.
3. Workshop and garden: Lawnmowers, portable tools (e.g., drills, screwdrivers, sanders), hedge trimmers, portable test meters.
4. Personal health and hygiene: Bathroom scales, toothbrushes, hair trimmers, blood-pressure monitors, heart pacemakers, shavers, hearing aids.
5. Medical: In-hospital rechargeable batteries are used to move medical instruments like ECG monitors with the patient.
6. Logistics and construction: Heavy-duty batteries supply power to various automobile devices for ignition and start.
7. Military and submarine Operation: Radios used for communication; infrared goggles are powered by batteries.

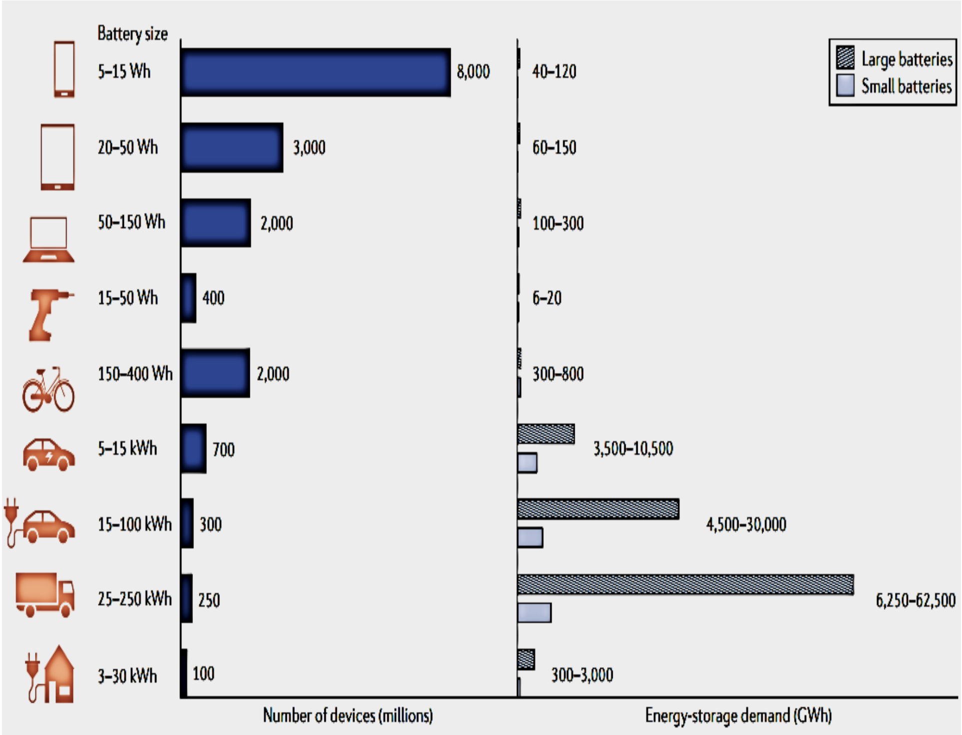

Figure 1.1 Estimated number of devices and related energy demand for 2016–2050[6].

1.3 Working of battery

A battery is an electrochemical device that have electrochemical oxidation-reduction reaction to transforms chemical energy contained in active materials directly into electric energy[7]. A cell is the core component of a battery, a single cell of the battery is composed of an electrolyte, a separator, a negative electrode, and a positive electrode[8]. A The electrolyte is an ionic-ally conducting and electronically insulating source that permits the red-ox reaction on both electrodes[9]. The separator enables the liquid electrolyte to penetrate and separates the anode and cathode from contacting each other[10]. Cell functions in two electrochemical ways; charging and discharging mode at the state of discharging, due to the oxidization of anode ions (Li^+/Na^+) releases in the electrolyte. These ions afterward move towards the cathode. In oxidation, electrons move through an electrical path from anode to cathode and attach with ions. These electrons move in an electrical circuit. This outside flow of electrons can be used as an energy source to get electricity for appliances (discharging) and batteries (charging). Figure 1.2 shows the working principal of sodium ion battery. The operation of charging mode is precisely the opposite, and it is also achievable that both discharging and charging processes occur simultaneously. Two charge carriers are serving in the electrochemical cell: ions and electrons. The moving ions transfer towards a particular direction in the electrolyte while the cell is operating the electrons transfer over the outside circuit.

In charging a sodium-ion battery, sodium ions are extracted from the positive electrode (cathode material) and passed by the electrolyte, reached into the negative electrode (anode material)[11]. When the current flow in an external circuit, the battery discharges spontaneously, i.e., on the anode, the oxidation reaction occurs, related to the sodium ions departs from the structure of the negative electrode and reached into the design of the cathode, which is decreased by the flow of electron in the external electrical circuit. According to the basics of chemistry, a reduction is the gain of electrons to an element, oxidation is the extraction of electrons from an element, and redox reaction is the gross result, in which there is a movement of electrons to one element (acceptor of electron, or oxidant) from another (donor of electron, or reductant). The electrode at which reduction happens is named the cathode; the one at which oxidation happens is known as the anode.

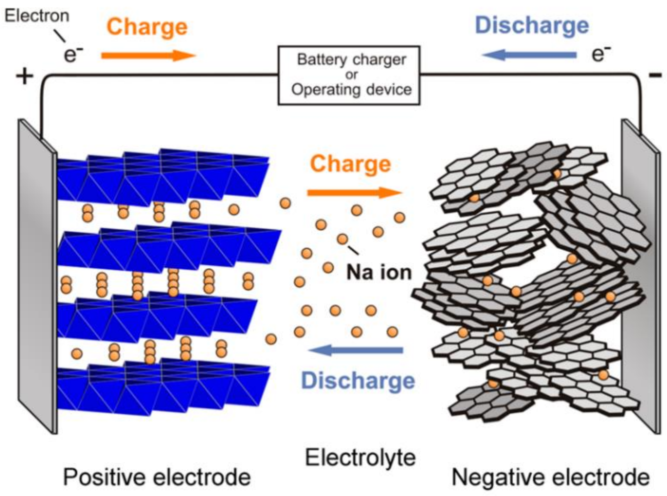

Figure 1.2 Schematic showing the working principle of the Sodium ion battery[12].

Material with constant current GCD plot with clear plateaus and CVs that have sharp, visibly divided reductive and oxidative peaks, should be categorized as battery or a faradaic electrode material. Charge storage in battery electrodes material shows a nonlinear relation, dissimilar to the capacitive charge storage. In sodium ion batteries (SIBs), sodium ion deintercalation/intercalation allows the redox reaction to major part of the electrode material in a chronological method which is diffusion controlled and slow leading to superior energy density[13]. Supercapacitors possess high power density because they have surface-controlled reaction and quicker diffusion compared to batteries. Figure 1.3 shows the charge storage and transfer mechanism of battery, supercapacitors and EDLC.

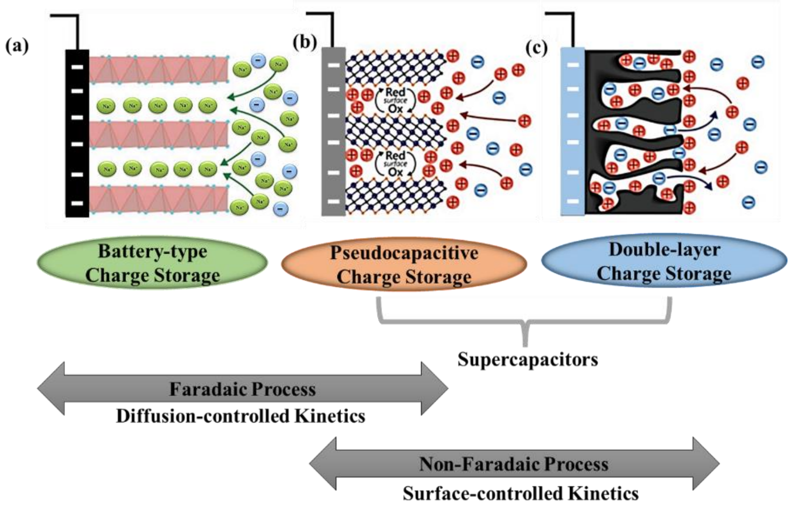

Figure 1.3 Charge storage and transfer mechanism in (a) Battery (b) Pseudocapacitor (c) EDLC.

1.4 Sodium Ion Battery: A replacement to Lithium Ion Battery

SIBs are counted as the future generation electrochemical energy storage system of selection. However, while from the cost perspective and sustainability SIBs are the most promising option to LIBs, further optimization, and modification in terms of electrochemical performance, more often in terms of energy density, are necessary. For the flourishing application of Na-ion batteries, the price per energy unit should be equal to or even less than that of the industrialized Li-ion batteries for the future-generation batteries, and thus material for cathode with a better capacity and cyclic number essentially be formulated. In the most recent five years, research and development on SIBs have gotten dynamic, and quick advancement in materials improvement and performance has been accomplished[14]. LIBs face hurdles related to mining the ores that contains metal and financial concerns attached to material insufficiency and the effect of reprocessing toxic chemical components on environment[15].

Manufacturing high-performance SIBs from harmless and abundant materials in earth (figure 1.4), such as a coalition of sodium, manganese, iron, titanium, and magnesium ores, decreases impact on environment and offers a worldwide opportunity to prepare affordable and safe batteries to both the developed and the developing nations of the world[16]. There is practically no uncertainty that the commercialization of SIBs is conceivable (figure 1.5 shows **c**omparison for energy density for the various battery prototypes). This may require a market specialty where SIBs show explicit benefits over LIBs or another setup kind of batteries. Cost-productive batteries dependent on bountiful components may be such a specialty that may get applicable later the off chance that asset supply chains for LIBs will be tested excessively; obviously, this requires an incorporated methodology[17].

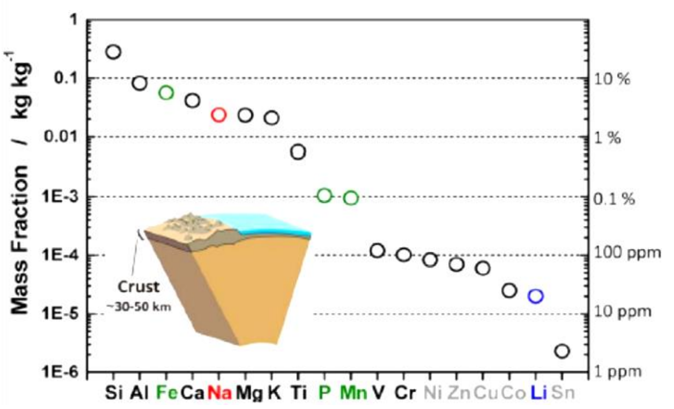

Figure 1.4 Earth crust elements abundance comparison[18].

In a functional cell, the metal oxide and graphite are coated onto foil of aluminum and copper. The foils act as a current collector, and it is easy to take out the negative and positive tabs from the current collectors. An organic salt of lithium is coated onto the separator sheet acts as the electrolyte. The industry of batteries is frequently overlooked at a level of research because it is essential to find new electrode materials with higher energy, to solve the obstacles in cell chemistries at a small scale. Nevertheless, when manufacturing large-scale cells, it is essential to achieve the optimal performance of the cell. This helps reduce obstruction to initial costs, as it is not required to create new facilities yet; the space between laboratory and commercial technologies still requires to be linkup to help material advancement and their utilization in more giant cells[14]. In addition, research organizations frequently need facilities that can be beneficial in large scale production of material. Research and manufacturing can be accelerated by improving links between academia and industry.

Slurries of the electrode in the coin-cell also have normalized formulations; dry powder blending and metro-logy also requires attention. They contain large amounts of carbon and binders to get over the Limitations of material, such as less conductivity. By Decreasing this quantity energy density of cells can be increased at large scales. However, such variation needs specific optimization and testing of slurry for every electrode[19]. After coating, calendaring, and the influence of drying as a technique to improve adherence and electrode density is also not habitually advised inside the research environment. Although processing and material are essential to the performance of the cell, other conditions, such as balancing of electrode, safety prospect, geometry related to a greater number of cycle and long-term storage that are not habitually studied at a small scale as well become essential. SIB technology is less mature, so little research can be done for many of the regions. However, it is better that a considerable lot of these can be straightforwardly moved from LIB exploration, and difficulties can be collectively handled. One of the main factors contributing to this ramp in production is the transition from internal combustion engine (ICE) automobiles to electric vehicles (EVs) from companies like Audi and GM, which will stop producing ICE vehicles in 2026 and 2035 respectively.

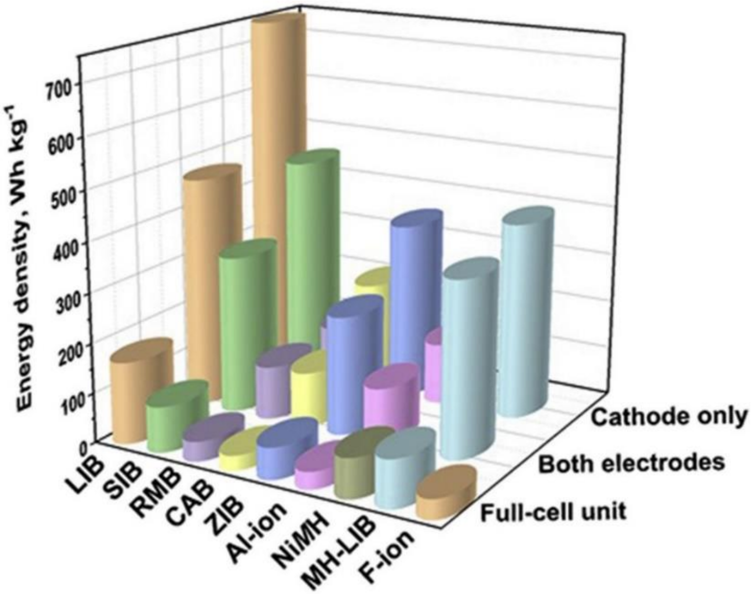

Figure 1.5 Comparison for energy density for the various battery prototypes[20]**.**

Why it is necessary to explore Sodium-Ion Batteries (SIB's)?

There are certain serious Limitations exist with Li-Ion Batteries (LIB) which are as follows:

- **Safety**: Needs protection circuit to keep current and voltage within safe limits, as Li is highly toxic and reactive[21].
- **Aging effect:** LIB's have aging effect, even if not in use storage in a cool place, 40% charge decreasesowing to self-discharge[22].
- **Costly to manufacture:** About 40 percent higher in price than nickel-cadmium as extraprotective layer is needed to fabricate the safe LIB's[23].
- **Lower operating temperature:** Generally operating temperature of LIBs are from 5 ºC to 45 ºC, while charging the temperature goes up and hence explosion is most common in

LIB’s[24].

Even though LIBs are good in performance, due to the above limitations, restricts the progress and utilization. To overcome these problems, we need an alternative to Li ions, and Na is next to Li hence research on SIB’s in needed without compromising the performance. In secondary battery technologies, when sodium replaces lithium, it requires completely new anode materials. The most remarkably suitable anode material, graphite in LIBs, is incapable of intercalating sodium metal ions between its nanosheets. It has been hard carbon or no graphitizable carbon, which can intercalate sodium ions[25].

1.5 Working of SIBs

In charging a sodium-ion battery, sodium ions are removed from the positive electrode (cathode material) and passed by the electrolyte, reached into the negative electrode (anode material). When the current flow in an external circuit, the battery discharges spontaneously, i.e., on the anode, the oxidation reaction occurs, related to the sodium ions departs from the structure of the negative electrode and reached into the design of the cathode, which is decreased by the flow of electron in the external electrical circuit. Further discovery regarding the energy density of sodium-ion batteries depends on the improvement of high-performance material for electrodes. SIBs have been studied again to provide a low-cost option that is less prone to risk supply and resources[26]. Theoretically, replacing lithium with sodium in a battery appears straight at first, but uncertain disruptions are often found in practical applications[27]. A rechargeable Na^+ ion cell consists of two materials capable of Na^+ ion insertion called negative electrode (cathode) and positive electrode (anode). A schematic representation of the operating principle of sodium ion battery is shown in figure 1.6. The electrolyte (pure ionic conductor) electronically isolates these electrodes. The stored chemical energy converts into electrical energy, and the performance of the entire assembly changes with varying the shape, state, composition, alignment of these components.

Figure 1.6 Schematic showing sodium ion battery cathode, anode, and electrolyte[27].

Cell functions in two electrochemical ways; charging and discharging mode at the state of discharging, due to the oxidization of anode Na^+ releases in the electrolyte. These ions afterward move towards the cathode. In oxidation, electrons move through an electrical path from anode to cathode and attach with Na^+. These electrons move in an electrical circuit. This outside flow of electrons can be used as an energy source to get electricity for appliances (discharging) and batteries (charging). The operation of charging mode is precisely the opposite, and it is also achievable that both discharging and charging processes occur simultaneously.

The overall chemical reaction for charging and discharging of $NaTMO_2$ is shown below,

$$TM = \text{Transition metal}$$

$$NaTMO_2 \underset{Discharge}{\overset{Charge}{\rightleftarrows}} Na_{1-x}TMO_2 + xNa^+ + xe^-$$

$$C + xNa^+ + xe^- \underset{Discharge}{\overset{Charge}{\rightleftarrows}} Na_xC$$

$$NaTMO_2 + C \underset{Discharge}{\overset{Charge}{\rightleftarrows}} Na_xC + Na_{1-x}TMO_2$$

1.6 Organization of Thesis

This thesis is structured in the following way:

1. Chapter 1 discusses about the introduction of energy storage devices, batteries and working of sodium ion batteries.
2. Chapter 2 discusses about the different types of cathode materials and layered oxides cathode for sodium ion battery and the motivation and objectives of the work.
3. In Chapter 3, experimental techniques have been discussing like synthesis of layered oxide, preparation of electrode and the characterization of material.
4. Chapter 4 discussed about the result obtained from different characterization methods of the prepared layered oxide material.
5. Chapter 5 provides the summery of the work done during this research and talks about the future scope.

Chapter 2

Review of past work and problem formulation

2.1 Literature Survey

In secondary battery technologies, when sodium replaces lithium, it requires completely new anode materials. The most remarkably suitable anode material, graphite in Li-ion batteries, is incapable of intercalating sodium metal ions between its nanosheets. It has been hard carbon or no graphitizable carbon, which can intercalate sodium ions[28]. Various cathode materials have been suggested to construct SIBs with high power/energy density, great energy conversion efficiency and a greater number of cycles[6]. table 2.1 shows the benefits and drawbacks of various types of cathode materials for SIBs. P2-type manganese-based oxides, which holds advantages of high energy density, improved reaction kinetics, low-price and eco-friendly, has been largely considered[29]. Though, it's still difficult to obtain an efficient approach to defeat the trouble of inadequate cycling stability, which triggered by degradation of structure caused from Jahn-Teller effect of Mn^{3+}[30]. Enhanced rate capability of SIBs for renewable energy also required for practical use. Furthermore, the air stability is also unsatisfactory for storage of materials, shipping and battery production due to the most of P2 materials are hygroscopic[31]. Figure 2.1 shown the advantages of various cathode materials used for SIBs. Inspired by the distinctive electrochemical performance of various materials with diverse crystal structure, hybrid type cathode was suggested to combine the benefits and overcome the drawbacks of collaborative component[32]. The analysis of P2/O3 composite cathode verify that the hybrid cathode provided improved electrochemical performance that the pure substance. Additionally, partial replacement of Mn with other cations (Al, Zn, Co, Mg, Li, etc.) is an efficient approach to report the related Jahn-Teller effect and increase the electrochemical properties of materials to some amount[33].

Table 2.1: Benefits and drawbacks of different types of cathode materials used in sodium ion battery.

Cathode Material	Benefits	Drawbacks
Prussian Blue Analogs[34]	Three- dimensional open structure, Mild and facile preparation method, Abundant interstitial sites, Strong structure stability.	Water impedes performance, Numerous vacancies / Coordination
Organic Compounds[35]	Stable redox potential, Excellent flexibility, Abundant reserve.	Rapid dissolution, Slow kinetics
Polyanionic Compounds[36]	Fast Na^+ diffusion kinetics, Prominent cycling stability, Strong structure stability, High energy density, Open 3D framework.	Poor electronic conductivity, Low specific capacity.
Transition Metal Oxide[37]	High theoretical capacity, Faster diffusion of Na^+ ions, Reasonable redox potential Low cost, Scalable, Well stability crystal structure.	Hygroscopic nature, Low reaction kinetics, Multiple phase formation, Complex cycling profile.

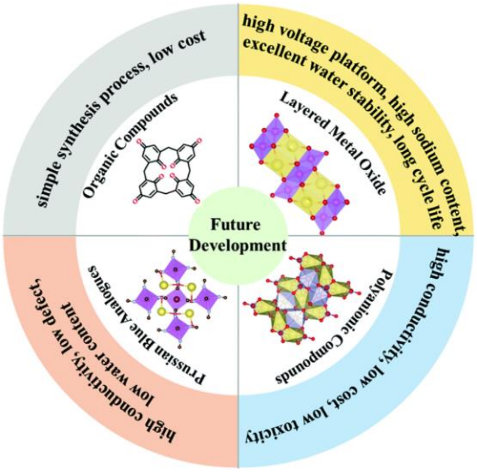

Figure 2.1 A comparison of different cathode materials for SIBs[38].

2.1.1 Transition metal layered oxide

Various cathode materials have been suggested to construct SIBs with high power/energy density, great energy conversion efficiency and a greater number of cycles. Amongst cathode materials for SIBs, layer structured Na_xTMO_2 (TM = Ni, Co, Mn, Fe, *etc*.) composites are favorable due to their long cycle lives and large energy densities. Comparable to the cathode materials of LIBs, the layered configuration of these cathode materials contains edge-sharing $MO6$ octahedral packing along with the c-axis and Na ions inserted in the middle of the $MO2$ layers[39].

Different polymorphs are feasible for a layered oxide (Na_xTMO_2) compound dependent on the crystal structure. TMOs usually show high reversible capacities. Compact structure makes them well suitable for purposes for which a superior volumetric density is necessary. Transition metal-based oxide with O3 and P2 type structure with the chemical formula of $Na_x\boldsymbol{TM}O_2$ (here, $\boldsymbol{TM}$ = Mg, Cu, Zn, Fe, Ni, Co, or sequence of several elements.), are being largely utilized for industrial purposes and are plentiful in nature. Layered sodium oxide materials can be categorized based on the position of Na^+ ions. The terminology for these materials is as follows: P and O related to Na’s trigonal and octahedral coordination, and the number 3 or 2 indicates to the number of repeating layers of transition metal in the unit cell. For example, in O3, it’s ABCABC, and in P2, it’s ABBA[40]. Categorization of $Na-M-O$ layered materials with sheets of edge-shared MO6 octahedral and phase change processes generated by sodium removal is shown in figure 2.2**.** Table 2.2 is a conclusion of the basic characteristics, Na content, and benefits/drawbacks of layered oxide materials in SIBs.

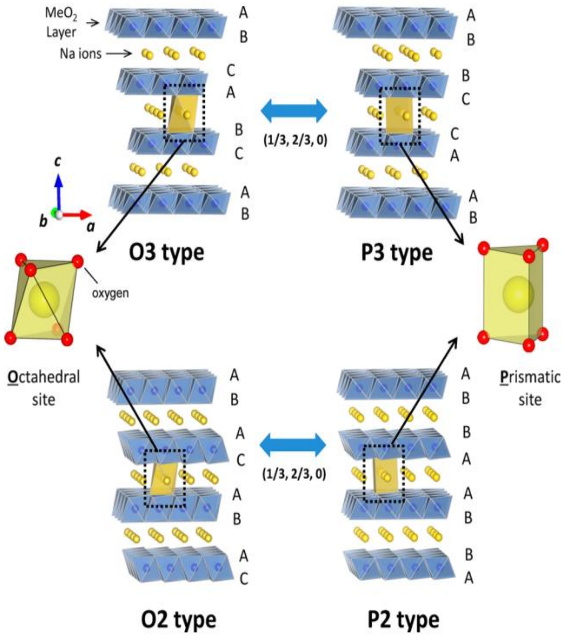

Figure 2.2 Categorization of Na−*M*−O materials with layers of edge-shared MO6 octahedral and phase change processes generated by sodium removal[18].

Generally, O3-type materials have more Na content than P2-phase materials. Layered P2-type compounds have exhibited increased electrochemical properties as, in general, they experience less phase changes when intercalating/deintercalating Na^+ ions than O3-type compounds[41]. For the P2 phase, it is much easier to retains its initial structure, and at the time of the sodium intercalation process. The electrochemical findings indicate that the P2 phase shows better cycling stability and rate capability. P2-based systems can meet the best power performance due to the specific sodium-ion surroundings that permit facile ionic mobility over rectangle-shaped faces between neighbouring trigonal prismatic environments[42].

P2 type phase with mixed transition metal elements allows reversible removal of more Na ion without any deformation in structure. More significantly, the larger inter-slab space offers a short diffusion barrier, which encourages quick diffusion of Na-ions in the P2 type phase[43]. Representation of typical structural growth throughout charge/discharge of O3-phase and P2-phase layered oxides shown in figure 2.3.

Table 2.2. A conclusion of the basic characteristics, Na content, and benefits/drawbacks of layered oxide materials in SIBs.

Material type	Structural property	Na content	Benefits	Drawbacks
P2	Prismatic sites, P63/mmc space group, ABBA stacking order.	0.3-0.7	Fast transfer of Na^+ ions, High range of working voltage.	Poor stability in air, Na^+/vacancy Ordering, O2-P2 phase transition.
O3	Octahedral sites, R3m space group, ABCABC stacking order.	1	High initial Capacity.	Poor air stability, Inferior capacity retention, Complex phase transition, Low-rate performance.

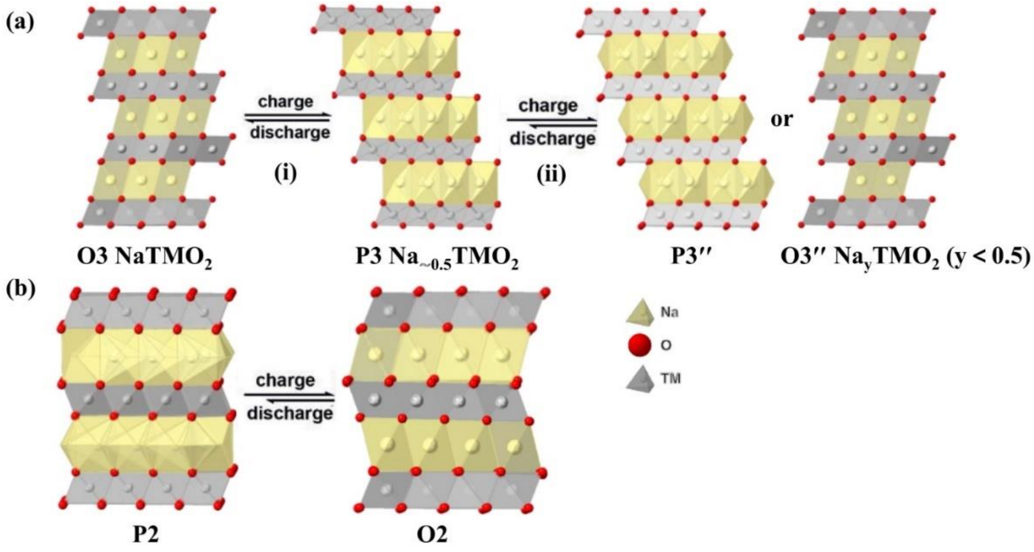

Figure 2.3 Representation of typical structural growth throughout charge/discharge of (a) O3-phase, and (b) P2-phase layered oxides[44].

Table 2.3. Electrochemical performance of various P2 and O3 phase layered TMOs.

Materials	**Cycle number**	**Voltage (V)**	**Current density (C or mA g^{-1})**	**First discharge capacity [mAh g^{-1}]**	**Capacity retention [%]**	**Type**	**Ref.**
$Na_{0.6}Li_{0.2}Mn_{0.8}O_2$	100	2-4.6	1/15C	190	100	P2	[45]
$Na_{0.45}Ni_{0.22}Co_{0.11}Mn_{0.66}O_2$	100	1.5-4.6	0.1C	200	80	P2	[46]
$Na_{0.55}Ni_{0.1}Fe_{0.1}Mn_{0.8}O_2$	100	1.5-4.3	0.1C	221.5	75	P2	[47]

$Na_{0.67}Mn_{0.65}Ni_{0.2}Mg_{0.15}O_2$	100	2-4.3	0.1C	125	94	P2	[48]
$Na_{2/3}Co_{2/3}Mn_{2/9}Ni_{1/9}O_2$	10	2-4.5	0.05C	140	85	P2	[49]
$Na_{2/3}Ni_{1/6}Mn_{2/3}Cu_{1/9}Mg_{1/18}O_2$	500	2.5-4.15	0.1C	64	81.4	P2	[50]
$Na[Li_{0.05}(Fe_{0.25}Ni_{0.25}Mn_{0.5})_{0.95}]O_2$	20	1.75-4.4	0.1C	180	90	O3	[51]
$Na_{0.9}Ca_{0.05}Ni_{1/3}Fe_{1/3}Mn_{1/3}O_2$	200	2-4	0.1C	127	92	O3	[52]
$Na_{0.75}Ni_{0.82}Co_{0.12}Mn_{0.06}O_2$	400	2-4	0.1C	171	65	O3	[53]
Na_4FeRuO_6	100	2-4	0.2C	120	80	O3	[54]
$Na_{0.67}Fe_{0.425}Mn_{0.425}Mg_{0.15}O_2$	50	1.5-4.2	0.1C	98	95	O3/P2	[55]
$Na_{2/3}Li_{0.18}Mn_{0.8}Fe_{0.2}O_2$	100	1.5-4.2	0.1C	125	70	P2/O3	[56]
$Na_{0.7}Li_{0.06}Mg_{0.06}Ni_{0.22}Mn_{0.67}O_2$	50	2-4.4	0.2C	129	97	P3/P2	[57]

$Na_{0.66}Mn_{0.5}Co_{0.5}O_2$	100	1.5-4.3	1C	156	55	P3/P2	[58]
$Na_{0.6}Mn_{0.75}Ni_{0.25}O_2$	500	2-4.1	0.2C	101	68	P2/P3	[59]
$Na_{0.66}Mn_{0.9}Mg_{0.1}O_2$	100	2-4.5	1C	162.9	65/1C	P2	[60]
$Na_{0.8}Co_{0.4}Ti_{0.6}O_2$	100	1.1-4	0.1C	100	80	O3	[61]
$Na_{2/3}[Fe_{0.22}Mn_{0.78}]O_2$	100	1.5-4.3	0.1C	187	91/0.1C	P2	[62]
$NaNi_{0.5}Mn_{0.5}O_2$	50	2.2-3.8	4.8 mA g^{-1}	125	75	O3	[63]
$Na_{2/3}Mn_{0.8}Fe_{0.1}Ti_{0.1}O_2$	300	2-4	0.1C	144.16	87.7/1C	P2	[64]
$Na_{0.67}Cu_{0.28}Mn_{0.72}O_2$	50	2-4.5	0.1C	109	98/1C	P2	[65]
$Na_{1.2}Mn_{0.4}Ir_{0.4}O_2$	50	1.5-4.4	0.1C	133	60/0.5C	O3	[66]
$Na_{0.67}Al_{0.1}Mn_{0.9}O_2$	100	2-4	12 mA g^{-1}	175	86/120 mA g^{-1}	P2	[67]
$Na_{2/3}[Mn_{0.8}Ni_{0.2}]O_2$	100	2-4.3	0.1C	162	75/0.1C	P2	[68]
$Na_{0.6}Ni_{0.22}Al_{0.11}Mn_{0.66}O_2$	50	1.5-4.6	20 mA g^{-1}	252	80/20 mA g^{-1}	P2	[69]
$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$	100	2-4	0.1C	136	80/1C	O3	[70]
$Na_{0.78}Al_{0.05}Ni_{0.33}Mn_{0.60}O_2$	50	2-4.5	0.1C	131.9	83.9/0.1C	P2	[71]
$Na_{0.67}Fe_{0.20}Ni_{0.15}Mn_{0.65}O_2$	900	2-3.8	0.1C	145	55/1C	P2	[72]

$NaNiO_2$	20	1.25-3.75	0.1C	123	93.5	O3	[73]
$Na_{0.67}[Ni_{0.1}Fe_{0.1}Mn_{0.8}]O_2$	200	1.5-4.3	0.1C	220	80/3C	P2	[74]
$Na_{0.97}Cr_{0.97}Ti_{0.03}O_2$	100	2-3.6	0.2C	125	96/0.2C	O3	[75]
$Na_{0.86}Co_{0.475}Mn_{0.475}Ti_{0.05}O_2$	200	1.5-4	0.5C	111.8	81.4/5C	P2	[76]
$Na_{0.82}Mn_{1/3}Fe_{2/3}O_2$	12	1.5-3.8	0.02C	132	92/0.02C	O3	[77]

From the above tables it can be observed that most of the well performing materials have doping of Nickel, Manganese, Magnesium, Iron, Titanium and Lithium. While the maximum energy density can be determined for Li-ion cathodes, various Na ion cathodes showing values that make them prospective applicants. TMOs normally possess high reversible capacities among all options available for sodium ion cathode. The compact structural framework of metal oxides makes them well appropriate for applications that requires a high volumetric density [78]. With this, a lot of research papers has been published on cathode, anode, and electrolyte material for various batteries by prestigious research institutes around the world. Future research is oriented for improved properties in battery chemistries include, for example, high capacity, high conductivity, low cost, large electrochemical stability, wide operating voltage range, long storage life, a wide range of operating temperature, long cycle life, overall safety, and high thermal stability.

2.2 Motivation of the work

Batteries are one of the most flexible energy storage devices, play a vital part in the shift from fossil-based fuels to renewable energy. SIBs are highly regarded replacement to the current popular LIBs as cost effective energy storing devices with excellent sustainability value with no unnecessary sacrifice in electrochemical performance. With the 2019 Nobel Prize in Chemistry for developing LIBs, ever-growing importance of portable, high-performance energy storage; it is now importance that we consider environment friendly and cost-effective solutions to the global energy storage demand[79]. Increasing demands for electric vehicles, portable electronic equipment and large-scale smart grids, etc. The Government of India Vision 2030 is aiming to accomplish full electrification of the public vehicle before 2030[80].

SIBs are considered as the future generation electrochemical energy storage system of selection. However, while from the cost perspective and sustainability SIBs are the most promising option to LIBs, further optimization, and modification in terms of electrochemical performance, more often in terms of energy density, are necessary. For the flourishing application of Na-ion batteries, the price per energy unit should be equal to or even more than that of the industrialized Li-ion batteries for the future-generation batteries, and thus material for cathode with a better capacity and cyclic number essentially be formulated. In the most recent five years, research and development on SIBs have gotten dynamic, and quick advancement in materials improvement and performance has been accomplished. LIBs face hurdles related to mining the ores that contains metal and financial concerns attached to material insufficiency and the effect of reprocessing toxic chemical components on environment. Figure 2.5 shows total and annual lithium utilization in 2015–2050 under the belief that only the requirement from electric vehicles will grow, although other uses stay constant Manufacturing high-performance SIBs from harmless and abundant materials in earth, such as a coalition of sodium, manganese, iron, titanium, and magnesium ores, decreases impact on environment and offers a worldwide opportunity to prepare affordable and safe batteries to both the developed and the developing nations of the world.

There is practically no uncertainty that the marketization of SIBs is conceivable. This may require a market specialty where SIBs show explicit benefits over LIBs or another setup kind of batteries. Cost-productive batteries dependent on bountiful components may be such a specialty that may get applicable later the off chance that asset supply and supply chains for LIBs will be tested excessively; obviously, this requires an incorporated methodology. The efforts are put together to develop and explore new, cheap substitute electrode materials with outstanding energy storage properties. Figure 2.4 shows the number of publications on SIBs and layered cathodes from 2000 to 2021 Recently, lots of transition metal oxides-based nano structure materials like, hydroxides, oxides, phosphates, sulphides, and many combinations have been made for energy storage pseudocapacitor. Some unique qualities make NFM exhibit rare characteristics, like electronic conductivity owning to better structural stability, various oxidation states and rich redox reactions, higher reversible capacity, and efficiently decreasing the polarization throughout charge/discharge.

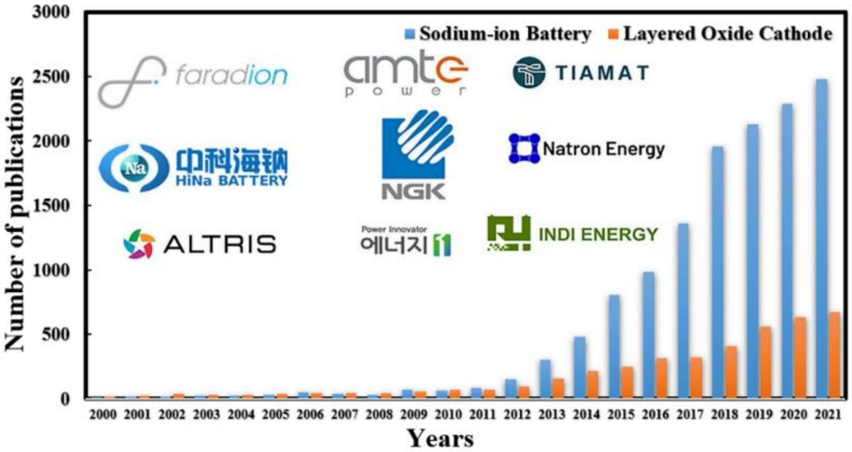

Figure 2.4 The number of publications on SIBs and layered cathodes from 2000 to 2021. (Data are encapsulated from Scopus).

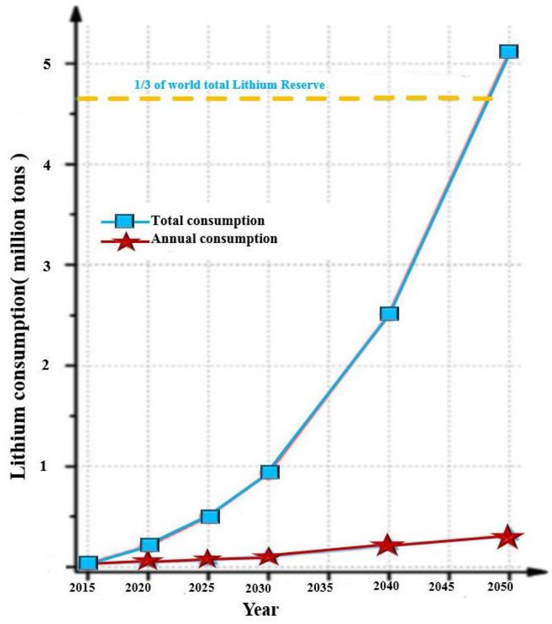

Figure 2.5 Total and Annual lithium utilization in 2015–2050 under the belief that only the requirement from EV will grow, although other uses stay constant. [41]

2.3 Objectives

The aimed objectives to develop sustainable sodium ion battery are as follows:

- To fabricate the high cycling performance, thermally stable, layered cathode; Na_xTMO_2, via yield efficient citric acid assisted sol-gel method.
- Structural and morphological characterization of the synthesized material by X-ray diffraction and FESEM.
- Electrochemical characterization (CV, GCD, and EIS) to determine the specific capacity, cyclability and stability test etc..
- To design layered cathode; Na_xTMO_2, to enhance the sodium ion battery performance in terms of high delivering capacity as well as high working voltage.

Chapter 3

Experimental Techniques

3.1. Synthesis of P2 type cathode material

The P2-type $Na_{0.67}Ni_{0.15}Fe_{0.15}Mn_{0.7}O_2$ (NFM) positive electrode material was made by a simple sol-gel method (figure 3.1), and as a chelating agent citric acid was utilized. Stoichiometric quantities of sodium acetate trihydrate ($NaOOCCH_3.3H_2O$, Alfa Aesar, 99%), Manganese acetate tetrahydrate ($C_4H_6MnO_4.4H2O$, Sigma Aldrich, >99%), Nickle acetate tetrahydrate ($(CH_3COO)_2Ni.4H_2O$, Sigma Aldrich,>98%) and Iron acetate ($Fe(CO_2CH_3)_{2,}$ Sigma Aldrich) were mixed together and stirred to homogenized for 2 h to 5 h. Later, the citric acid ($C_6H_8O_7.H_2O$, Alfa Aesar 99%) was added for the homogenization of metal acetate solution and was permitted to concentrate the procedure by strong stirring at 80 ^oC for 10 h to 12 h. A surplus of the sodium precursor was carried along with the stoichiometric quantity, to compensate Na^+ ion loss in the high-temperature calcination procedure. At last, the attained gel precursor was dried at 120 ^oC for 12 h to 15 h and heated at 450 ^oC to 550 ^oC for 6 h to 10 h in furnace after this material is calcined in muffle furnace at 750 ^oC to 900 ^oC temperatures to get the P2-type NFM material.

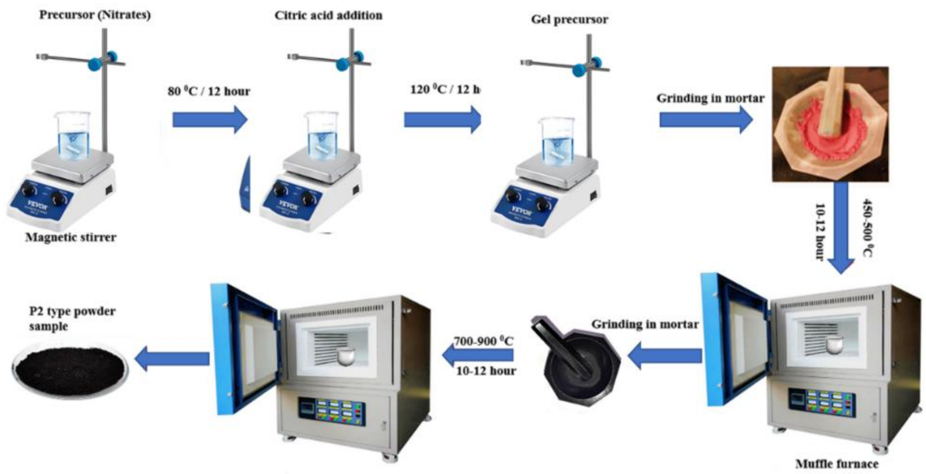

Figure 3.1 Experimental method used to synthesize P2 type layered oxide cathode material for Na ion battery.

3.2 Preparation of electrode

The preparation of electrode is distributed in two major steps. The first step implies the blending of the several components within the solvent to achieve the electrode slurry. The second step is linked to casting of electrode slurry on the current collector, drying and calendaring. The appropriate mixture of active material, solvent, conductive additive, and binder, gives good electrode slurry, as shown in figure 3.2. The sequence of mixing of the various components through preparation of electrode slurry crucial and alters the performance of the cell. Usually, conductive additive and active material are added and dispersed in the solvent/binder solution. The stirring and dispersion of the slurry components affect the rheological properties of the electrode, and therefore the battery performance.

The chemical and physical properties of the active material are also important for achieving high-quality electrodes. The active material performs as sodium basin in the electrode slurry, duty of the binder is to bind the conductive additive and the active material and to advance the mechanical strength and the adhesion between the current collector and electrode slurry. After all, the conductive additive is utilized for enhancing the electrical conductivity of the electrode. Once the electrode slurry is ready, it is pasted on the current collector and heated to evaporate the solvent.

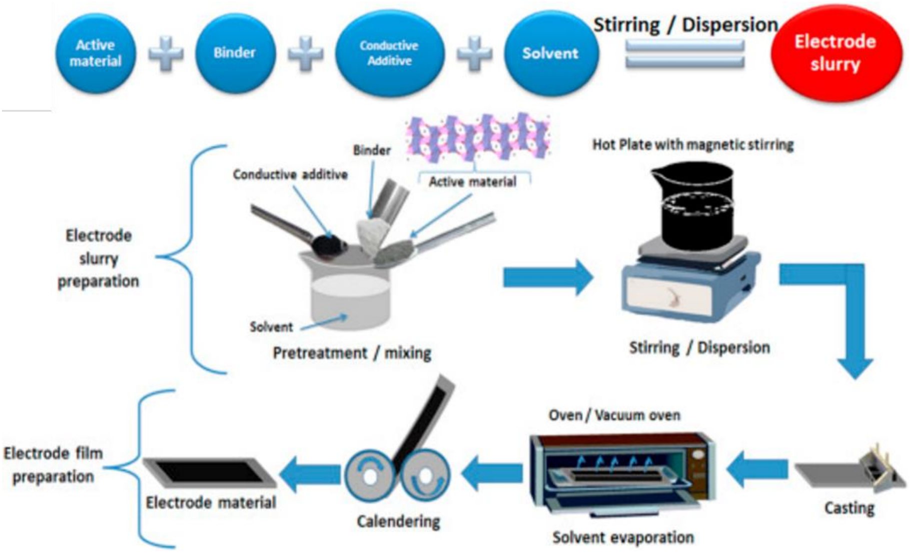

Figure 3.2 Electrode slurry preparation process[81].

3.3 Physicochemical characterization

3.3.1 X-Ray Diffraction technique:

X-ray powder diffraction (XRD) is the most valuable methods to characterise the powder samples. It is efficiently utilized for the phase analysis, structural determination, recognition of desired orientation, and also determination of crystalline size of the powder samples. The locations and the intensities of the peaks are utilized to recognize the phase, structure etc., of the material. XRD is a basic method, that is particularly helpful for analysing the crystal structure of condensed system. Nanomaterials demonstrate crystalline phases, which may be distinct from their bulk counterparts. This technique used to know the crystal structure, lattice parameters and the average particle size of given powder using XRD. XRD instrument is shown in figure 3.3. It provides us data about the lattice defects, lattice parameter, crystallite size, lattice strain and the kind of molecular bond of crystalline phase. The operating principle of the XRD (figure 3.4) is simple in which a monochromatic X-ray generated by the impact of accelerated electrons with heavy metal like Cu and which then filtered and collimated by nickel filters. If these X-rays beam with a characteristic wavelength λ hits the solid with an incident angle θ then the scattered radiation is defined by Bragg's law. The XRD patterns will be gathered on an X-ray powder diffractometer using Cu Kα radiation (λ = 1.54050 Å) for the phase formation and to check the crystallinity. In XRD pattern very sharp and intense peak suggests that the synthesized material is more crystalline in nature and calcination temperature is the optimum for the formation of pure phase. This crystalline material is favourable for good sodium intercalation and deintercalation. By XRD refinement crystal parameters can also be defined and can be compared at different temperatures

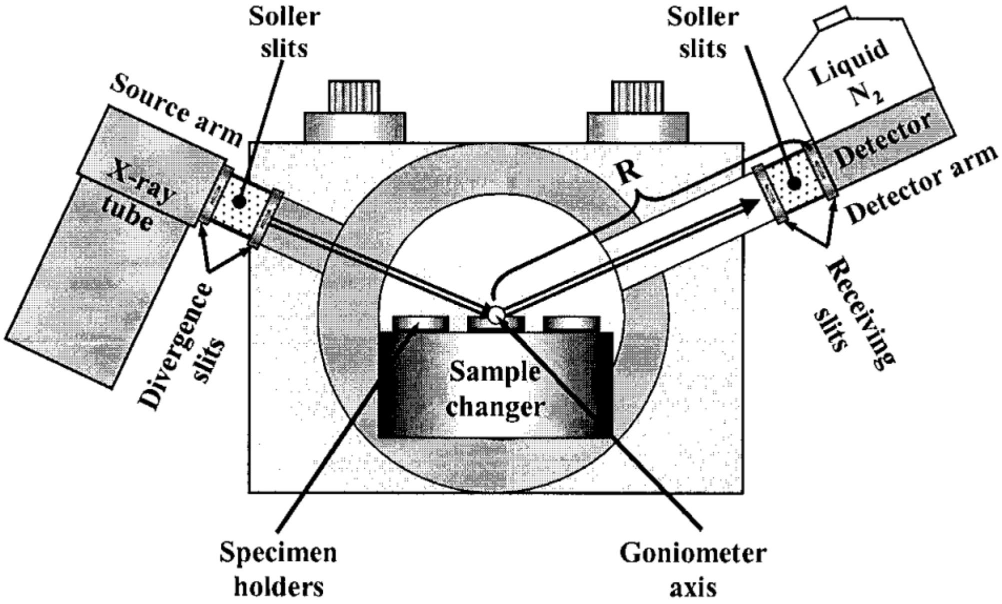

Figure 3.3 Schematic of X-ray diffraction instrumentation[82].

Bragg's law is the operating principle of X-ray diffractometer. The common correlation between the angle of incidence, wavelength of the incident X-rays, and space between the crystal lattice planes of atoms is well-recognized as Bragg's Law and stated as:

$$n\lambda = 2d\sin\theta \quad \dots\dots\dots (1)$$

Where, d = inter planar spacing of the crystal in angstroms

λ = wavelength of the incident X-rays in angstroms

θ = angle between the surface of the crystal and incident rays in degrees

n = an integer (Usually equal 1)

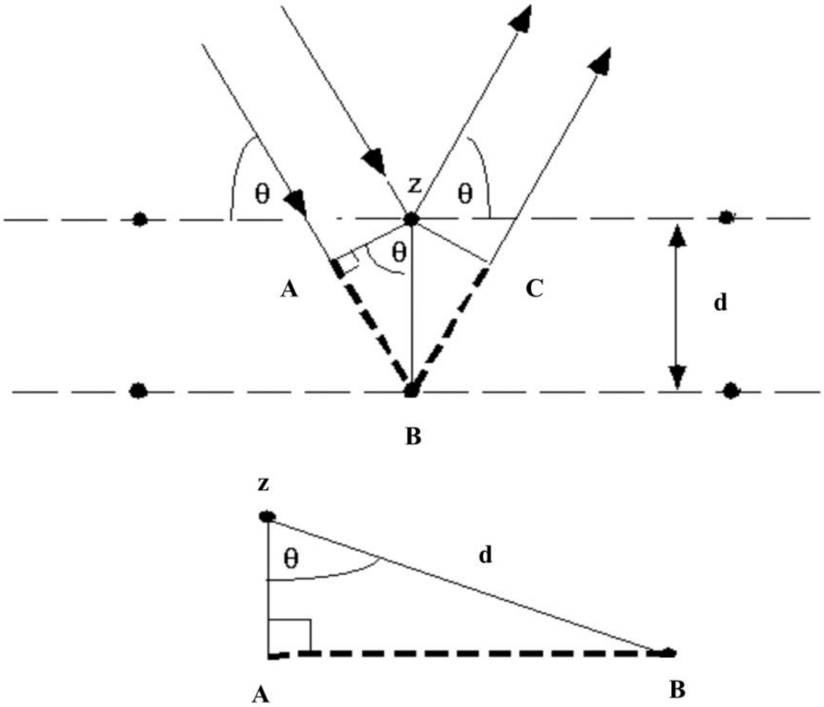

Figure 3.4 Working principal X-ray Diffraction (Braggs Law).

3.3.2 Field Emission Scanning Electron Microscopy (SEM)

FESEM is a kind of electron microscope that generates images of a sample by scanning the surface with a concentrated beam of electrons. The electrons interact with atoms in the sample, making different signals that include knowledge about the composition and surface topography of sample. The electron beam is scanned in a raster scan pattern, and the position of beam is combined with the identified signal to generate an image. FESEM can attain resolution better than 1 nanometre. Specimens can be seen in high vacuum in traditional FESEM, or in wet conditions or low vacuum in varying pressure or environmental FESEM, and at a broad range of cryogenic or high temperatures with specialized instruments. FESEM utilizes a focused beam of high-energy electrons to produce a various signals at the surface of solid samples. The signals that come from interactions of electron and sample show data about the sample involving external morphology, orientation of materials and crystalline structure. Figure 3.5 shows the working of FESEM. In many applications, data are gathered over a selected area of the surface of the sample, and a 2-D image is produced that shows spatial changes in these properties. Areas varying from nearly 1 cm to 5 microns in width can be imaged in a scanning mode utilizing traditional SEM techniques.

Fundamental Principles of FESEM

Accelerated electrons in an FESEM bring considerable amounts of kinetic energy, and this energy is dispersed as various signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals comprise backscattered electrons (BSE), secondary electrons (that produce SEM images), diffracted backscattered electrons (EBSD that are used to know orientations and crystal structures of material), photons, heat and visible light. Secondary electrons and backscattered electrons are usually used for imaging samples. Secondary electrons are most valuable for showing topography and morphology on samples and backscattered electrons are important for illustrating contrasts in composition in multiphase samples (*i.e.* for rapid phase discrimination). The morphology of the surface of the materials was examined by field-emission scanning electron microscopy (FESEM; Karl Zeiss JEOL).

Essential components of FESEM include the following:

- Room free of ambient magnetic and electric fields.
- Display/Data output devices.
- Electron Source ("Gun").
- Electron Lenses.
- Sample Stage.
- Signals detectors.
- Vacuum System.
- Cooling system.

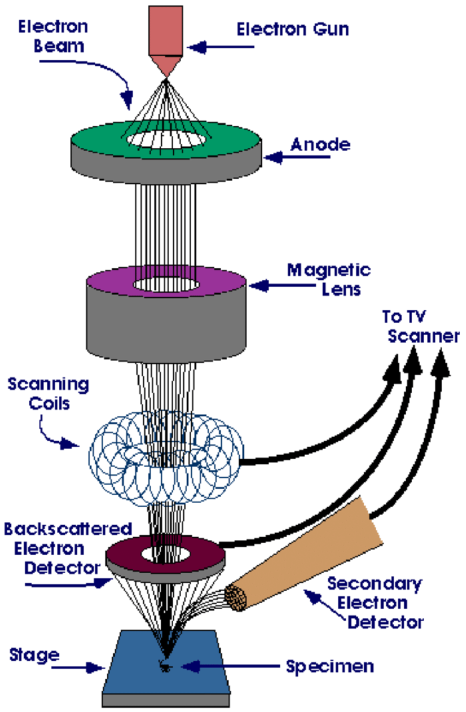

Figure 3.5 Schematic showing working of Scanning Electron Microscopy. [83]

3.4 Electrochemical performance analysis:

Computer-controlled galvanostat/potentiostat with a typical three-electrode system coupled to an electrochemical cell is used to perform electrochemical measurement. The as-prepared NFM electrode coated on Ni foam acting as a working electrode, platinum wire used as a counter electrode and saturated calomel electrode used as a reference electrode. 2 M KOH is used as aqueous electrolyte to carry out the measurements. The electrochemical workstation, AutoLab PGSTAT302N, Metrohm is used to carry out cycling stability studies, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge discharge (GCD) at room temperature as shown in figure 3.6. CV analysis have assisted to observe the redox performance and electrochemical kinetics of NFM. The CV plot for the NFM is shown at several scan rates varying from lesser 2 mV/s to 100 mV/s and the voltage range of -1 to 0.42 V. From the CV plot, the non-rectangular profile explains the faradaic type of behaviour which caused in battery-type performance. The CV plot shows the couple of redox peaks, attached to the reversible transformation of transition metal due to the reduction and oxidation procedures.

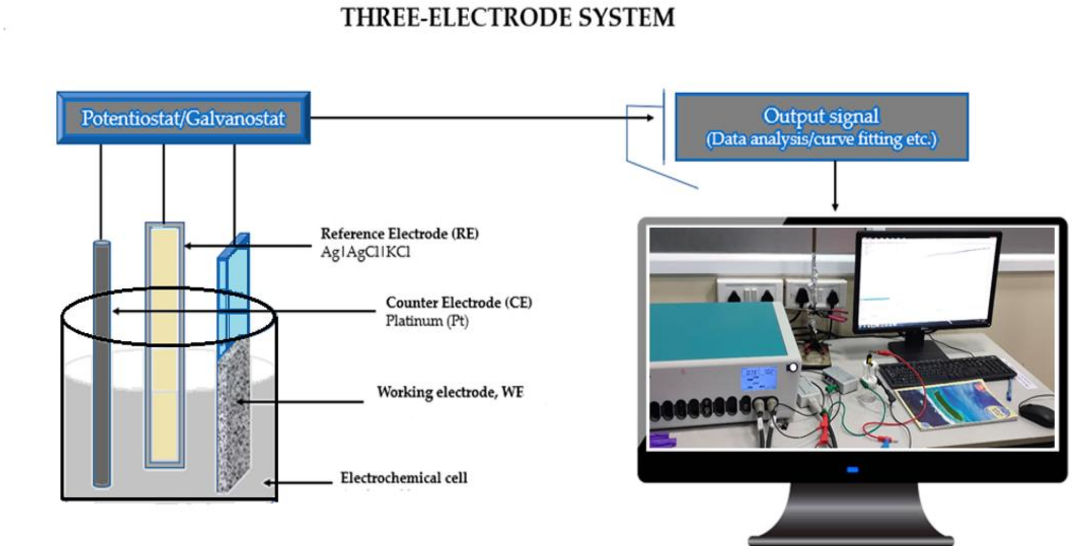

Figure 3.6 A Computer controlled galvanostat/potentiostat with a typical three-electrode system linked to an electrochemical cell.

In summery material synthesis and the electrode preparation process is successfully established, the basis characterization tools like XRD, FESEM and electrochemical analysis have been discussed.

Chapter 4

Results and Discussion

In this chapter we will discuss the result obtained by various physiochemical characterization techniques like XRD, FESEM and electrochemical characterization techniques for the P2 type layered oxide sample $Na_{0.67}Ni_{0.15}Fe_{0.15}Mn_{0.7}O_2$.

4.1 XRD Analysis for structural characterization

X-ray diffraction of the $Na_{0.67}Ni_{0.15}Fe_{0.15}Mn_{0.7}O_2$ at 850°C demonstrates phase pure without impurity. The XRD Patterns were indexed with space group *P63/mmc*, hexagonal crystal structure. The materials annealed at 850°C shows good crystalline material. From XRD Rietveld refinement *a* and *c* lattice constants are 2.885±0.007 Å and 11.218±0.008 Å. In XRD pattern very sharp and intense peak suggests that the synthesized material is more crystalline in nature and calcination temperature 850°C is the optimum for the formation of pure P2 phase of NFM ($Na_{0.67}Ni_{0.15}Fe_{0.15}Mn_{0.7}O_2$). This kind of crystalline material is favourable for good sodium intercalation and deintercalation and we expect that the synthesized material should exhibit good electrochemical activity during cycling. The synthesized material crystallizes into hexagonal crystal phase and the pattern is indexed on the basis of P2- $Na_{0.67}Ni_{0.15}Fe_{0.15}Mn_{0.7}O_2$ phase which matches well with JCPDS file No. 27-0751. Hexagonal cell parameters are calculated from XRD Rietveld refinement (figure 4.1) using FullProf software.

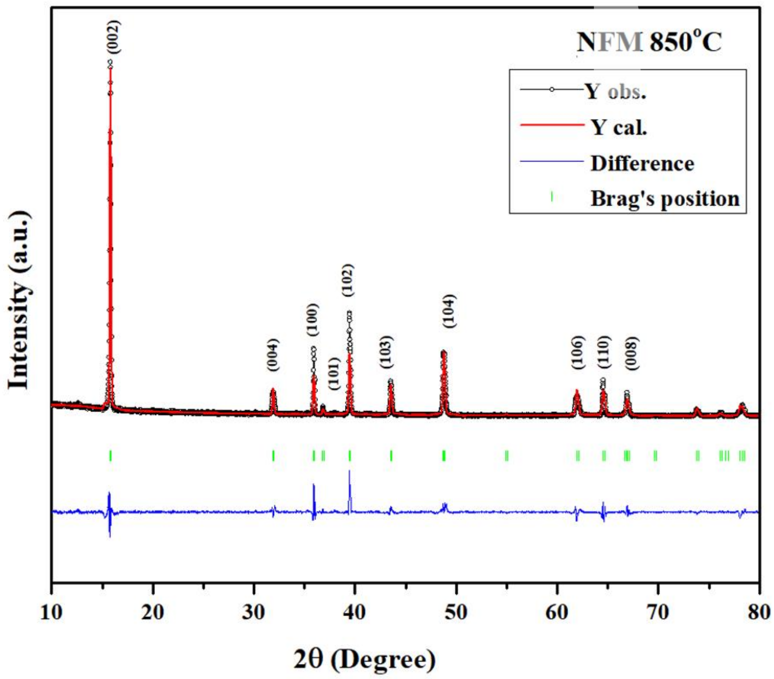

Figure 4.1 Rietveld refined XRD of the $Na_{0.67}Ni_{0.15}Fe_{0.15}Mn_{0.7}O_2$ (NFM) at 850 °C.

4.2 FESEM Analysis for morphological characterization

The FESEM studies shows that the material prepared at 850 °C shows well grown grain morphology and may lead for good battery performance. FE-SEM images of NFM sample calcinated at 850˚C displays that particle are evenly distributed and having well specified hexagonal shape. The small white marks are present on the surface of the particle that may be a slight amount of Na_2CO_3 phase. The FESEM images of $Na_{0.67}Ni_{0.15}Fe_{0.15}Mn_{0.7}O_2$ cathode material shown in figure 4.2 that confirms the development of phase by calcination.

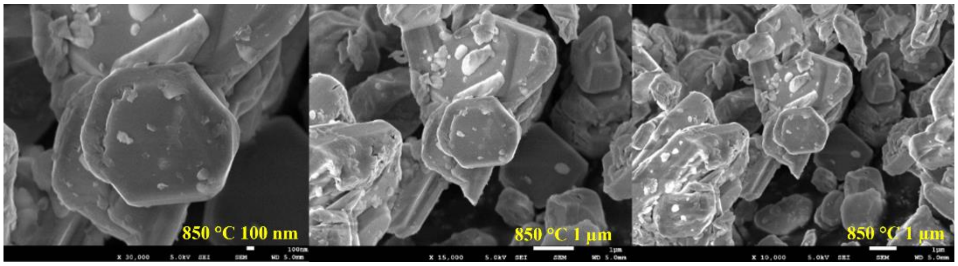

Figure 4.2 FESEM images of $Na_{0.67}Ni_{0.15}Fe_{0.15}Mn_{0.7}O_2$ synthesized at different temperatures

4.4 Electrochemical analysis:

The area under curve in the CV plot used to identify reaction kinetics and compute the specific capacity of the NFM material. The P2 type structure of as prepared layered oxide offers a specific capacity 353.5 mAh/g of at a scan rate of 2 mV/s and 52.47564 mAh/g at the scan rate 100 mV/s. Typical faradaic battery-like feature can be observed from in the typical CV plot, displaying two pair of major redox peaks as indicated in figure 4.3. The small variation between cathodic and anodic peaks favours the reversibility and pseudocapacitive characteristics of the positive electrode, take the lead to a rapid reversible redox process. With increase in scan rate, the oxidation peak in the CV moves to more positive potential owning to a redox reaction process regulated by a charge transport mechanism. The reduction peak indicates nearly no change; the wide redox peaks can be linked to high conductivity and to the intercalation nature of pseudocapacitive materials consist of a faradaic mechanism with no phase change. Various voltage plateaus caused by the presence of biphasic domains and first order transition through the de-intercalation and intercalation activities.

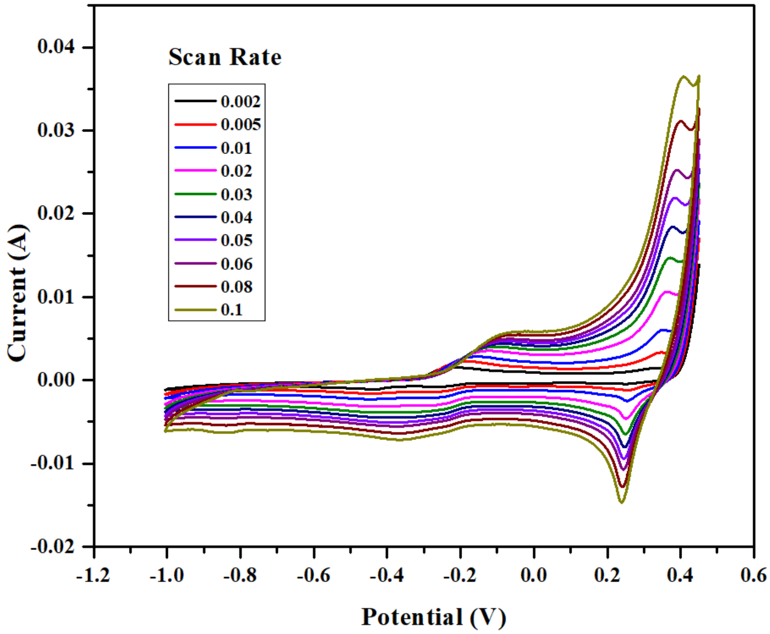

Figure 4.3 CV plot of P2-NFM at various scan rates in 2 M KOH solution with 1 mg active mass loading in voltage range 1.42 V.

At less sodium quantity, single-phase domains are stable, that leads to drop in voltage, although the sloped section signifies the solid solution behaviour. As the scan rate increases from 2-100mV/s, a peak shift can be observed, and this is because of the polarization process at electrolyte/electrode interface and ohmic resistance, that is resulted in the reduction in specific capacity due to the fast rate of electron transfer diffusion/kinetics. Figure 4.4 demonstrates the graph of scan rate vs specific capacity, noticing that at smaller scan rate full migration and diffusion of electrolytic ions into the NFM electrode recognized.

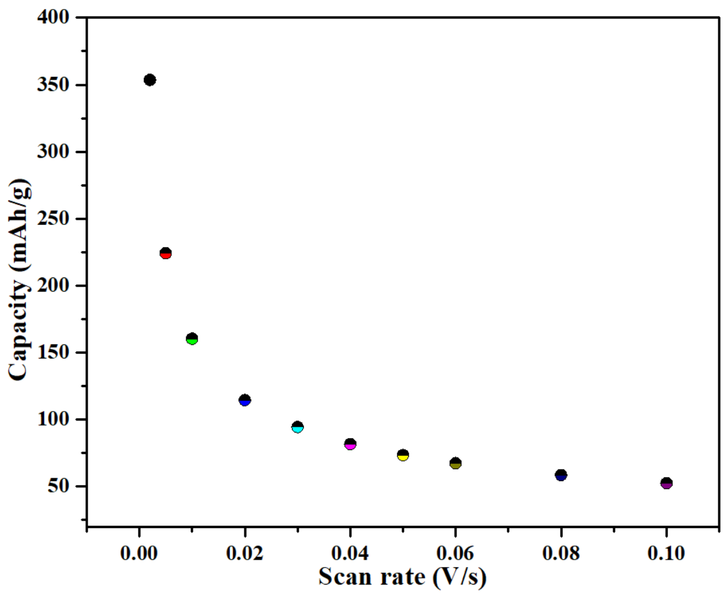

Figure 4.4 Specific capacity vs scan rate plot for NFM.

GCD plot for battery type faradaic materials generally exhibit hills of constant voltage linked to the redox reactions that are appearing through cycling[84]. In battery-type systems due to the different peak potential, the potentials of the discharging and charging reactions are not same. This change in voltage is described as polarization; the roots of polarization in battery appears from variations in the kinetics of the electrochemical redox reactions happening through discharging and charging (diffusion-controlled or/and charge transfer- kinetics)[8]. For NFM electrode from GCD plot at different current density (figure 4.5), specific capacity is 289.855 mAh g^{-1} at current density of 1 A/g and 139.13 mAh g^{-1} at high current density of 3 A/g respectively in 1.38 V voltage range.

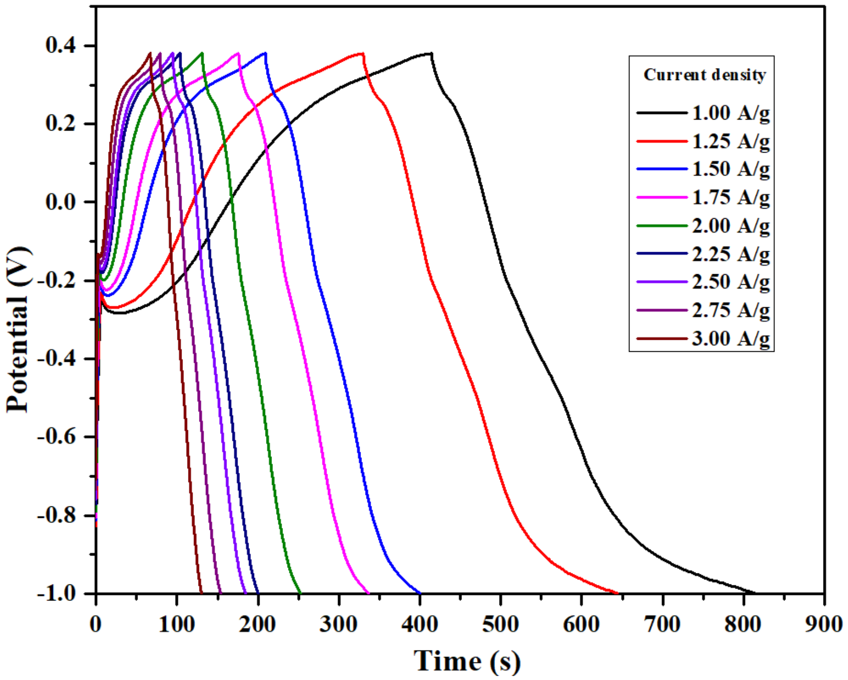

Figure 4.5 GCD plot of NFM at different current density from -1V to 0.38.

With increases in current density the specific capacity slowly reduces (Figure 4.6) and the reduction in specific capacity can be attributed as at lesser current densities the ions can enter into nearly all the internal holes and entire of the surface of NFM electrode thus, retrieving nearly all the active location for storage of charge[85]. While, at higher current densities, the consumption of NFM electrode material is limited to the ions and surface will not get sufficient period of time to get into the internal segment of the structure. The capacity reduction could be ascribed to the reduction of active sites, electrochemical dissolution of NFM electrode materials, increased resistance, and phase transformation of the electrode materials.

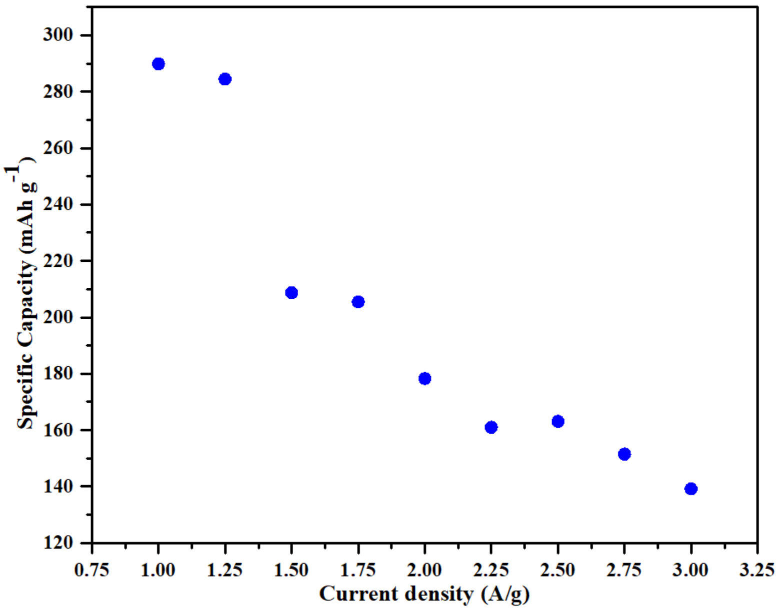

Figure 4.6 Specific capacity *vs*. current density plot for NFM.

EIS is a potential analytical method in characterising electrochemical cells in different frequencies. Generally, Nyquist plot have real and imaginary impedances at different frequencies in the range within 10 mHz to 100 kHz in an open circuit model with an AC voltage of 10 mV were used for the NFM electrode. EIS spectra of the NFM electrode were plotted after and before 1000 number of cycles of discharge and charge to achieve a comprehension into the performance. The semicircle at high frequency region shows R_{ct} that is related to the electro active surface area of the electrode owning to the faradaic redox process of the NFM electrode. To compute R_s find the intercept at high frequency on the real axis. Nyquist plot of NFM cathode material is shown in Figure 4.7. Before cycling, the charge transfer resistance is too high however, after cycling it drastically reduces. The increased resistance before cycling is due to the formation of stable SEI on the cathode surface which hinders the sodium ion intercalation and deintercalation[86].

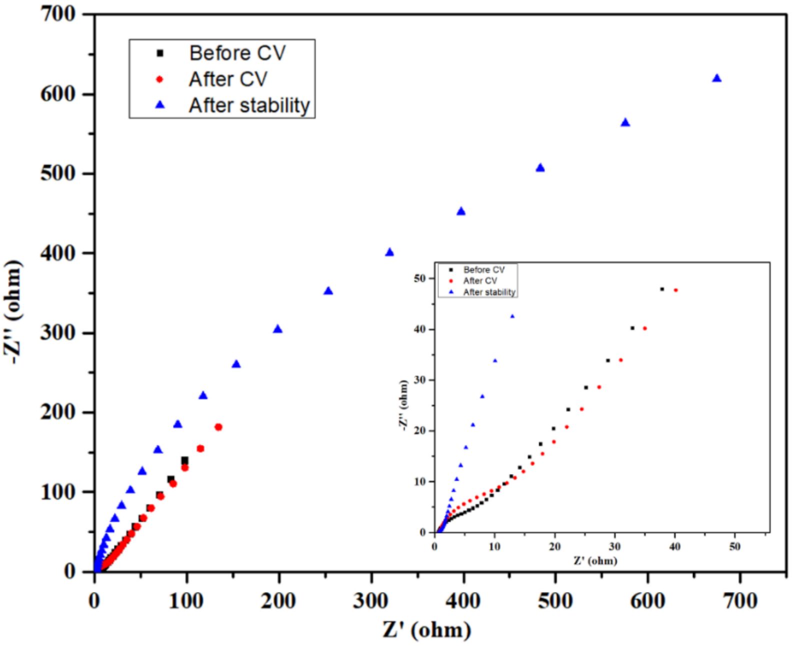

Figure 4.7 Nyquist graph of NFM and inset displays the enlarged image of low-frequency zone.

In summary, the physicochemical and electrochemical characterization of the as prepared material has been done, XRD pattern demonstrates phase pure without impurity. The materials annealed at 850 ºC shows good crystalline material. FE-SEM images of synthesized NFM, calcinated at 850˚C and morphology signifies that particle are evenly distributed and having well specified hexagonal shape. Electrode material shows good specific capacity from CV and GCD and EIS discusses about the charge transfer resistance.

Chapter 5

Summery and Scope of Future Work

Due to the inevitable natural restriction of LIBs, SIBs are believed as a major applicant for grid-size storage for renewable energy. SIB was studied along with LIBs in the 80s, but SIBs were out of research and development because of lower electrochemical performance. Current problems related to the demand and supply of lithium and the transition metals commonly used to make material for cathode for LIBs have accelerated the research and manufacturing organizations to focus on alternative chemistries for the battery. Consequently, the irregular and limited concentration of the raw materials used in the LIB technology is the primary reason for the revived focus in Na chemistry, even though it should be mentioned that various studies and future predictions claim that the lithium insufficiency supply should not happen within the next five decades, which would be even postponed when optimizing the process to recycle LIBs. On the other side, the accelerated requirement for lithium is the reason for the substantial price increment, which is undoubtedly a problem. These favour the SIB technology, which is beneficial because of highly abundant and inexpensive raw materials. In many battery technologies, layered TMOs ($Na_x\mathit{TM}O_2$; here, *TM*= Mn, Ti, Co, Ni, Fe, Al, V, Cr, and a grouping of different elements from earth crust) are used also layered O3 | P2 cathode chemistry is at the leading position for the substantial improvement of the SIB performance over the past decades. PBAs are a challenging set of composites to review for SIBs because of the extremely tunable characteristics of their synthesis and the complicated network of chemical interactions with the environment and inside the material. Yet, their probability as positive electrodes in ahead lithium-ion systems are evident in terms of performance and cost. Therefore, the considerable difficulty will be to develop a solid basic knowledge of these complicated interactions, allowing material advancements that promote processes practiced using novel advanced electrolytes. Polyatomic anion cathodes resume providing a path to improve working potential by capitalizing on the inductive effect and awarding stable structure of the material. There is compensation for the capacities, accomplished with the dense polyatomic anion component compared to layered oxides. Still, recent efforts to adapt extra Na-ions, for example, the use of proper dopants is attractive.

In summery thesis have five chapters that briefly discusses about the SIBs and the layered oxide cathode materials for SIBs.

Future scope: The close structural similarities between layered lithium-ion cathodes and O3 | P2 materials have assist to modify their commercial and scientific evolution. However, the higher complexity in the structure of O3 | P2 materials, emerging from the capability of sodium ions to follow elongated octahedral and trigonal prismatic coordination, generate many difficulties and gives major opportunities. The difficulties resulting from the combinational complication of the cation permutations can also be possibilities to produce SIBs that can compete with the good quality LIBs. In add-on to synthetic evolution that enables access to superior samples and novel polymorphs, shape tailoring, and size of particle will allow further modifications, such as better power densities. In future the work will be carried out to address these issues. In future the work will be carried out to address these issues.

REFERENCES

[1] R.S. Kalubarme, C.-J. Park, P.M. Shirage, Two-dimensional mesoporous carbon electrode for high energy density electrochemical supercapacitors, Journal of Nanoscience and Nanotechnology, 15 (2015) 1253-1260.

[2] M. Hannan, M.M. Hoque, A. Mohamed, A. Ayob, Review of energy storage systems for electric vehicle applications: Issues and challenges, Renewable and Sustainable Energy Reviews, 69 (2017) 771-789.

[3] X. Luo, J. Wang, M. Dooner, J. Clarke, Overview of current development in electrical energy storage technologies and the application potential in power system operation, Applied energy, 137 (2015) 511-536.

[4] M. Armand, J.-M. Tarascon, Building better batteries, nature, 451 (2008) 652-657.

[5] C.L. Mantell, Batteries and energy systems, (1982).

[6] C. Vaalma, D. Buchholz, M. Weil, S. Passerini, A cost and resource analysis of sodium-ion batteries, Nature reviews materials, 3 (2018) 1-11.

[7] D. Sarma, A. Shukla, Building better batteries: A travel back in time, in, ACS Publications, 2018, pp. 2841-2845.

[8] M. Winter, R.J. Brodd, What are batteries, fuel cells, and supercapacitors?, Chemical reviews, 104 (2004) 4245-4270.

[9] A. Ponrouch, D. Monti, A. Boschin, B. Steen, P. Johansson, M.R. Palacín, Non-aqueous electrolytes for sodium-ion batteries, Journal of Materials Chemistry A, 3 (2015) 22-42.

[10] L. Zhang, X. Li, M. Yang, W. Chen, High-safety separators for lithium-ion batteries and sodium-ion batteries: advances and perspective, Energy Storage Materials, 41 (2021) 522-545.

[11] Y. Fang, L. Xiao, Z. Chen, X. Ai, Y. Cao, H. Yang, Recent advances in sodium-ion battery materials, Electrochemical Energy Reviews, 1 (2018) 294-323.

[12] K. Abraham, Intercalation positive electrodes for rechargeable sodium cells, Solid State Ionics, 7 (1982) 199-212.

[13] D. Chao, W. Zhou, F. Xie, C. Ye, H. Li, M. Jaroniec, S.-Z. Qiao, Roadmap for advanced aqueous batteries: From design of materials to applications, Science advances, 6 (2020) eaba4098.

[14] J. Deng, W.B. Luo, S.L. Chou, H.K. Liu, S.X. Dou, Sodium-ion batteries: from academic research to practical commercialization, Advanced Energy Materials, 8 (2018) 1701428.

[15] B.E. Murdock, K.E. Toghill, N. Tapia-Ruiz, A Perspective on the Sustainability of Cathode Materials used in Lithium-Ion Batteries, Advanced Energy Materials, 11 (2021) 2102028.

[16] Y. Huang, Y. Zheng, X. Li, F. Adams, W. Luo, Y. Huang, L. Hu, Electrode materials of sodium-ion batteries toward practical application, ACS Energy Letters, 3 (2018) 1604-1612.

[17] Y.Y. Wang, B.H. Hou, J.Z. Guo, Q.L. Ning, W.L. Pang, J. Wang, C.L. Lü, X.L. Wu, An ultralong lifespan and low-temperature workable sodium-ion full battery for stationary energy storage, Advanced Energy Materials, 8 (2018) 1703252.

[18] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Research development on sodium-ion batteries, Chemical reviews, 114 (2014) 11636-11682.

[19] G.-W. Lee, J.H. Ryu, W. Han, K.H. Ahn, S.M. Oh, Effect of slurry preparation process on electrochemical performances of LiCoO2 composite electrode, Journal of Power Sources, 195 (2010) 6049-6054.

[20] A. El Kharbachi, O. Zavorotynska, M. Latroche, F. Cuevas, V. Yartys, M. Fichtner, Exploits, advances and challenges benefiting beyond Li-ion battery technologies, Journal of Alloys and Compounds, 817 (2020) 153261.

[21] P. Balakrishnan, R. Ramesh, T.P. Kumar, Safety mechanisms in lithium-ion batteries, Journal of power sources, 155 (2006) 401-414.

[22] R. Singh, Lithium Ion Batteries: Answer to Communications-Energy Crunch.

[23] F. Duffner, N. Kronemeyer, J. Tübke, J. Leker, M. Winter, R. Schmuch, Post-lithium-ion battery cell production and its compatibility with lithium-ion cell production infrastructure, Nature Energy, 6 (2021) 123-134.

[24] A.M. Aris, B. Shabani, An experimental study of a lithium ion cell operation at low temperature conditions, Energy Procedia, 110 (2017) 128-135.

[25] P. Yu, W. Tang, F.-F. Wu, C. Zhang, H.-Y. Luo, H. Liu, Z.-G. Wang, Recent progress in plant-derived hard carbon anode materials for sodium-ion batteries: a review, Rare Metals, 39 (2020) 1019-1033.

[26] D. Karabelli, S. Singh, S. Kiemel, J. Koller, A. Konarov, F. Stubhan, R. Miehe, M. Weeber, Z. Bakenov, K.P. Birke, Sodium-based batteries: in search of the best compromise between sustainability and maximization of electric performance, Frontiers in Energy Research, 8 (2020) 605129.

[27] J.-Y. Hwang, S.-T. Myung, Y.-K. Sun, Sodium-ion batteries: present and future, Chemical Society Reviews, 46 (2017) 3529-3614.

[28] K. Song, C. Liu, L. Mi, S. Chou, W. Chen, C. Shen, Recent progress on the alloy-based anode for sodium-ion batteries and potassium-ion batteries, Small, 17 (2021) 1903194.

[29] R.J. Clément, P.G. Bruce, C.P. Grey, manganese-based P2-type transition metal oxides as sodium-ion battery cathode materials, Journal of The Electrochemical Society, 162 (2015) A2589.

[30] B. Bochu, J. Buevoz, J. Chenavas, A. Collomb, J. Joubert, M. Marezio, Bond lengths in ‘CaMn3’(Mn4) O12: A new Jahn-Teller distortion of Mn3+ octahedra, Solid State Communications, 36 (1980) 133-138.

[31] K. Chayambuka, G. Mulder, D.L. Danilov, P.H. Notten, Sodium-ion battery materials and electrochemical properties reviewed, Advanced Energy Materials, 8 (2018) 1800079.

[32] Y. Xiao, N.M. Abbasi, Y.F. Zhu, S. Li, S.J. Tan, W. Ling, L. Peng, T. Yang, L. Wang, X.D. Guo, Layered oxide cathodes promoted by structure modulation technology for sodium-ion batteries, Advanced Functional Materials, 30 (2020) 2001334.

[33] X. Li, X. Ma, D. Su, L. Liu, R. Chisnell, S.P. Ong, H. Chen, A. Toumar, J.-C. Idrobo, Y. Lei, Direct visualization of the Jahn–Teller effect coupled to Na ordering in Na5/8MnO2, Nature materials, 13 (2014) 586-592.

[34] J. Peng, W. Zhang, Q. Liu, J. Wang, S. Chou, H. Liu, S. Dou, Prussian Blue Analogues for Sodium-Ion Batteries: Past, Present, and Future, Advanced Materials, 34 (2022) 2108384.

[35] Q. Zhao, Y. Lu, J. Chen, Advanced organic electrode materials for rechargeable sodium-ion batteries, Advanced energy materials, 7 (2017) 1601792.

[36] Q. Ni, Y. Bai, F. Wu, C. Wu, Polyanion-type electrode materials for sodium-ion batteries, Advanced Science, 4 (2017) 1600275.

[37] Q. Liu, Z. Hu, M. Chen, C. Zou, H. Jin, S. Wang, S.L. Chou, S.X. Dou, Recent progress of layered transition metal oxide cathodes for sodium-ion batteries, Small, 15 (2019) 1805381.

[38] J. Xiao, X. Li, K. Tang, D. Wang, M. Long, H. Gao, W. Chen, C. Liu, H. Liu, G. Wang, Recent progress of emerging cathode materials for sodium ion batteries, Materials Chemistry Frontiers, 5 (2021) 3735-3764.

[39] T. Shimono, D. Tanabe, W. Kobayashi, H. Nitani, Y. Moritomo, Electronic State of P2-Type Na x M O2 (M= Mn and Co) as Investigated by In situ X-ray Absorption Spectroscopy, Journal of the Physical Society of Japan, 82 (2013) 124717.

[40] C. Delmas, C. Fouassier, P. Hagenmuller, Structural classification and properties of the layered oxides, Physica B+ c, 99 (1980) 81-85.

[41] Q. Liu, Z. Hu, M. Chen, C. Zou, H. Jin, S. Wang, S.L. Chou, Y. Liu, S.X. Dou, The cathode choice for commercialization of sodium-ion

batteries: layered transition metal oxides versus Prussian blue analogs, Advanced Functional Materials, 30 (2020) 1909530.

[42] S. Guo, Y. Sun, J. Yi, K. Zhu, P. Liu, Y. Zhu, G.-z. Zhu, M. Chen, M. Ishida, H. Zhou, Understanding sodium-ion diffusion in layered P2 and P3 oxides via experiments and first-principles calculations: a bridge between crystal structure and electrochemical performance, NPG Asia Materials, 8 (2016) e266-e266.

[43] Y. Yang, W.-F. Wei, Electrochemical mechanism of high Na-content P2-type layered oxides for sodium-ion batteries, Rare Metals, 39 (2020) 332-334.

[44] J. Xu, D.H. Lee, R.l.J. Clément, X. Yu, M. Leskes, A.J. Pell, G. Pintacuda, X.-Q. Yang, C.P. Grey, Y.S. Meng, Identifying the critical role of Li substitution in P2–Na x [Li y Ni z Mn1–y–z] O2 (0< x, y, z< 1) intercalation cathode materials for high-energy Na-ion batteries, Chemistry of Materials, 26 (2014) 1260-1269.

[45] E. de la Llave, E. Talaie, E. Levi, P.K. Nayak, M. Dixit, P.T. Rao, P. Hartmann, F. Chesneau, D.T. Major, M. Greenstein, Improving energy density and structural stability of manganese oxide cathodes for Na-ion batteries by structural lithium substitution, Chemistry of Materials, 28 (2016) 9064-9076.

[46] L.G. Chagas, D. Buchholz, L. Wu, B. Vortmann, S. Passerini, Unexpected performance of layered sodium-ion cathode material ináionic liquid-based electrolyte, Journal of Power Sources, 247 (2014) 377-383.

[47] J.Y. Hwang, J. Kim, T.Y. Yu, Y.K. Sun, A new P2-type layered oxide cathode with extremely high energy density for sodium-ion batteries, Advanced Energy Materials, 9 (2019) 1803346.

[48] Y. Wen, J. Fan, C. Shi, P. Dai, Y. Hong, R. Wang, L. Wu, Z. Zhou, J. Li, L. Huang, Probing into the working mechanism of Mg versus Co in enhancing the electrochemical performance of P2-Type layered composite for sodium-ion batteries, Nano Energy, 60 (2019) 162-170.

[49] S. Doubaji, M. Valvo, I. Saadoune, M. Dahbi, K. Edström, Synthesis and characterization of a new layered cathode material for sodium ion batteries, Journal of Power Sources, 266 (2014) 275-281.

[50] Y. Xiao, Y.F. Zhu, H.R. Yao, P.F. Wang, X.D. Zhang, H. Li, X. Yang, L. Gu, Y.C. Li, T. Wang, A stable layered oxide cathode material for high-performance sodium-ion battery, Advanced Energy Materials, 9 (2019) 1803978.

[51] S.-M. Oh, S.-T. Myung, J.-Y. Hwang, B. Scrosati, K. Amine, Y.-K. Sun, High capacity O3-type Na [Li0. 05 (Ni0. 25Fe0. 25Mn0. 5) 0.95] O2 cathode for sodium ion batteries, Chemistry of Materials, 26 (2014) 6165-6171.

[52] L. Sun, Y. Xie, X.Z. Liao, H. Wang, G. Tan, Z. Chen, Y. Ren, J. Gim, W. Tang, Y.S. He, Insight into Ca-Substitution Effects on O3-Type NaNi1/3Fe1/3Mn1/3O2 Cathode Materials for Sodium-Ion Batteries Application, Small, 14 (2018) 1704523.

[53] J. Yang, M. Tang, H. Liu, X. Chen, Z. Xu, J. Huang, Q. Su, Y. Xia, O3-Type Layered Ni-Rich Oxide: A High-Capacity and Superior-Rate Cathode for Sodium-Ion Batteries, Small, 15 (2019) 1905311.

[54] J. Xu, Z. Han, K. Jiang, P. Bai, Y. Liang, X. Zhang, P. Wang, S. Guo, H. Zhou, Suppressing Cation Migration and Reducing Particle Cracks in a Layered Fe-Based Cathode for Advanced Sodium-Ion Batteries, Small, 16 (2020) 1904388.

[55] D. Zhou, W. Huang, X. Lv, F. Zhao, A novel P2/O3 biphase Na0. 67Fe0. 425Mn0. 425Mg0. 15O2 as cathode for high-performance sodium-ion batteries, Journal of Power Sources, 421 (2019) 147-155.

[56] M. Bianchini, E. Gonzalo, N.E. Drewett, N. Ortiz-Vitoriano, J.M.L. del Amo, F.J. Bonilla, B. Acebedo, T. Rojo, Layered P2–O3 sodium-ion cathodes derived from earth abundant elements, Journal of Materials Chemistry A, 6 (2018) 3552-3559.

[57] Y.-N. Zhou, P.-F. Wang, Y.-B. Niu, Q. Li, X. Yu, Y.-X. Yin, S. Xu, Y.-G. Guo, A P2/P3 composite layered cathode for high-performance Na-ion full batteries, Nano Energy, 55 (2019) 143-150.

[58] X. Chen, X. Zhou, M. Hu, J. Liang, D. Wu, J. Wei, Z. Zhou, Stable layered P3/P2 Na 0.66 Co 0.5 Mn 0.5 O 2 cathode materials for sodium-ion batteries, Journal of Materials Chemistry A, 3 (2015) 20708-20714.

[59] D. Wang, H. Chen, X. Zheng, L. Qiu, J. Qu, Z. Wu, Y. Zhong, W. Xiang, B. Zhong, X. Guo, Simultaneous Component Ratio and Particle Size Optimization for High-Performance and High Tap Density P2/P3 Composite Cathode of Sodium-Ion Batteries, ChemElectroChem, 6 (2019) 5155-5161.

[60] K. Kaliyappan, T. Or, Y.P. Deng, Y. Hu, Z. Bai, Z. Chen, Constructing safe and durable high-voltage P2 layered cathodes for sodium ion batteries enabled by molecular layer deposition of alucone, Advanced Functional Materials, 30 (2020) 1910251.

[61] X. Zhang, S. Guo, P. Liu, Q. Li, S. Xu, Y. Liu, K. Jiang, P. He, M. Chen, P. Wang, Capturing Reversible Cation Migration in Layered Structure Materials for Na-Ion Batteries, Advanced Energy Materials, 9 (2019) 1900189.

[62] J.U. Choi, Y.J. Park, J.H. Jo, L.-Y. Kuo, P. Kaghazchi, S.-T. Myung, Unraveling the role of earth-abundant Fe in the suppression of Jahn–Teller distortion of P′ 2-Type Na2/3MnO2: experimental and theoretical studies, ACS applied materials & interfaces, 10 (2018) 40978-40984.

[63] P.F. Wang, H.R. Yao, X.Y. Liu, J.N. Zhang, L. Gu, X.Q. Yu, Y.X. Yin, Y.G. Guo, Ti-Substituted NaNi0. 5Mn0. 5-xTixO2 Cathodes with Reversible O3− P3 Phase Transition for High-Performance Sodium-Ion Batteries, Advanced Materials, 29 (2017) 1700210.

[64] M.H. Han, E. Gonzalo, N. Sharma, J.M. López del Amo, M. Armand, M. Avdeev, J.J. Saiz Garitaonandia, T. Rojo, High-performance P2-phase Na2/3Mn0. 8Fe0. 1Ti0. 1O2 cathode material for ambient-temperature sodium-ion batteries, Chemistry of Materials, 28 (2016) 106-116.

[65] W. Zheng, Q. Liu, Z. Wang, Z. Wu, S. Gu, L. Cao, K. Zhang, J. Fransaer, Z. Lu, Oxygen redox activity with small voltage hysteresis in Na0. 67Cu0. 28Mn0. 72O2 for sodium-ion batteries, Energy Storage Materials, 28 (2020) 300-306.

[66] X. Zhang, Y. Qiao, S. Guo, K. Jiang, S. Xu, H. Xu, P. Wang, P. He, H. Zhou, Manganese-Based Na-Rich Materials Boost Anionic Redox in High-Performance Layered Cathodes for Sodium-Ion Batteries, Advanced Materials, 31 (2019) 1807770.

[67] X. Liu, W. Zuo, B. Zheng, Y. Xiang, K. Zhou, Z. Xiao, P. Shan, J. Shi, Q. Li, G. Zhong, P2-Na0. 67AlxMn1− xO2: Cost-Effective, Stable and High-Rate Sodium Electrodes by Suppressing Phase Transitions and Enhancing Sodium Cation Mobility, Angewandte Chemie International Edition, 58 (2019) 18086-18095.

[68] A. Konarov, J.U. Choi, Z. Bakenov, S.-T. Myung, Revisit of layered sodium manganese oxides: achievement of high energy by Ni incorporation, Journal of Materials Chemistry A, 6 (2018) 8558-8567.

[69] I. Hasa, S. Passerini, J. Hassoun, Toward high energy density cathode materials for sodium-ion batteries: investigating the beneficial effect of aluminum doping on the P2-type structure, Journal of Materials Chemistry A, 5 (2017) 4467-4477.

[70] H. Wang, X.-Z. Liao, Y. Yang, X. Yan, Y.-S. He, Z.-F. Ma, Large-scale synthesis of NaNi1/3Fe1/3Mn1/3O2 as high performance cathode materials for sodium ion batteries, Journal of The Electrochemical Society, 163 (2016) A565.

[71] Y. Shi, S. Li, A. Gao, J. Zheng, Q. Zhang, X. Lu, L. Gu, D. Cao, Probing the structural transition kinetics and charge compensation of the P2-Na0. 78Al0. 05Ni0. 33Mn0. 60O2 cathode for sodium ion batteries, ACS Applied Materials & Interfaces, 11 (2019) 24122-24131.

[72] C. Luo, A. Langrock, X. Fan, Y. Liang, C. Wang, P2-type transition metal oxides for high performance Na-ion battery cathodes, Journal of Materials Chemistry A, 5 (2017) 18214-18220.

[73] P. Vassilaras, X. Ma, X. Li, G. Ceder, Electrochemical properties of monoclinic NaNiO2, Journal of The Electrochemical Society, 160 (2012) A207.

[74] J.U. Choi, J.H. Jo, Y.J. Park, K.S. Lee, S.T. Myung, Mn-rich P′ 2-Na0. 67 [Ni0. 1Fe0. 1Mn0. 8] O2 as high-energy-density and long-life cathode material for sodium-ion batteries, Advanced Energy Materials, 10 (2020) 2001346.

[75] Y. Shao, Z.-f. Tang, J.-y. Liao, C.-h. Chen, Layer-structured Ti doped O3-Na1− x Cr1− x Ti x O2 (x= 0, 0.03, 0.05) with excellent electrochemical performance as cathode materials for sodium ion batteries, Chinese Journal of Chemical Physics, 31 (2018) 673-676.

[76] T. Fang, S. Guo, K. Jiang, X. Zhang, D. Wang, Y. Feng, X. Zhang, P. Wang, P. He, H. Zhou, Revealing the Critical Role of Titanium in Layered Manganese-Based Oxides toward Advanced Sodium-Ion Batteries via a Combined Experimental and Theoretical Study, Small Methods, 3 (2019) 1800183.

[77] B.M. De Boisse, J.-H. Cheng, D. Carlier, M. Guignard, C.-J. Pan, S. Bordere, D. Filimonov, C. Drathen, E. Suard, B.-J. Hwang, O3–Na x Mn 1/3 Fe 2/3 O 2 as a positive electrode material for Na-ion batteries: structural evolutions and redox mechanisms upon Na+(de) intercalation, Journal of Materials Chemistry A, 3 (2015) 10976-10989.

[78] V.R.R. Boddu, D. Puthusseri, P.M. Shirage, P. Mathur, V.G. Pol, Layered NaxCoO2-based cathodes for advanced Na-ion batteries: review on challenges and advancements, Ionics, 27 (2021) 4549-4572.

[79] P. Poizot, J. Gaubicher, S. Renault, L. Dubois, Y. Liang, Y. Yao, Opportunities and challenges for organic electrodes in electrochemical energy storage, Chemical reviews, 120 (2020) 6490-6557.

[80] P. Shukla, S. Dhar, M. Pathak, K. Bhaskar, Electric vehicles scenarios and a roadmap for India, UNEP DTU Partnership, (2014).

[81] A. Gören, C. Costa, M.M. Silva, S. Lanceros-Méndez, State of the art and open questions on cathode preparation based on carbon coated lithium iron phosphate, Composites Part B: Engineering, 83 (2015) 333-345.

[82] V. Pecharsky, P. Zavalij, Fundamentals of powder diffraction and structural characterization of materials, Springer Science & Business Media, 2008.

[83] A. Billah, Investigation of multiferroic and photocatalytic properties of Li doped BiFeO3 nanoparticles prepared by ultrasonication, in, Dissertação de Mestrado, Bangladesh University of Engineering and Technology, 2016.

[84] Y. Jiao, J. Pei, D. Chen, C. Yan, Y. Hu, Q. Zhang, G. Chen, Mixed-metallic MOF based electrode materials for high performance hybrid supercapacitors, Journal of Materials Chemistry A, 5 (2017) 1094-1102.

[85] L. Guan, L. Yu, G.Z. Chen, Capacitive and non-capacitive faradaic charge storage, Electrochimica Acta, 206 (2016) 464-478.

[86] Z. Wang, H. Yang, Y. Liu, Y. Bai, G. Chen, Y. Li, X. Wang, H. Xu, C. Wu, J. Lu, Analysis of the stable interphase responsible for the excellent electrochemical performance of graphite electrodes in sodium-ion batteries, Small, 16 (2020) 2003268.