

Fe-BASED PHOSPHATE MATERIALS FOR SODIUM-ION BATTERIES

Ph.D. Thesis

By
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**DEPARTMENT OF METALLURGICAL ENGINEERING AND
MATERIALS SCIENCE
INDIAN INSTITUTE OF TECHNOLOGY INDORE**

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Fe-BASED PHOSPHATE MATERIALS FOR SODIUM-ION BATTERIES

A THESIS

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

by
ARCHANA RAJENDRA KANWADE



**DEPARTMENT OF METALLURGICAL ENGINEERING AND
MATERIALS SCIENCE
INDIAN INSTITUTE OF TECHNOLOGY INDORE
APRIL 2026**



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled “**Fe-BASED PHOSPHATE MATERIALS FOR SODIUM-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 August 2021 to April 2026 under the supervision of Prof. Parasharam M. Shirage, Professor, Department of Metallurgical Engineering and Materials Science, 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.

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Date: April 06, 2026

Archana Rajendra Kanwade

DEDICATED TO
MY FAMILY
AND
ALL WHO BELIEVED IN ME

LIST OF PUBLICATIONS

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Paper 1: Archana R. Kanwade, Ravi C. Dutta, Sawanta S. Mali, Jyoti V. Patil, Chang Kook Hong, Parasharam M. Shirage*, Insights into Electrolyte-Dependent Interfacial Chemistry in High-voltage $\text{Na}_3\text{VFe}(\text{PO}_4)_3$ Cathode through Combined Experimental and Theoretical Studies, *Journal of Materials Chemistry A*, (2026). (Published online) <https://doi.org/10.1039/D6TA00219F> (IF=9.5)

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Paper 5: Archana Kanwade, Sheetal Gupta, Akash Kankane, Abhishek Srivastava, Subhash Chand Yadav, Parasharam M. Shirage*, Phosphate-based cathode materials to boost the electrochemical performance of sodium-ion batteries, *Sustain. Energy Fuels*, 6, (2022), 3114–3147. <https://doi.org/10.1039/D2SE00475E> (IF=5.1)

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1. Prof. Parasharam M. Shirage, **Archana R. Kanwade**, “Moderate temperature process for producing battery-grade hard carbon from post-consumer tea waste and uses thereof”, Indian Patent Application Number-202621025257.

LIST OF CONFERENCE/WORKSHOP/COURSES ATTENDED

1. Oral presentation in the Asian Conference on Electrochemical Power Sources 13 (ACEPS13) held at the Indian Institute of Science, Bengaluru, India, during January 11th-14th, 2026.
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3. Poster presentation in the International Union of Materials Research Societies – International Conference in Asia, 2024 (IUMRS ICA 2024) held on 3rd-6th December 2024, at Indore, India.
4. Oral presentation in the International Conference on Advanced Materials Synthesis, Characterizations, and Applications held at Queensland University of Technology, Brisbane, during 25th-27th September 2024.
5. Participated in Prime Minister's Research Fellow Symposium 2024 held at the Indian Institute of Technology Indore from 7th to 8th March 2024.
6. SERB-sponsored Karyashala (High-End Workshop) on "Energy Material Synthesis, Characterization, and Device Fabrication" Organized by Prof. Parasharam M. Shirage, Department of Metallurgical Engineering and Materials Science, during 3rd-8th July 2023.
7. Oral presentation in the International Conference on Advanced Materials Synthesis, Characterizations, and Applications held at Savitribai Phule Pune University, Pune, during 15th-17th October 2022.

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ACRONYMS/ABBREVIATIONS

2D	Two-dimensional
3D	Three-dimensional
BE	Binding energy
CB	Carbon black
CPE	Constant phase element
CV	Cyclic voltammetry
DEC	Diethyl carbonate
DI-water	De-ionized water
DMC	Dimethyl carbonate
DSC	Differential Scanning Calorimetry
DTG	Derivative of thermogravimetric
EC	Ethylene carbonate
EDS/EDX	Energy dispersive X-ray spectroscopy
EES	Electrochemical energy storage
EIS	Electrochemical impedance spectroscopy
ESS	Energy storage systems
FEC	Fluoroethylene carbonate
FESEM	Field emission scanning electron microscopy
FWHM	Full-width half maxima
HC	Hard carbon
HRTEM	High Resolution Transmission Electron Microscopy
JCPDS	Joint committee on powder diffraction standards
LIB	Lithium-ion battery
NMP	N-methyl-2-pyrrolidone
OCV	Open circuit voltage
PBA	Prussian blue analog
PC	Propylene carbonate
PE	Polyethylene

PP	Polypropylene
ppb	parts per billion
ppm	parts per million
PVDF	Polyvinylidene difluoride
<i>RHE</i>	Reference hydrogen electrode
SAED	Selected Area Electron Diffraction
SBR	Styrene-butadiene rubber
SEI	Solid electrolyte interphase
SIB	Sodium-ion battery
TGA	Thermogravimetric Analysis
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Chapter 1

Introduction



This chapter introduces rechargeable battery technology in depth, with particular focus on sodium-ion batteries (SIBs). The fundamental working principles and key components of SIBs are briefly discussed, with special emphasis on the role of electrode materials in determining battery performance. An in-depth literature review of the different cathode materials is given, with emphasis on the structural characteristics, merits, and demerits of these materials. Particular attention is given to major classes of cathode materials, including layered oxides, tunnel-structured structures, and polyanionic structures. Their electrochemical characteristics, structural stability, and applicability for sodium-ion

storage are highlighted in the discussion. Based on existing literature, the key research challenges and gaps in the development of high-performance cathode materials are identified. Finally, the scope, objectives, and motivation of the present research work are outlined, followed by a brief description of the overall structure and organization of the thesis.

1.1 Introduction to electrochemical energy storage

The swiftly increasing global population, industrialization, and technological advances have contributed to the constant rise in global energy demand. At present, the majority of this energy demand is still met by fossil fuel-based resources such as coal, oil, and natural gas. The extensive consumption of these non-renewable resources has raised significant concerns about the environment, including the emission of greenhouse gases, global warming, and climate change. Consequently, the transition toward clean, sustainable, and renewable energy sources has become an urgent global priority. Energy storage plays an important role in current energy infrastructure because it allows decoupling of energy generation from consumption, thereby ensuring the reliability, stability, and continuity of power supply.[1] Overall, energy storage technologies enable excess energy generated during low demand to be stored and used during surging demand or when energy generation is insufficient.

Solar and wind power have also shown potential alternatives because of their availability and minimal environmental effect. The intermittent and unpredictable nature of these energy sources however, offers great difficulties in integrating them into existing power grids on large-scale. The mismatch between energy generation and consumption necessitates the development of efficient energy storage systems that can store excess energy and deliver it on demand. Energy storage technologies can be categorized into mechanical, thermal, and electrochemical systems with regard to energy storage form, as shown in **Figure 1.1**. Storage of energy in the form of potential or kinetic energy is stored in mechanical energy storage systems, e.g. pumped hydro storage, compressed air energy storage, and flywheels that are normally used on large scale grid. Thermal energy storage systems store energy as heat or cold using sensible heat, latent heat, or thermochemical processes, and are widely used in solar thermal power plants and building energy management.[2]

Among these, electrochemical energy storage devices, particularly rechargeable batteries, play a crucial role in addressing this challenge.[3] These systems convert electrical energy into chemical energy during the charging process and reconvert it back into electrical energy during discharging. Electrochemical energy storage devices, including batteries and supercapacitors, offer several advantages such as high energy conversion efficiency, rapid response, modularity, scalability, and suitability for both portable and stationary applications.[4] Owing to these advantages, EES has emerged as a key enabling technology for next-generation energy systems and plays a pivotal role in supporting sustainable and low-carbon energy solutions.[5]

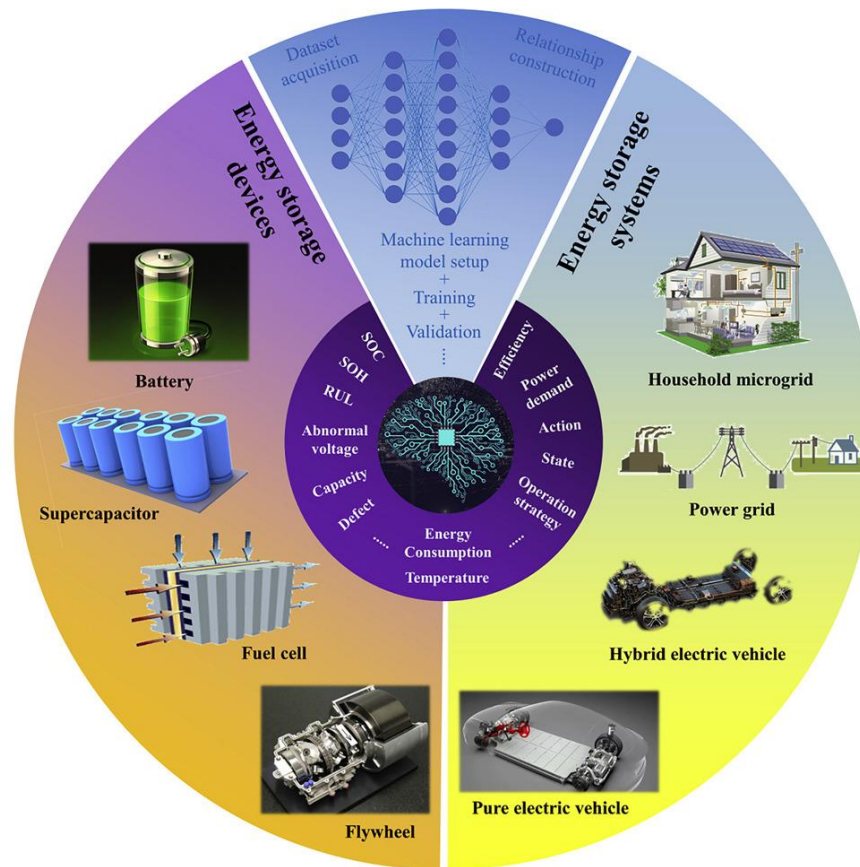


Figure 1.1 Schematic of various types of energy storage systems and devices.[4]

1.2 Battery Technologies

Battery technology is one of the widely used EES systems due to its ability to store electrical energy in a compact, efficient, and reversible manner. It is used in a wide range of technologies, including portable electronics, grid-level energy storage, and electric vehicles. Since Alessandro Volta first demonstrated batteries in 1800, their complex chemical processes are still being studied to improve energy density, sustainability, and lifetime as outlined in **Figure 1.2 (a)**. [6] The general working principle of a battery is based on reversible electrochemical redox reactions occurring at two electrodes: the anode and the cathode, which are separated by an electrolyte and an ion-permeable separator. During discharge, oxidation reactions occur at the anode, releasing electrons that flow through the external circuit to perform electrical work, while reduction reactions occur at the cathode. Simultaneously, charge-compensating ions migrate through the electrolyte from one electrode to the other to maintain electrical neutrality. During charging, an external electrical energy source drives these reactions in the reverse direction, thereby restoring the chemical potential of the active materials. The nature of the electrode materials, electrolyte composition, and interfacial phenomena largely governs the electrochemical behavior and performance of the battery. [7] Scientists are using new tools to better understand the electrical and chemical processes in batteries, enabling a new generation of highly efficient electrical energy storage.

From a practical perspective, there are two main categories of battery technology: Primary battery technology and secondary battery technology. [8,9]

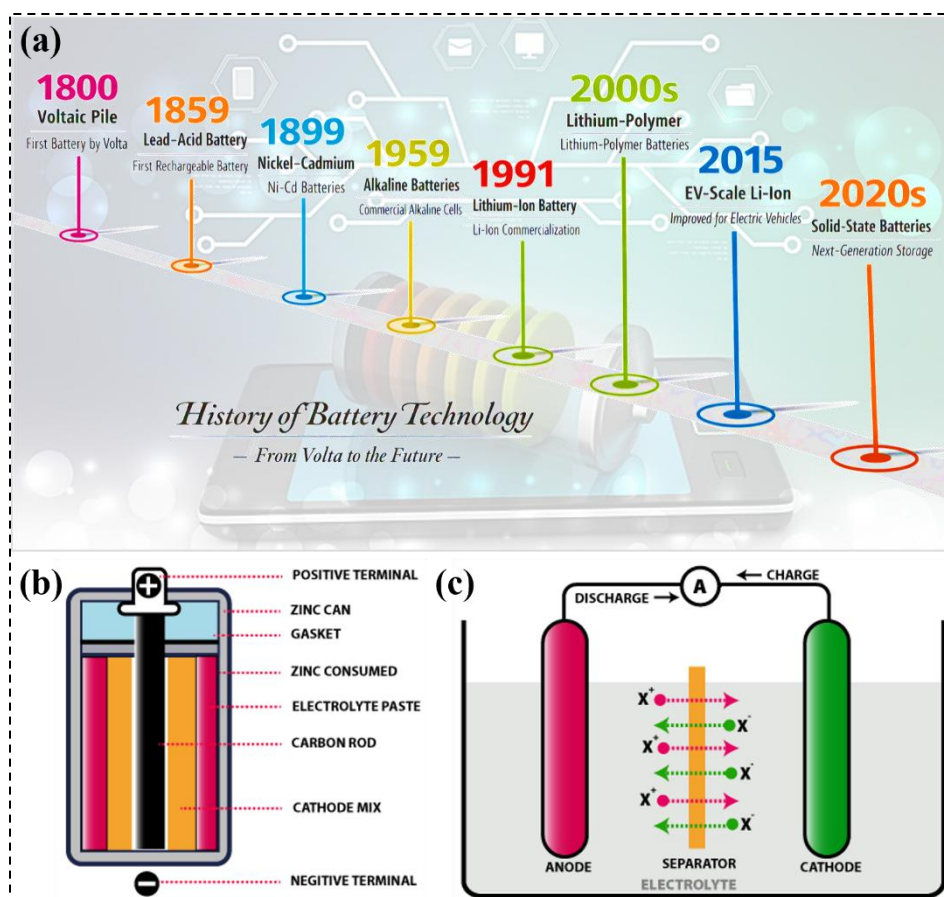


Figure 1.2 (a) Illustration of the history of battery technology, schematic of (b) primary battery and (c) secondary battery technologies.

1.2.1 Primary Battery Technology

Primary batteries are also called non-rechargeable batteries as shown in **Figure 1.2 (b)**. They are designed for single use; once the energy is depleted, they must be discarded, as they cannot be recharged. They are produced in an ionized form, and their storage capacity can hold the energy released by the amount of reactants placed in them during manufacturing. The electrochemical reactions involved are virtually irreversible after the discharge, thereby requiring cell replacement rather than reuse under normal operating conditions. This technology includes alkaline batteries, zinc-carbon batteries, and lithium metal batteries, which are widely employed in low- to medium-drain applications such as household electronics, remote controls, and small medical devices.[8]

1.2.2 Secondary Battery Technology

These batteries are known to be rechargeable, as shown in **Figure 1.2 (c)**, since they can be recharged after being discharged by simply reversing the current flow through the battery. They are stored in discharged condition during assembly and then used. It implies that it can be reused several times until its end of life by refilling it after each discharge. At the end of their life, the materials inside these batteries can be recycled and used to produce new batteries or for other suitable applications. Therefore, they are environmentally friendly and economical in the long term, compared to primary batteries. It encompasses nickel-metal hydride, lead-acid, lithium-ion, and solid-state batteries, which are being extensively deployed in electronic equipment and grid-scale energy storage.

The lithium-ion batteries have been very successful among the secondary batteries due to their high energy content, long cycle life and high capacities. Despite these advantages, there are a few significant factors that limit the extensive use of lithium-ion batteries as grid-scale and stationary energy storage.[10] The low lithium supply and its uneven geographical distribution are among the main issues. The increased use of lithium-based technology has driven up material costs and the susceptibility of their supply chains, especially when used on a large scale. In addition to lithium scarcity, the use of expensive and environmentally sensitive transition metals such as cobalt and nickel in conventional lithium-ion battery cathodes further increases production costs and raises sustainability concerns.[11] The extraction and processing of these materials are linked to significant environmental and ethical concerns, including resource depletion and the destruction of the ecology. Another significant drawback of lithium-ion batteries is safety. The use of flammable organic electrolytes and the potential for thermal runaway under abusive conditions make large-format batteries particularly challenging from a safety perspective. Furthermore, lithium-ion batteries are not as cost-efficient in stationary

energy storage systems, where high energy density is less important than cost, safety, and long-term stability.[12]

These shortcomings have prompted intensive research on alternative rechargeable batteries that can supplement or replace lithium-ion batteries for large-scale energy storage. In this regard, SIBs have emerged as a promising candidate, as they inherently offer key benefits as an abundance of materials, relatively low costs, and environmental sustainability.[13]

1.3 Sodium-ion batteries: Next-generation EES

SIBs have attracted considerable interest as a next-generation electrochemical energy storage technology, especially in large-scale and stationary applications. Sodium resources are abundantly available worldwide, making SIB technology a promising and cost-effective alternative to LIBs.[14,15] Owing to their close resemblance to LIBs in terms of the electrochemical working mechanisms, SIBs have attracted significant attention from research community over the past few years. Sodium is one of the most abundant elements on Earth, with natural reserves estimated to be nearly three orders of magnitude greater than those of lithium. It ranks as the fourth most abundant element in the Earth's crust and is widely distributed in nature. For instance, the United States alone possesses approximately 23 billion metric tons of soda ash, enabling easy access to sodium-based precursors and highlighting the feasibility of large-scale fabrication of SIBs.

Even though NIBs and LIBs are similar in terms of cell designs and electrochemical mechanisms, the type of charge carriers differs significantly. The ionic radius of sodium ions (1.02 Å, coordination number 6) is larger than that of lithium ions (0.76 Å, coordination number 6) and this results in different interfacial behavior, ion-based transport kinetics, and structural stability of host materials in repeated intercalation and deintercalation reactions. In addition, sodium has a more significant atomic weight (23 g/mol) than lithium (6.9 g/mol) and the standard electrochemical potential (-2.71 V vs SHE) of sodium is less than that of lithium (-3.02 V vs

SHE). These intrinsic differences influence the achievable energy and power densities of SIBs. Moreover, the practical capacity of a battery is also highly determined by the chemical nature and the crystallographic structure of the electrode materials used.[16]

The different parts of SIBs include the electrode materials, which are a controlling factor in deciding the general energy density, operating voltage, stability during cycling, and the safety of the device. Therefore, the development of high-performance, stable, and cost-effective electrode materials remains a key research focus for advancing SIB technology toward practical applications.

1.3.1 Components of SIBs

According to **Figure 1.3 (a)**, SIB consists of the cathode, anode, current collectors, electrolyte, and separator. Each of these elements contributes to the general functioning of the SIBs. The anode and the cathode are the two electrodes that are porous in nature in order to store more charge carriers. During the charging process, the sodium-ion is inserted into the host material of the anode, and during the discharge process, it is extracted and inserted into the cathode. The electrolyte assists in the movement of ions between the electrodes, and the separator prevents short-circuiting of the electrical circuit while allowing ion flow.[17]

Among these components, the cathode material plays a decisive role in determining the overall electrochemical performance of SIBs, including energy density, operating voltage, cycling stability, and safety characteristics. The electrochemical potential of the cathode largely governs the cell voltage, while its structural stability and redox activity directly affects the capacity retention and rate capability. Therefore, the development of suitable cathode materials is critical for the practical realization of high-performance SIBs. SIBs also need cathode materials with open crystal structures, which can accommodate the comparatively large sodium ions, unlike lithium-ion batteries. The structural stress caused by repeated insertion and removal of sodium ions exerts significant strain

on the cathode lattice, which is why structural robustness and chemical stability are necessary conditions. Consequently, extensive research has been devoted to identifying cathode materials that can simultaneously deliver high capacity, stable cycling performance, and long-term durability.[18]

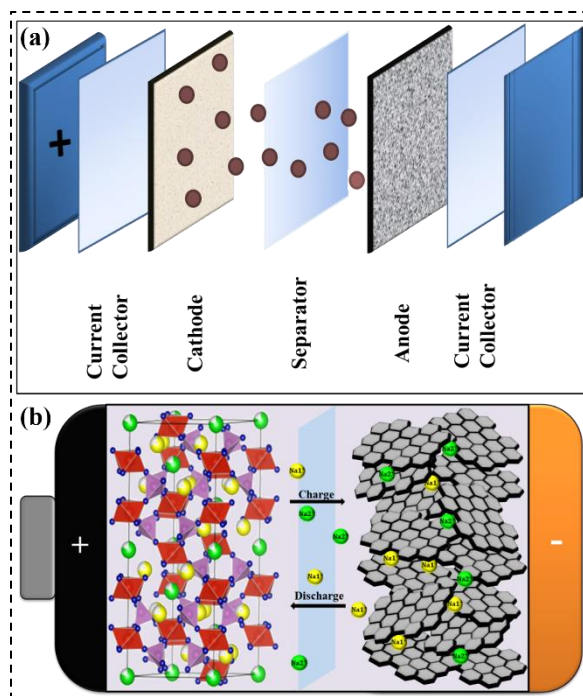


Figure 1.3 Schematic representation of (a) components, and (b) the working mechanism of SIBs

1.3.2 Working Mechanism of SIBs

A battery is an electrochemical device that consumes chemicals and converts chemical energy into direct electric current. A SIB is an energy storage system that works on the principle of electrochemical charge/discharge reactions due to the movement of sodium ions as the charge carriers. The basic battery system consists of components such as an anode, a cathode, an electrolyte, current collectors, and a separator. The working principle of the SIB is analogous to that of the LIB. A schematic of the SIB is shown in **Figure 1.3 (b)**. A sodium-ion cell is typically set up in the discharged state. The cathode is the sodium-ion source that contains transferable sodium ions, while the anode is sodium-free. For initial

charging, the power source induces electron migration from the cathode to the anode via an external circuit. Charge neutrality is maintained by releasing sodium ions from the cathode into the electrolyte. These sodium ions reach the anode layers through the electrolyte as the ion-conducting channel. The electrons reach the anode from the cathode through the external circuit, and the sodium ions also reach the anode and become intercalated within the anode layers by capturing the electrons. Accordingly, oxidation and reduction reactions take place at the cathode and anode, respectively. More and more sodium ions are released from the cathode and stored in the anode via the intercalation mechanism, and the battery is charged.[19] During discharge, the power source is removed, and the load is connected across the two terminals of the cell. The migration of electrons and sodium ions is reversed; the electrons migrate from the anode to the cathode through an external circuit, as they cannot pass through an electrolyte, and electricity is generated in the load. The sodium ions start moving from the anode to the cathode through the electrolyte, and after capturing the electrons, they become sodiated to the cathode materials. After the sodiation of all the sodium ions on the cathode materials, both electrodes return to their initial discharged state.[20] In this case, oxidation and reduction reactions occur at the anode and cathode, respectively.

1.3.3 Acceleration of SIB development

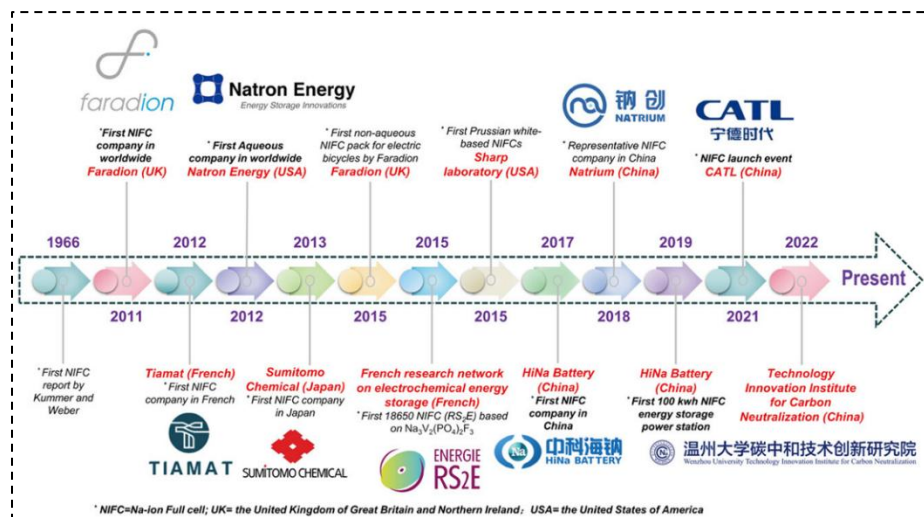


Figure 1.4 Worldwide development history of the NIFCs.[21]

The rapid development of SIBs is one of the strategic measures responding to the barriers of lithium-ion battery, such as lithium scarcity, vulnerability of the supply-chain, and increased cost, making SIBs a less expensive alternative to for grid storage and affordable mobility. Sodium's abundance-approximately 400 times greater than lithium-combined with low raw material costs and manufacturing compatibility requiring only about 10% additional capital expenditure for retrofitting existing lithium-ion lines, has propelled SIBs from laboratory research to commercial deployment since the 2010s revival of 1980s origins as shown in **Figure 1.4**.^[22] China holds 53% of world SIB patent figures on the back of landmark discoveries like that of Delmas with reversible Na intercalation in Na_xCoO_2 (1980s), Stevens and Dahn with the discovery of hard carbon anode (2000) and Yabuuchi with the discovery of a high-energy P2-layered cathode (2012).^[23]

The recent materials breakthroughs, such as layered transition metal oxides, polyanionic phosphates, such as $\text{Na}_2\text{FePO}_4\text{F}$, Prussian blue analogues, and optimized hard carbon/alloy anodes, have provided significant improvements in specific capacity, operating voltage, cycling stability of over 4000 cycles, and low-temperature operation of $-40\text{ }^\circ\text{C}$, and while electrolyte and interface engineering are combating SEI formation issues.^[24] This development follows industrial advances: Naxtra battery of CATL went into mass production in December 2025 with 175 Wh/kg density enabling 500 km EV range and 10,000 cycles; BYD unveiled the first sodium-ion forklift in January 2026 with $-40\text{ }^\circ\text{C}$ to $60\text{ }^\circ\text{C}$ operation, 4C charging and 10-year warranty; Peak Energy rolled out the first grid-scale 3.5 MWh system in SolarTAC in 2025; and others such Bloomberg NEF estimates that by 2030, SIBs will capture more than 50 GWh or 23% of the stationary storage.^[21]

These advances make SIBs particularly compelling for grid-scale renewable integration, where low cost and long cycle life mitigate solar/wind intermittency, as well as for industrial vehicles and entry-level

electric vehicles, which benefit from 30% lower system costs, aluminum current collectors, and reduced critical material dependence. Hybrid lithium-sodium configurations further optimize performance across applications. Although energy density still trails premium lithium-ion batteries and battery management systems require chemistry-specific optimization, SIBs are firmly established as complementary technology targeting cost- and sustainability-driven markets, directly supporting ongoing polyanionic cathode research like your NFMP work for practical sodium-ion advancement.

1.4 Electrochemical Kinetic and Performance Parameters

For an electrode, the intrinsic properties are the faradaic capacity and voltage profiles. However, the storage capacity and open-circuit voltage are measurable quantities. Using these quantitative evaluations, the electrochemical properties of the electrode materials can be estimated. This highly depends on the kinetic and thermodynamic properties of intercalation compounds as represented in **Figure 1.5**.

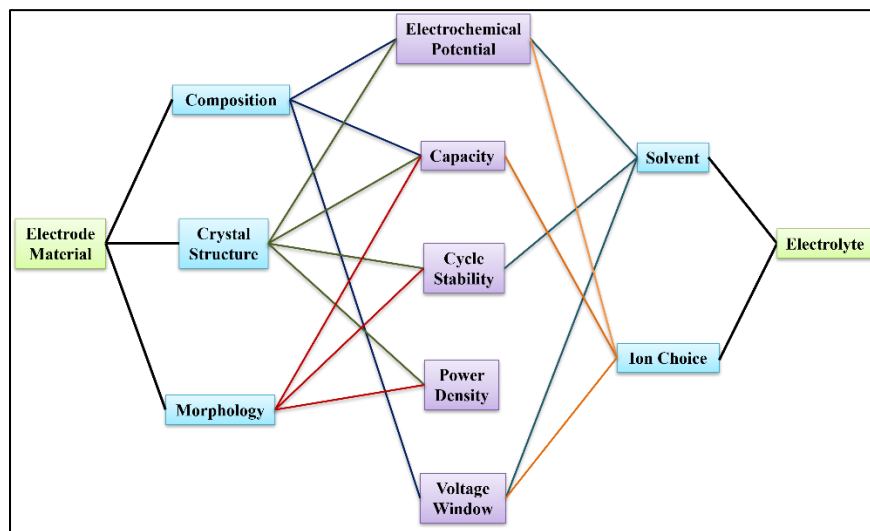


Figure 1.5 The electrochemical kinetics and performance parameters of the electrode materials.

The performance of batteries can be defined by the following parameters:[8,9,25]

- **Theoretical Specific Capacity:** capacity is the amount of current that a battery can deliver over a specific time period.

The theoretical specific capacity is the maximum charge-storage capacity of an electrode material, determined by its stoichiometry and the number of electrons involved in the redox reaction.

$$Q_{Theoretical} = \frac{nF}{3.6 m} \quad (1.1)$$

where,

n is the number of electrons transferred per formula unit, F is Faraday's constant (96,485 C/mol), m is the molar mass of the active material (g/mol), and the factor 3.6 converts coulombs to mAh.

This parameter provides an upper limit for practical capacity and is useful for evaluating material utilization efficiency.

- **Practical specific capacity:** The practical or specific capacity is experimentally measured during galvanostatic charge-discharge cycling and is expressed in mAh/g.

$$Q = \frac{I \times t}{m} \quad (1.2)$$

Where I is the applied current (mA), t is the discharge time (h), and m is the mass of active material (g).

The difference between theoretical and practical capacity arises from kinetic limitations, incomplete utilization of active sites, and irreversible side reactions.

- **Charge and discharge rate:** It defines how fast energy can be charged/discharged and is measured using the C-rate. The C-rate is a unitless ratio that relates the charge or discharge current to the battery's nominal capacity, where a higher C-rate means a faster charge or discharge.
- **Cell Voltage (V):** The cell voltage of a battery is determined by the difference in electrochemical potentials of the cathode and anode materials. It represents the driving force for electron flow during

battery operation and directly influences the achievable energy density.

$$V_{cell} = V_{cathode} - V_{anode} \quad (1.3)$$

Where $V_{cathode}$ and V_{anode} are the equilibrium potentials of the cathode and anode, respectively, referenced to the same standard electrode. The average operating voltage is typically obtained from the discharge voltage profile and is used for energy density calculations.

- **Energy Density (E):** Energy density defines the amount of energy stored per unit mass of the battery and is a key metric for portable and transportation applications.

$$E = Q \times V_{average} \quad (1.4)$$

Where Q is the specific capacity (mAh/g) and V_{avg} is the average discharge voltage (V).

Energy density is commonly reported in Wh/kg.

- **Power Density (P):** Power density indicates the rate at which energy can be delivered and is particularly important for high-rate applications.

$$P = E \times t \quad (1.5)$$

where E is the energy density (Wh/kg), and t is the discharge time (h). Power density is expressed in W/kg.

- **Coulombic Efficiency (η):** Coulombic efficiency reflects the reversibility of electrochemical reactions and is defined as the ratio of discharge capacity to charge capacity.

$$\eta (CE)\% = \frac{Q_{discharge}}{Q_{charge}} \times 100 \quad (1.6)$$

High coulombic efficiency indicates minimal irreversible capacity loss and stable electrode-electrolyte interfaces.

- **Cycle Life and Capacity Retention:** Cycle life of a battery is the number of charge and discharge cycles that a battery can complete before losing performance and reaching a certain state of health,

while capacity retention quantifies the remaining capacity after a given number of cycles.

$$\text{Capacity Retention (\%)} = \frac{Q_n}{Q_1} \times 100 \quad (1.7)$$

Where Q_n is the capacity after the n^{th} cycle and Q_1 is the initial capacity.

- **Rate Capability:** Rate capability evaluates the ability of a battery to maintain capacity at higher current densities and is related to ion diffusion and charge-transfer kinetics.

$$\text{Rate capability (\%)} = \frac{Q_{\text{high rate}}}{Q_{\text{low rate}}} \times 100 \quad (1.8)$$

These parameters collectively determine battery performance and suitability for the application. The electrochemical performance of batteries is governed by intrinsic material properties, electrode architecture, and interfacial phenomena. A comprehensive understanding of these metrics is essential for the rational design and optimization of advanced battery systems.

1.5 Anode

In a battery, the anode acts as the negative electrode with oxidation occurs during the discharge process. The sodium atoms lose electrons at this electrode, and the electrons pass through the external circuit to form electric current. Metallic sodium has a very low redox potential (-2.71 V vs. SHE) and large theoretical specific capacity and energy density, which makes it thermodynamically an attractive anode material to use in SIBs.[26] Nevertheless, sodium metal is very reactive to most of the liquid electrolytes that may result in formation of dendrite during repeated cycling. These dendrites can enter the separator, through which internal short circuits can be generated and even thermal runaway may take place. As a result of these safety issues, only laboratory scale studies have been performed to use metallic sodium anodes and cannot yet be used in commercial SIB systems.

To overcome these limitations, significant research efforts have focused on developing alternative anode materials with safer and more stable sodium storage mechanisms. Among various candidates, carbon-based materials, particularly hard carbon (HC), have emerged as promising anodes for SIBs. Graphite is an anode material that is commonly used in lithium-ion batteries (LIBs) due to its layer structure, with the interlayer of 3.35 Å. This separation is however not adequate enough to successfully intercalate the bigger Na^+ ions (~ 2.04 Å in diameter). Research density functional theory has also indicated that, graphite has poor sodium intercalation energetics, which makes it poor as an anode in SIBs. The sodium storage of the graphite is extremely low in spite of the fact that compounds, like NaC_{15} , NaC_{30} , and NaC_{80} can also form.[27] By comparison, glucose-derived hard carbon shows pseudo-intercalation behavior and promises to perform well in both LIBs and SIBs, which provides a reversible capacity of approximately 300 mAh/g in sodium-ion systems. A lot of work has therefore been directed toward enhancing the hard carbon-based anodes to SIB applications.[26,28]

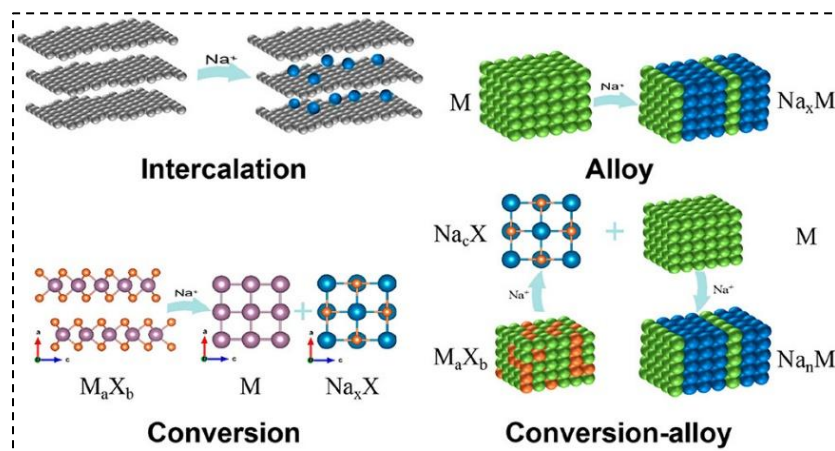


Figure 1.6 Types of anode materials for SIBs.[26]

Based on their sodium storage mechanisms, anode materials can generally be categorized into four types as shown in **Figure 1.6**: [29,30]

1. **Intercalation-type anodes:** These materials accommodate Na^+ ions within their structure without major structural rearrangements. Examples include hard carbon (HC), titanium dioxide (TiO_2), and sodium titanate ($\text{Na}_2\text{Ti}_3\text{O}_7$).
2. **Conversion-type anodes:** These undergo redox reactions accompanied by complete phase transformations during sodiation. Examples include iron oxide (Fe_2O_3) and transition metal dichalcogenides.
3. **Alloy-type anodes:** These materials form sodium-based alloys during Na^+ insertion, typically accompanied by significant volume expansion. Examples include tin-based compounds (SnS , SnO_2) and Sb_2O_4 .
4. **Conversion-alloy type anodes:** These materials combine conversion reactions (phase transformations) with alloying mechanisms (Na-alloy formation) during sodiation, offering high capacities but facing challenges like volume expansion. Examples include $\text{Sn}@ \text{FeS}_2$ composites, Bi_2O_3 , and Cu_6Sn_5 alloys.

Although the anode plays a vital role in battery operation, the present thesis primarily focuses on the development of cathode materials for SIBs. In the electrochemical studies conducted in this work, sodium metal chips were used as both the counter and reference electrodes in a Na half-cell configuration.

1.6 Electrolyte

Electrolytes are the ionic conduction medium, which facilitates the movement of Na^+ ions between anode and cathode during battery operation. They are not directly involved in the process of energy storage, but their physicochemical characteristics have a great impact on the overall performance of battery. Electrolytes may be in liquid, solid, or gel form but

liquid electrolytes are the most common at present due to their high conductivity of ions and good electrode wetting properties. A perfect electrolyte must have a number of crucial characteristics:[31]

- A wide electrochemical stability range.
- Large ionic conductivity, ideally greater than 10^{-3} S/cm.
- Reduced electrical conductivity to reduce the risk of self-discharge and short circuiting.
- Chemical and thermal stability with other cell components.
- High wettability and low viscosity to allow easy ion transfer.
- Low toxicity, non-inflammable, and economical
- The ability to form a stable solid electrolyte interphase (SEI).

Different SIBs liquid electrolytes include sodium salts dissolved in organic solvents and many of them are supplemented with functional additives to improve performance.[16] Sodium perchlorate (NaClO_4), sodium hexafluorophosphate (NaPF_6), sodium bis(trifluoromethanesulfonyl) imide (NaTFSI), and sodium bis(fluorosulfonyl) imide (NaFSI) are common sodium salts. The salts are normally dissolved in cyclic carbonate solvents mixtures like ethylene carbonate (EC) and propylene carbonate (PC) as well as linear carbonate solvents like dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC). Such combinations of solvents are useful in maximizing viscosity, dielectric properties and ion solvation behavior.[32]

Functional additives such as fluoroethylene carbonate (FEC) are often introduced to modify the electrode-electrolyte interfacial chemistry. FEC improves the reversibility of Na^+ insertion by facilitating a stable layer of SEI and minimizing parasitic side reactions.[33] Other alternative electrolytes that have been investigated in SIBs usage are ionic liquids due to their high thermal stability, non-flammability as well as large electrochemical stability windows. Their practical implementation is, however, at the moment of high viscosity and cost.

1.7 Current Collector and Separator

This is a vital element of electrodes within a battery that collects electrons produced during an electrochemical reaction and transport them to the external circuit. Current collector selection depends on the following properties: electrical conductivity, corrosion resistance, electrochemical stability, mechanical strength, and cost. Typically, copper (Cu) and aluminum (Al) are used as current collectors for anodes and cathodes, respectively, due to their excellent conductivity and affordability. Traditionally, copper has been used as a current collector of the anode but this is relatively heavy and more costly compared to aluminum. In the recent past, aluminum has also been considered as an anode current collector in SIBs, which will enhance the cost and weight of the battery.

The separator is an ionically permeable but electrically insulating membrane that physically separates the positive and negative electrodes to avoid internal short circuits and permits the migration of Na^+ ions between electrodes. In addition, the separator acts as an electrolyte reservoir, facilitating efficient ionic transport. A good separator must be highly porous (around 40-60 per cent), have small pore size (around 1 μm) to inhibit dendrite growth, be very wettable to ions to increase ion conductivity with a high degree of mechanical and thermal stability.[34] Commonly used separators include borosilicate glass fiber, microporous polypropylene (PP), and polyethylene (PE). Advanced alternatives such as polymer composite membranes and ceramic-coated separators are also being developed to improve safety and performance.

1.8 Cathode Materials for SIBs

Cathode materials for SIBs can be broadly classified into three main categories based on their crystal structure and sodium storage mechanism: layered transition metal oxides, Prussian blue and its analogues, and polyanionic compounds.

1.8.1 Layered Transition Metal Oxides

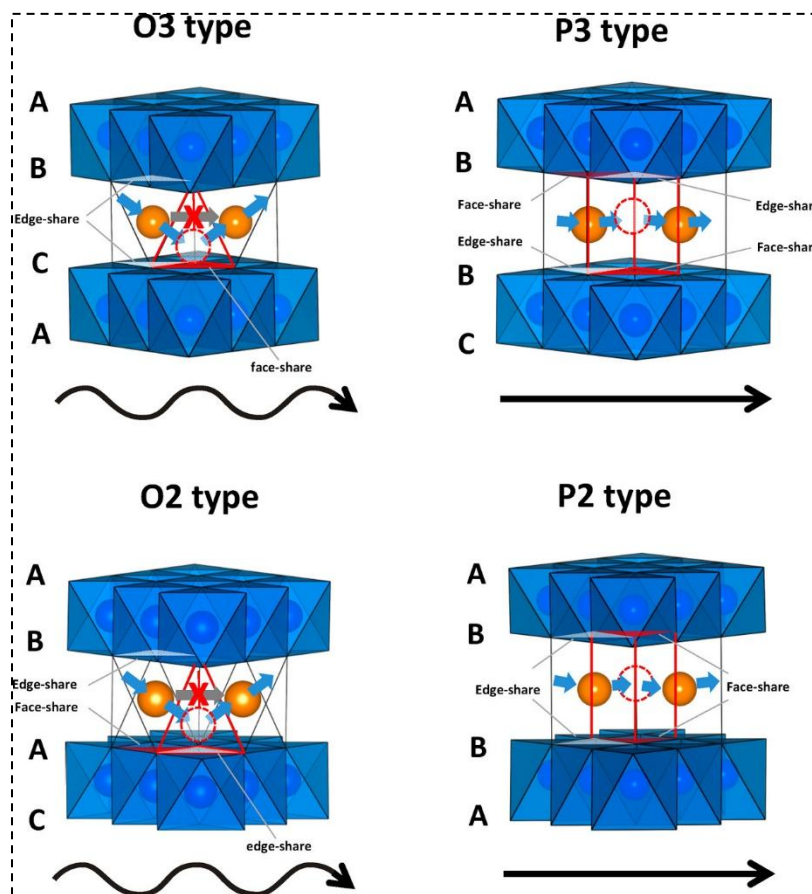


Figure 1.7 Na migration paths in different layered structures.[17]

The remarkable commercial success of layered oxide cathodes in LIBs has sparked significant scientific interest in layered NaMO_2 materials ($\text{M} = \text{Co}$, Fe , Mn , Ni , *etc.*, or their combinations).[35] In particular, low- or cobalt-free layered materials, including those based on environmentally friendly iron and manganese, have demonstrated exceptional reversible capacity and prolonged cycle life. These contributions augment the promising application potential of layered oxide cathodes for large-scale energy storage systems. Layered structures typically consist of stacked sheets comprising edge-sharing MO_6 octahedra. Layered transition metal oxides (TMOs) Na_xMO_2 (here, $\text{M}_{1/4}$ transition metals, can be single or multiple metal elements) are expected to be promising cathode materials for SIBs.

The specific structure has small ion diffusion channels and a bigger surface area during sodiation/ desodiation that are advantageous for stabilizing cycling capacity.[36] The prosperity of LiCoO_2 unsurprisingly inspires research into its sodium equivalent, NaCoO_2 . Layered sodium oxide materials can be categorized according to the position of Na^+ ions. According to the classification proposed by Delmas *et al.*, Na-layered oxides can be categorized into distinct structures based on the surrounding Na environment, namely O3-type (ABCABC), P2-type (ABBA), O2-type (ABAC), and P3-type (ABBCC) structures, as illustrated in **Figure 1.7**. [17] The terminology for these materials is as follows: P and O refer to Na's trigonal and octahedral coordination, and the number 3 or 2 refers to the repetition of layers of transition metal in the unit cell. It is worth noting that in lithium-containing layered compounds, the smaller ionic size of Li^+ ions prohibits their occupation of trigonal prismatic sites.[37]

Layered transition metal oxides have large theoretical capacities and relatively large operating voltages. However, these materials face significant challenges under high-voltage conditions, particularly regarding transition-metal migration and voltage decay.[36] At higher voltages, decomposition of the electrolytes produces HF which causes the dissolution of transition-metal ions, particularly, Ni and Mn, through the Jahn-Teller effect.[38] The result of these dissolved ions is that they are transported into the electrolyte causing the following undesirable effects; the irreversible anionic redox reactions, hysteresis of voltages and low cycling stability.[39] Mobility of the transition metals compromises the electrochemical functionality and integrity of the material and presents a critical challenge to a stable, high-voltage operation. Another important problem of layered oxides is known as voltage decay that is caused by interaction between oxygen release and transition metals valence changes.[40] The range of energy of redox pairs greatly determines the degree of volt drop. The variation of the energy of pairs of redox highly determines the voltage decay. As an example, the losses of Mn and Co are

significant since they are large in terms of energy difference. This deterioration is aggravated by oxygen release as redox pairs like $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ are used to compensate the charges, causing structural damage.[37] Particle morphology is also changed with the release of oxygen resulting in the formation of fractures and the expansion of exposed surface area, which further impairs the cycling stability and lifetime of such materials.[41]

1.8.2 Prussian Blue Analogues

Prussian blue analogues have an open three-dimensional structure, which allows the rapid diffusion of sodium-ions and therefore these can be used in high-rate applications. This structure offers advantages of increasing volume and structural stability when intercalating and deintercalating Na^+ ions, with low-spin $\text{Fe}(\text{ii})$ ions on the corners of corner-shared octahedra and high-spin $\text{Fe}(\text{iii})$ ions on the corners of corner-shared dodecyhedra bridged by linear (C N) complexes.[42] An example of a Prussian blue shown in **Figure 1.8**, $\text{K}[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6] \cdot y\text{H}_2\text{O}$, comprises a cubic framework (space group Fmm) of altern Further, the cyano ligands reveal the faces of the elementary cubes, which gives ways in which the Na^+ ions move between the half-filled body-center positions.[43]

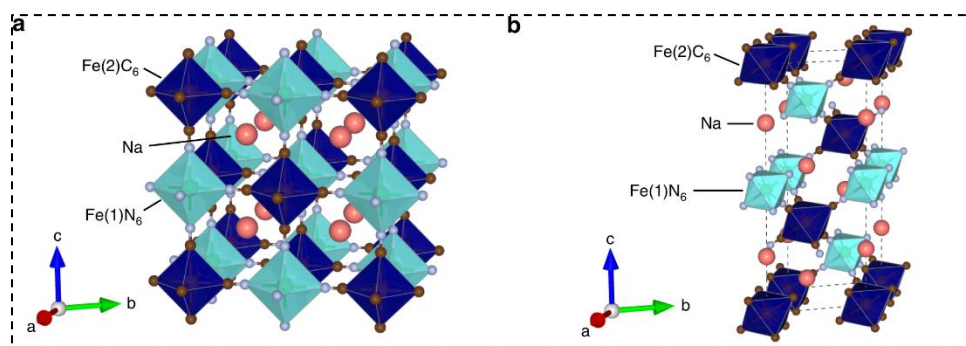


Figure 1.8 Schematic structure of $\text{Na}_{2-x}\text{FeFe}(\text{CN})_6$ (Na in red, C in brown, N in grey, Fe1 and Fe2 in cyan and blue, respectively).[43]

However, poor structural integrity is characteristic of these materials because coordinated water molecules and vacancies are a characteristic feature that may result in decreased cycling stability and decreased practical capacity. Under high voltage conditions, PBAs face a system of special obstacles such as structural defects, slow redox kinetics, and low electronic conductivity. $\text{Fe}(\text{CN})_6$ vacancy defects and crystalline water are usually introduced during the synthesis that undermines the performance of the material. Crystalline water fills sodium storage sites and clogs ion transport channels, and $\text{Fe}(\text{CN})_6$ defects undermine structural stability, particularly in charge-discharge cycling.[44] All these structural defects intensify electrolyte breakdown, HF leakage and resultant material dissolution at high voltages and greatly lowering battery efficiency. High voltage also inhibits the redox reaction kinetics in PBAs and results in low charge discharge efficiency. The ions of transition metals like Mn^{3+} are particularly prone to Jahn Nielsen Teller effects, deteriorating the cycling behavior of the material. Moreover, PBAs lack strong complexes because the metal ions and the ligands do not have strong bonds, which results in low electrical conductivity. This problem is aggravated by high voltage which causes structural collapse and additional disruption of sodium storage as well as the electronic pathways.[45] A combination of these effects accelerates the reduction of the electrochemical performance, which makes it clear that new solutions are required to handle these shortcomings.

1.8.3 Polyanionic Compounds

Polyanionic compounds have garnered significant attention in the field of LIBs due to their excellent thermal stability and higher redox potential resulting from the inductive effect of the XO_4 or XO_3 polyanion. These advantageous properties have spurred extensive investigations into polyanionic framework compounds, including phosphates, fluorophosphates, sulfates, and other novel polyanionic cathode systems for Na^+ ions.[46] In addition, the presence of facile

Na⁺ diffusion pathways and the tunability of local coordination environments present key benefits for SIBs. The exploration of polyanionic framework compounds for SIBs finds inspiration from their successful implementation in LIBs. However, it is important to note that many Na-based polyanionic cathode materials exhibit unique properties compared to their lithium-ion counterparts. For example, naturally occurring phosphate NaMPO₄ (M = Fe, Mn, Co, *etc.*) adopts the thermodynamically stable maricite structure, which lacks free Na⁺ migration pathways and exhibits negligible electrochemical performance, unlike the olivine-structured LiMPO₄.^[47] The latter demonstrates one-dimensional lithium transport paths, leading to superior electrochemical performance. This discrepancy arises from the inverse positioning of transition metal M²⁺ ions and alkali metal Na⁺ ions in the maricite structure, in contrast to olivine structure materials.^[48] Consequently, although various olivine NaMPO₄ cathode materials for SIBs have been reported, most of them necessitate chemical or electrochemical Li/Na exchange methods to be synthesized from LiMPO₄.

NASICON compounds, characterized by their open 3D frameworks, feature corner-sharing MO₆ octahedra and XO₄ tetrahedra, which create abundant Na⁺ diffusion tunnels as shown in **Figure 1.9 (a)**.^[49] Originally recognized for their fast Na⁺ ion transport properties, these materials have more recently gained attention as cathode materials. In fact, NASICON phosphate materials were initially explored as hosts for Li intercalation by Padhi *et al.*, utilizing redox couples such as V⁴⁺/V³⁺, V³⁺/V²⁺, Fe³⁺/Fe²⁺, Ti⁴⁺/Ti³⁺, Nb⁴⁺/Nb³⁺, and Nb⁵⁺/Nb⁴⁺.^[46] For instance, Li₃V₂(PO₄)₃ (*P2₁/n*) features a three-dimensional structure consisting of mildly distorted metal octahedra and phosphorus tetrahedra, interconnected through shared apical oxygen atoms to form a (M–O–P–O)_{*n*} bonding framework. One Li(1) ion forms a tetrahedron with four surrounding oxygen atoms, while Li(2) and Li(3) adopt highly distorted tetrahedral environments.^[50] In contrast, the typical NASICON-type Na₃V₂(PO₄)₃ (*R $\bar{3}$ c*) material consists of isolated

VO₆ octahedra and PO₄ tetrahedral units interconnected through corner sharing, creating the framework anion [V₂(PO₄)₃]³⁻. One Na⁺ ion occupies the M1 (6b) site, while the other two reside in the M2 (18e) site within the interstitial positions. These distinct structural characteristics contribute to the unique physical and electrochemical properties exhibited by NASICON Na-ion compounds, necessitating comprehensive investigations.[51] Additionally, the introduction of fluorine (F) elements into phosphates can form fluorophosphates with higher redox potentials, attributed to the presence of highly electronegative fluorine atoms.

Polyanion-type electrode materials are compound that contains a series of tetrahedron anion units (XO₄)ⁿ⁻ or their derivatives (X_mO_{3m+1})ⁿ⁻ (X = S, P, Si, As, Mo, or W) with strong covalent-bonded MO_x polyhedra (M represents a transition metal).[52] Due to strong covalently bonded oxygen with the transition metal M and the nonmetal X, they show higher thermal stability compared to other cathode materials, which makes them popular where safety is a concern.[46] Also their minor structural changes during their insertion and deinsertion of sodium ions due to the robust 3D structure is another advantage. Polyanionic materials generally show lower gravimetric densities due to their heavier polyanionic groups.

The higher redox potential of the polyanionic compounds can be explained with molecular orbital theory according to **Figure 1.9 (b)**. Interactions among the 3d orbital of a transition metal and the 2sp orbital of oxygen (M-O) causes the energy splitting of molecular orbitals into bonding and antibonding orbitals. A highly covalent M-O bond will lead to larger spilling which in turn will decrease the energy difference (ΔE) between the antibonding orbitals and the Fermi level of sodium (vacuum state), thus reducing the voltage as ΔE proportional to the redox potential of the metals.[53] When an electronegative polyanionic group is introduced to the framework, the M-X bond weakens the M-O bond, as it increases the

electron density on the transition metal; thus, the antibonding orbitals rise to a lower extent, which raises the redox potential of the transition metal as depicted in **Figure 1.9 (c)**.

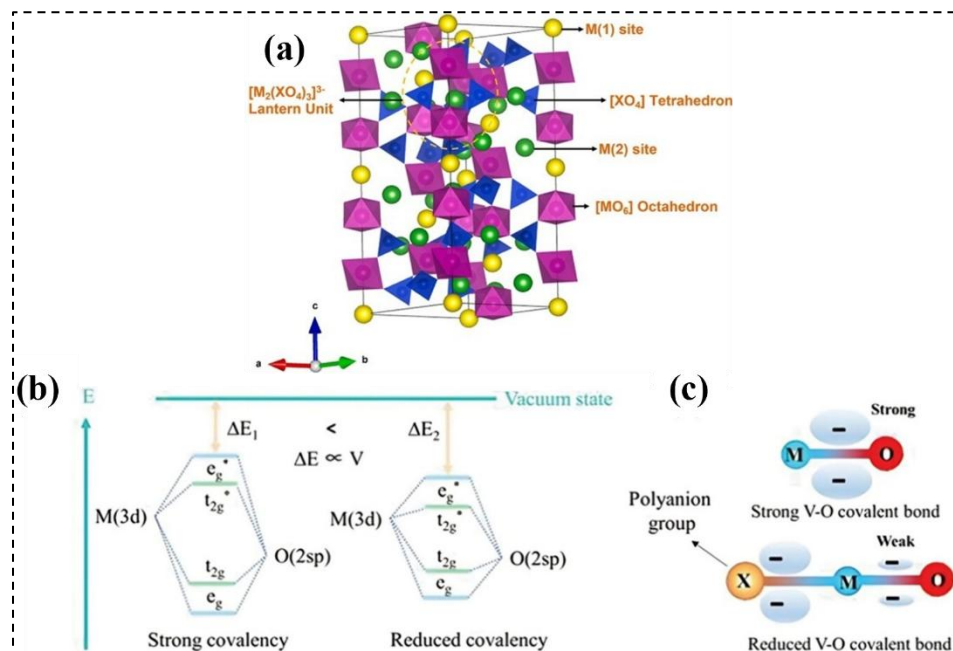


Figure 1.9 (a) NASICON crystal structure with rhombohedral symmetry. The lantern unit is highlighted by the dash line,[52] (b) Schematic illustration of the changes of molecular orbits and (c) covalency of M-O bond.[53]

Polyanionic compounds exhibit distinct challenges under high-voltage conditions, primarily due to slow redox reaction kinetics and oxygen release. The rigid structure of polyanionic materials tends to hinder redox reaction dynamics and slow down the charge transfer rate that occurs during the charging and discharging. This sluggish nature reduces the energy efficiency and applicability of such materials in high performance systems. Besides, redox reactions with oxygen release can involve high-valence transition metals like Fe^{4+} and Ni^{4+} at high voltages. Such oxygen release causes structural rearrangements and irreversible capacity loss, further worsening the electrochemical performance of polyanionic compounds.[47,49] The simultaneous occurrence of electrolyte oxidation

compounds these issues, accelerating degradation and reducing the overall stability of materials.

Although PBAs, polyanionic compounds, and layered transition-metal oxides have the potential as high-voltage cathode materials for SIBs, each class has its own challenges. These problems can only be resolved by an in-depth understanding of the structural, electrochemical, and interfacial processes which take place under high voltages. Overcoming these obstacles and realizing the full potential of high-voltage cathode materials requires future work on the material design, synthesis methods, and electrolyte optimization.[42,54]

1.9 Polyanionic phosphate compounds

Polyanionic cathode materials are characterized by the presence of anionic groups such as phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), or silicate (SiO_4^{4-}) units within their crystal structures.[24,47] Among these, phosphate-based materials have been given significant consideration in SIBs due to their high structural stability, safety, and electrochemical stability.

The phosphate group is bonded with strong P-O covalent bonds, and these bonds stabilize the crystal lattice and inhibit oxygen release at high voltages. Such structural strength leads to better thermal stability and high safety as compared to oxide-based cathode materials. Also, the inductive effect of the phosphate group decreases the energy of the transition-metal redox couple, increasing the operating voltage with no effect on structural integrity, as detailed further.

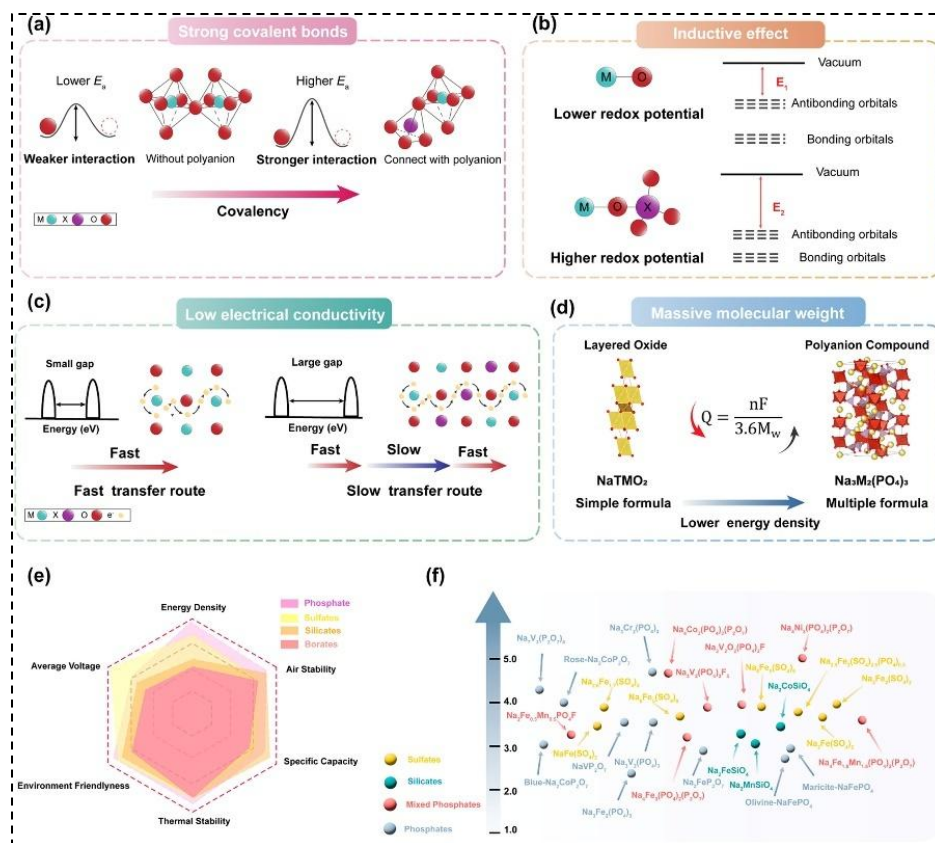


Figure 1.10 (a) Schematic diagram showing the influence of the M–O covalency with polyanion. (b) Schematic diagram of the inductive effect. E is the energy needed to drive one electron to a vacuum state. E is proportional to the voltage. (c) Schematic diagram of possible electron transfer route in polyanionic materials. (d) The formula to calculate the theoretical capacity, Q : theoretical capacity (mAh g^{-1}), n : the number of transferred electrons from one molecule, M_w : molecular weight (g mol^{-1}). (e) Overview of key properties of different polyanionic compounds for SIBs. (f) Diagram of the average voltages (vs. Na^+/Na) of various polyanionic cathode materials.[24]

1.9.1 Properties of polyanionic compounds

- High thermal and structural stability

In polyanionic compounds, the strong X–O covalent bonds, along with the connectivity between anion units and MO_x polyhedra, enable the formation of open and robust structural frameworks. Compared to layered oxide compounds, the oxygen atoms in the polyanion units exhibit a more

pronounced interaction with the highly electronegative X atoms, which significantly increases the activation energy barrier for oxygen release (**Figure 1.10 (a)**). This enhanced bonding stabilizes the oxygen within the lattice even at elevated temperatures, effectively preventing structural degradation and ensuring superior thermal stability and safety.[55] Besides, the open 3D frameworks with abundant lattice interstices facilitate continuous Na^+ diffusion, effectively reducing volume changes and mitigating complex phase transitions during long-term cycling, thereby improving the durability and stability of polyanionic cathodes.

- High redox potential

The strong X–O covalent bonds in polyanionic compounds not only improve the structural stability but also promote the redox potential of transition metals via the inductive effect (**Figure 1.10 (b)**). According to molecular orbital theory, the covalent interactions between M 3d and O 2p orbitals lead to the splitting of molecular orbitals, giving rise to bonding and antibonding orbitals. The splitting energy between antibonding and bonding orbitals depends on the properties of M–O covalent bonds. Specifically, the stronger M–O covalency can increase the splitting energy, causing more electrons to fill the bonding orbitals while raising the antibonding orbitals. Consequently, the energy difference (E_1) between antibonding orbitals and vacuum will decrease, resulting in a lower redox potential. When X atoms with stronger electronegativity are introduced to form M–O–X bonds, the inductive effect comes into effect and makes the M–O bonds more ionic. The repulsion between bonding and antibonding orbitals is weakened, and the energy difference (E_2) increases, contributing to a higher redox potential. Based on this principle, strongly electronegative groups such as F^- or SO_4^{2-} have been introduced into polyanionic cathodes to further increase the inductive effect, aiming to achieve batteries with promoted operating voltage and thus enlarged energy density.

- Low electrical conductivity

In polyanionic compounds, the covalent X–O bonds localize electrons on oxygen atoms due to the high electronegativity of the X elements, creating a wide band gap that impedes electronic delocalization (**Figure 1.10 (c)**). Additionally, the presence of anionic groups disrupts the continuous electron conduction pathways, forcing charge transport to proceed via isolated hopping sites. For instance, in the sodium superionic conductor (NASICON)-type $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP), oxygen atoms are shared with the PO_4 tetrahedra rather than between VO_6 octahedra. As a result, electrons transfer via a slower V–O–P–O–V pathway instead of the more direct and faster V–O–V route. Since the transport of electrons is blocked by the anion units, polyanionic cathodes typically exhibit low electrical conductivities, leading to large charge/discharge polarizations, limited capacity, and poor rate capability. Effective strategies for this issue will be presented afterward.

- Relatively low specific capacity

The “weight penalty” (smaller theoretical specific capacity) arising from the presence of large-mass inactive anionic groups is another limitation of polyanionic cathodes. Compared with layered oxides, polyanionic compounds typically possess larger formula weights due to their complex compositions and multi-atom anionic units, resulting in a lower theoretical specific capacity (**Figure 1.10 (d)**). For an electrode material, the theoretical specific capacity (Q) can be calculated by Eq. (1).

$$Q = \frac{nF}{3.6 M_w} \quad (1.9)$$

where n is the number of electrons involved in the redox reaction, F is the Faraday constant, and M_w is the molecular weight of the electrode material. The large molecular weight of polyanionic groups inevitably restricts the theoretical specific capacities of polyanionic cathodes. Fortunately, the energy density of the battery is determined by both specific capacity and operating voltage. Hence, it is still possible to realize batteries with competitive energy densities despite the relatively low specific capacities.

As discussed above, the four characteristics of polyanionic cathodes are closely connected to their electrochemical performance. In general, several principles should be taken into account for preparing an ideal cathode material, including (1) high operating voltage and large specific capacity for enlarged energy density, (2) high thermal and structural stability for long-term durability, (3) low cost for large-scale production, and (4) environmental friendliness without pollution.[56] Comprehensively considering these factors for polyanionic cathodes, including phosphates, sulfates, silicates, and borates (**Figure 1.10 e and f**), phosphates and sulfates stand out as the most promising candidates for practical applications. In the following sections, a detailed review of the advancements in phosphate and sulfate-based polyanionic cathodes for SIBs will be presented.

1.9.2 Fe-based phosphate compounds

Phosphate-based polyanionic materials exhibit a wide range of structural frameworks, including NASICON-type, olivine-type, and other three-dimensional open frameworks. These structures provide well-defined sodium-ion diffusion pathways, facilitating reversible sodium-ion insertion and extraction. Moreover, compositional design can be flexibly designed to partially replace transition metals, permitting the electrochemical properties of capacity, voltage, and cycling stability to be fine-tuned.[57] Vanadium-based polyanionic cathodes, such as $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, and mixed V-based fluorophosphates, establish current performance benchmarks of SIBs because of their high operating voltages (typically over 3.4 V vs. Na^+/Na), rapid diffusion of Na^+ in NASICON structures, and high rate capability. These advantages largely stem from the high redox potentials of the $\text{V}^{3+}/\text{V}^{4+}$ and $\text{V}^{4+}/\text{V}^{5+}$ couples, combined with strong inductive effects from polyanions and, in some cases, additional anions such as F^- . [51] Although V-based polyanionic phosphates, including $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and related derivative are generally considered as standard benchmarks in cathode development, because they operate at high operating voltages and have a high rate capability, their dependence on the less

abundant, expensive, and toxic vanadium greatly restricts the potentials of sustainable, grid scale application.

Other transition metals such as Mn, Co, and Ni have also been explored in polyanionic phosphate frameworks, either as primary redox centers or as co-substituents. Manganese has relatively high redox potentials, $\text{Mn}^{2+}/\text{Mn}^{3+}$, and is relatively inexpensive but Mn-based cathodes are prone to Jahn-Teller distortions, phase transitions, and capacity loss especially when operating at high voltages or high rates. Cobalt and nickel could enhance electronic conductivity and energy density, but they cost much more, are less sustainable, and have long-standing environmental and ethical issues in their mining and supply chains. These drawbacks support the role of iron as a more convenient and scalable solution in particular when it is partially replaced by Mn or V to achieve synergetic effects in mixed-polyanionic or multi-cation systems.[55,57]

The iron is earth-abundant (≈ 5 wt% in the Earth's crust), inexpensive, and environmentally benign, making Fe-based polyanionic cathodes inherently more suitable for cost-sensitive and large-volume SIB markets. The Fe-based polyanionic phosphate compounds have become promising cathode material in SIBs offering structural strength, cost, safety, and electrochemical properties that are highly compatible with the practical demands of large-scale energy storage. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox pair, combined with the polyanionic structure, makes Fe-based polyanionic phosphate compounds appealing. The high structural stability, thermal stability, and inherent safety of phosphate and mixed polyanionic groups (e.g., $\text{PO}_4/\text{P}_2\text{O}_7$, PO_4/SO_4) are due to the strong covalent P-O bond, which offers these qualities even during high rate cycling and overcharge conditions, a key feature in stationary storage and high safety.[58] The $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox potential is not as high as that of $\text{V}^{3+}/\text{V}^{4+}$ or $\text{V}^{4+}/\text{V}^{5+}$, but the operating voltage of the Fe-based phosphates can be greatly increased by the polyanionic inductive effect, which allows multi-electron redox activity to compete effectively with dense frameworks. Further, the preferred

electronic configuration and capacity of iron to undergo mixed-valency states enable electrochemical versatility to be tuned by substituting cations and mixing polyanions to enable high-performance cathodes to be designed.[59]

From a sustainability standpoint, Fe-based polyanionic phosphates significantly lower reliance on critical or geopolitically sensitive elements such as V, Co, and Ni, which are more expensive, less abundant, and often associated with higher environmental and social costs. In large-scale, long-lifetime grid storage, where energy density is less of a concern than in high-end electric vehicles, and where cost, safety, and cycle life are the dominant factors, this advantage of resource is a strong case in favour of Fe-based chemistries over V-based counterparts.[60]

The literature increasingly indicates that Fe-based polyanionic phosphates can provide rivalry in terms of electrochemical activity and still maintain obvious benefits in terms of price and sustainability. Fe-based mixed phosphates such as $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ have robust open frameworks with interconnected channels of Na^+ migration, which allow good rate capability and cycling stability both in bulk and thin-film systems.[61,62] Systematic investigations on phosphate-based mixed polyanion systems have demonstrated that the redox potentials, as well as electronic/ionic conductivity and structural stability during repeated Na^+ insertion/extraction could be maximized by incorporating other transition metals (e.g., Mn, V) and multiple anionic groups (PO_4 , P_2O_7 , SO_4) in the system.

In NASAICON-type $\text{Na}_3\text{M}_2(\text{PO}_4)_3$, Fe substitution has been intensively studied as a technique to moderate cost and toxicity without impairing or indeed improving electrochemical performance. As an example, Fe-modified NASICON compounds, including $\text{Na}_3\text{Fe}_{0.8}\text{V}_{1.2}(\text{PO}_4)_3/\text{C}$, show that replacement of V by Fe can still retain fast Na^+ diffusion (migration barriers of about 0.14 eV), reduce charge-transfer resistance and provide high rate capability, and cycling stability, even

though average operating voltage increases moderately.[63] Similarly, Fe mixed phosphates and metaphosphates were demonstrated to attain competitive capacities and stable cycling with carbon coating or nano-structuring to overcome inherent electronic conductivity constraints.[64]

Recent literature on polyanionic cathodes for practical SIBs repeatedly notes that Fe-based phosphates are the most promising cathodes for commercial use, particularly in applications that emphasize safety, durability, and cost rather than maximizing energy density. In this regard, Fe based polyanionic phosphate materials like $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ and similar FeMn or FeV solid solutions are especially attractive since they combine structural and resource/environmental merits of phosphate frameworks with the multi-cation redox synergistic for capacity advantages offered by using multi-cation redox. All these attributes justify the interest in Fe-based polyanionic phosphates as promising cathode materials for next-generation SIBs and provide a strong scientific and technological foundation for the work reported in this thesis.

1.10 Research Gaps and Motivation

Despite extensive research on SIB cathode materials, several complex issues remain that reduce their full-scale implementation and long-term sustainability. $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ is one of the most commonly studied cathode materials, which has excellent structural stability, a high operating voltage, and a good cycling capability. Nevertheless, its dependence on vanadium, which is relatively expensive, toxic, and less abundant, raises serious concerns regarding cost, environmental impact, and resource longevity as it seeks to develop vanadium-reduced or vanadium-free systems, which still achieve positive electrochemical behavior.

Besides the compositional issues, the electrochemical performance of the high-voltage polyanionic cathodes is highly dependent on the compatibility with the commonly used electrolyte. Interfacial reactions between electrode materials and electrolytes may cause surface degradation, decomposition of electrolytes and interfacial resistance

especially at high operating voltages. Although it is essential, there are still no systematic studies on the compatibility of electrolytes and electrode-electrolyte interfacial stability of vanadium-reduced or modified cathode systems, representing significant research gap.

Another way of making SIBs sustainable is by fully substituting vanadium with elements that are earth-abundant, cost-effective, and environmental-friendly like iron and manganese. Nevertheless, these replacements usually lead to lower electronic conductivity and slow diffusion kinetics of sodium-ion, which negatively impact rate capability and capacity utilization. To overcome these drawbacks, heteroatom doping (e.g., nitrogen) has become a potential solution to increase electronic conductivity, alter local electronic structure, as well as enhance charge-transfer kinetics, without affecting structural integrity. However, the mechanisms behind the effect of heteroatom doping on electrochemical performance is yet to be explored.

Interestingly, a number of the new polyanionic and framework-based materials of the electrode demonstrate dual electrochemical capability with poised sodium storage ability under high voltage and low voltage range conditions based on the operating window. Although this multi-purpose behavior opens up the prospects of designing multi-functional electrodes, in-depth research on such duality, including the effects of duality on redox reversibility, structural integrity, and cycling stability, is lacking.

In addition, the inherently poor electronic conductivity of most polyanionic substances still impairs their practical capability and high-rate functionality. There has been little exploration in the design of state-of-the-art conductive carbon networks despite carbon coating commonly being used, an example of such hierarchical carbon network is nitrogen-doped hierarchical architecture when using Fe/Mn. Developing effective carbon networks can provide a promising solution in improving electron transfer, active material

utilization, and capacity to increase reversible currents at high current densities.

These unsolved challenges highlight the necessity of systematically investigating the new vanadium-free cathode materials with better electrolyte compatibility, higher electronic conductivity due to heteroatomic doping, and versatile electrochemical functions. These gaps have been systematically filled in the present study through the development of vanadium-free and N-doped carbon-coated cathodes, nitrogen-doped carbon-coated $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ (NFMP@NC) cathodes, that serve as the solution to vanadium-free composition, N-doping, improved sustainable carbon structures, and stability of electrolyte interface by multi-technique characterization (XRD, XPS, EIS, GITT). By delivering high-performance, scalable SIB cathodes for grid-scale applications, this work advances sustainable SIB technologies toward practical commercialization.

1.11 Scope and Aim of the thesis

The scope of this thesis is focused on advancing the fundamental understanding and development of sustainable cathode materials for SIB applications. Emphasis is on the overcoming of the main shortcomings of traditional cathode chemistries especially in terms of material cost, environmental impact, electronic conductivity, and interfacial stability.

The aim of the work is to develop alternative designs for SIB cathodes, focusing on a vanadium-free system based on earth-abundant, environmentally benign elements. Much attention is paid to the enhancement of electrochemical performance in terms of compositional modifications, electronic structure tuning, and surface/interface engineering. The research also includes the analysis of the interaction of electrode and electrolyte to allow stable and consistent battery functioning in real-world conditions.

Moreover, this thesis area is also necessitating the exploration of methods to improve charge transport kinetics and practical capacity through

conductive network engineering, such as carbon-based architectures. This study aims to add value to the design of high-performance, cost-effective and scalable cathode materials to be used in the next-generation SIBs by combining material chemistry, electrochemical analysis and structural optimization.

1.11.1 Thesis Objectives

The thesis reports the investigation of the following objectives to address the challenges identified in the literature survey. The primary objective of this research is to develop, fabricate, and optimize Fe-based phosphate materials as efficient electrode systems for SIBs with enhanced electrochemical performance, stability, and rate capability. The specific objectives are:

1. To explore the electrolyte compatibility and the electrolyte-dependent interfacial chemistry of high redox-potential $\text{Na}_3\text{FeV}(\text{PO}_4)_3$ cathodes in SIBs.
2. To investigate the effects of heteroatom doping and interface-induced structural changes in $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ cathodes on electrochemical behavior and sodium-ion diffusion kinetics.
3. To explore the influence of heteroatom doping on sodium-ion storage properties of $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ as an anode material.
4. To examine the role of conductive carbon network engineering in enhancing the electrochemical performance of $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ electrodes.
5. To develop and optimize Fe-based polyanionic electrode material and perform extensive physicochemical characterizations to understand their structural, chemical, thermal and electronic characteristics.
6. To carry out detailed electrochemical analyses, including redox behavior investigation, sodium-ion diffusion kinetics, capacity evaluation, and long-term cycling stability.

By addressing these objectives, this research aims to develop cost-effective, high-performance, and sustainable Fe-based polyanionic electrode materials for next-generation SIB applications.

1.11.2 Structure of the Thesis

The work has been divided into six chapters, encompassing the introduction (Chapter 1) and the conclusions and future scope (Chapter 6). The chapter-wise organization is summarized as follows:

Chapter 1: Introduction

The chapter introduces the necessity of developing sustainable and cost-effective electrochemical energy-storage systems, highlighting SIBs as a promising alternative to LIBs. The history, operating principles, and performance evaluation parameters of SIBs are discussed in detail. The fundamental elements of a battery and their roles are described and then cathode materials used in SIBs are categorized. The advantages and drawbacks of the various cathode material classes are carefully discussed, with a specific focus on the issues and opportunities associated with polyanionic compounds. Finally, the scope, aims, and objectives of the present thesis are clearly defined.

Chapter 2: Experimental and Characterization Techniques

In this chapter, the synthesis methodologies that were used to prepare Fe-based polyanionic electrode materials are described, with most of the wet-chemical routes being sol-gel and hydrothermal. The steps of electrode preparation and coin cell fabrication are described. Furthermore, physicochemical and electrochemical characterization techniques that were employed to evaluate the structural, morphological, chemical, and electrochemical properties of the synthesized materials are discussed.

Chapter 3: Electrolyte-Electrode Interfacial Chemistry in High-Voltage $\text{Na}_3\text{FeV}(\text{PO}_4)_3$ Cathodes for SIBs

This chapter presents the synthesis of $\text{Na}_3\text{FeV}(\text{PO}_4)_3$ cathode material by the sol-gel method and focuses on the electrolyte compatibility

and electrolyte-dependent interfacial chemistry. The effects of electrolyte selection on the electrode-electrolyte interface and the electrochemical performance of polyanionic cathodes in a SIB are systematically examined. Furthermore, the effect of partial V substitution on sodium-ion diffusion behavior is elucidated using combined experimental observations and computational studies.

Chapter 4: Dual Functionality of $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ -Based Materials for Sodium-Ion Batteries

This chapter is divided into two parts as the materials demonstrated dual functionality for SIBs.

Part A: Heteroatom Interface Engineering for Enhanced Na^+ Diffusion in $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ Cathode

This chapter reports a systematic investigation of the synthesis of heteroatom-doped carbon-coated $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ cathode materials using a hydrothermal process. The effects of heteroatom doping on phase formation, morphology, crystallinity, electronic structure, and interfacial properties are thoroughly discussed. A comparative electrochemical study on the modified and the pristine $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ is presented, demonstrating enhanced operating voltage, improved capacity retention, and superior cycling stability, highlighting their potential as high-performance cathodes for SIBs.

Part B: Heteroatom Doping Strategy for Enhanced Sodium-Ion Storage in $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ Anode

This chapter explores the application of heteroatom-doped carbon-coated $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ as an anode material in SIB. The study focuses on applying synergistic multi-redox reactions to improve the sodium storage performance. The synthesis approach, physicochemical characterization, and electrochemical behavior are discussed in detail, demonstrating promising a promising reversible capacity, rate capability,

and cycling stability. This chapter represents the first systematic study of this material and strategy as an anode to SIBs.

Chapter 5: Graphene-Embedded $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ for Enhanced Sodium-Ion Battery Performance

This chapter examines the impact of the conductive carbon network on the physicochemical and electrochemical characteristics of $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ cathode for SIB. The structural features and electrochemical behavior of $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ are discussed. The advantages of incorporating graphene as a conductive additive are highlighted, particularly in reducing electronic resistance and facilitating efficient electron transport. The contributions of an interlinked carbon network to increased sodium-ion transport, Fe redox activity, rate performance, and long-term cycling stability are carefully examined.

Chapter 6: Conclusions and Scope for Future Work

This chapter summarizes the key findings and critically assesses the electrochemical performance of the developed Fe-based polyanionic electrode material for SIBs. The chapter concludes by outlining future research directions aimed at further improving electrode materials and advancing SIB technology toward practical and commercial applications.

By addressing the outlined objectives, this thesis contributes to the advancement of SIB technology through the rational design, interfacial engineering, and performance optimization of advanced electrode materials.

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Chapter 2

Experimental and Characterization Techniques

In this chapter, the experimental procedures employed for the synthesis of electrode materials and the characterization techniques used for physicochemical and electrochemical analyses of advanced electrode materials for SIBs are described in detail. Fe-based phosphate materials were successfully synthesized using wet-chemical routes such as sol-gel and hydrothermal methods under controlled conditions. The structural, chemical, thermal, and electronic properties of the synthesized materials were systematically investigated using various characterization techniques, including thermogravimetric analysis (TGA), X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDS), Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Furthermore, the procedures for electrode preparation, coin-cell fabrication, and electrochemical characterization, comprising cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) measurements, and electrochemical impedance spectroscopy (EIS), are presented. Density functional theory (DFT) calculations, used to support experimental findings and elucidate sodium-ion diffusion behavior and electronic structure, are also described. This chapter establishes the experimental foundation for interpreting structure-performance relationships of the electrode materials discussed in the subsequent chapters.

2.1 Introduction

The development of high-performance electrode materials for SIBs requires systematic synthesis strategies combined with comprehensive physicochemical and electrochemical characterization. Experimental methods are important for understanding the structural-property relations that govern the electrochemical behaviour of electrode materials. Specifically, synthesis conditions, crystallographic structure, morphology, elemental composition, and the surface chemistry have a considerable impact on the kinetics of sodium-ion diffusion, electronic conductivity, and the overall battery performance.

The chapter presents the experimental strategies used to prepare the polyanionic phosphate-based cathode materials and the experimental procedures employed to investigate their structural, chemical, and electrochemical properties. In the current study, the investigated materials were $\text{Na}_3\text{FeV}(\text{PO}_4)_3$, $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ and its heteroatom-doped derivatives, and $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3/\text{graphene}$ composites, produced by the sol-gel and hydrothermal process. These synthesis methods have been commonly used in the synthesis of phosphate-based electrode material because of their potential to attain homogeneous compositions, controlled particle sizes, and high phase purity.

Following the materials synthesis, a series of advanced characterization methods was used to explore the structural, morphological, and chemical properties of the prepared materials. Thermal stability and decomposition behavior of precursors in the presence of high temperatures were studied by thermogravimetric analysis (TGA), and powder X-ray diffraction (XRD) was used to analyze the crystal structure, lattice parameters, and phase purity. The morphology on the surface, and distribution of particle size were studied using field-emission scanning electron microscopy (FESEM), meanwhile, high-resolution transmission

electron microscopy (HRTEM) examined structural characteristics at the nanoscale and lattice composition. Elemental composition and distribution were studied by energy-dispersive X-ray spectrophotometry (EDS), and Raman spectroscopy, Fourier-transform infrared spectrophotometry (FTIR), and X-ray photoelectron spectrophotometry (XPS) were used to study the vibrational modes, chemical bonding, and surface oxidation states. Besides physicochemical characterization, the process of electrode preparation and fabrication of coin-cells is outlined in detail. The electrochemical performance was investigated with the help of cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) measurements, and electrochemical impedance spectroscopy (EIS), which will give an insight into redox reactions, kinetics of sodium-ion diffusion, charge transfer resistance, and overall battery performance. Moreover, the density functional theory (DFT) computations were conducted in order to complement the experimental findings and to understand more about the electronic structure and the migration pathways of sodium-ions in the electrode materials. The combination of theoretical modeling and experimental observation gives an understanding of the structure-performance relationship of the synthesized materials in a manner that is comprehensive. In general, this chapter forms the experimental basis of the synthesis, characterization, and electrochemical assessment of the electrode materials that are employed in this thesis, which underlie the discussion of their sodium-ion storage ability in the subsequent chapters.

2.2 Material Synthesis via Wet Chemical Methods

The synthesis techniques employed for preparing electrode materials play a significant role in influencing their structural, morphological, and electrochemical characteristics in SIBs. In this thesis, two main synthesis routes were primarily utilized: (i) the sol-gel method and (ii) the hydrothermal method. These approaches were selected because of their advantages in producing phosphate materials with high phase purity

and well-controlled composition. The following sections provide a brief description of these synthesis techniques.

2.2.1 The Sol-Gel Synthesis Method

The sol-gel method is a wet-chemical technique that is extensively used for the development of high-quality nanomaterials. This method is called a sol-gel method as during the synthesis of the phosphate nanoparticles, the liquid precursor is transformed to a sol, and the sol is ultimately converted into a network structure that is called a gel. Conventional precursors for the generation of nanomaterials using the sol-gel method are metal acetates, nitrates or carbonates. The synthesis process of nanoparticles via the sol-gel method can be completed in several steps. In the first step, the hydrolysis of the metal precursors takes place in water to form a sol. In the next step, condensation takes place, resulting in an increase in the solvent viscosity to form porous structures that are left to age. During the condensation or polycondensation process, hydroxo- (M-OH-M) or oxo- (M-O-M) bridges form, resulting in metal-hydroxo- or metal-oxo-polymer formation in solution. During the aging process, polycondensation continues, with changes to the structure, properties, and porosity. During aging, the porosity decreases, and the distance between the colloidal particles increases. After the aging process, drying takes place, in which water and organic solvents are removed from the gel. Lastly, calcination is performed to achieve nanoparticles. Fig. 9 shows film and powder formation using the sol-gel method. The factors that affect the final product obtained via the sol-gel method are the precursor nature, hydrolysis rate, aging time, pH, and molar ratio between H_2O and the precursor. It is an economically friendly method and has many other advantages, such as the produced material being homogeneous in nature, the processing temperature being low, and the method being a facile way to produce composites and complex nanostructures.

2.2.1.1 Synthesis of $Na_3FeV(PO_4)_3$

$\text{Na}_3\text{FeV}(\text{PO}_4)_3$ was synthesized through a facile sol-gel route followed by a two-step annealing. The starting materials $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$: NH_4VO_3 : CH_3COONa : $\text{NH}_4\text{H}_2\text{PO}_4$ were taken in the molar ratio of 1:1:3.1:3, respectively. The citric acid as a complexing agent was added at 20% of the total metal precursors. Initially, the citric acid was dissolved in 80 mL of DI water under constant stirring. NH_4VO_3 was then added to the above solution and subjected to stirring for 30 minutes at 70 °C to facilitate the reduction of V^{5+} to V^{3+} . Subsequently, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, CH_3COONa and $\text{NH}_4\text{H}_2\text{PO}_4$ were added sequentially to the solution. After complete dissolution, the solution was kept on stirring for another 30 minutes and then heated at 80 °C until the formation of a gel. Then the resulting gel was ground and subjected to the two-step annealing under an Argon atmosphere. The material is preheated at 300 °C for 4 hours to remove organic content, and this intermediate material is then annealed at 500 °C for 8 hours in a tubular furnace, with a ramping rate of 3 °C per minute. Finally, the obtained $\text{Na}_3\text{FeV}(\text{PO}_4)_3$ powder was collected and ground for further characterization.

2.2.1.2 Synthesis of graphene-embedded $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$

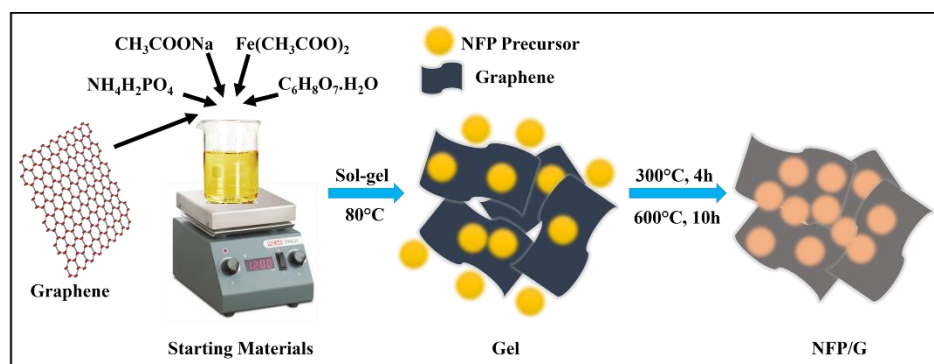


Figure 2.1 Schematic illustration of the sol-gel synthesis process for the graphene-embedded $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ composite

The synthesis of the $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3/\text{G}$ composite employed a citric acid-assisted sol-gel approach, as depicted in **Figure 2.1**. Initially, a precise molar ratio mixture of CH_3COONa , $\text{Fe}(\text{CH}_3\text{COO})_2$, and $\text{NH}_4\text{H}_2\text{PO}_4$ (3:2:3) was dissolved in 50 mL of deionized water at ambient temperature.

Subsequently, 8 wt% graphene powder, relative to the total raw materials, was incorporated into the solution and subjected to ultrasonication for 1 h at room temperature to ensure homogeneous dispersion. After this step, citric acid solution was added to the mixture with the pH maintained at 4 to enable gel formation. The resultant sol was then dried at 80 °C to a gel-like form, heated at 100 °C and ground into fine powder. The obtained powder was finally subjected to thermal treatment at 300 °C for 4 h, followed by annealing at 600 °C for 10 h to obtain the desired compound structure. Moreover, $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ without graphene was also synthesized using the same procedure for comparison study. It is an effective methodological strategy that produces a controlled synthesis of the $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3/\text{G}$ compound to improve its applicability in further characterization and performance assessment studies in SIB applications.

The phosphate-based cathode materials investigated in this thesis were synthesized using a citric acid-assisted sol-gel route, which enabled homogeneous precursor mixing and the formation of phase-pure compounds with desirable electrochemical properties. Although the synthesis employed deionized water as the solvent and relatively simple processing conditions, large-scale implementation may still be influenced by solvent usage, drying requirements, and thermal treatment costs. Therefore, future studies should focus on developing more scalable and cost-effective synthesis strategies, along with comprehensive techno-economic and environmental assessments, to facilitate the practical deployment of these materials in sodium-ion batteries.

2.2.2 The Hydrothermal Process

The hydrothermal process uses molecular-level precursors that are dissolved in water to synthesize nanoparticles via a bottom-up mechanism. The reaction is conducted in a closed and highly pressurized vessel (autoclave), which helps decompose the precursor and/or drive the chemical reaction at high temperature and pressure. The conditions favour greater solubility, reactivity and crystallization of the precursors allowing

controlled formation of materials. This method is extensively used in the production of nanomaterials, such as metals, metal oxides, semiconductors, ceramics, and in certain instances, polymer-based materials. Among the benefits of the hydrothermal technique, one can highlight the ability to obtain nanomaterials with different morphologies, including nanoparticles, nanorods, nanowires, and nanospheres. Synthesis parameters, such as the type of solvent, reaction temperature and pressure, precursor concentration, pH, surfactant or structure-directing agent, have a strong impact on the physicochemical properties of the synthesized materials. A liquid-phase nucleation and growth process usually dictates the hydrothermal process. The first step involves the nucleation of a small nanocrystalline nucleus through the decomposition of a precursor by supersaturation of the initial solution or subsequent reaction products. Subsequently, these nuclei grow via diffusion-controlled processes within the liquid medium, ultimately yielding well-crystallized nanomaterials with controlled size and morphology. During the reaction, dissolved chemical precursors or molten species in the liquid phase undergo continuous thermal motion, which facilitates crystal growth and phase evolution.

2.2.2.1 Synthesis of $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3@ \text{NC}$

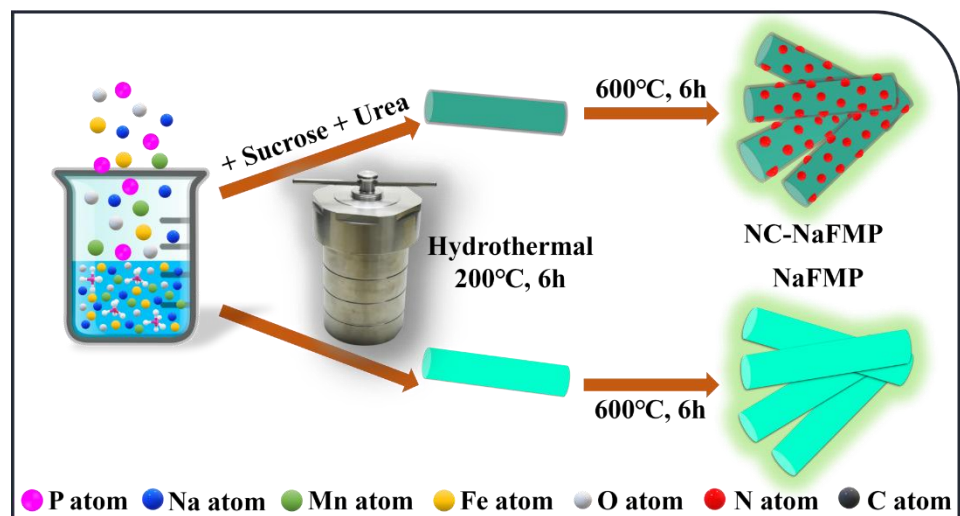


Figure 2.2 Schematic illustration of the hydrothermal process followed by heat treatment for $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ and $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3@ \text{NC}$.

$\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3@\text{NC}$ was synthesized through a hydrothermal process as illustrated in **Figure 2.2**, employing $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, MnCO_3 , and $\text{FeC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ as initial materials, sucrose and urea as carbon and nitrogen sources, respectively. In a standard synthesis for NFMP@NC, the molar ratio of Na:Fe:Mn:P was maintained at 2:1.5:1.5:3 in a 50 mL deionized (DI) water solution labeled as A, which was then subjected to stirring. At the same time, a mixture of sucrose and urea in 5 mL of DI water, which was referred to as solution B, was prepared. Thereafter, solution B was carefully added to solution A with constant stirring and allowed to incubate for 30 min. This solution was then put into a Teflon-lined stainless-steel autoclave and maintained at 200 °C for 6 h. On cooling to room temperature, the solution was filtered and washed several times with DI water and ethanol followed by drying at 100 °C under a vacuum for 12 h. The dried sample was subjected to a 5 h calcination at 600 °C under a flow of N_2 . Additionally, NFMP was synthesized using the same method but without the inclusion of sucrose and urea.

2.2.2.2 Synthesis of $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ and its derivatives

As illustrated in **Figure 2.3**, all NFMP materials were synthesized via the hydrothermal process followed by high-temperature annealing. Sol A and B solutions were prepared in 30 mL of deionized water (DI) each. 0.22g of MnCO_3 (Sigma–Aldrich, $\geq 99.9\%$) and 0.35g of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Sigma–Aldrich, $\geq 99.9\%$) were mixed in 30 mL of DI water and stirred for 30 min to form Sol A. Similarly, 0.62g of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (SRL, 99%) and 0.68g of NaNO_3 (Sigma-Aldrich, $\geq 99.0\%$) were added to 30 mL of DI water and mixed for 30 min to form Sol B. Subsequently, Sol B was added dropwise to Sol A under continuous stirring for an additional 15 min to ensure homogeneity. After moving to an autoclave lined with Teflon, the solution was hydrothermally treated for 6 h at 200 °C. The product was allowed to cool to room temperature before being thoroughly cleaned three times with DI water and dried for 12 h at 80 °C. The dried powder was then annealed at 700 °C for 5 h under a N_2 atmosphere to obtain the final NFMP.

To synthesis N and S-doped carbon-coated NFMP samples, the synthesis process incorporated 10 wt.% urea (Merck) or thiourea (Merck) with 20 wt.% sucrose (0.39g) into Sol B. The resulting materials are NFMP@NC (N-doped) and NFMP@SC (S-doped). A 1:1 mixture of urea and thiourea was further used to prepare an N and S co-doped carbon-coated material, denoted as NFMP@NSC.

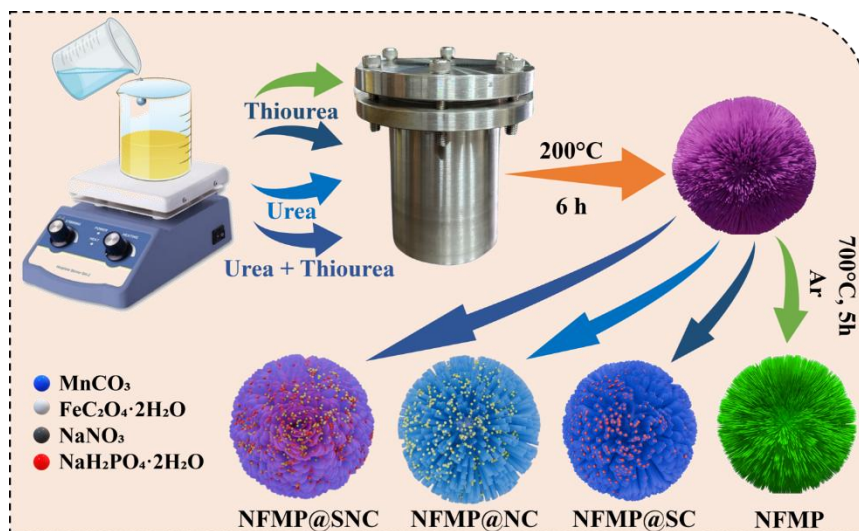


Figure 2.3 Schematic illustration of the hydrothermal process followed by heat treatment for $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ and its derivatives.

2.3 Electrode Preparation and Coin Cell Fabrication

Prior to electrochemical evaluation in SIBs, the cathode materials must undergo systematic electrode fabrication and cell assembly processes. These steps are crucial for obtaining consistent and reliable electrochemical performance results.

2.3.1 Device Fabrication

Electrode fabrication is a key step in probing the intrinsic electrochemical characteristics of the cathode materials. The procedure consists of multiple controlled steps designed as depicted in **Figure 2.4** to ensure electrode uniformity, reproducibility, and dependable electrochemical measurements.

2.3.1.1 Electrode Slurry Preparation

The working electrode was fabricated by homogeneously mixing active material, polyvinylidene fluoride (PVDF) (Aldrich) as a binder, and Super P as a conductive additive in appropriate ratio (8:1:1 for $\text{Na}_3\text{VFe}(\text{PO}_4)_3$, $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ and 7:2:1 for $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ in an appropriate amount of N-methyl-2-pyrrolidone (NMP) (Sigma Aldrich, 99.5%) to prepare a slurry.

2.3.1.2 Electrode Preparation

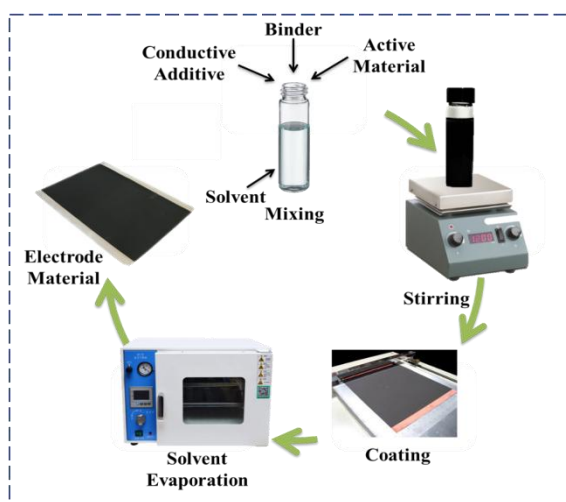


Figure 2.4 Schematic illustration of the process of electrode preparation.

The slurry was then coated onto Al foil (for cathode), and copper foil (for anode) using a doctor blade. The coated electrodes were dried at 100 °C for 12 h under vacuum conditions to remove NMP solvent and to enhance the binder adhesion. After drying, the electrodes were uniformly pressed via a hot roller press to obtain uniform thickness, better adhesion with the current collector, and better particle-to-particle contact. Then, the electrode was punched into the disc of diameter of 0.16 mm and resulting active mass loading of each working electrode were measured. The typical active mass loading per electrode was measured to be in the range of 1.5–2.5 mg/cm². All electrode discs were stored in a dry, inert atmosphere

(argon-filled glove box) until cell assembly to prevent moisture and air degradation.

2.3.1.3 Coin Cell Assembly

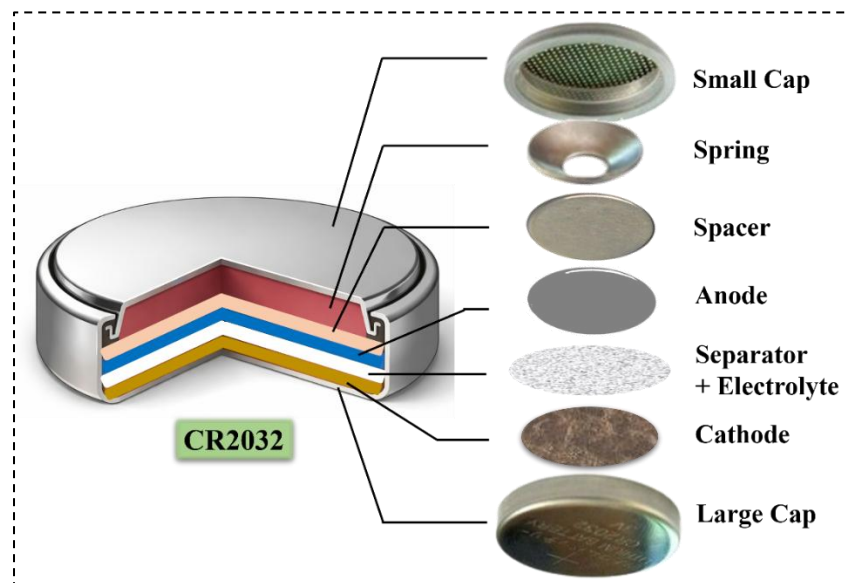


Figure 2.5 Sodium half-cell assembly process.

CR2032-type coin cells (20 mm diameter and 3.2 mm thickness) were assembled in a nitrogen-filled glove box for electrochemical performance evaluation. The cells were configured as sodium half-cells, in which highly pure sodium metal chips were employed as both the counter and reference electrodes. A glass microfiber membrane was used as the separator, while the electrolyte consisted of 1 M NaClO_4 dissolved in a mixed solvent of propylene carbonate (PC) and ethylene carbonate (EC) in a 1:1 (v/v) ratio. All components of the SIB were carefully assembled in a coin-cell configuration under strictly controlled inert conditions. The whole assembly procedure was conducted in an N_2 -filled glove box where the level of oxygen and moisture were kept at a level of less than 0.1 ppm in order to suppress undesired side reactions. Upon assembling the coin cells, they were sealed using a hydraulic crimping machine and left to rest over a period of 12 h before undergoing electrochemical testing. The sequential steps involved in the Na half-cell assembly are illustrated in **Figure 2.5**. Moreover, the electrochemical behavior of $\text{Na}_3\text{VFe}(\text{PO}_4)_3$ is optimized by

employing alternative electrolyte systems and this is discussed in details in Chapter 3.

To reliably estimate cell voltage, it is necessary that the electrode and assembly be ideal conditions:: (i) highly pure and electrochemically stable sodium metal counter/reference electrode is used; (ii) the cell is assembled under an and free environment (either nitrogen or argon) to avoid contamination of the cell by oxygen and moisture; (iii) uniform and stable contact between electrodes and electrolyte to minimise interfacial resistance; (iv) a stable electrolyte composition to prevent parasitic reactions; and (v) electrodes that exhibit reversible and reproducible electrochemical behavior. In such regulated conditions, electrochemical potentials determined are a valid measure of intrinsic redox activity of the cathode material relative to the Na^+/Na couple.

2.4 Materials Characterization Techniques

The physical and chemical properties of the electrode materials synthesized for SIBs were studied systematically using several advanced physicochemical characterization methods. The techniques were employed to examine structural properties in terms of phase composition, crystal symmetry, thermal properties, particle size, surface morphology, and atomic structure, and also chemical properties, including stoichiometry, oxidation state of elements, and chemical environment of electropositive elements. The thermal properties such as thermal stability, precursor decomposition behaviour as well as formation of phase-pure materials were measured through Thermogravimetric Analysis (TGA), Derivative Thermogravimetric (DTG). The phase purity, crystal structure and lattice parameters were measured using Powder X-ray Diffraction (XRD) with a wavelength of 1.542 Å. Particle morphology, surface features, particle size distribution, elemental distribution and empirical stoichiometry were studied using Field Emission Scanning Electron Microscopy (FESEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS). Raman

spectroscopy was performed to investigate the bonding characteristics and vibrational modes of the material. Furthermore, Transmission Electron Microscopy (TEM), High-Resolution TEM (HRTEM), and Selected Area Electron Diffraction (SAED) were used to examine nanoscale structural features, including atomic arrangements, lattice interplanar spacing, and detailed crystallographic information. The chemical states and oxidation environments of the constituent elements were analyzed using X-ray Photoelectron Spectroscopy (XPS). A brief overview of these characterization techniques is provided in the following subsections.

2.4.1 Thermogravimetric analysis

Thermogravimetric Analysis (TGA) measures the change in a sample's mass as a function of temperature or time under precisely controlled conditions, revealing thermal stability, decomposition behavior, and compositional changes. It is widely used in materials science to study phase transitions and purity without focusing on specific end products.[1]

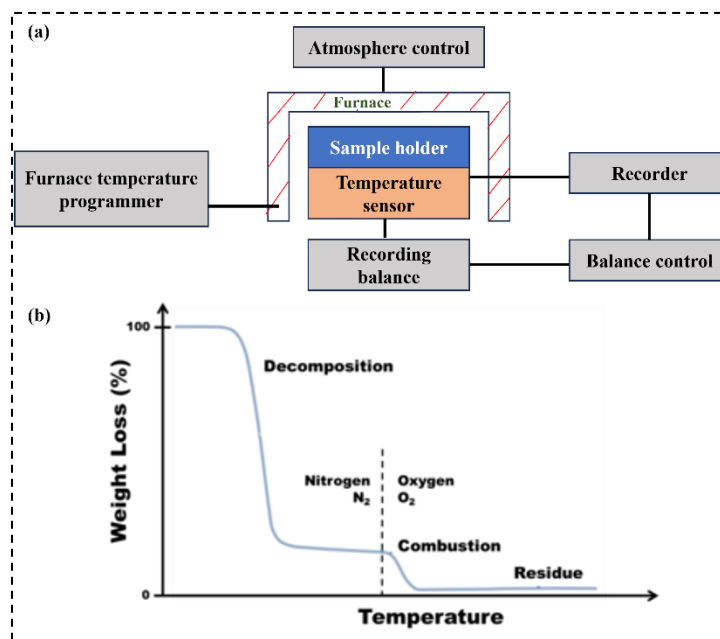


Figure 2.6 (a) Schematic diagram of the TGA setup and (b) a typical TGA curve.

TGA operates by placing a sample on a sensitive microbalance inside a temperature-programmable furnace, where mass is continuously

recorded during heating or isothermal holds. The system's key components, as shown in the provided **Figure 2.6 (a)**, include the furnace for precise temperature control via a programmer, a sample holder with integrated temperature sensor, atmosphere control for inert or reactive gases, and a recorder tied to balance control for data logging.

This setup produces a characteristic TGA curve of mass percentage versus temperature as shown in **Figure 2.6 (b)**, with the derivative thermogravimetric (DTG) curve identifying inflection points of rapid mass loss events. TGA curves provide quantitative data on composition, thermal stability, and decomposition kinetics by tracking mass changes versus temperature. From a typical TGA profile like Figure X, key parameters include initial mass loss percentage for volatiles (e.g., moisture/oils at 100-200°C), intermediate losses for polymers/organics (300-500°C), combustible fraction (500-700°C), and final ash residue (inorganics >700°C), revealing overall purity and filler content. Temperature of 5% or 10% weight loss (T5, T10) indicates onset of degradation, while plateau regions show stability limits.[2]

2.4.2 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) is an essential method in materials science that uses a non-destructive technique to investigate the atomic structure of a crystalline solid. XRD determines unknown phases, crystal structures, and microstructural properties such as crystallite size and lattice strain by studying the pattern formed in the diffraction of X-rays upon interacting with a lattice of a sample. It was discovered by Max von Laue in 1912 and developed by the Braggs, and has since been essential in characterizing polycrystalline powders, thin films and composites in as many fields as battery material to pharmaceuticals, and provides fingerprint-individualization of the sample without modification.[3]

The fundamental concept of XRD is based on the wave-like interference of the X-rays scattered by electron encircles of the atoms of a periodical crystal lattice. When the monochromatic X-rays beam is incident

on the sample at a glancing angle θ , the interferences between successive atomic plane distances spaced by d occur constructively only when the distance change along the path between the X-ray source and detector is an integer multiple of the X-ray wavelength λ , according to the Bragg law:[4]

$$n\lambda = 2d \sin\theta \quad (2.1)$$

where n is the reflection order. This leads to sharp diffraction peaks at detector angle 2θ , whose positions are inversely proportional to d -spacing, and intensity is proportional to the number of scatterers and their geometry. For powdered samples with random crystallite orientations, the method produces a complete set of reflections, forming a characteristic pattern unique to each phase, as illustrated in the diffraction geometry of **Figure 2.7 (a)**. [5]

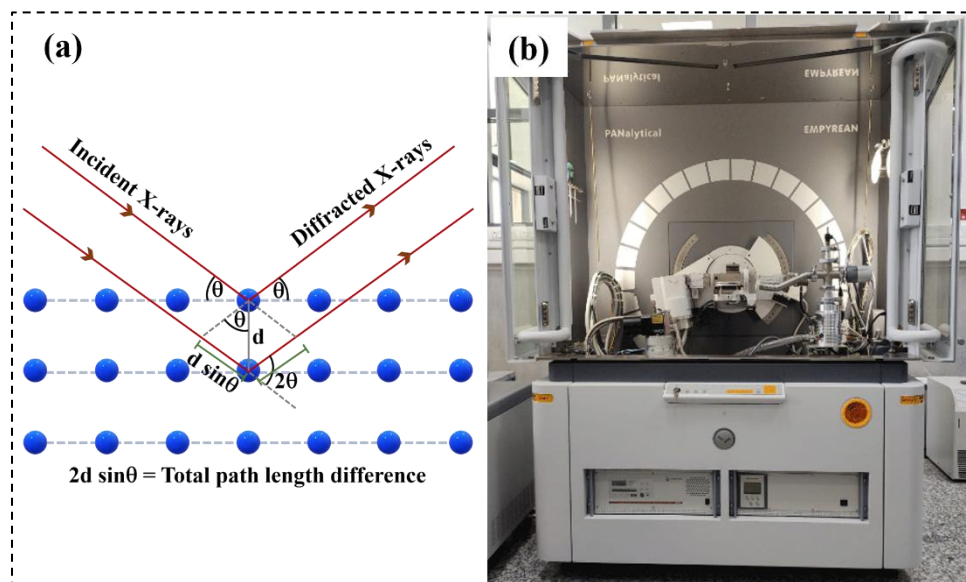


Figure 2.7 (a) Schematic representation of XRD principle showing the diffraction of incident X-rays from crystal lattice planes according to Bragg's law, (b) Photograph of the powder X-ray diffractometer used for structural characterization of the synthesized electrode materials.

A typical Bragg-Brentano powder diffractometer works by placing the sample on a flat holder and irradiating it with filtered $\text{Cu K}\alpha$ from an X-ray tube with a detector moving over a range of 2θ at some controlled speed. The goniometer ensures synchronous movement of the source and detector

to maintain constant θ incidence, with collimating slits sharpening the beam and a monochromator eliminating K_{β} radiation for cleaner peaks. Diffracted photons strike the detector (usually a scintillation counter or, more recently, a linear array), the sample is rotated to average the intensity versus 2θ in real time, and computer software is used to implement Lorentz-polarization corrections and strip off background. The full setup, depicted in **Figure 2.7 (b)**, completes a high-resolution scan in 5-60 minutes, calibrated against silicon standards for precise angular accuracy.[6]

From the resulting XRD diffractogram, a wealth of quantitative structural data emerges: peak positions directly compute d-spacings via Bragg's law, matched against ICDD databases for phase identification and semi-quantitative analysis, while full-pattern Rietveld refinement handles multi-phase quantification down to trace levels. Crystallite size and microstrain derive from peak breadth analysis using the Scherrer equation:[3]

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2.2)$$

($K \approx 0.94$, β = FWHM) and Williamson-Hall plots, respectively, revealing nanoscale domains or defect-induced broadening. Compositional variations or thermal expansion, lattice parameters of indexing multiple peaks, relative intensities of preferred orientation or texture, broad humps under peaks, and amorphous fractions are estimated by the RIR method with internal standards. Other information would be residual stress due to systematic shifts in the peaks and polymorphism in organics, all of which were non-destructively extracted from the pattern produced by the instrument in Figure X(b).

2.4.3 Field emission scanning electron microscopy

FESEM, coupled with EDS and color mapping, is the next level of surface characterization methods in materials science, providing high-resolution images and elemental analysis (**Figure 2.8**). FESEM offers sub-nanometer topographic and morphological information, and EDS is capable of detecting typical X-rays emitted by sample atoms during electron

bombardment, which allows mapping chemical compositions. Color mapping is a visualization technique that allows visualization of the elemental distributions spatially, and these techniques are essential in analyzing electrode microstructures, particle morphology, and impurities in materials without destroying the samples.[7,8]

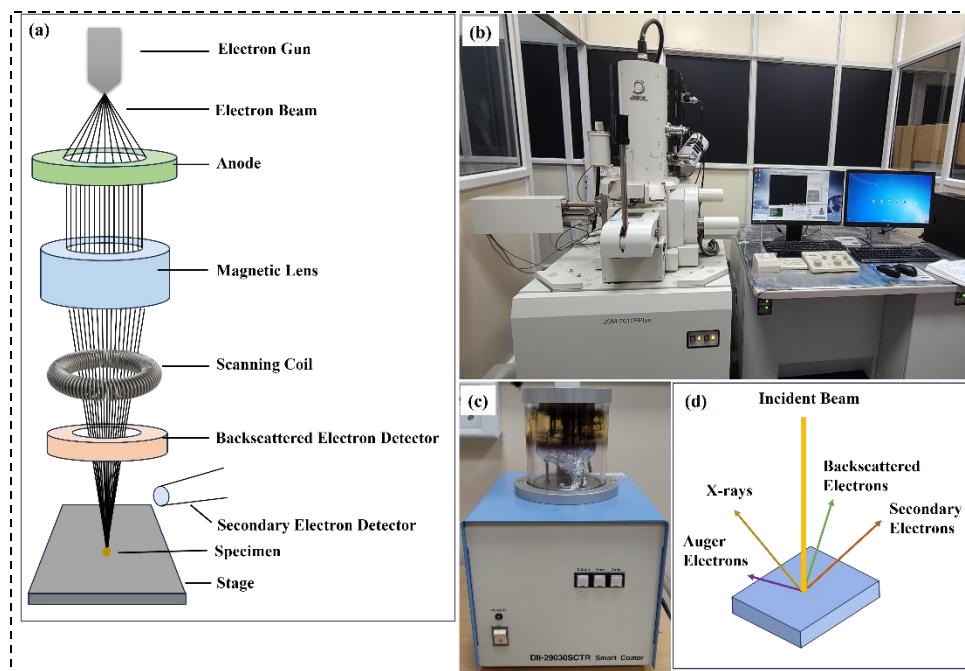


Figure 2.8 (a) Schematic illustration of the FESEM working principle showing electron beam interaction with the sample surface and signal generation. (b) Photograph of the FESEM instrument used for morphological characterization of the synthesized materials. (c) A sputter coater was used to coat the sample with gold prior to FESEM analysis. (d) Schematic representation of various signals generated from the sample surface during electron beam interaction.

FESEM works by accelerating field-emitted electrons from a sharp tungsten or Schottky emitter using a high-voltage lens system (0.5-30 kV) to create a raster-scanning probe (1-10 nm diameter) which scans the sample surface as shown in **Figure 2.8 (a)**. The topography is displayed by secondary electrons (SE, 50 eV), which show the detector yield variations and the compositional contrast as atomic number differences by the backscattered electrons (BSE, >50 eV) (**Figure 2.8 (d)**). EDX/EDS is based

on beam-induced ionization that ejects inner-shell electrons (e.g., K, L) and then follows the filling in of higher-energy outer electrons into vacancies, releasing characteristic X-rays (e.g., Mn K α at 5.9 keV); a silicon drift detector (SDD) with a beryllium window measures energies (133-20 keV) in a spectrum, which is deconvoluted by ZAF (atomic number, absorption, fluorescence) corrections. Color mapping superimposes normalized elemental intensities onto SE/BSE images giving a visual representation of RGB colors to peaks to aid spatial correlation.[9,10]

Within FESEM-EDS, the cold/hot field emission gun, electromagnetic condensers and octopole deflectors are used to image the sample on a stub at 5-15 kV and 1-10 pA using a vacuum chamber (105 Torr). SE signals are optimized through an Everhart-Thornley detector on topography images: the BSE feeds a four-quadrant solid-state detector for Z-contrast. Simultaneous EDX acquisition builds spectra in 1-5 minutes via liquid nitrogen-cooled or Peltier SDD, with pulse processing stripping escape peaks and summing artifacts. Software uses Gaussian peaks to measure wt%/at% as standardless k-ratios of the Cliff-Lorimer method after acquisition, then produces color maps by thresholding intensities.[11]

FESEM delivers nanoscale morphology, particle size distributions (mean via ImageJ feret diameters), agglomeration states, porosity from cross-sections (fractal analysis), and surface features like grain boundaries or defects from SE/BSE contrasts at 1 nm resolution. FESEM provides nanoscale morphology, the size distributions of particles (mean consisting of ImageJ feret diameters), agglomeration conditions, porosity using cross-sections (fractal analysis), and surface properties such as grain boundaries or defects based on SE/BSE contrasts at 1 nm. It is found that EDX spectra can be used to determine elemental composition, and impurities, with a profile of diffusion (e.g., color mapping provides information about spatial distributions). Quantitative EDS maps are computed from intensity gradients to determine phase fractions and diffusion coefficients, all non-destructively from raster-scanned electron-sample interactions.[7,9]

2.4.4 Raman Spectroscopy

This is a powerful vibrational spectroscopy method applicable to materials science to investigate molecular structure, phase composition, and chemical bonding at a molecular scale. It uses, unlike infrared spectroscopy, inelastic light scattering to report on vibrational modes to give complementary information on symmetric stretches and lattice phonons. Raman analysis is widely used in the characterization of battery electrodes, nanomaterials, polymers, as well as, in studies of local environments, polymorphism, stress states, and defects, and requires little sample preparation.[12]

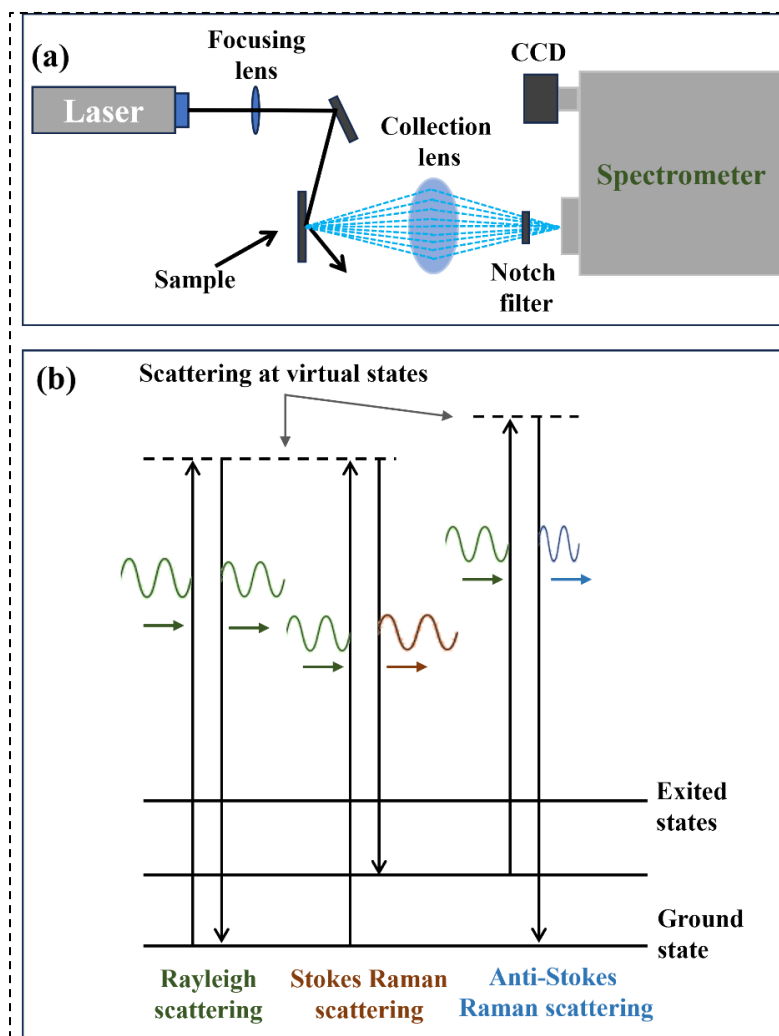


Figure 2.9 (a) Schematic illustration of the Raman spectroscopy working principle showing laser interaction with the sample surface and signal

generation. (b) Schematic representation of scatterings generated from the sample surface during electron beam interaction.

Raman scattering is a phenomenon that results when monochromatic laser light (usually 532 nm green or 785 nm near-IR) interacts with the molecular vibrations or phonons within a sample, which causes the temporary virtual electronic excitation of photons and inelastic re-emission of the photons with altered energies (**Figure 2.9 (a)**). The energy difference, Stokes (lower energy, red-shifted) or that of an anti-Stokes (higher energy, blue-shifted) line equals vibrational quanta ($10\text{-}4000\text{ cm}^{-1}$), which is determined by the polarizability change during vibration and not by the change in the dipole moment. Rayleigh scattering is incident-frequency elastic scattering that has been filtered to select weak Raman signals (10^{-6} of total).[13] The way virtual state transitions cause Stokes-dominant spectra at room temperature with positions, widths, and intensities fingerprinting bond strengths, disorder and local symmetry, independent of water or aqueous conditions, is shown in **Figure 2.9 (b)**.

A confocal Raman microscope focuses a diffraction-limited beam ($0.5\text{-}1\text{ }\mu\text{m}$ laterally, $1\text{ }\mu\text{m}$ depth) of a collimated laser beam on the sample with objective lenses. The collected light is re-directed back through collection optics, and a notch filter is used to remove Rayleigh (more than 10 times stronger), after which a spectrometer makes the light pass through a grating ($1200\text{-}1800$ grooves/mm) to count photons on a cooled CCD detector. Spectral acquisition integrates to prevent photo-damage, and grating blaze is optimum to the Stokes region ($100\text{-}4000\text{ cm}^{-1}$). A confocal Mapping scans stage or beam in x-y-z ($0.2\text{-}10\text{ }\mu\text{m}$ steps), building hyperspectral datasets; software applies cosmic ray removal, baseline correction (polynomial), and peak fitting (Lorentzian/Gaussian) for quantitative maps. The setup in Figure X illustrates laser focusing, notch filtering, and spectrometer separation of Rayleigh, Stokes, and anti-Stokes components.[14]

Raman spectra provide quantitative information about the molecular and structural structure: the positions of the peaks are used to determine the phases and functional groups (e.g. D/G ratio to characterize the disorder of carbon), the FWHM is used to determine the crystallinity or amorphicity in terms of quantifying the phonon lifetime, and the relative concentrations or orientations are determined by the ratios of the intensity of the peaks.[15] Quantitative analysis calculates bond fractions based on integrated areas, defect densities based on I_D/I_G , and the number of layers of 2D materials based on the 2L/1L ratios. Confocal depth profiling measures both thickness and interfaces non-destructively, and polarization-resolved spectra reveal anisotropy, both based on the Stokes-shifted inelastic scattering of the CCD following spectral dispersion.

2.4.5 Transmission electron microscopy

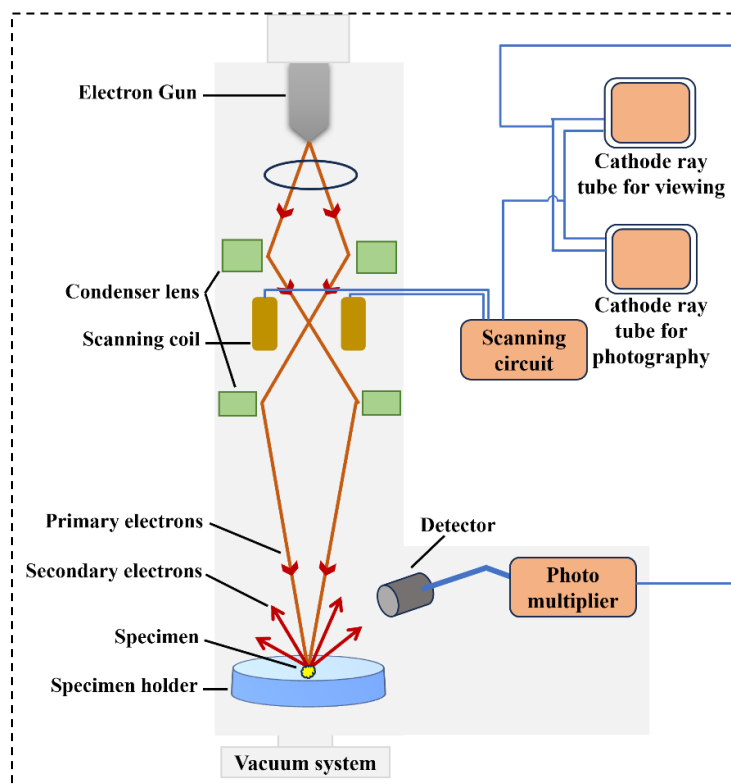


Figure 2.10 Schematic illustration of the HRTEM working principle showing electron beam interaction with the sample surface and signal generation.

HRTEM is an advanced imaging technique used in materials science to examine crystal lattice fringes, defects, and nanostructures of thin specimens at an atomic scale resolution. Working in the high-energy electron beam mode with ultra-thin samples (thinner than 100 nm), HRTEM provides images of atomic columns and atomic planes along with other lower-resolution techniques such as SEM. Necessary in battery research, nanomaterials, and catalysis, it offers an unparalleled view of phase distribution, grain boundaries and interface structure, but needs careful sample preparation to eliminate artifacts.[7]

HRTEM uses the wave type of electrons accelerated to 80-300 kV that would pass through the sample and interact constructively at the objective lens defocus to create phase-contrast images of lattice planes as close as 0.1 nm. As depicted in **Figure 2.10**, the electron beam interacts through elastic (diffraction) and inelastic (energy loss) interactions, but high-resolution is achieved through phase-contrast transfer by the objective lens, in which aberrations (spherical, chromatic) resonate with contrast at certain spatial frequencies. Bright-field imaging shows dark atomic projections under the influence of projected potential are controlled by the Schrodinger equation of electron waves; these patterns are also used in SAED, which simultaneously measures the reciprocal lattice to establish the structure. The power spectra of Fourier transforms of HRTEM images are reminiscent of diffraction and allow a direct determination of d-spacings and symmetry.[16]

A coherent electron probe is produced using a field-emission gun (Schottky or cold FEG) in a vacuum (10^{-7} Torr) and focused on the sample by twin lenses; the electrons are magnified and focused with electromagnetic objective and projector lenses onto a phosphor screen or direct electron detector. The samples are tilted on 3 mm Cu grids (lacy carbon or holey films) through a double-axis goniometer; scans are operated using aberration correctors to give a sub-Å resolution. There are acquisition modes such as through-focal series (defocus -5 to -100 nm) to re-construct

CTF, low-dose imaging to reduce beam damage, and energy-filtered TEM (EFTEM) to remove plasmon. Images are simulated by software through multislice algorithm (e.g., Dr. Probe) which matches experimental micrographs to crystal models so that accurate images can be studied.[8]

HRTEM has a direct visualization of atomic positions lattice fringes verify phases, terminating planes identify facets, and moire fringes identify lattice mismatch at surfaces. A defect analysis can measure dislocations (Burgers vectors of strain fields), stacking faults, and twins through image contrast, and particle size distributions and morphologies through edge detection on low-magnification overviews. Orientation relationships are measured with a pattern index of SAED, local strain fields are measured with image processing (FFT filtering, denoising), and composition is measured with CBED (convergent beam patterns). Quantitative phase contrast provides thickness and 3D tomography of the shapes of nanoparticles and their porosity in a non-destructive manner by measuring the transmitted electron wavefront perturbed by the projected potential of the sample.[6]

2.4.6 X-ray Photoelectron Spectroscopy (XPS)

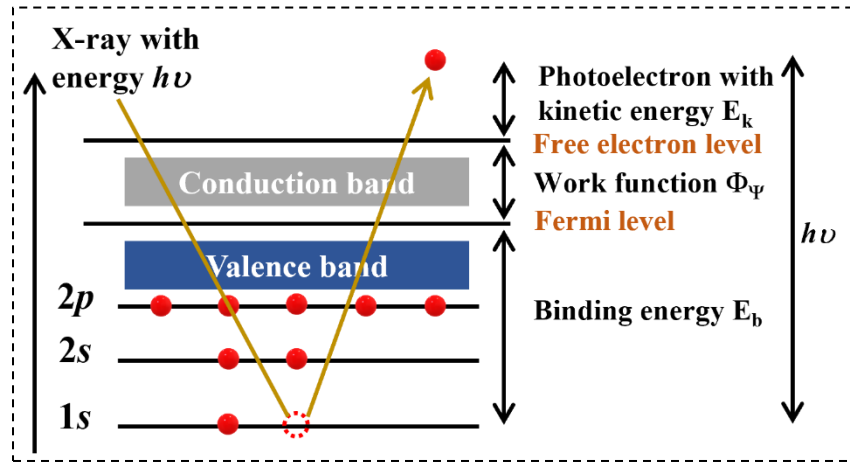


Figure 2.11 Schematic illustration of the working principle of XPS.

XPS is a surface-sensitive technique that investigates the elemental composition, chemical states, and electronic structure of materials. XPS offers quantitative analysis of surface chemistry, oxidation state, and

bonding environment, and is invaluable in the study of thin films, catalysts, battery electrodes, and interfaces in the materials science community by performing this analysis on samples irradiated with monochromatic X-rays and emitted photoelectrons.[17]

XPS is based on the principle of photoelectric effect, in which incident X-rays (typically Al K α at 1486.6 eV or Mg K α at 1253.6 eV) knock off core-level electrons in atoms, with the kinetic energy (KE) proportional to binding energy (BE),[18]

$$BE = h\nu - KE - \phi \quad (2.3)$$

Here, $h\nu$ is the photon energy and, ϕ is the work function. The binding energy is element-dependent and varies with the chemical environment, as a result of differences in orbital energies driven by electronegativity and coordination (**Figure 2.11**). Only surface layers lose photoelectrons by inelastic mean free path ($\sim 1\text{-}3$ nm), and additional contrast is also given by Auger electrons and secondary electrons; spectra have peaks with spin-orbit splitting (e.g. 2p $_{3/2}$, 2p $_{1/2}$) and shake-up satellites in valence transitions.[19]

The ultra-high vacuum chamber (10^{-9} Torr) is flooded by a monochromatic X-ray source and covered by the photons onto the sample, which is placed on a manipulator with ion gun (Ar $^{+}$, 0.5-5 kV), that cleans the sample. Photoelectrons hemispherically analyzed can be made to reach a concentric analyzer (pass energy 20-100 eV) via entrance lenses and then dispersed by electrostatic fields onto microchannel plate detectors. Elements are scanned over 0-1400 eV (1 eV step), and then high-resolution regions (0.1 eV step) are scanned to peak-fit. Charge neutralization, low-energy electrons or flood gun is used as insulators; Shirley background is subtracted using software, atomic quantification using a sensitivity factor of adventitious C 1s at 284.6 eV with calibration to adventitious C 1s.[20]

XPS provides chemical speciation based on binding energy differences, oxidation state based on multiplet splitting, and stoichiometry based on the ratio of area, corrected for transmission. Sequential sputtering creates depth profiles that indicate layer thicknesses and interfaces; angle-

resolved XPS (take-off angles 15° - 90°) provides better depth selectivity (1-10 nm). Valence-band spectroscopy reveals band positions and density-of-states, and non-destructive mapping (lens mode, 10 mm resolution) reveals lateral inhomogeneities. Quantitative analysis of alloy compositions, contamination layers, and functional group densities can be determined using the N 1s or O 1s deconvolution.[21]

2.4.7 Fourier transform infrared spectroscopy

FTIR spectroscopy is an absorption technique that is commonly used in materials science to determine functional groups, chemical bonds, and molecular structure by analyzing characteristic vibrational resonances. By interacting with infrared light, FTIR can generate spectra that serve as molecular fingerprints for qualitatively and quantitatively analysing organic, inorganic, and polymeric substances. It is non-destructive, can be applied to solids, liquids, or gases, with only minimal preparation, and is complemented by other techniques such as Raman, probing the change in dipole moment during asymmetric vibrations, and is therefore important in the study of surface chemistry, phase transitions, and reaction mechanisms.[13]

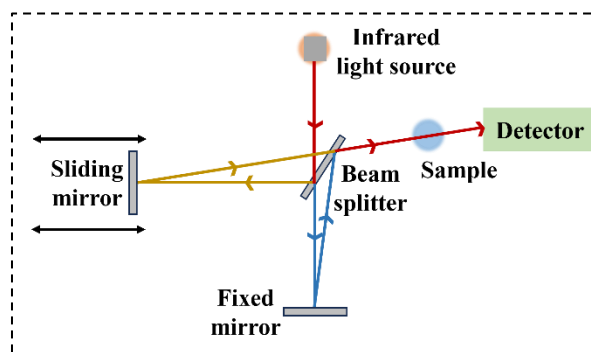


Figure 2.12 Schematic illustration of the working principle of FTIR.

FTIR relies on the absorption of infrared radiation (4000 - 400cm^{-1} , mid-IR region) by molecular bonds, which excite them out of ground state to vibrational excited states by stretching, bending, scissoring, or rocking modes (**Figure 2.12**). When the IR frequency is identical to the vibrational transition dipole, the result is absorption producing peaks whose position

(wavenumber $\propto \sqrt{k/\mu}$, k = force constant, μ = reduced mass) indicates bond strength and mass, intensity reflects concentration and change in dipole, and shape reveals environment (e.g., hydrogen bonding broadens O-H). Unlike dispersive IR, FTIR uses a Michelson interferometer: broadband IR from a global source splits at a 50/50 beamsplitter (KBr or ZnSe), reflects off fixed and moving mirrors, recombines with path-dependent phase differences (optical path difference, OPD), and yields an interferogram via detector, Fourier-transformed mathematically into a single-beam spectrum via fast Fourier transform (FFT) for all wavelengths simultaneously, enhancing signal-to-noise by Fellgett's advantage.[22]

A typical FTIR spectrometer directs IR from a heated ceramic source (global, 1200-1500 K) through an interferometer onto the sample compartment, where transmission (KBr pellet, thin film), reflectance (ATR with diamond/ZnSe crystal, single or multi-bounce), or diffuse reflection (DRIFTS) modes accommodate diverse forms. The moving mirror scans ± 0.5 -2 cm OPD at constant velocity (e.g., 0.3 cm/s), modulating interference; a DTGS or MCT detector records the time-domain interferogram. Background single-beam spectra (empty beam) subtract from sample interferograms post-FFT, yielding absorbance, with apodization and zero-filling optimizing resolution.[23]

FTIR spectra provide detailed chemical insights: peak positions identify functional groups (e.g., C=O 1700-1750 cm^{-1} , O-H 3200-3600 cm^{-1} broad, Si-O 1000-1100 cm^{-1}), the fingerprint region (1500-400 cm^{-1}) confirms identity via band patterns, and intensities enable quantification via Beer's law ($A = \epsilon bc$, ϵ = molar absorptivity). Ratioing bands assesses relative concentrations or reaction completion; band shifts ($>10 \text{ cm}^{-1}$) signal hydrogen bonding, conjugation, or oxidation state changes, while FWHM quantifies crystallinity (sharper for ordered phases). 2D mapping (ATR-FTIR or focal plane arrays) visualizes inhomogeneities, depth profiling via ATR angle variation extracts layer thicknesses, and deconvolution (curve-fitting Gaussian-Lorentzian) computes polymorphism or hydration states

from subtle asymmetries, all derived non-destructively from the Fourier-transformed interferogram capturing modulated IR absorption across the molecular vibrational manifold.[23,24]

2.4.8 N₂ adsorption-desorption isotherm

One of the important gas adsorption techniques in materials science is the BET surface area analysis, a technique to determine the specific surface area and porosity of powdered or porous materials. It expands on the concept of gas molecules coating surfaces, which will assist the researchers in studying the impact of texture on material performance in applications such as catalysis and energy storage. It is a non-destructive, simple method used frequently to describe the accessibility of the internal structure.[25]

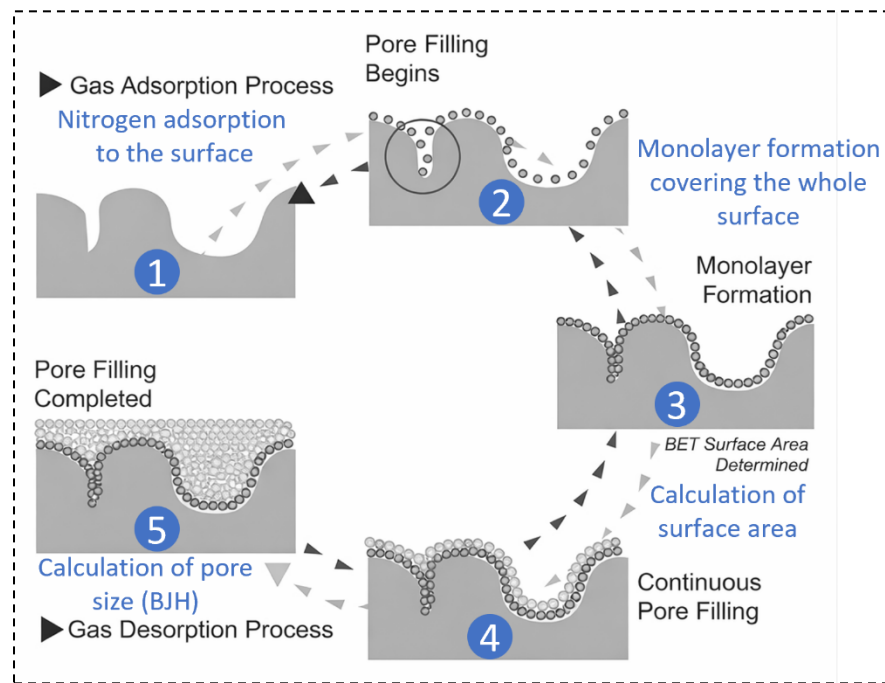


Figure 2.13 Schematic illustration of the working principle of N₂ adsorption-desorption isotherm.

BET extends the monolayer adsorption concept to multiple layers of gas molecules, such as nitrogen at liquid nitrogen temperature as represented in **Figure 2.13**. The first layer sticks strongly to the surface, while outer layers behave like liquid. By plotting adsorption data at low relative pressures, a straight line forms, from which the monolayer amount

is found, leading directly to the total surface area calculation. The method assumes uniform multilayer growth and no chemical reactions, focusing purely on physical adsorption.[26]

The sample is first cleaned by heating in vacuum to remove impurities, then cooled to liquid nitrogen temperature. Precise doses of nitrogen gas are added step-by-step, and the pressure drop measures how much gas adsorbs at each level. Both adsorption and desorption branches build the isotherm curve, with software fitting the linear region to extract surface data. The process, shown step-by-step in Figure X, goes from initial surface coverage through multilayer buildup and pore filling to final desorption.[27]

BET provides the specific surface area, distinguishing total accessible area from micropores via comparison plots. Pore size and volume come from the isotherm shape and hysteresis loop during desorption, revealing meso or macropore networks. The adsorption strength indicates surface energy uniformity, while curve types classify material porosity. These insights link directly to practical properties like reactivity and capacity, all derived simply from the gas uptake behavior without complex assumptions.[26]

2.5 Electrochemical Characterization Techniques

Electrochemical evaluation of cathode materials plays a vital role in evaluating the overall battery system's performance and degradation pathways. It provides the critical insight into the aspects of charge storage dynamics, capacity, energy and power densities, interfacial processes, cycling stability, and long-term stability of the electrodes.[28] It also explains the redox properties, Na^+ -ion transport properties, and phase transitions of these materials.[29] We performed cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) on the sodium half-cells of the synthesized cathode materials. CV shows redox peaks, reversibility, and reaction kinetics, as

shown by the shape and position of the current-voltage profile peaks.[30] EIS measures the resistive and capacitive components of the electrode-electrolyte interface, such as the charge transfer resistance, diffusion barriers of Na^+ , and the formation of solid electrolyte interphase (SEI).[31] GCD assessments determined specific capacity, long-term cyclability, and coulombic efficiency, with rate performance tests also performed via GCD. The CV and EIS measurements utilized an Autolab electrochemical workstation (Figure 2.14 (a)), while an 8-channel battery tester (Figure 2.14 (b)) handled GCD and related battery evaluations.

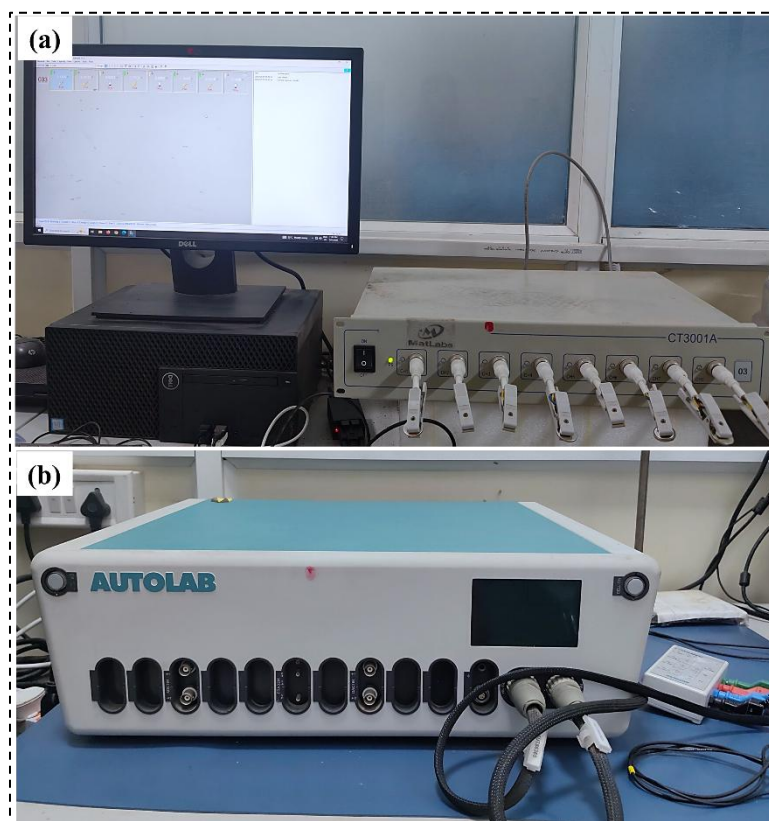


Figure 2.14 (a) Electrochemical workstation (Potentiostat) and (b) LAND 8-channel battery tester used for the electrochemical analysis.

2.5.1 Cyclic Voltammetry (CV)

CV is an important electrochemical technique used to investigate the redox behavior, electrochemical kinetics, and sodium ion storage mechanism of electrode materials in SIBs. In this technique, the potential

of the working electrode is swept linearly over time between two potential limits, and the resulting current is recorded.

During the forward and reverse scans, sodiation (reduction) and desodiation (oxidation) reactions occur at the electrode surface, producing characteristic cathodic and anodic peaks in the voltammogram (**Figure 2.15 (a,b)**). The position, shape, and intensity of these peaks provide valuable information about the electrochemical reversibility, reaction kinetics, and Na⁺ ion diffusion behavior in the electrode material.[32]

The scan rate (ν) in cyclic voltammetry is defined as:

$$\nu = \frac{dE}{dt} \quad (2.4)$$

where ν = scan rate (V s⁻¹) E = applied potential (V)
 t = time (s)

Parameters Calculated from CV

Several important electrochemical parameters for SIBs can be obtained from cyclic voltammetry.[33]

1. Diffusion Coefficient of Sodium Ions

The diffusion coefficient of Na⁺ ions in the electrode material can be estimated using the Randles–Ševčík equation:[34]

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C \nu^{1/2} \quad (2.5)$$

where I_p = peak current (A), n = number of electrons transferred A = electrode surface area (cm²) D = diffusion coefficient (cm²/s) C = concentration of Na⁺ ions (mol/cm³) ν = scan rate (V/s)

From the slope of the plot I_p vs $\nu^{1/2}$, the diffusion coefficient D of sodium ions can be calculated.

2. Charge Storage Mechanism (b -value Analysis)

The relationship between peak current and scan rate is expressed as:[35]

$$i = a \nu^b \quad (2.6)$$

where i = current (A), ν = scan rate (V/s) a, b = adjustable constants

Taking logarithm:

$$\log(i) = b \log(\nu) + \log(a) \quad (2.7)$$

The b -value indicates the charge storage mechanism:

- $b = 0.5 \rightarrow$ diffusion-controlled process (battery-type behavior)
- $b = 1 \rightarrow$ surface capacitive process

3. Capacitive and Diffusion Contribution

The current response can also be separated into capacitive and diffusion-controlled contributions using the equation:[34]

$$i(V) = k_1 v + k_2 v^{1/2} \quad (2.8)$$

where $k_1 v$ = capacitive contribution, $k_2 v^{1/2}$ = diffusion-controlled contribution

This analysis helps determine how much of the charge storage originates from surface reactions versus ion diffusion.

4. Specific Capacity from CV

The specific capacity of the electrode material can be estimated from the CV curve using:[36]

$$Q = \frac{\int I(V) dV}{mv} \quad (2.9)$$

Where, Q = specific capacity (C/g or mAh/g), $I(V)$ = current response, m = mass of active material (g), v = scan rate (V/s)

Importance of CV in SIBs

Cyclic voltammetry provides important information about:

- Redox potentials of electrode materials
- Reversibility of sodiation/desodiation reactions
- Sodium-ion diffusion kinetics
- Charge storage mechanisms
- Electrochemical stability of electrodes

Therefore, CV is widely used to evaluate the electrochemical performance and sodium-storage behavior of electrode materials in SIBs.

2.5.2 Galvanostatic Charge-Discharge (GCD)

GCD measurements are widely used to evaluate the electrochemical performance, specific capacity, and cycling stability of electrode materials in SIBs. In this technique, the battery is charged and discharged at a constant

current density within a fixed voltage window while the corresponding voltage response is recorded as a function of time.[37]

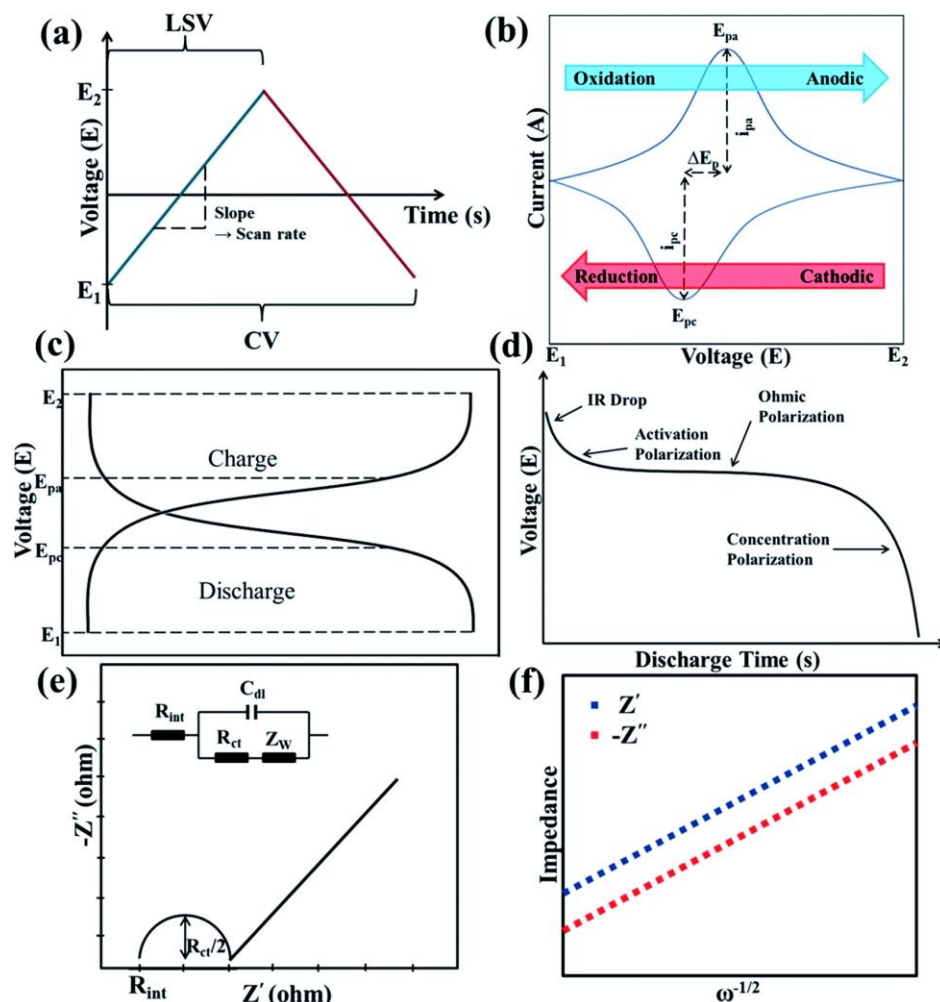


Figure 2.15 (a) Voltage profile applied in LSV and CV measurements. (b) A typical plot of current response vs. voltage. (c) Voltage *versus* integral current curves. (d) A typical galvanostatic discharge plot of the battery. (e) Randles circuit with the corresponding EIS. (f) Bode plot showing a linear relationship between Z_{re} or Z_{im} and $\omega^{-1/2}$.

During the charging process, sodium ions are extracted from the electrode (desodiation), whereas during the discharging process, sodium ions are inserted into the electrode (sodiation). The resulting charge-discharge curves provide important information regarding the reversibility

of electrochemical reactions, energy storage capability, and rate performance of the electrode material. The shape of the GCD curves and the presence of voltage plateaus correspond to the redox reactions occurring during sodium ion insertion and extraction (**Figure 2.15 (c,d)**). Symmetric charge and discharge profiles generally indicate good electrochemical reversibility and stability of the electrode material.[38,39]

Parameters Calculated from GCD

Several important electrochemical parameters for SIBs can be determined from galvanostatic charge-discharge measurements.[40]

1. **Specific Capacity:** The specific capacity of the electrode material can be calculated from the discharge curve using the equation (1.2). This parameter represents the amount of charge stored per unit mass of the electrode material.
2. **Energy Density:** The energy density of the electrode material can be estimated from the discharge curve using equation (1.4). Energy density represents the total energy stored per unit mass of the electrode material.
3. **Power Density:** Power density describes how quickly energy can be delivered and is calculated using equation (1.5). Higher power density indicates better rate capability of the electrode material.
4. **Coulombic Efficiency:** Coulombic efficiency indicates the reversibility of the electrochemical reaction and can be calculated using equation (1.6). A coulombic efficiency close to 100% indicates highly reversible electrochemical reactions.

Importance of GCD in SIBs

Galvanostatic charge-discharge analysis provides crucial information about:

- Specific capacity of electrode materials

- Coulombic efficiency and reversibility
- Energy and power density
- Rate capability of the battery
- Long-term cycling stability

Therefore, GCD measurements are essential for evaluating the practical electrochemical performance of electrode materials in SIBs.

2.5.3 Electrochemical Impedance Spectroscopy (EIS)

EIS is a powerful technique used to investigate the electrochemical kinetics, charge transfer resistance, ion diffusion, and interfacial properties of electrode materials in SIBs. In this technique, a small sinusoidal alternating current (AC) voltage is applied to the electrochemical system over a wide range of frequencies, and the resulting current response is measured. The impedance response of the system is analyzed as a function of frequency to obtain information about various resistive and capacitive processes occurring at the electrode-electrolyte interface. The EIS data are usually presented in the form of a Nyquist plot, where the real part of impedance (Z') is plotted against the imaginary part (Z'').[41,42]

A typical Nyquist plot consists of a semicircle in the high-frequency region and a straight line in the low-frequency region (**Figure 2.15 (e,f)**). The semicircle corresponds to the charge transfer resistance and double-layer capacitance, while the inclined straight line represents the Warburg impedance related to sodium-ion diffusion within the electrode material.[43]

Parameters Obtained from EIS

Several important electrochemical parameters related to SIBs can be extracted from EIS analysis.[44]

1. Solution Resistance (R_s): The intercept of the Nyquist plot with the real axis at high frequency represents the solution resistance.

$$Z = R_s \quad (2.10)$$

Where R_s = electrolyte resistance or solution resistance

This resistance includes contributions from the electrolyte, separator, and electrical contacts within the battery cell.

2. Charge Transfer Resistance (R_{ct}): The diameter of the semicircle in the Nyquist plot corresponds to the charge transfer resistance, which is related to the kinetics of the electrochemical reaction at the electrode surface.

$$R_{ct} = \frac{RT}{nFi_0} \quad (2.11)$$

where R = universal gas constant (8.314 J mol/K), T = temperature (K), n = number of electrons transferred, F = Faraday constant (96485 C/mol), i_0 = exchange current density Lower R_{ct} values indicate faster charge transfer kinetics and better electrochemical performance.

3. Warburg Impedance (Z_w): The straight line observed in the low-frequency region of the Nyquist plot is associated with Warburg impedance, which arises from the diffusion of sodium ions in the electrode material.

The Warburg impedance is expressed as:

$$Z_w = \sigma \omega^{-1/2} (1 - j) \quad (2.12)$$

where σ = Warburg coefficient, ω = angular frequency ($\omega = 2\pi f$), j = imaginary unit

4. Sodium Ion Diffusion Coefficient: The diffusion coefficient of sodium ions (D_{Na^+}) can be calculated from the Warburg coefficient using the following equation:

$$D_{Na^+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2} \quad (2.13)$$

where D_{Na^+} = sodium ion diffusion coefficient (cm^2/s), A = electrode surface area (cm^2), C = concentration of sodium ions (mol/cm^3), σ = Warburg coefficient. This parameter provides information about the rate of sodium-ion transport within the electrode material.

Importance of EIS in SIBs

Electrochemical impedance spectroscopy provides valuable insights into:[45]

- Internal resistance of the battery system
- Charge transfer kinetics at the electrode surface
- Ion diffusion behavior in electrode materials
- Interfacial properties between electrode and electrolyte
- Overall electrochemical performance of SIBs

Therefore, EIS is an essential technique for understanding the electrochemical processes and improving the performance of SIB materials.

2.6 Density functional theory (DFT) analysis

To investigate the Na ion adsorption mechanism and kinetic barriers in the $\text{Na}_3\text{FeV}(\text{PO}_4)_3$ and $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ materials, we performed rotationally invariant DFT+U calculations using the Vienna Ab Initio Simulation Package (VASP). For $\text{Na}_3\text{FeV}(\text{PO}_4)_3$, the initial structure was obtained by replacing 50% of Vanadium atoms in $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ with Fe atoms. The unit cell used for all the calculations consisting of 12 Na atoms, 4 Fe atoms, 4 V atoms, 12 P atoms, and 48 O atom. For $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$, the initial structure was obtained from the Cambridge Crystallographic Data Centre (CCDC), reference number 1946641. A unit cell comprising 8 Na atoms, 6 Fe atoms, 6 Mn atoms, 12 P atoms, and 48 O atoms was used for all calculations. Structural minimization was performed on this structure by allowing the ionic positions, as well as the size and shape of the simulation cell, to relax. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, revised for solids (PBEsol), was used in

conjunction with the projector augmented-wave (PAW) method. An energy cutoff of 520 eV was employed for the plane-wave basis set. The convergence criteria for electronic and ionic relaxations were set to 10^{-6} eV and $0.01 \text{ eV } \text{\AA}^{-1}$, respectively. To determine the minimum energy paths and the associated kinetic energy barriers for Na-ion diffusion in NVFP, the climbing image nudged elastic band (CI-NEB) method was employed. A spring constant of $5 \text{ eV} \cdot \text{\AA}^{-2}$ was used between the images. Na-ion migration between two adjacent sites was considered, and five intermediate configurations were generated between the initial and final states. Selective dynamics were applied during the NEB calculations, where only the migrating Na ions were allowed to relax, while the positions of non-migrating atoms, as well as the size and shape of the simulation cell, were kept fixed.

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Chapter 3

Electrolyte-Electrode Interfacial Chemistry in High-Voltage $\text{Na}_3\text{FeV}(\text{PO}_4)_3$ Cathode

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Insights into electrolyte-dependent interfacial chemistry in a high-voltage $\text{Na}_3\text{VFe}(\text{PO}_4)_3$ cathode through combined experimental and theoretical studies

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NASICON-type materials are very promising cathodes for sodium-ion batteries (SIBs) owing to their stable 3D framework and rapid Na^+ diffusion. Although high-voltage $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) has been extensively investigated for good capacity ($\sim 117 \text{ mAh g}^{-1}$) as well as outstanding rate capability, its practical use is limited because of the expensive and toxic vanadium. Hence, replacing V with Fe in $\text{Na}_3\text{VFe}(\text{PO}_4)_3$ (NVFP) presents a more sustainable composition with dual redox activity while maintaining high voltage. Herein, phase-pure NVFP is synthesized via a facile sol-gel method, delivering a specific capacity of $108.43 \text{ mAh g}^{-1}$ and energy density of $\sim 317 \text{ Wh kg}^{-1}$ at 0.1C . Furthermore, NVFP demonstrated excellent rate capability with outstanding retention of 88.01% over 100 cycles and 86.11% over 2000 cycles at 0.5C and 3C , respectively. For the first time, NVFP is comprehensively investigated in various carbonate-based electrolytes for the understanding of its influence on Na^+ diffusion kinetics and overall electrochemical performance. Additionally, the post-cycling analysis and detailed computational study provided crucial insights into the structural stability, diffusion kinetics, and sodium-ion transport mechanisms of NVFP, highlighting its strong potential as a cathode material for future commercialization of SIB systems.

In this chapter, phase-pure $\text{Na}_3\text{VFe}(\text{PO}_4)_3$ (NVFP) is synthesized via a facile sol-gel method, delivering a specific capacity of 108.43 mAh/g and energy density of $\sim 317 \text{ Wh/kg}$ at 0.1C , as determined from Na half-cell measurements using sodium metal as the counter/reference electrode. Furthermore, NVFP demonstrated excellent rate capability with outstanding retention of 88.01% over 100 cycles and 86.11% over 2000 cycles at 0.5C , and 3C , respectively. For the first time, NVFP is

comprehensively investigated in various carbonate-based electrolytes for the understanding of its influence on Na⁺ diffusion kinetics and overall electrochemical performance. Additionally, the post-cycling analysis and detailed computational study provided crucial insights into structural stability, diffusion kinetics, and sodium-ion transport mechanisms of NVFP, highlighting its strong potential as a cathode material for future commercialization of SIB systems.

3.1 Introduction

As discussed in Chapter 1, the shift to renewable energy and electric transportation has escalated the demand for economical, sustainable, and efficient energy storage systems. While lithium-ion batteries (LIBs) have been commercialized and used for almost all practical applications, the rising costs, localised distribution, and limited supply of lithium have driven research in finding alternatives.[1] In the context of abundance, low cost, and compatibility with LIB technology, SIBs are promising alternatives. However, the development of high-voltage cathode material that can deliver high energy density and structural stability with a long-life span is essential for advancing high-performance SIBs. In this regard, the 3D stable framework, safer and tunable electrochemical properties of the polyanionic compounds $\text{Na}_x\text{M}_2(\text{AO}_4)_3$ (M = transition metal, A = P, S, Si) make them suitable cathode materials for SIBs.[2] The 3D open architectures of NASICON-type materials are remarkable because they provide enhanced structural stability and quick Na^+ diffusion across extended life cycles.

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) is a well-known NASICON material for SIBs due to its favourable electrochemical properties with a high operating voltage of ~ 3.4 V versus Na^+/Na , ascribed to the $\text{V}^{3+}/\text{V}^{4+}$ redox activity.[3] The monoclinic crystal structure of NVP is built from the corner-sharing of VO_6 octahedra and PO_4 tetrahedra, resulting in a robust 3D network with large interstitial sites that accommodate mobile Na^+ ions. This leads to the high density as well as superior rate capability of NVP, making it a potential candidate for practical SIB applications in both half-cell and full-cell applications. However, its widespread adoption for sustainable SIB deployment is hindered by some limitations, such as intrinsic electronic conductivity, high cost, and toxicity of vanadium. To address these limitations, significant attempts have been made to partially or fully substitute vanadium with more abundant and inexpensive transition metals. This includes $\text{Mn}^{2+}/\text{Mn}^{3+}$, Fe^{3+} , Mg^{2+} , Ti^{4+} , Mo^{6+} , Al^{3+} , and Cr^{3+} , which

have been utilized as cation doping at the V site to improve the overall electrochemical performance of NVP. [4–8]

A recent study reported $\text{Na}_4\text{MnV}(\text{PO}_4)_3$ with increased operating voltage, but the Jahn-Teller distortion leads to structural instability and rapid capacity fading.[9] On the other hand, Cr substitution at the V site demonstrated enhancement in structural robustness of $\text{Na}_3\text{Cr}_{0.5}\text{V}_{1.5}(\text{PO}_4)_3$, but with a low operating voltage.[10] Moreover, $\text{Na}_3\text{VTi}(\text{PO}_4)_3$ delivered improved cycling stability with reduced operating voltage.[11] Among various transition metal substitutions, Fe stands out as an attractive candidate due to its abundant precursors, cost-effectiveness, and non-toxicity.[12] It also introduces additional redox activity by partially improving capacity as well as energy density. The partial substitution of Fe at the V site leverages the dual redox couple $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{V}^{3+}/\text{V}^{4+}$, demonstrating high operating voltage and theoretical capacity of around 128 mAh/g attributed to the extraction of more than two sodium ions per formula unit.[13] Furthermore, the presence of Fe improves the sustainability profile of the material and may enhance electronic conductivity, thereby facilitating faster charge/discharge kinetics and making Fe-doped NVP a promising cathode for next-generation SIBs.[7,14]

Although Fe-doped NVP materials show promising attributes, their practical application depends on the selection of a compatible electrolyte, which governs the interfacial stability, ionic conductivity, and overall electrochemical performance.[15] Extensive research has been carried out on the compatibility of carbonated-based electrolytes with NASICON compounds, where electrolytes need to offer wide electrochemical stability, inhibit side reactions, and enable fast Na^+ mobility.[16,17] The crucial factor in achieving long-term cycling stability with high coulombic efficiency is the formation of a stable electrode-electrolyte interface, which becomes more important while operating at higher voltages that may activate additional redox couples. According to recent reports on the

electrochemical performance of NVP and its derivatives, the role of selection of suitable sodium salt, solvent, and functional additives for electrolyte composition is primarily considered in modulating the interfacial behavior and surpassing side reactions.[18,19] Optimizing these components can significantly improve the structural integrity and electrochemical performance of NASICON-type materials. Therefore, the rational understanding of the impact of the interaction of electrolyte system with the electrode kinetics is crucial for practical implementation of Fe-doped NVP-based SIBs.

In the present investigation, an experimental as well as computational study of $\text{Na}_3\text{VFe}(\text{PO}_4)_3$ (NVFP) as a cathode material for SIBs is performed, in the context of balancing cost, environmental impact, and electrochemical functionality. The present approach incorporates a facile sol-gel synthesis of phase-pure NVFP and its comprehensive study of the compatibility of various carbonated-based electrolytes containing FEC additive. Through multi-faceted evaluation in half-cell configurations, this study aims to examine the electrolyte-dependent ionic transport and cathode-electrolyte interface (CEI) chemistry that unveils the superior rate capability and long-term cycling stability demonstrated here.[20] Moreover, the computational insights into Fe substitution effects on the local electronic structure and Na^+ site occupancy reveal the origin of high-voltage reversible redox behavior extending beyond the conventional $\text{V}^{3+}/\text{V}^{4+}$ couple, enabling enhanced capacity and structural robustness. Furthermore, the integration of post-electrochemical analysis highlights practical applicability and scalability of NVFP by positioning it as a compelling candidate for next-generation sustainable SIBs. The present findings contribute to the advancement of next-generation SIBs by highlighting the synergistic role of material composition and electrolyte optimization in achieving high energy density, safety, and long cycle life.

3.2 Experimental Section

3.2.1 Materials synthesis

The experimental procedures, including the selection of precursors, synthesis strategies, slurry preparation, electrode fabrication, cell assembly, physicochemical characterization, and electrochemical evaluation techniques for the $\text{Na}_3\text{VFe}(\text{PO}_4)_3$ cathode material, were discussed in detail in Chapter 2. The physicochemical characterization of the $\text{Na}_3\text{VFe}(\text{PO}_4)_3$ cathode involved powder XRD, FESEM, EDS, XPS, and HRTEM.

3.2.2 Coin cell fabrication

The electrochemical measurements were performed using electrodes with an active material loading of approximately $0.6\text{-}0.7\text{ mg/cm}^2$ ($\approx 1.2\text{-}1.4\text{ mg}$ per 16 mm diameter electrode). Prior to evaluating the electrochemical performance of $\text{Na}_3\text{VFe}(\text{PO}_4)_3$ in CR2032 half-cells, optimization of the electrolyte system was carried out using various electrolyte formulations. The four electrolyte systems are 1M NaClO_4 in (i) PC, (ii) EC:PC (1:1), (iii) EC:DMC (1:1), and (iv) EC:DEC (1:1), each containing 2% of fluoroethylene carbonate (FEC) as an additive. Among these electrolyte systems, $\text{Na}_3\text{VFe}(\text{PO}_4)_3$ demonstrated notable electrochemical activity in EC:DMC electrolyte system.

3.3 Results and Discussion

3.3.1 Physicochemical Analyses

3.3.1.1 Structural Analysis

The XRD pattern of NVFP and its Rietveld refinement (**Figure 3.1 (a)**) confirmed that NVFP crystallizes in a rhombohedral crystal structure with space group $R\text{-}\bar{3}C$. [21] The refined structural parameters exhibited good agreement with the experimental data, as reflected by the relatively low χ^2 (3.5), R_p (11.7%) and R_{wp} (9.9%) values obtained from the Rietveld analysis. The corresponding refined unit cell parameters are $a = 8.736 \pm 0.004\text{ \AA}$, $b = 8.736 \pm 0.004\text{ \AA}$, and $c = 21.744 \pm 0.007\text{ \AA}$. The XRD pattern displayed sharp as well as distinct diffraction peaks, and the lack of any impurity peaks further indicates a highly crystalline and phase-pure NVFP

material. The crystal structure illustrated in **Figure 3.1 (b)**, reveals that the FeO_6/VO_6 octahedra are connected through the corner sharing with PO_4 tetrahedra.[22] The Na atoms located in the interstitial cavities form the 3D robust NASICON framework, facilitating rapid Na^+ diffusion and structural stability during the electrochemical charging-discharging process.

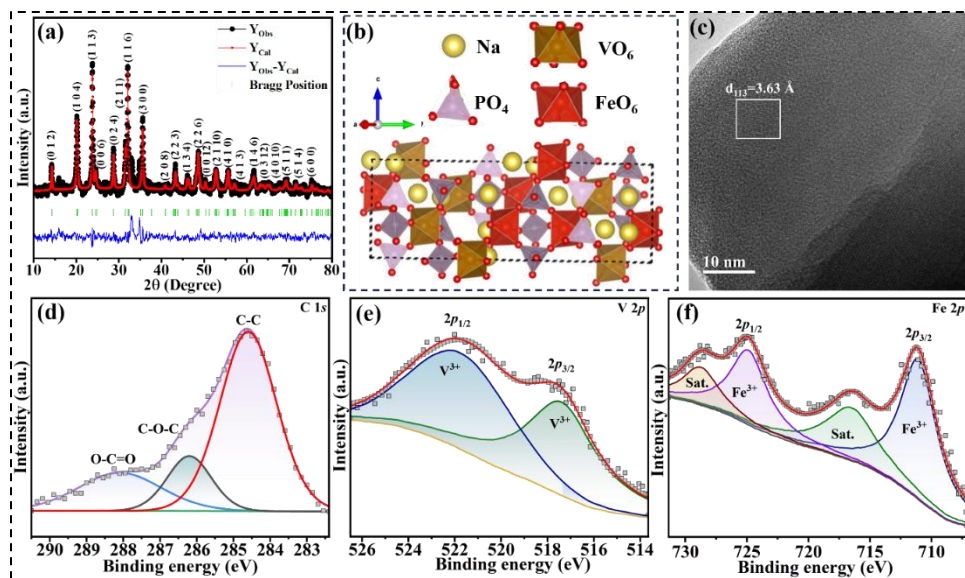


Figure 3.1 (a) Rietveld refinement of NVFP, (b) crystal structure, (c) HRTEM image, deconvoluted XPS of (d) C 1s, (e) V 2p, and (f) Fe 2p of NVFP.

HRTEM analysis depicted in **Figure 3.1 (c)** indicates the lattice fringes with interplanar spacings of 3.63 Å, corresponding to the crystallographic plane (113) of the rhombohedral structure. Additionally, the SAED pattern shown in **Figure 3.2 (a)** confirms the crystalline nature of NVFP. The calculated interplanar spacings of 3.68 and 2.79 Å can be indexed to the (113) and (116) crystallographic planes, respectively. These results confirm the crystallinity of NVFP, which is in agreement with the XRD analysis.

3.3.1.2 Chemical Analysis

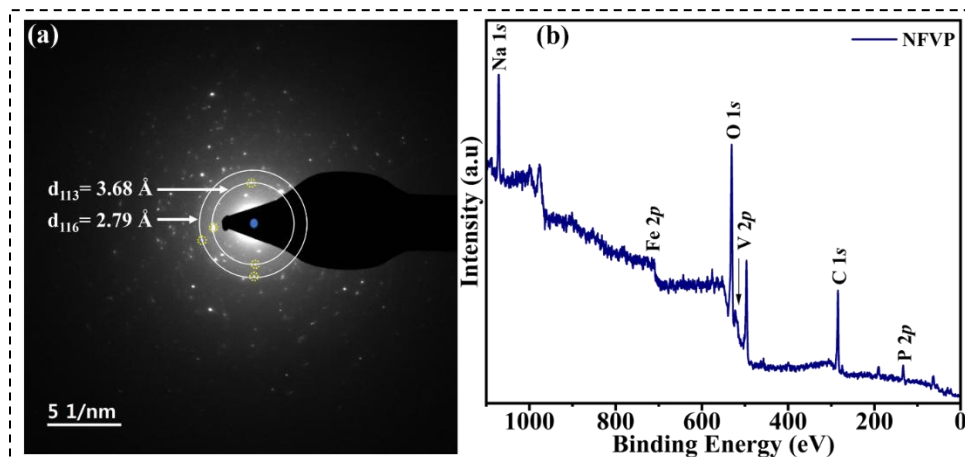


Figure 3.2 (a) SAED pattern, and (b) survey scan of NVFP.

Moreover, the XPS analysis clarified the surface chemical composition and electronic states of NVFP. **Figure 3.2 (b)** presents the presence of all key elements on the surface of NVFP. The high-resolution C 1s XPS spectrum depicted in **Figure 3.1 (d)** exhibits a predominant C-C peak at 284.6 eV with C-O-C and O-C=O at 286.5 eV and 288.3 eV, respectively, ascribed to residual surface carbon species. Moreover, the V 2p spectrum represented in **Figure 3.1 (e)** demonstrates that V is present predominantly in the +3 oxidation state with characteristic peaks at 517 and 522 eV. Similarly, the Fe 2p spectrum shown in **Figure 3.1 (f)** reveals the presence of the +3 oxidation state of Fe, with peaks at 711 eV and 725 eV, respectively, accompanied by satellite features of Fe^{3+} . These oxidation states of V and Fe, specifically the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{V}^{3+}/\text{V}^{4+}$ couples, are critical as they directly influence the redox activity and electrochemical performance of NVFP in SIB applications.[13]

3.3.1.3 Surface Morphology Analysis

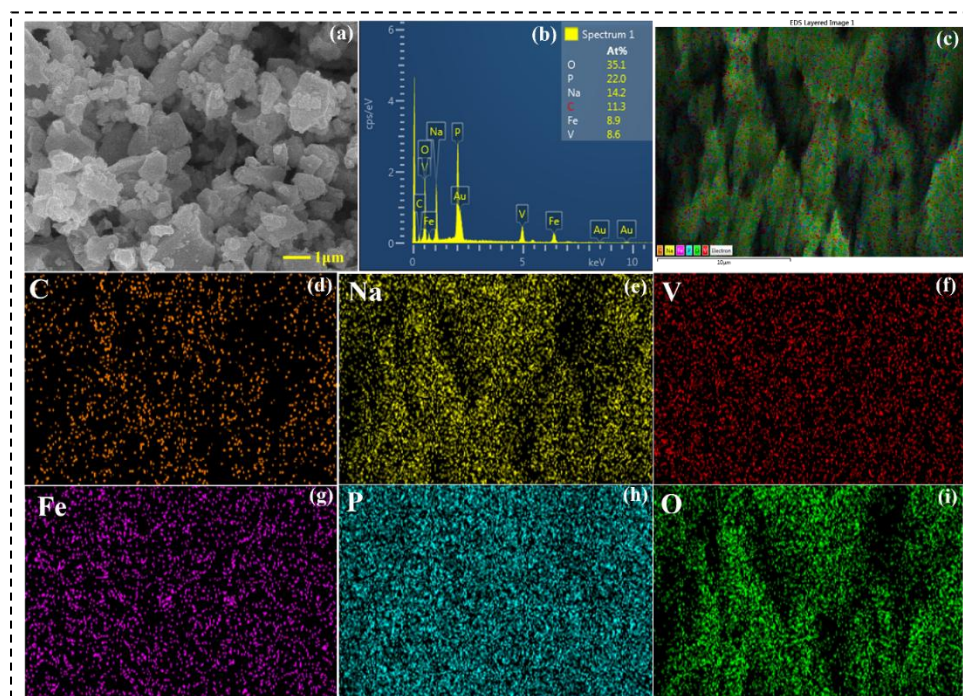


Figure 3.3 (a) FESEM image, (b) EDX analysis, (c) color mapping of elements, (d) C, (e) Na, (f) V, (g) Fe, (h) P, and (i) O of NVFP.

Surface morphological features were characterized using FESEM, as shown in **Figure 3.3 (a)**, revealing that the NVFP particles consist of irregularly shaped microparticles with uniform distribution. This architecture is advantageous for electrochemical analysis, as it promotes the active surface area, leading to shorter sodium-ion diffusion pathways and improving electrolyte-electrode contact. Further, the EDX analysis of NVFP confirms the elemental composition of NVFP to be close to the expected stoichiometry, as shown in **Figure 3.3 (b)**, and the color mapping (**Figure 3.3 (c-i)**) shows a homogeneous distribution of Na, Fe, V, P, and O elements throughout the sample. Together, these physicochemical characterizations validate the successful synthesis of phase-pure NVFP with desirable structural, compositional, and morphological features for high-performance SIB applications.

3.3.2 Electrochemical Analysis

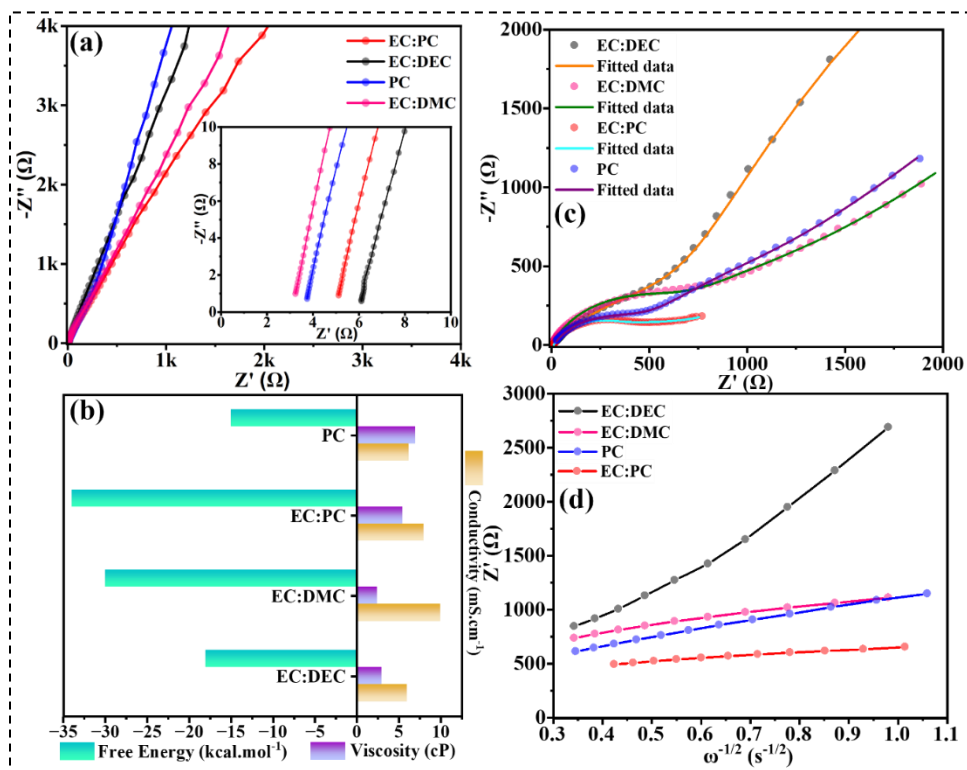


Figure 3.4 (a) Nyquist plots of all electrolytes (Inset: Magnified Nyquist plot), (b) parameters of carbonate solvents used in SIBs, (c) Nyquist plots of NVFP1 in all electrolytes, (d) plot of Z' vs $\omega^{-1/2}$ for NVFP1 in all electrolytes

The electrochemical performance of the NVFP cathode material was evaluated in the half-cell configuration of the CR2032 prototype. Initially, to investigate the effect of voltage range on the electrochemical performance of NVFP, two voltage cutoff windows were employed: 2.0-4.0 V (NVFP1) and 2.0-4.3 V (NVFP2). For achieving high-performance SIB, a stable electrode-electrolyte interface is one of the critical requirements. Hence, in this study, the NVFP1 was tested in four electrolyte systems, each containing 1M NaClO₄ salt dissolved in different combinations of carbonate solvents, including polyethylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC). The four electrolyte systems are 1M NaClO₄ in (i) PC, (ii) EC:PC (1:1), (iii)

EC:DMC (1:1), and (iv) EC:DEC (1:1), each containing 2% of fluoroethylene carbonate (FEC) as an additive. Here, the primary role of the additive is to suppress electrolyte decomposition as well as to improve the ionic conductivity of electrolytes and interfacial stability. The ionic transport properties of these electrolytes for SIBs are known to be significantly influenced by the viscosity, ionic conductivity, and solvation free energy of the solvents that are reported by the previous studies,[23] as represented in **Figure 3.4 (b)**.

Table 3.1 Fitted impedance parameters determined from EIS of NVFP1 half cells.

Solvent(s) Parameters	EC:DEC	EC:DMC	EC:PC	PC
$R_{\Omega} (\Omega)$	10.46 (0.41%)	5.14 (0.48%)	9.18 (0.55%)	12.28 (0.53%)
$R_{CEI} (\Omega)$	471.51 (4.28%)	515.95 (4.21%)	663.52 (2.21%)	495.30 (1.81%)
$R_{ct} (\Omega)$	711.93 (4.65%)	290.21 (2.01%)	395.61 (2.5%)	467.94 (5.27%)
$\sigma (\Omega.s^{1/2})$	2873.35	481.88	568.34	655.05
$D_{Na^+} (cm^2/s)$	1.01×10^{-18}	3.59×10^{-17}	2.58×10^{-17}	1.94×10^{-17}
χ^2	1.42×10^{-3}	1.94×10^{-3}	4.07×10^{-3}	2.08×10^{-3}

The theoretical findings offer a primary baseline for the experimental results. The ionic conductivity of the electrolyte systems, as depicted in **Figure 3.4 (a)**, was characterized via electrochemical impedance spectroscopy (EIS) using stainless-steel symmetric cells at 25 °C.[24] Further, the Nyquist plots for NVFP1 in all electrolytes are shown in **Figure 3.4 (c)**. In this study, EC:DMC system demonstrated the lowest ionic resistance among four electrolytes, which is in agreement with the lowest viscosity and highest conductivity, according to the reported literature. This is attributed to strong ion dissociation from EC and low-viscosity ion transport from DMC.[23,25] Moreover, the addition of 2% FEC further improves the CEI formation, stimulating enhanced interfacial

stability and reduced charge transfer resistance, which contributes to better overall kinetics. Unexpectedly, the electrolyte containing only PC demonstrated lower ionic resistance than EC:PC, even though theoretically EC:PC should exhibit higher conductivity than PC with more negative solvation free energy.[26] This observed discrepancy can be ascribed to the strong coordination between Na ions and solvent molecules in the EC:PC mixture, which can limit the desolvation at the electrode-electrolyte interfaces, resulting in higher interfacial resistance.[23] Furthermore, the stronger solvation of FEC may reduce its accessibility to the electrode surface, which limits the optimal formation of an CEI layer. In contrast, PC enables easier Na^+ desolvation and more effective FEC reduction, leading to thinner, more conductive CEI layers, which is reflected in the EIS results.[27] The observed highest resistance for the EC:DEC system is in accordance with its poor ion dissociation and low dielectric constant. Further, it causes high ion pairing, reducing the concentration of Na^+ available for conduction, impeding transport, and limiting FEC functionality at the interface. Even though FEC stabilizes the interface, its effectiveness is hindered in this system with inferior salt dissociation and unfavorable solvation dynamics, leading to the unstable or resistive CEI.[20,28] The Nyquist plots of NVFP1 in all electrolytes were fitted using an equivalent electrochemical circuit represented in **Figure 3.4** with obtained elements: the ohmic resistance (R_Ω) related to the ionic resistance of electrolyte used, the charge-transfer resistance (R_{ct}) at NVFP1-electrolyte interface, the resistance correlated with the formation of CEI on the surface of electrode (R_{CEI}), double-layer charge at NVFP1/electrolyte interface (CPE_{CEI}), spatial capacitance at NVFP1 layer (CPE_{ct}), and Warburg impedance (W) attributed to the Na^+ diffusion in NVFP1 channels.[13,29] The fitted EIS parameters of NVFP1, along with the error in all electrolyte systems, are tabulated in **Table 3.1**. Additionally, the Warberg factors (σ) are determined from the plot of $\omega^{-1/2}$ vs Z' (**Figure 3.4 (d)**). Then, the sodium-ion diffusion coefficients (D_{Na^+}) are determined using **equation**

(2.13). The D_{Na^+} value is $3.59 \times 10^{-17} \text{ cm}^2/\text{s}$, the highest for the EC:DMC system and the lowest for the EC:DEC system. This signifies the importance of assessing not only bulk transport properties but also interfacial chemistry while designing an optimized electrolyte system for SIBs.

The electrochemical behavior of NVFP electrodes in different electrolyte solvents were evaluated by assembling the coin cells. **Figure 3.5** depicts the galvanostatic charge-discharge (GCD) profiles and rate performance of NVFP in all four electrolytes within a voltage window of 2-4 V. Among them, NVFP1 in EC:DMC solvent delivered the highest initial specific capacity of 97.14 mAh/g at 0.1C with superior rate capability among all other electrolytes (**Figure 3.5 (c)**). The specific capacity obtained at 0.1C in solvents PC, EC:DEC, and EC:PC are 82.92, 68.19, and 59.98 mAh/g, respectively. The rate capability of NVFP1 in all electrolytes, as shown in **Figure 3.5 (a-d)**, follows the typical trend of decreasing specific capacity with increasing C-rates, reflecting the ionic mobility limitations of each electrolyte. The achieved superior performance of NVFP1 in EC:DMC electrolyte is well supported by both experimental and theoretical research in SIBs in the context of favourable viscosity, conductivity balance, enhanced Na^+ transport, and reduced polarization losses during cycling.[23,25,27] Further, to get an insight into the effect of electrolyte solvents on structural and cycling performance, the NVFP1 cathode was cycled at 0.5C for 100 cycles in all electrolytes. Specifically, NVFP1 in EC:DMC retained 95.24% capacity after 100 cycles. The NVFP1 in PC, EC:PC, and EC:DEC retained 95.04%, 92.96% and 89.06% of their initial discharge specific capacity, respectively, after 100 cycles with nearly 100% CE in all electrolytes (**Figure 3.5 (e)**). These findings clearly demonstrate that the electrolyte composition plays a pivotal role in the performance of NASICON-type cathodes. The combination of strong salt dissociation of EC and low viscosity of DMC, coupled with the potential to form CEI of FEC, makes this electrolyte solution the most promising of those experimented with. Both previously reported experimental and theoretical

predictions as well as current experimental validation support this.

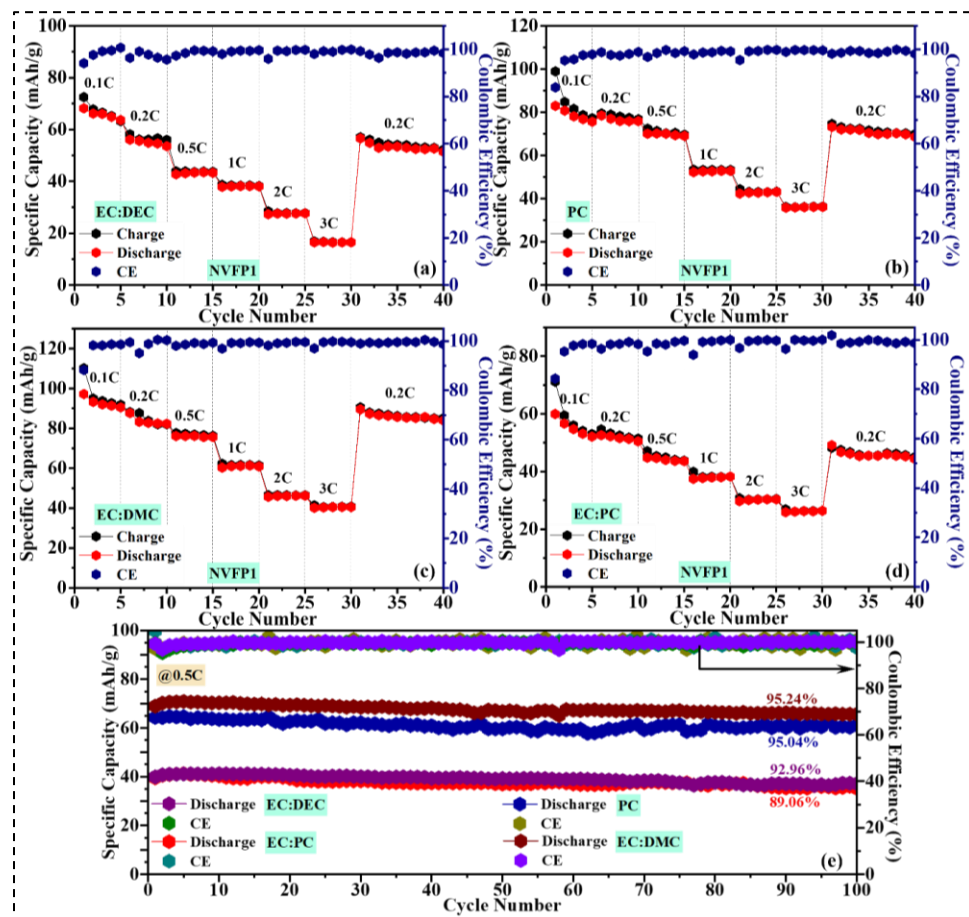


Figure 3.5 Rate capability plot of NVFP1 in various C-rates in (a) 1M NaClO₄ in EC:DEC with 2% FEC, (b) 1M NaClO₄ in PC with 2% FEC, (c) 1M NaClO₄ in EC:DMC with 2% FEC, (d) 1M NaClO₄ in EC:PC with 2% FEC, and (e) cyclic stability of NVFP1 in all electrolytes for 100 cycles at 0.5C.

Although PC gives satisfactory performance, its viscosity is slightly higher, which hinders rate capability. Conversely EC:DEC and EC:PC is limited in both interfacial and transport properties, which adversely affect their electrochemical performance.[23–28] To gain deeper insights into the electrochemical reaction mechanism and the multistage Na⁺ extraction/insertion process of NVFP1, cyclic voltammetry (CV) and differential capacity (dQ/dV) analyses were performed as shown in **Figure**

3.6. Figure 3.6 (a) presents the CV curve of the NVFP1 cathode at a scan rate of 0.1 mV/s within the voltage range of 2.0-4.0. The profile exhibits three distinct pairs of anodic (oxidation) and cathodic (reduction) peaks, indicating a stepwise redox mechanism. The first redox peak at around 2.4-2.5 V attributed to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ and the most intense peak at around 3.3-3.5 V corresponds to the $\text{V}^{3+}/\text{V}^{4+}$. [13] The observed area under the CV curve is higher for the EC:DMC configuration among others. The high degree of symmetry between the anodic and cathodic scans suggests excellent electrochemical reversibility of the NASICON framework.

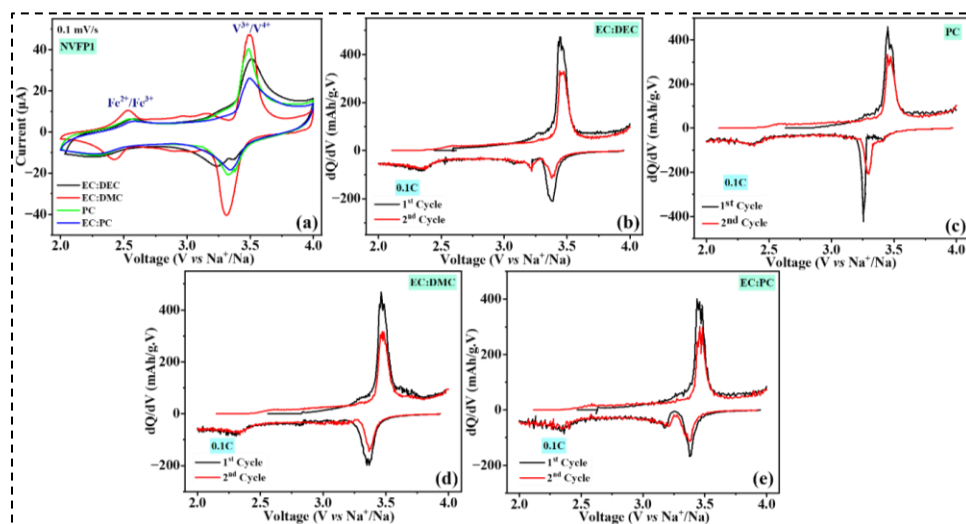


Figure 3.6 (a) CV of NVFP1 in all electrolyte systems at 0.1 mV/s, differential CV of NVFP1 in (b) EC:DEC, (c) PC, (d) EC:DMC, and (e) EC:PC electrolyte systems at 0.1C.

Furthermore, the redox behaviour is corroborated by dQ/dV curves for all configurations which are derived from GCD profiles at 0.1 C, represented in **Figure 3.6 (b-e)**. [30] The dQ/dV analysis are in line with GCD, CV analysis, and EIS analysis for NVFP1 in different electrolyte systems in terms of capacity, conductivity and reversibility. In general, the findings highlight the need to optimally design electrolyte systems to be used with high-voltage NASICON cathodes, in which interfacial chemistry and bulk ion transport should be optimally matched. The results also point

to the importance of FEC in stabilizing the interface, which is effective depending on the solvent environment and solvation dynamics.[16,17,31]

3.3.3 Post-electrochemical analysis

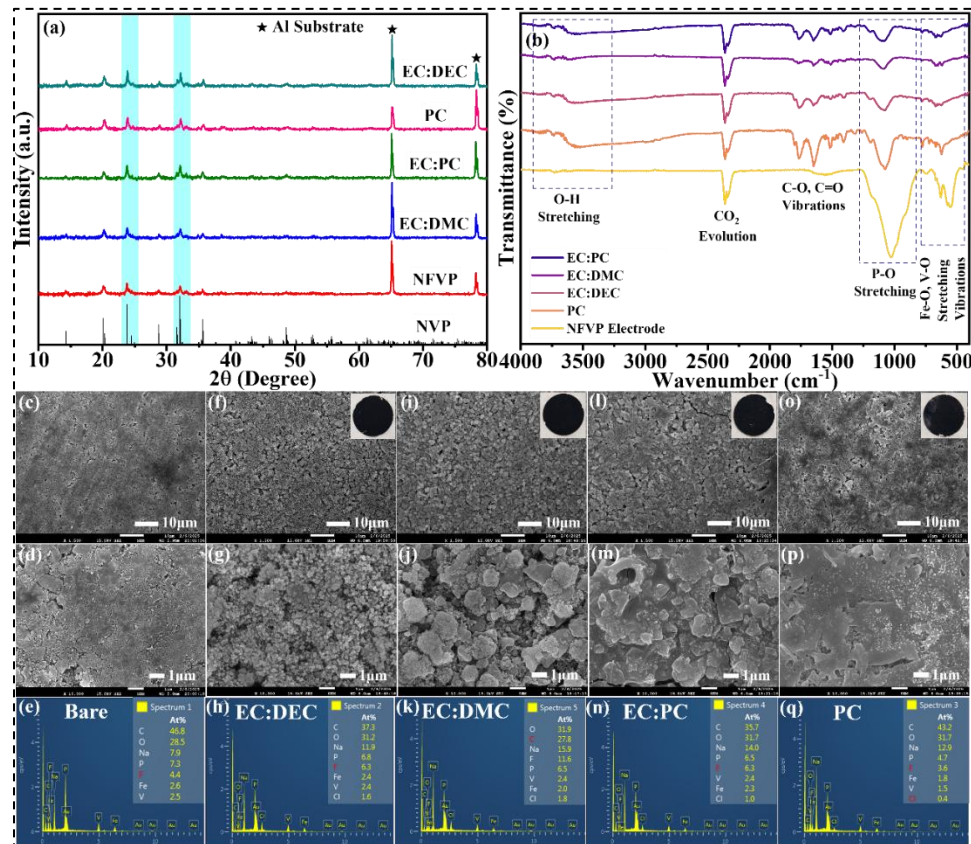


Figure 3.7 (a) Combined XRD patterns, (b) Combined FTIR analysis post-electrochemical testing, (c,d) FESEM image, (e) EDX of bare NVFP1 electrode, FESEM images of NVFP1 electrode in (f,g) 1M NaClO₄ in EC:DEC with 2% FEC, (i,j) 1M NaClO₄ in EC:DMC with 2% FEC, (l,m) 1M NaClO₄ in EC:PC with 2% FEC, (o,p) 1M NaClO₄ in PC with 2% FEC, (h,k,n,q) EDX of NVFP1 in 1M NaClO₄ in EC:DEC, EC:DMC, EC:PC, PC each with 2% FEC respectively.

To characterize the phase purity, morphological, and chemical features of NVFP1 after electrochemical testing in various carbonate-based electrolytes, XRD, FTIR, FESEM, and XPS analyses were carried out. It provided useful information about the structural properties and the interface

chemistry of NVFP following electrolyte cycling. The XRD data in **Figure 3.7 (a)** confirm the existence of intermittent diffraction peaks and the lack of new phases or broadening of peaks which proves that the bulk crystal structure is maintained despite the presence of solvent environment.[10] This highlights the structural robustness of NASICON materials, which undergo sodium insertion and extraction with minimal lattice disruption. The occurrence of peaks with the star symbol with the meaning of the aluminium substrate is anticipated and does not hamper with the interpretation of the active phase of NVFP.

The FTIR spectra displayed in **Figure 3.7 (b)** indicate significant variations in surface chemistry and interfacial stability of the electrode depending on the electrolytes used. The O-H stretching observed at a broad band around 3580 cm^{-1} , referring to the adsorbed surface moisture or the hydroxyl species (such as NaOH, metal hydroxides) resulting from electrolyte side reactions. The sharp peak at 2356 cm^{-1} is indicative of CO_2 evolution from electrolyte breakdown and parasitic reactions occurring during cycling. It is also worth noting that the peak of EC:DMC is comparatively weaker and, therefore, suggests that this electrolyte system is efficient to suppress any undesirable side reactions and foster a more stable CEI. The resolution of C-O, C=O bands in $1500\text{--}1800\text{ cm}^{-1}$ indicates a formation of CEI and complex organic and inorganic compounds such as R-COO^- and ROCO^{2-} formed as a result of the electrolyte decomposition; consequently, the interfacial environment appears not to be the most disturbed by cycling, which makes the complex most chemically stable.[27] The phosphate-related vibrational bands observed near 1200 cm^{-1} further support the preservation of the phosphate framework, and transition metal-oxygen bonds remain intact.[32,33] Particularly, in EC:DMC, the interfacial environment appears least perturbed by cycling, suggesting a higher chemical stability. Overall, this elegantly illustrates how the careful selection of electrolyte composition directly influences both the structural integrity and interfacial chemistry of NASICON-type cathodes, ultimately

determining their effectiveness in SIB applications. Further, the morphological analysis was conducted to investigate the impact of electrolyte selection on the surface structure and chemistry of the electrode, which supports these findings.[25] **Figure 3.7 (c,d) and (e)** shows the FESEM images and EDS of bare NVFP electrode respectively before any electrochemical testing. FESEM images of electrodes cycled in EC:DMC (**Figure 3.7 (i,j)**) and EC:DEC (**Figure 3.7 (f,g)**) exhibit the uniform, fine-grained surface texture, indicative of a compact and homogeneous CEI. It is correlating with the superior electrochemical performance of NVFP in EC:DMC. In contrast, electrodes cycled in EC:PC (**Figure 3.7 (l,m)**) and especially in pure PC (**Figure 3.7 (p,q)**) show a rougher surface with larger agglomerates, visible cracks and voids, featuring unstable and potentially mechanical degradation of the interface. Furthermore, EDS analysis reinforces these observations, showing that EC:DMC (**Figure 3.7 (h)**) and EC:DEC (**Figure 3.7 (k)**) samples retain higher sodium and phosphorus content, suggesting minimal loss of active material. The elevated percentage of fluorine in EC:DMC is also evidence of the presence of FEC-derived protective CEI constituents and the electrolyte decomposition.[20]

To determine the composition and chemical nature of the CEI formed on NVFP1 under various electrolyte configurations, ex-situ XPS was conducted (**Figure 3.8**). The presence of the elements: Na, V, Fe, P, O, C, and F is confirmed by the survey spectra (**Figure 3.8 (a)**). Among the electrolytes studied, the F 1s intensity is highest for EC:DMC, suggesting that the CEI formed in this electrolyte is relatively enriched in NaF. This suggests that the EC:DMC electrolyte facilitates the selective breakdown of the salt and the formation of a stable interphase with a high inorganic fluoride content, and, as such, is reported to produce greater interfacial stability and lower parasitic side reactions. The C 1s high-resolution spectra (**Figure 3.8 (b)**) were deconvoluted into three major peaks.

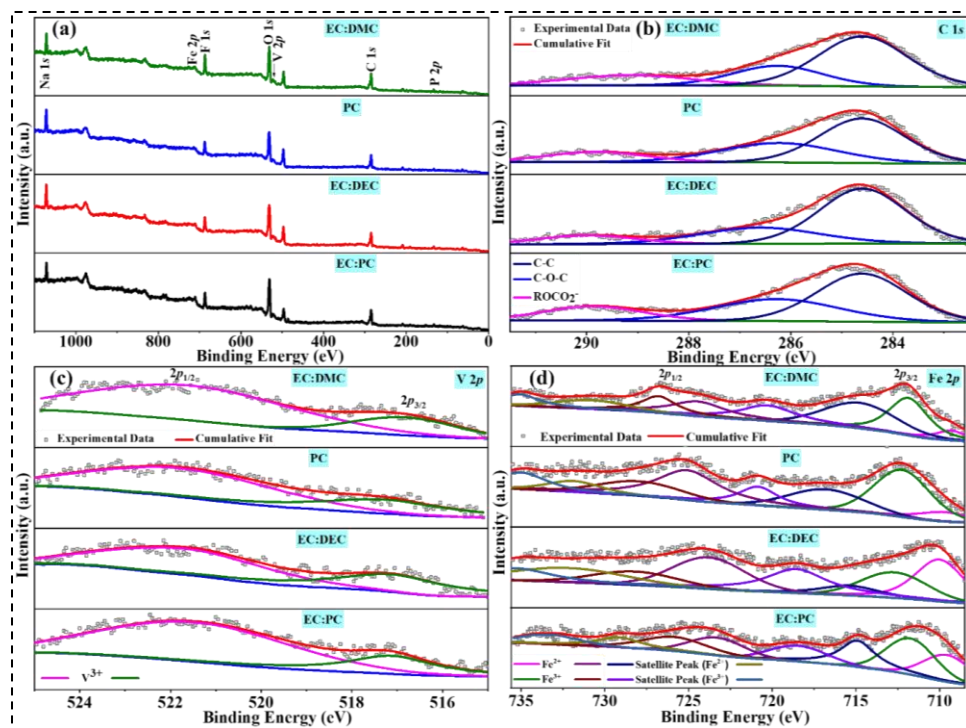


Figure 3.8 (a) Survey spectra, combined high-resolution XPS of (b) C 1s, (c) V 2p, and (d) Fe 2p of NVFP1 in all four electrolyte configurations.

The highest at 284.6 eV corresponds to the C-C bond, which is the remaining carbon content of the conductive additive or adventitious carbon. The peak at approximately 286.4 eV attributed to C-O-C, and is present in the CEI layers as a result of partial decomposition of the solvent. The third deconvoluted peak at around 289.9 eV, corresponds to the ROCO_2^- species for PC, EC:PC, EC:DEC, which is formed through the breakdown of the carbonate-based solvents. On the other hand, in EC:DMC, this peak shifts slightly to approximately 289.25 eV and may be attributed to lower decomposition in the solvent system. Such variations imply that the electrolyte constituents have a great influence on the chemical states and stability of the organic constituents of the CEI. According to the high-resolution V 2p spectra (**Figure 3.8 (c)**), V predominantly remains in a V^{3+} oxidation form following complete discharge. This validates the data of reversible redox transitions of V through cycling which aligns with the GCD profiles as V^{3+} is oxidized to V^{4+} and then to V^{5+} as the cell is charged

and reduced to V^{3+} as the cell is discharged. Moreover, the high-resolution Fe 2p spectra (**Figure 3.8 (d)**) indicate that there is a coexistence of Fe^{2+} and Fe^{3+} along with their respective satellite peaks, and this confirms that the NVFP1 has the mixed-valence state of Fe after cycling.[34] It is shown that both oxidation states are present, demonstrating that Fe is actively involved in redox processes during cycling. Overall, the XPS findings have shown that the electrolyte composition has a significant impact on the formation and the chemical composition of the CEI, EC:DMC has a preference towards the formation of a NaF-rich interphase, which is often advantageous to interfacial stability and long-term cycling. Simultaneously, the oxidation states of the transition metals are relatively conserved, indicating that the inherent electrochemical characteristics of NVFP1 are retained, and the redox behavior of the bulk material is mostly influenced by the interphase rather than by bulk redox. These findings can offer valuable guidance on the choice of electrolyte to optimize the nature of CEI and improve the performance of SIBs.

All these structural and compositional analyses confirm the trends of electrochemistry. In general, EC:DMC electrolyte system supports the formation of a stable, ion-conductive, and protective CEI, reducing interfacial degradation and promoting Na^+ transport efficiency. Conversely, the less efficient electrolyte systems lead to surface instability, resistance, and diminished performance of NASICON-type phosphate cathodes in SIBs.[18] These findings highlight the crucial role of electrolyte formulation in preserving structural integrity and optimizing interfacial chemistry for NASICON-type phosphate cathodes in SIBs.

3.3.4 Extended Electrochemical Evaluation of NVFP in EC:DMC

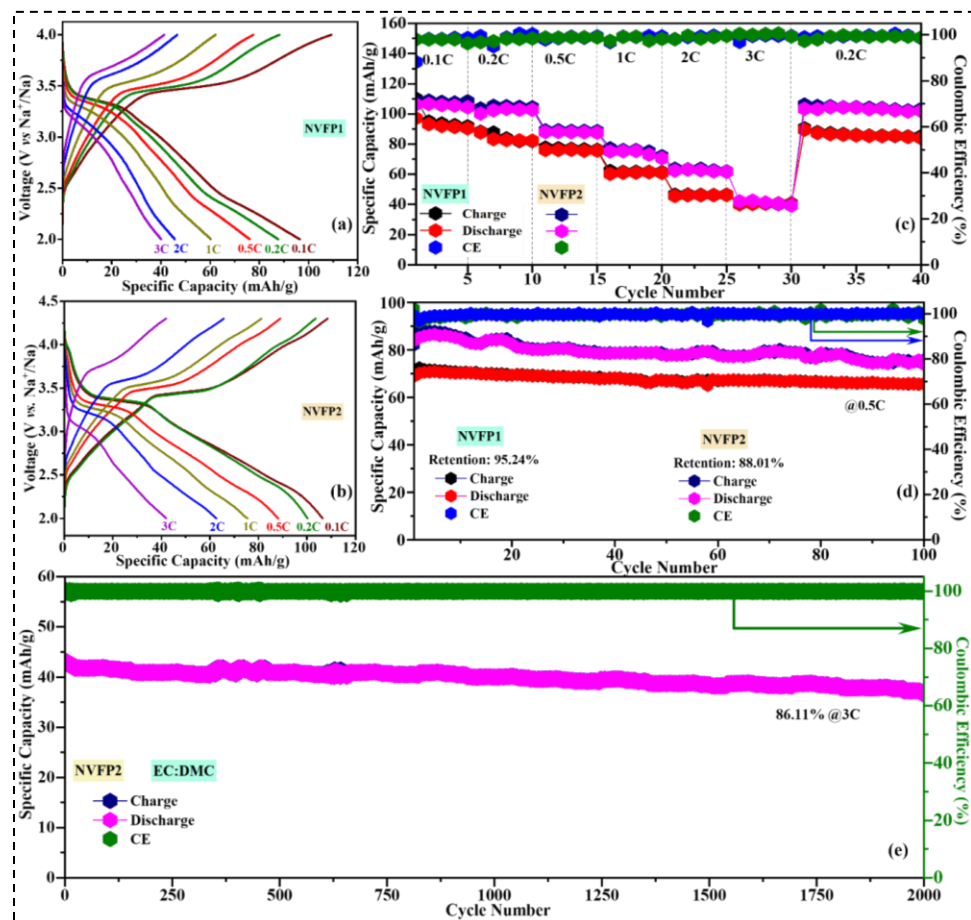


Figure 3.9 GCD profile of (a) NVFP1, (b) NVFP2, (c) combined rate capability plot, (d) cyclic stability of NVFP1 and NVFP2 for 100 cycles at 0.5C, (e) cyclic stability of NVFP2 at 3C for 2000 cycles in 1M NaClO₄ in EC:DMC with 2% FEC.

Based on the above-discussed electrochemical analysis and post-electrochemical analysis, extended testing on NVFP2 was conducted in 1M NaClO₄ in EC:DMC with 2% FEC electrolyte. As shown in **Figure 3.9 (a) and (b)**, both NVFP1 and NVFP2 exhibit a clear plateau in the voltage range of 3.4-3.5V corresponding to the redox activity of V³⁺/V⁴⁺. In case of NVFP2, an additional plateau enables around 3.95-4.1V, attributed to the activation of the V⁴⁺/V⁵⁺ redox couple due to the higher cutoff voltage. This contributes to the higher specific capacity of 108.43 mAh/g at 0.1C, due to

the higher cut-off voltage and more extensive sodium ion extraction and greater utilization of redox reactions compared to 97.14 mAh/g for NVFP1. The observed specific capacity 108.43 mAh/g and energy density 317 Wh/kg were obtained from Na half-cell measurements using sodium metal as the counter/reference electrode.

Table 3.2 Comparison of the electrochemical performance of the present study with previously reported materials and their derivatives.

Composition	Voltage Window (V)	Average Operating Voltage (V vs Na ⁺ /Na)	Specific Dis. Capacity (mAh/g) @C rate	Retention, Cycle Number@C rate	Ref.
Na ₃ VFe(PO ₄) ₃	~ 3.2	1.8-3.9	105@0.1C	87.6 %, 400@5C	[34]
Na ₃ VFe(PO ₄) ₃	~ 3.4	2.2-3.8	103@1C	95%, 2000@1C	[35]
Na ₃ VCr(PO ₄) ₃	~ 3.4	2.5-4.3	90@0.1C	-	[36]
Na ₃ VMn _{0.5} Ti _{0.5} (PO ₄) ₃ /C	~ 3.4	1.5-4.15	144.3@0.13C	88.13%, 500@0.85C	[37]
Na ₃ VFe _{0.5} Ti _{0.5} (PO ₄) ₃ /C	~ 3.4	1.5-4.15	145@ 0.12C	92%, 6000@11.2C	[38]
Na ₃ VFe(PO ₄) ₃	~ 3.3	2.0-4.3	108.43@0.1C	86.11%, 2000@3C	This Work

When assessing rate capability performance of both NVFP1 and NVFP2, the high coulombic efficiency is maintained with increasing C-rates, underscoring the excellent reversibility and kinetic capacities of the NVFP material as observed in **Figure 3.9 (c)**. However, in the case of NVFP2, more significant capacity fading is observed at higher C-rates, which may be due to the increased polarisation or kinetic limitations resulting from the expanded voltage range. Furthermore, the cycling stability at 0.5C for 100 cycles demonstrates capacity retention of 95.24%

and 86.11% for NVFP1 and NVFP2, respectively, reflecting the durability and stability of NVFP as depicted in **Figure 3.9 (d)**. The slightly lower capacity retention for NVFP2 points to the high-voltage side reactions or electrolyte decomposition at higher voltage. The first-cycle charge and discharge capacities were 58.42 and 47.05 mAh/g, respectively, corresponding to an initial Coulombic efficiency of 80.54%, indicating the extent of irreversible capacity loss associated with electrolyte decomposition and CEI formation during the initial cycle. Further, the coulombic efficiencies close to 100% show the highly reversible electrochemical processes as well as limited irreversible losses. Nevertheless, the cyclic stability of NVFP2 in **Figure 3.9 (e)** at a higher C rate of 3C for 2000 cycles demonstrates outstanding capacity retention of 86.11%. Overall, these results further suggest the long-term stability and retention, making NVFP1 suitable for durable SIBs, while the higher capacity and long-life span of NVFP2 are suitable for enhancing the energy density of SIBs. **Table 3.2** presents the comparison of the present study with previously reported compositions and its derivatives, where V is 50% substituted with Fe,[34,35] Cr,[36] Mn/Ti,[37] and Fe/Ti.[38] This reveals the comparable electrochemical performance of NVFP, and this composition can further be optimized by multi-element substitutions and carbon compositing for further performance enhancement.

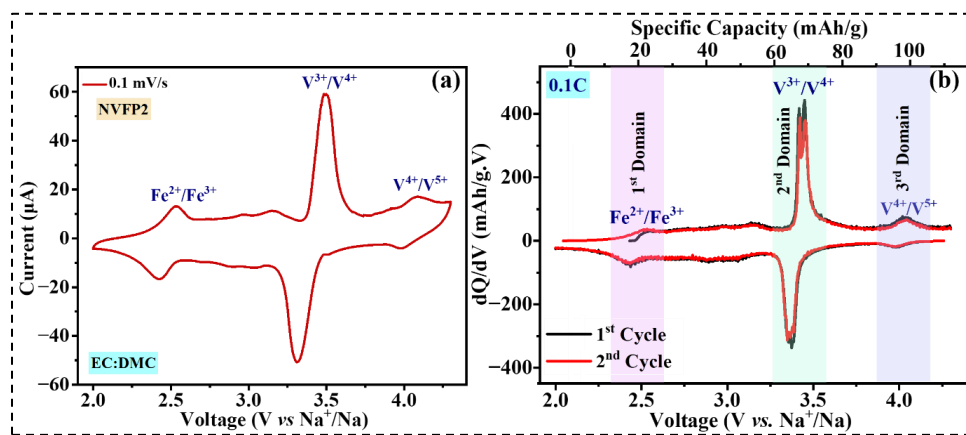


Figure 3.10 (a) CV profile at 0.1 mV/s, and (b) differential CV at 0.1C for NVFP2.

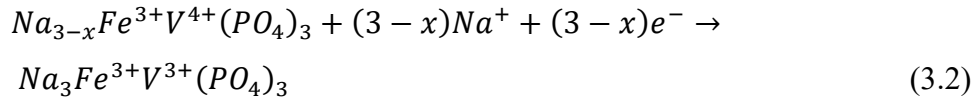
Furthermore, **Figure 3.10 (a)** illustrates the CV curve of NVFP2 cathode at the scan rate of 0.1 mV/s in the voltage range of 2.0-4.3 V vs. Na⁺/Na. The profile shows three redox pairs with anodic (oxidation) and cathodic (reduction) peaks. The initial two peaks at around 2.4/2.5 V have been referred to the reversible Fe²⁺/Fe³⁺ redox couple. The redox pair of highest intensity was centered at 3.4/3.5 V, corresponding to the V³⁺/V⁴⁺ redox reaction, and the broad peaks at higher potentials (around 4.0 V) are associated with the V⁴⁺/V⁵⁺ redox reaction.[39] The excellent electrochemical reversibility of the NASICON structure is indicated by the high level of symmetry between the anodic and cathodic scans. The redox performance is also supported by the dQ/dV curve in **Figure 3.10 (b)**, which was derived from the GCD profile at 0.1 C. The dQ/dV curve identifies three voltage ranges that are consistent with the CV data: 1st Domain (~2.3-2.6 V): This is the first capacity contribution due to the oxidation of Fe. 2nd Domain (~3.3-3.5 V): This is the main contribution of capacity due to the oxidation of V³⁺/V⁴⁺. 3rd Domain: The steepness of these peaks suggests a stable phase change in the migration of the remaining Na⁺ ions through the V⁴⁺/V⁵⁺ couple, yielding an overall specific capacity of more than 100 mAh/g.[14] During charging, the voltage domains are 2.53 V, 3.45 V, and 4.04 V, corresponding to Fe and V redox activity, respectively. Moreover, 2nd domain consists of three subdomains. It begins with a small solid-solution domain, a plateau of voltage, and then a sloping curve typical of materials with many crystallographic sites for sodium. In the early stages of the 2nd domain, a little Na⁺ is removed from the NVFP2 structure without the crystal phase changing. This is a single-phase (solid-solution) reaction in which the lattice parameters shrink slightly as V³⁺ oxidizes to V⁴⁺. This is represented in a dQ/dV curve as the first rise/slope to the actual peak. The steepest and strongest part of the 2nd domain peak indicates a first-order transition. This is a two-stage process, in which a Na-rich and a Na-poor

phase exist. This is a flat voltage plateau in a GCD curve because the chemical potential remains constant as a phase of the compound is converted to the other. In the dQ/dV plot, this is the sharp peak at 3.45 V, which shows that a significant amount of charge is transferred at a nearly constant voltage. When the second extraction of sodium ions reaches completion, the system returns to a sloping region. This is seen by the gradual decline of the dQ/dV peak. It often indicates that the structure is reorganizing or that the remaining Na^+ ions are occupying sites with varying energetic environments, leading to a steady rise in voltage as concentration decreases. The near overlap between the 1st cycle (black) and 2nd cycle (red) dQ/dV curves indicates that the material exhibits better structural stability and cycling performance. This multi-redox center utilization confirms that NVFP2 effectively leverages both Fe and V ions to achieve high energy density.

3.3.5 Role of Fe Substitution in Enabling High-Voltage Redox Activity

In pristine NVP, primarily the $\text{V}^{3+}/\text{V}^{4+}$ redox couple is electrochemically active within the typical voltage window ($\sim 3.4\text{V}$ vs Na^+/Na). In contrast, the $\text{V}^{4+}/\text{V}^{5+}$ redox couple is generally inaccessible under standard cycling conditions due to structural and electronic constraints. This corresponds to the unfavourable local coordination and electronic configuration of V in the NASICON framework within an accessible voltage window, which underlies the reversibility and thermodynamic feasibility of oxidizing $\text{V}^{4+}/\text{V}^{5+}$.^[40] However, partial substitution of Fe^{3+} at V^{3+} site in NVFP alters the electronic environment and sodium ion distribution, particularly modifying the occupancy and ordering of sodium ion sites. This substitution results in a more stable structure accommodating ample sodium extraction, with stabilization of the V^{5+} oxidation state. The electronic configuration and redox potential of Fe^{3+} in NVFP not only enhance electronic conductivity but also aid in lowering the activation energy for Na^+ migration. According to the GCD profile of

NVFP2, the reversible activation of redox couple V^{4+}/V^{5+} is enabled at around 3.8-4.0V vs Na^+/Na . [41] Additionally, maintaining sufficient Na^+ content at the Na_2 crystallographic site is very important for stabilizing the high oxidation state of V and allowing for the reversible V^{4+}/V^{5+} redox process. [33] This is enabled by Fe substitution at the V site. This synergistic redox activity of Fe^{2+}/Fe^{3+} and $V^{3+/4+/5+}$ not only increases the accessible capacity but also widens the operational voltage window, resulting in the enhancement of electrochemical performance of NVFP. [13] Moreover, the enhanced Na^+ retention at specific crystallographic sites stabilizes the framework against irreversible structural transitions. These effects are observed in the electrochemical performance of NVFP2. In summary, Fe substitution plays a crucial role in enabling high-voltage electrochemical activity in NVFP, contributing both to capacity enhancement and improved structural robustness, making it a strong candidate for next-generation SIB cathodes. **Equation (1) and (2)** shows the sodium storage mechanism while charging and discharging processes, respectively. [38]

$$Na_3Fe^{3+}V^{3+}(PO_4)_3 \rightarrow Na_{3-x}Fe^{3+}V^{4+}(PO_4)_3 + (3-x)Na^+ + (3-x)e^- \quad (3.1)$$


3.4 Effect of carbonate-solvent on battery performance

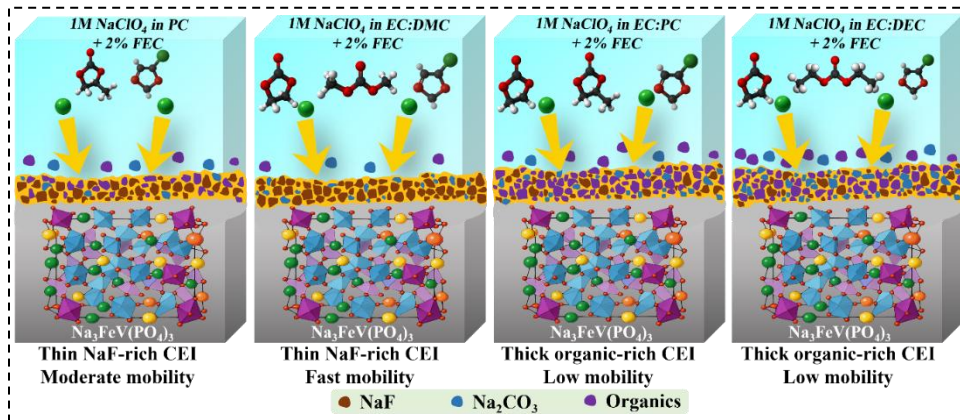
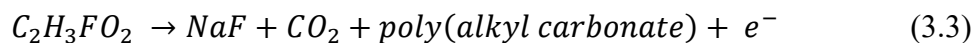
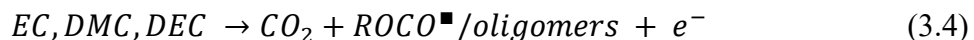


Figure 3.11 The illustrated reaction mechanism of (a) 1M NaClO₄ in PC with 2% FEC, (b) 1M NaClO₄ in EC:DMC with 2% FEC, (c) 1M NaClO₄ in EC:PC with 2% FEC, (d) 1M NaClO₄ in EC:DEC with 2% FEC electrolytes on the surface of the NVFP1 cathode.

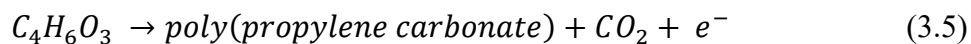
During electrochemical operation of NVFP cathodes, sodium ion storage is accompanied by the formation of CEI, which arises from oxidative decomposition of the electrolyte at potentials approaching the Fe²⁺/Fe³⁺, V³⁺/V⁴⁺ redox couple (~3.4 V vs. Na/Na⁺).[20] **Figure 3.11 (a-d)** illustrates the plausible mechanism of CEI formation for the presented study of NVFP in electrolyte systems, PC, EC:DMC, EC:PC and EC:DEC respectively. Upon migration and desolvation of Na⁺ ions at the cathode surface, FEC undergoes preferential oxidation, given in **equation (3)**, leading to defluorination and the generation of NaF, CO₂, and polycarbonate-type oligomers.[25]



The NaF formed constitutes the dominant inorganic passivation phase, ensuring interfacial stability and facilitating Na⁺ transport. Concurrently, solvent molecules also undergo oxidative decomposition.[31] In EC:DMC or EC:DEC blends, the primary products are CO₂ and short-chain carbonate fragments, giving rise to a thin, NaF-rich CEI with minor contributions from Na₂CO₃, which forms secondarily via CO₂ reactions with basic surface species (**equation (4)**).[42]



In contrast, PC-containing electrolytes promote oxidative polymerization, yielding poly(propylene carbonate), CO₂, and inorganic carbonates, which result in a thicker, more polymeric and elastic CEI (**equation (5)**).



The sodium salt NaClO₄ remains largely stable within the operating window of NVFP, with only negligible ClO_x fragments observed under severe

overcharge conditions. Overall, the CEI is NaF-rich, ion-permeable, and electronically insulating; it remains relatively thin in EC:DMC or EC:DEC electrolytes, but becomes thicker and more polymer-rich in PC- or EC:PC-based systems.[27] Importantly, Fe substitution within the NASICON lattice of NVFP enhances structural stability and reduces catalytic electrolyte decomposition, thereby preserving the integrity and composition of the CEI and ensuring favorable sodium-ion kinetics during long-term cycling.

3.5 Theoretical study of NVFP

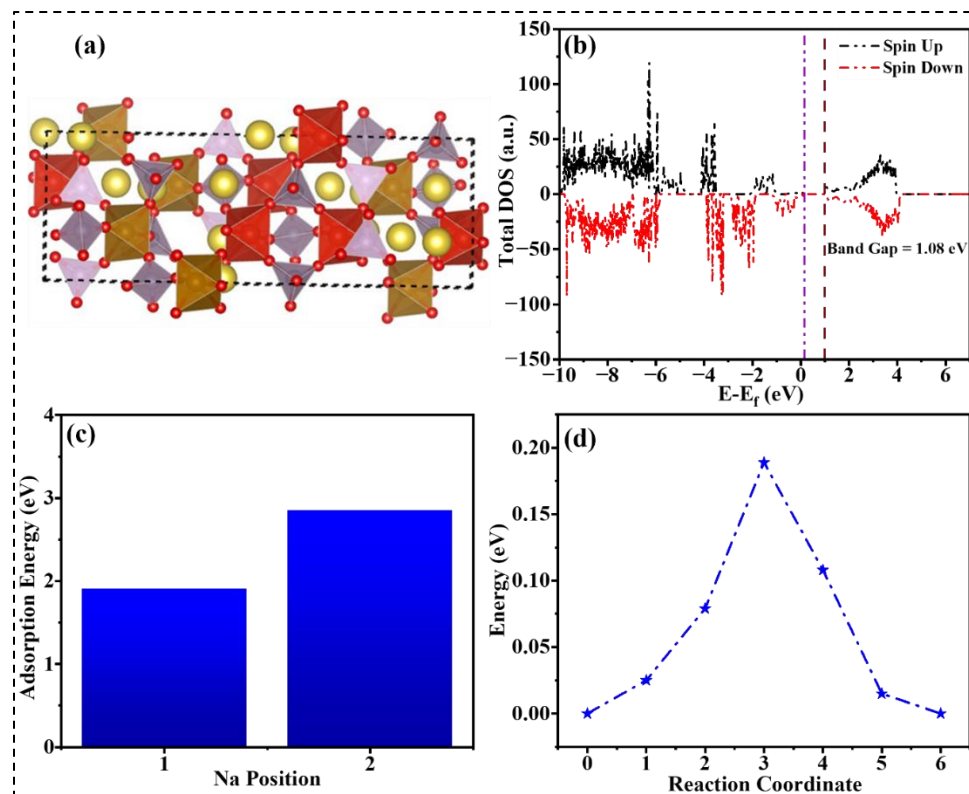


Figure 3.12 (a) Crystal structure of NVFP, (b) DOSs, (c) adsorption energy of sodium in Na1 and Na2 sites and d) Na⁺ diffusion energy profile with calculated migration barriers for NVFP.

First-principles calculations are performed to further understand the structural, electronic, and Na adsorption/diffusion properties of the NVFP material.[13] **Figure 3.12 (a)** depicts the optimised crystal structure of

NVFP, with lattice parameters $a = 8.7756 \text{ \AA}$, $b = 8.7855 \text{ \AA}$ and $c = 21.722 \text{ \AA}$, and with angles $\alpha = \gamma = 90^\circ$, and $\beta = 120^\circ$, indicating a rhombohedral crystal structure. A good agreement between simulations performed and experimentally observed lattice parameters highlights the accuracy of the model employed to represent the NVFP structure. Furthermore, the DOSs are evaluated, as depicted in **Figure 3.12 (b)**.

A narrow band gap of $\sim 1.08 \text{ eV}$ is observed in NVFP, which accounts for experimentally observed enhanced electrical conductivity and, consequently, improved electrochemical performance of NVFP. To elucidate the (de)intercalation behaviour of Na ions in the NVFP, we calculate the adsorption energy at two possible inequivalent Na ion sites, Na1 and Na2, by inserting an additional Na ion. The first site, Na1, is situated in an octahedral-like environment formed by two VO_6 octahedra and two PO_4 tetrahedra, whereas Na2 is located eight-fold coordinated polyhedron. It is observed that the Na1 sites have lower adsorption energy compared to the Na2 sites (**Figure 3.12 (c)**), indicating that during intercalation, the Na2 sites are filled first. In contrast, the Na1 sites, where sodium ions are less tightly bound, form the primary diffusion pathways. We then evaluated the diffusion pathways between the Na1 and Na2 sites, along with the corresponding energy barriers, as shown in **Figure 3.12 (d)**. A migration energy barrier of $\approx 0.2 \text{ eV}$ was found for Na-ion diffusion. Energy barriers of $0.2\text{-}0.34 \text{ eV}$ have been reported for Na ion in NVP.[43] We note that the relatively low Na ion migration barrier ($\approx 0.2 \text{ eV}$) does not fully explain the experimentally observed polarization behaviour.[44] This is because, under realistic experimental conditions, polarization is largely controlled by mass-transport limitations within the electrolyte and at the CEI, phenomena that are absent from bulk DFT calculations.

Despite promising advances demonstrated by NVFP, several intrinsic and extrinsic challenges remain for the practical deployment of SIBs. Although NVFP has a strong 3D NASICON structure that allows

quick Na^+ transportation and structural stability, the general energy density of SIBs remains lower than state-of-the-art LIBs mainly due to the increased ionic radius and mass of sodium. This essentially restricts possible volumetric and gravimetric performance, which requires continuous improvement in materials to bridge this performance gap. In addition, the CEI is useful in governing long-term cycling stability and rate capability in a critical manner. The current investigation of overall electrolyte analysis shows that solvent viscosity, ionic conductivity, solvation dynamics have direct effects on Na^+ desolvation and transport across the CEI, which affect the charge-transfer resistance and capacity retention. Despite the enhancement of interfacial stability by FEC additive formation of a NaF-rich CEI, solvent property mismatches can cause CEI heterogeneity, which affects the uniformity of ionic transport and mechanical integrity during long-lasting cycling[20,25] and highlights the fragility of the trade-off between maximizing the energy density and maintaining interfacial stability. Scalability and cost also become a problem when it comes to industrial-scale adoption. Although the costly V may be substituted by the readily available Fe to increase its sustainability and competitiveness on costs, the synthesis of SIBs on a large scale requires maintaining phase purity and morphology control, which are directly linked to electrochemical performance.[45] The comparative recent implementation of SIBs into the commercial market only shows that supply chains in the form of cathode material, electrolyte components, and battery management system are still in their formative stages and need to be standardized in order to facilitate mass production. Further, sodium propensity to create dendrites and electrolyte compatibility with high voltage cathodes is still a research aspect that is being studied, to ensure the cycle remains stable as well as the stability of electrolyte that is essential to enable commercial viability is achieved.[18] Despite these challenges, strong cycle stability of NVFP through the dual Fe and V redox activity and enhanced electrolyte interactions is a major stride that is being made towards research feasibility.

Further studies are needed to combine new nano architectonics of cathodes, alternative FEC-compatible electrolytes with bespoke solvation characteristics and scalable synthesis pathways to unlock the complete potential of NASICON-based cathodes such as NFVP in sustainable, high-performance SIBs.[19]

3.6 Conclusions

In this chapter, phase-pure robust NASICON-type NVFP material is synthesized via the sol-gel method for sustainable and high-performance SIBs. This material not only improves electronic conductivity through Fe substitution and sodium site occupancy but also enables reversible high-voltage redox activity beyond the conventional $V^{3+/4+}$ couple. Additionally, a systematic study of the compatibility of NVFP with carbonate-based electrolytes is carried out, revealing the influence of ion transport properties, CEI formation, and cycling stability of NVFP. Further, electrochemical analysis of this material revealed a high specific capacity of 108.43 mAh/g with an energy density of 317 Wh/kg at 0.1C in 1M NaClO₄ in EC:DMC with 2% FEC. Also, it demonstrated a remarkable rate capability and outstanding capacity retention of 88.01% over 100 cycles and 86.11% over 2000 cycles at 0.5C and 3C, respectively. Post-electrochemical structural, interfacial analyses, and theoretical calculations revealed the mechanisms driving robust framework as well as efficient sodium storage of NVFP. Overall, these comprehensive insights provide pathway for the rational design of cathode materials and electrolytes, advancing sustainable SIB technology towards practical applications.

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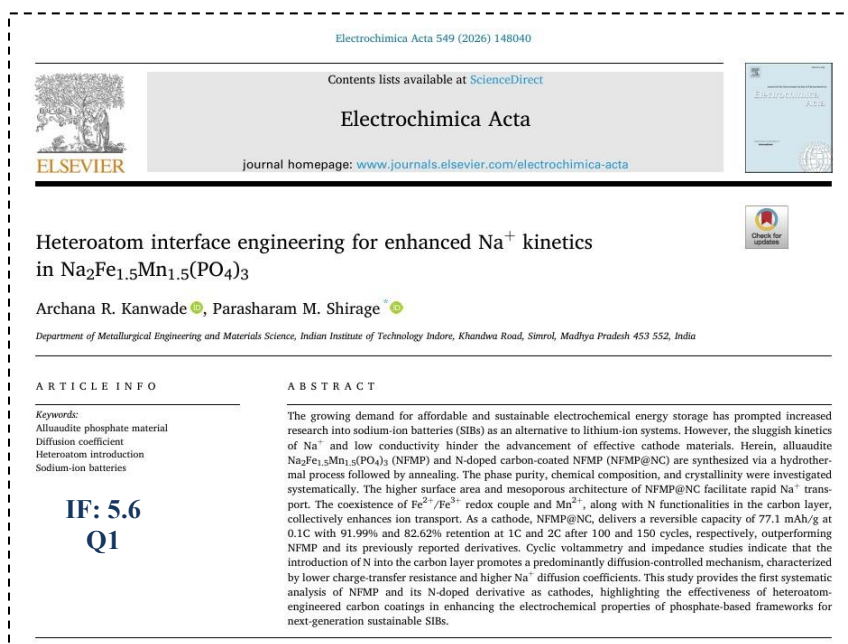
Chapter 4

Dual Functionality of $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ -Based Materials for Sodium-Ion Batteries

In Chapter 3, $\text{Na}_3\text{VFe}(\text{PO}_4)_3$ demonstrated that partial substitution of V with Fe effectively reduces vanadium content, making the material more cost-effective. Notably, it delivered a capacity comparable to $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ while maintaining long-term cycling stability. However, the issue of low electronic conductivity remains unresolved. Therefore, this chapter focuses on completely replacing V with abundant, redox-active elements, along with heteroatom engineering to enhance electrochemical performance. This chapter highlights the dual functionality of $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ (NFMP)-based materials as both cathode and anode for SIBs through heteroatom-doped carbon engineering. As a cathode, N-doped carbon-coated NFMP (NFMP@NC) exhibits improved Na^+ transport, conductivity, and electrochemical performance owing to its mesoporous structure and enhanced surface characteristics. As an anode, N, S co-doped carbon-wrapped NFMP (NFMP@SNC) with a 3D morphology facilitates efficient electron/ion transport and structural stability, leading to high capacity and stable cycling at low potential. Overall, these results demonstrate the versatility of NFMP as a multifunctional electrode material for high-performance SIBs.

Part A

Heteroatom interface engineering for enhanced Na^+ diffusion in $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ cathode



This chapter presents $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ (NFMP) and N-doped carbon-coated NFMP (NFMP@NC) synthesized via a hydrothermal process followed by annealing. The phase purity, chemical composition, and crystallinity were investigated systematically. The higher surface area and mesoporous architecture of NFMP@NC facilitate rapid Na^+ transport. The coexistence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple and Mn^{2+} , along with N

functionalities in the carbon layer, collectively enhances ion transport. As a cathode, NFMP@NC, delivered a reversible capacity of 77.1 mAh/g at 0.1C with 91.99% and 82.62% retention at 1C and 2C after 100 and 150 cycles, respectively, outperforming NFMP and its previously reported derivatives. Cyclic voltammetry and impedance studies indicated that the introduction of N into the carbon layer promotes a predominantly diffusion-controlled mechanism, characterized by lower charge-transfer resistance and higher Na^+ diffusion coefficients. This study provides the first systematic analysis of NFMP and its N-doped derivative as cathodes, highlighting the effectiveness of heteroatom-engineered carbon coatings in enhancing the electrochemical properties of phosphate-based frameworks for next-generation sustainable SIBs.

4.1 Introduction

As discussed in Chapter 3, in recent years, various categories of phosphate-based compounds have been actively researched, including orthophosphates, pyrophosphates, NASICONs, and fluorophosphates, among others. Many of these compounds exhibit excellent electrochemical stability, and greater operating potential in 3.0-3.5 V vs. Na/Na⁺. Polyanionic-type phosphate alluaudites are one of these materials with an open and stable framework structure positioning them as good prospects as cathode materials in SIBs. They have low-energy pathways of Na⁺ migration and a covalent framework structure, which adds to their thermal stability. The general formula for phosphate alluaudites is A(2)A(1)M(1)M(2)₂(PO₄)₃, where the large A(2) includes Na, K, and vacancies, and A(1) contains Na, Mn, and Ca. Mn²⁺ and Fe²⁺ can occupy M(1), and large M(2) can be occupied by Fe³⁺, Mn²⁺, Mg²⁺, and Li¹⁺, among others.[1] The A⁺ ions facilitate one-dimensional transfer pathways that promote ion transport, while the covalent phosphate framework imparts stability and safety advantages. Consequently, the exploration of phosphate alluaudites has gained importance from both a fundamental and practical perspective.

Several alluaudite phosphate compounds have been investigated with different transition metals, including V, Ti, Co, Fe, and Mn, etc. The synthesis, structural, and crystal chemistry study has been carried out for Na₂VFe₂(PO₄)₃/C,[2] (Na_{12x}Li_x)CdIn₂(PO₄)₃,[1] Na_{2-x}Fe₃(PO₄)₃,[3–6] Na₂Ni₂Fe(PO₄)₃,[7] Na₂Mn₂Fe(PO₄)₃,[7] and Na₂Ni_xMn_{2-x}Fe(PO₄)₃,[8] etc. Among them, a few have been tested as cathode material for both LIBs and SIBs. For instance, Na₂VFe₂(PO₄)₃/C delivered a specific capacity of 65.8 mAh/g at 5 mA/g in the SIB system with multiple redox contributions (Fe²⁺/Fe³⁺, V²⁺/V³⁺, and V³⁺/V⁴⁺).[2] The abundant and eco-friendly Fe-based phosphate, Na_{1.47}Fe₃(PO₄)₃, achieved an irreversible capacity of 98.22 mAh/g at 0.1C but exhibited sluggish kinetics with a sodium-ion diffusion coefficient of 5.56×10^{-14} cm²/s, necessitating further

improvement in its kinetics.[4] Similarly, $\text{Na}_2\text{Ni}_2\text{Fe}(\text{PO}_4)_3$ delivered 48.7 mAh/g at 0.1C, which restricts its application in practical SIBs.[7] In this context, the abundant and multi-redox active Fe and Mn-based phosphate alluaudites are of particular interest. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$ couples contribute to a wide operational potential window and promising specific capacities.[9] Moreover, synergistic substitution of Fe and Mn can enhance structural stability by balancing ionic radii and tuning redox activity.[10]

In a recent study, the cost-effective $\text{Na}_2\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ has been investigated as a cathode material for LIBs. This material delivered 70 mAh/g at C/15 with good capacity retention at C/5 after 50 cycles.[11] However, systematic investigation of $\text{Na}_2\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ in SIB systems is uncommon, leaving a significant knowledge gap regarding its structural evolution, ion transport behavior, and long-term stability with sodium. Considering the more demanding diffusional and structural requirements of Na^+ insertion/extraction compared to Li^+ , suitable modifications and performance evaluations of $\text{Na}_2\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ cathodes are both timely and necessary.[12,13] Therefore, the low electronic conductivity appears to be the primary disadvantage of alluaudite material, despite its appealing structural properties for alkaline metal intercalation/deintercalation. Improvements in conductivity and size reduction to the nanoscale are indeed required to enhance the electrochemical performance.[14]

A widely adopted strategy to overcome these drawbacks is surface engineering through carbon coating. The carbon layer serves as a protective barrier to mitigate electrolyte corrosion through electron-conducting networks.[15] Furthermore, the studies have reported on the introduction of heteroatoms in the carbon layer, which not only improves conductivity but also serves as favorable adsorption/desorption sites for Na^+ ions.[16–18] S and N co-doped carbon-coated $\text{Na}_2\text{VTi}(\text{PO}_4)_3$ has been studied as an anode material for SIBs.[19,20] It showed good rate capability with superior sodium storage. It reported that graphitic N enhances electrical conductivity, while pyrrolic and pyridinic N functionalities provide defect

sites that increase active surface sites and promote rapid charge transfer.[21–24] A number of recent studies have demonstrated that N-doped carbon modification is an effective strategy to enhance the electrochemical performance of polyanionic phosphate electrodes. For example, N-doped carbon coated $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes have shown significantly improved rate capability and cycling stability due to the synergistic effects of enhanced electronic conductivity and abundant defect sites in the N-doped carbon shell.[25–29] Similarly, N-doped carbon-coated $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ [30] and related $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$ -type fluorophosphates[31] have been reported to deliver higher capacities and better long-term stability, highlighting the role of N heteroatoms in modulating band structure and interfacial Na^+ transport. In addition, N-modified carbon-coated $\text{NaTi}_2(\text{PO}_4)_3$ [32] and other phosphate electrodes further confirm that introducing N functionalities into the carbon layer can simultaneously improve conductivity and provide favorable adsorption/desorption sites for alkali ions. Hence, N-doped carbon modification combines the benefits of a conductive network and heteroatom functionalities, simultaneously enhancing electronic conductivity, sodium-ion transport, and interfacial kinetics. However, despite these advances in NASICON and related phosphate systems,[33] N-doped carbon engineering has rarely been explored for Fe-Mn alluaudite phosphates such as $\text{Na}_2\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ in SIBs,[21] and the impact of N-doped carbon on their structure-property relationships (Na^+ diffusion, charge-transfer resistance, and pseudocapacitive behavior) remains largely unclear.[34] This gap motivates the present work, in which the material is designed to leverage both the robust alluaudite framework and the advantages of N-doped carbon to achieve improved electronic conductivity, accelerated Na^+ transport, and optimized interfacial kinetics.[35,36]

In this work, pristine $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ (NFMP) and N-doped C-coated NFMP (NFMP@NC) were synthesized via a hydrothermal process followed by annealing in an inert atmosphere. A comprehensive analysis,

including structural, morphological, and chemical characterization, was conducted to confirm the successful synthesis of the materials. Further, these materials are tested as cathode materials for SIBs and their electrochemical properties were evaluated systematically. NFMP@NC has better electrochemical performance, good rate capability and cycling stability with a higher sodium-ion diffusion coefficient than pristine NFMP. Notably, the study reveals how N-doped carbon coating is utilized to modulate the structure-property relationship. The results obtained in this regard contribute to the overall improvement in phosphate-based cathodes for SIBs and highlight NFMP@NC as a promising electrode for the next-generation safe, low-cost, and long-lasting batteries.

4.2 Experimental Section

4.2.1 Materials synthesis

The experimental procedures, including the selection of raw chemical precursors, synthesis methodology, slurry preparation, and electrode fabrication for the $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ cathode material, were briefly described in Chapter 2. $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ and $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ @NC cathode materials were synthesized using the hydrothermal method followed by heat treatment, and their physicochemical properties were systematically investigated using several advanced characterization techniques.

4.2.2 Coin cell fabrication

For electrochemical evaluation, sodium CR2032 half-cell configurations were assembled inside an N_2 -filled glove box. The cells consisted of 16 mm diameter sodium metal discs serving as both the counter and reference electrodes, 1 M NaClO_4 dissolved in a 1:1 (v/v) mixture of EC/DMC as the electrolyte, and a 19 mm diameter glass fiber separator. The electrochemical performance of the fabricated cells was evaluated using CV, EIS, and GCD measurements.

4.3 Results and Discussion

4.3.1 Physicochemical Analyses

4.3.1.1 Structural analysis: XRD

The NFMP and NFMP@NC materials were synthesized via a hydrothermal process followed by annealing in N₂ atmosphere. Their structural, morphological, and chemical properties were investigated through various characterization techniques. **Figure 4.1 (a)** shows the XRD patterns of both materials. The XRD matches well with the reference CIF No. 9003657, confirming a monoclinic crystal structure. Furthermore, the diffraction patterns were refined using the Rietveld method. Changes in the cell parameters of NFMP@NC are observed, which can be attributed to both physical and chemical effects resulting from the carbon layer and subsequent annealing treatment.[24] A slight change in lattice parameters is observed for NFMP@NC. The phosphate framework in the material undergoes a slight mechanical strain due to the carbon coating, resulting in mild expansion along specific crystallographic directions. This is observed through the slightly larger a and c parameters of NFMP@NC compared to those of NFMP. These nearly 1% variations arise from surface-related effects during the carbonization process. The elevated temperature and formation of the N-doped carbon layer relax residual microstrain in the pristine particles and introduce mild surface-induced stress, leading to anisotropic lattice adjustments.[37] In contrast, a minor change in monoclinic angle β and b parameter shows anisotropic responses of the lattice to these stresses. The almost unchanged monoclinic angle β confirms that the phosphate framework remains intact and that the observed shifts originate from interfacial strain rather than any bulk structural modification.[38] Such lattice modifications may affect the distribution of sodium ions at the surface and interface. Overall, these effects result not only in a robust structure but also in improved electron and ion transport

pathways, which are reported for carbon-coated alluaudite cathode materials.[37]

Table 4.1 Calculated cell parameters of NFMP and NFMP@NC.

	a (Å)	b (Å)	c (Å)	$\beta(^{\circ})$
NFMP	11.930	12.697	6.417	114.318
NFMP@NC	12.009	12.612	6.452	114.273

4.3.1.2 Structural analysis: HRTEM

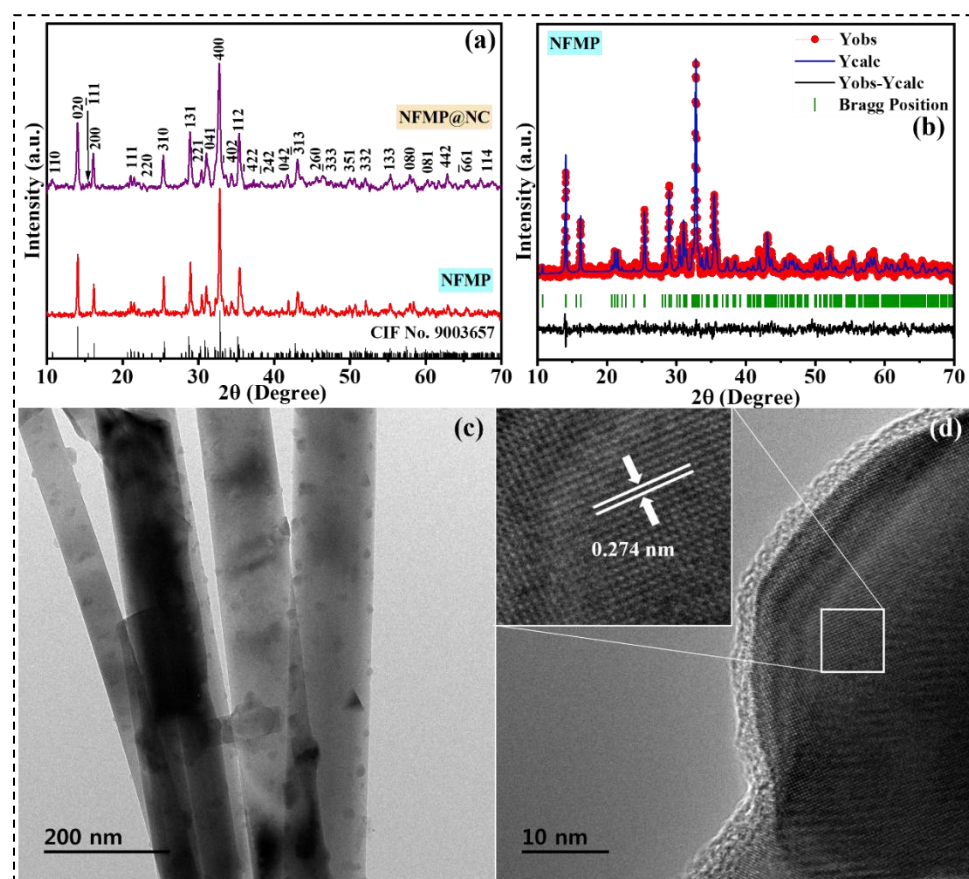


Figure 4.1 (a) Combined XRD patterns of NFMP and NFMP@NC, (b) Rietveld refinement of NFMP, (c) TEM image, (d) HRTEM analysis of NFMP@NC (Inset: Zoomed in HRTEM analysis)

Furthermore, the crystallinity of the materials was investigated using HRTEM analysis. **Figure 4.2 (b)** shows the NFMP nanorods with smooth and clean surfaces. In contrast, **Figure 4.1 (c)** shows slightly

rougher surfaces, indicating a conformal carbon coating on the NFMP particle with nitrogen particles embedded within it. The HRTEM analysis reveals interplanar spacings of 0.271 nm and 0.274 nm, corresponding to the (240) planes of NFMP (**Figure 4.2 (c)**) and NFMP@NC (**Figure 4.1 (d)**), respectively. A carbon layer of approximately 3 nm is visible on the surface of the NFMP in the NFMP@NC material. This carbon layer serves as both a conductive network and a protective layer, thereby maintaining the structural stability of NFMP during repeated deintercalation and intercalation of Na^+ . Additionally, the nitrogen doping in the carbon layer introduces heteroatom functionalities along with defect sites, which are expected to increase electronic conductivity.[21] Collectively, these structural modifications enhance the sodium storage sites, thereby improving the electrochemical kinetics of NFMP as a cathode for SIBs.

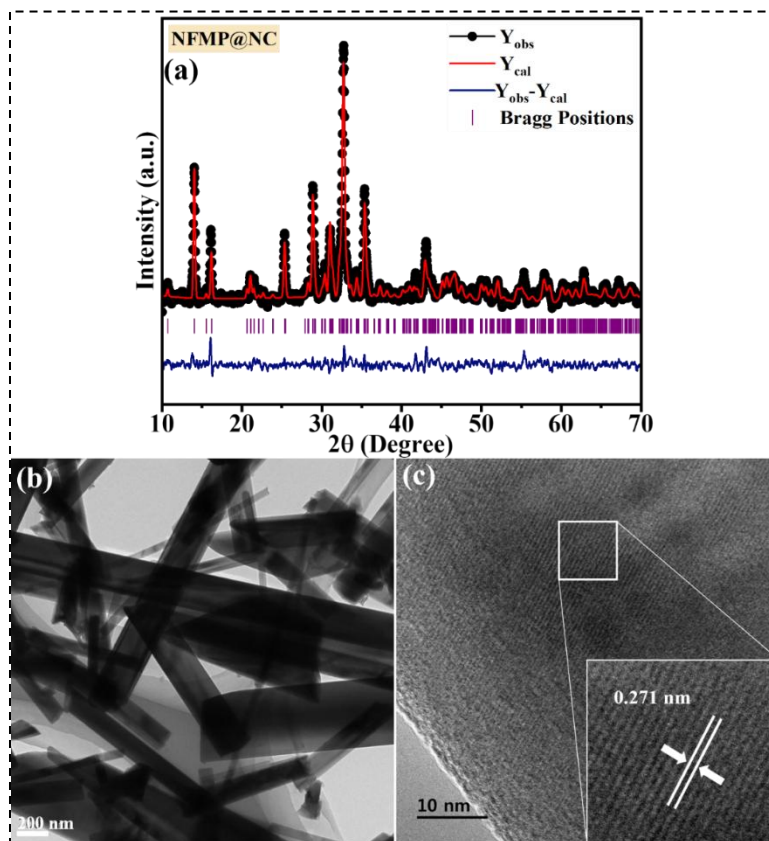


Figure 4.2 (a) Rietveld refinement of NFMP@NC, (b) TEM image, and (c) HRTEM image of NFMP.

4.3.1.3 Morphological analysis

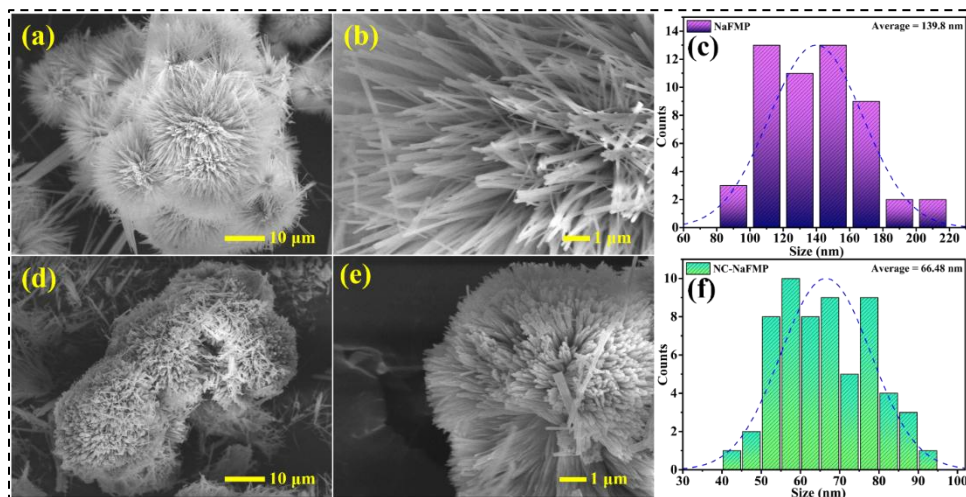


Figure 4.3 (a, b) FESEM images, (c) particle size distribution of NFMP, (d, e) FESEM images, (f) particle size distribution of NFMP@NC

The morphological structures of the samples were investigated using FESEM, as illustrated in **Figure 4.3**. **Figure 4.3 (a & b)** exhibits a 3D urchin-like morphology of NFMP composed of thin and well-defined nanofibers. The nanofibers have an average thickness of 139.8 nm, as determined and illustrated in **Figure 4.3 (c)**. In contrast, NFMP@NC retains urchin-like morphology consisting of rougher and densely distributed nanofibers as shown in **Figure 4.3 (d & e)**, but with reduced average thickness of 66.5 nm (**Figure 4.3 (f)**). EDS elemental mapping of both materials further confirms the desired composition of NFMP and NFMP@NC as represented in **Figure 4.4**. Such a morphological configuration is anticipated to shorten Na^+ ion diffusion pathways by reducing the nanofiber width and enhancing electronic transport mobility by establishing a distinctive three-dimensional conducting carbon network. This comprehensive characterization highlights the structural integrity and elemental homogeneity, which are crucial for improving the electrochemical performance of the NFMP and NFMP@NC.

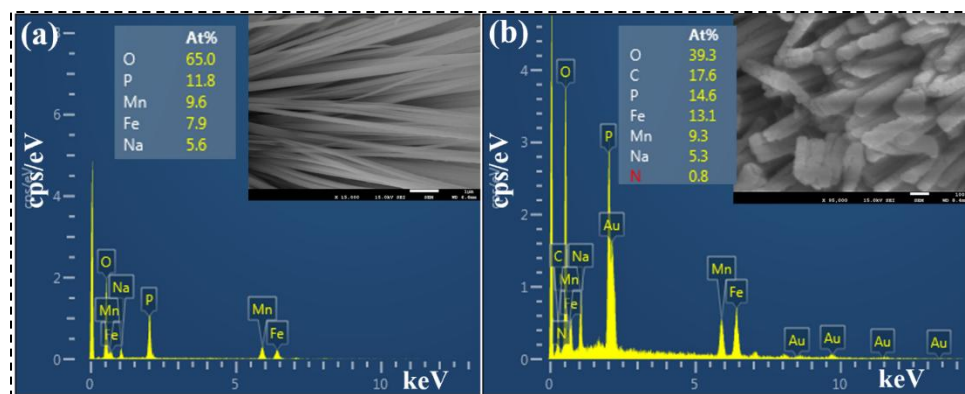


Figure 4.4 EDS analysis of (a) NFMP, and (b) NFMP@NC.

4.3.1.4 Chemical Analysis

The oxidation states of transition elements are crucial for determining the sodium storage performance of the cathode material. Insights into the chemical properties of both materials were gained by analyzing them using XPS. **Figure 4.5** shows the survey scan of both materials, confirming the presence of all key elements. Furthermore, the high-resolution XPS spectrum of the C 1s of NFMP reveals the presence of adventitious carbon at 284.6 eV, attributed to C-C with 47.65% and C-O at 286.2 eV (27.92%), and C=O at 288.8 eV (24.43%), as shown in **Figure 4.5 (a)**, which confirms the surface carbon species. The Fe 2p spectrum shows the presence of Fe in the mixed oxidation state of Fe^{2+} and Fe^{3+} , as shown in **Figure 4.5 (b)**. The Fe 2p_{1/2} and 2p_{3/2} peaks are located at 725.7 eV and 711.8 eV, respectively, with a binding energy separation of 13.9 eV. The ratio of total $\text{Fe}^{2+}/\text{Fe}^{3+}$ is 49.55%/50.45%. The two characteristic satellite peaks are located at 717 eV and 731 eV, confirming the coexistence of Fe^{2+} and Fe^{3+} in NFMP.[11] Similarly, the Mn 2p deconvoluted into Mn 2p_{1/2} and 2p_{3/2} with 35.02% and 64.98% at 653.5 eV and 641.9 eV, respectively, with a binding energy splitting of 11.6 eV. Here, Mn is predominantly present in the Mn^{2+} state, while the satellite peaks at 646 eV and 657 eV suggest the coexistence of Mn^{2+} and Mn^{3+} , as presented in Figure 3(c). These mixed oxidation states of Fe and Mn are beneficial for

electrochemical performance, as they exhibit redox activity during charge storage in NFMP.

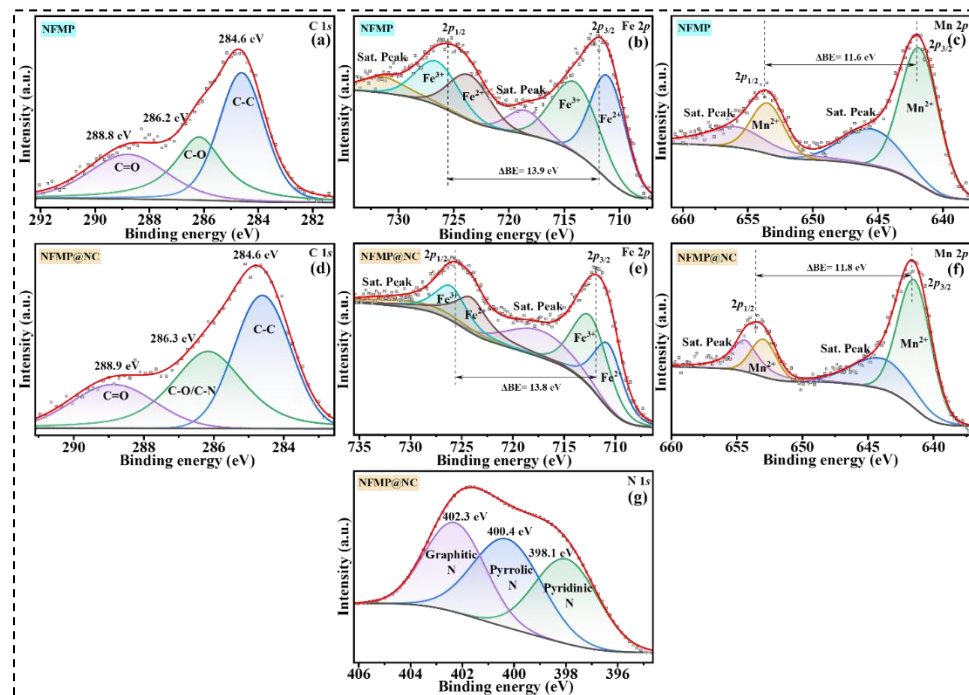


Figure 4.5 Deconvoluted XPS spectra of (a) C 1s, (b) Fe 2p, (c) Mn 2p of NFMP, Deconvoluted XPS spectra of (d) C 1s, (e) Fe 2p, (f) Mn 2p, and (g) N 1s of NFMP@NC.

Further XPS analysis reveals that the introduction of the N-doped carbon coating induces only minor changes in the surface oxidation-state distribution of Fe and Mn. For NFMP@NC, the C 1s spectra in **Figure 4.5 (d)** show an increase in the C-O/C-N component, which is 36.15% and a decrease in the C=O content to 17.80% after coating, reflecting the formation of N-derived surface functionalities and a more polar carbon environment. Further, the Fe²⁺ and Fe³⁺ contributions shift slightly to 48.31% and 51.69% as shown in **Figure 4.5 (e)**. A similar trend is observed for Mn, where the Mn 2p_{1/2} and Mn 2p_{3/2} components change to 33.37% and 66.63% in NFMP@NC as depicted in **Figure 4.5 (f)**.^[39] These small increases in the higher oxidation-state fractions are attributed to the mild oxidative environment during carbonization and the electron-withdrawing nature of N-containing functional groups on the coated carbon layer.

Notably, the N 1s are deconvoluted into three forms, which are pyrrolic N, pyridinic N, and graphitic N at 398.1, 400.4, and 402.3 eV, respectively. These include the graphitic N, which enhances the electronic conductivity of the substance, the pyrrolic and pyridinic N, which generate defect sites in the C layer and allow the transport of sodium ions, and subsequently lead to improved electrochemical performance of NFMP@NC.[40] Overall, the slight shift in Fe/Mn oxidation states, together with the modified carbon bonding structure, indicates that N-doping primarily alters the surface chemical environment without significantly disrupting the intrinsic redox activity of the NFMP framework. The synergistic effect between the C layer and N introduction is expected to enhance the conductivity and electrochemical reaction rates of NFMP@NC in SIBs.

4.3.1.5 N₂ adsorption-desorption isotherm

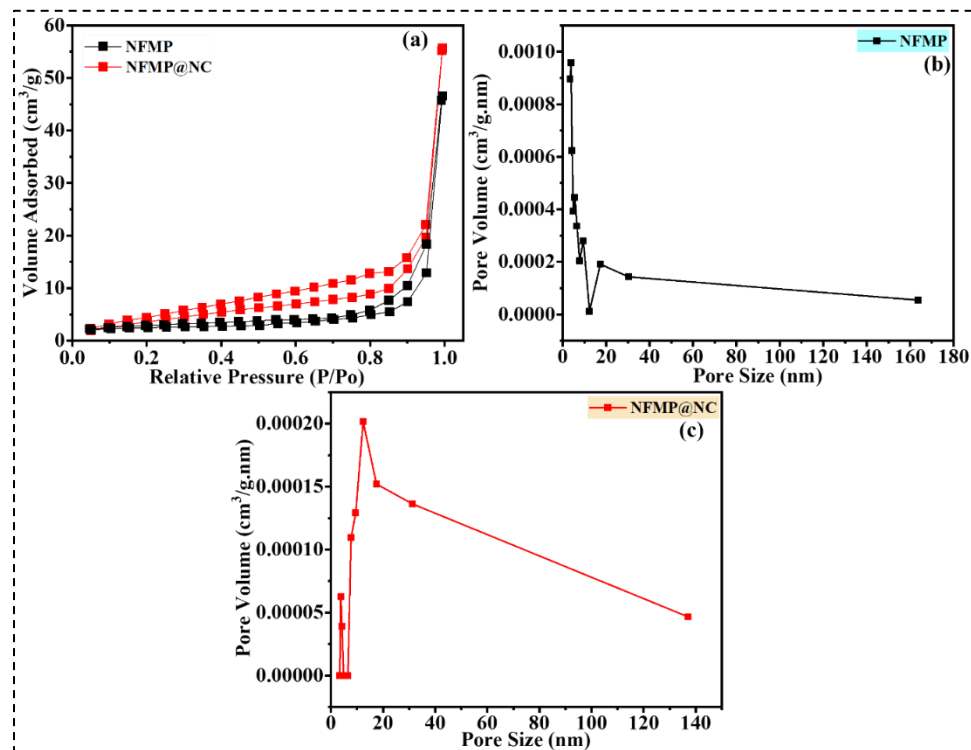


Figure 4.6 (a) BET analysis of NFMP and NFMP@NC, BJH pore size distribution of (b) NFMP, and (c) NFMP@NC.

Additionally, both samples were identified by specific surface area and the pore structure using nitrogen adsorption-desorption isotherm, which

is presented in **Figures 4.6 (a)**. The Brunauer-Emmett-Teller (BET) analysis revealed that NFMP@NC exhibits a specific surface area of 19.292 m²/g, which is higher than that of pristine NFMP (9.453 m²/g). The Barrett-Joyner-Halenda (BJH) cumulative pore size distribution further confirmed the presence of mesopores with pore diameters of approximately 7.9 nm and 9.8 nm for NFMP and NFMP@NC, respectively as depicted in **Figures 4.6 (b) and (c)**. Such mesoporous structures play a crucial role in sodium-ion storage. These mesoporous frameworks are important in the storage of sodium-ions. These internal mesopores are what promote the diffusion of electrolytes to the active substances, thus improving the electrochemical properties of the materials. NFMP@NC has a greater surface area on which active sites to transport sodium-ion are more accessible, and the interconnected mesopores facilitate the penetration of the electrolytes and shorten ion-diffusion pathways. This synergistic effect enables fast transport of Na⁺ and enhances the electrode-electrolyte interface kinetics, which also leads to an increase in electrochemical performance in SIBs.

4.3.2 Electrochemical Characterizations

4.3.2.1 GCD Analysis

The electrochemical properties of NFMP and NFMP@NC were investigated as cathode materials for SIBs in the CR2032 half-cell configuration using sodium metal as the counter electrode. The cathode materials are tested in 1 M NaClO₄ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and propylene carbonate (PC) within a voltage window of 1.5-4.3 V. The electrochemical properties were investigated through GCD, rate capability, and cyclic stability analyses. The GCD profile of NFMP recorded at various C-rates, ranging from 0.1C to 2C, is depicted in **Figure 4.7 (a)** and shows a well-defined charge-discharge plateau. The NFMP electrode delivers a specific capacity of 58.7 mAh/g at 0.1C, primarily arising due to the contribution of redox activity of Fe²⁺/Fe³⁺ and Mn²⁺/Mn³⁺. On the other hand, the specific capacity of NFMP@NC is 77.1 mAh/g at 0.1C (**Figure 4.7 (b)**). For NFMP, the polarization between charge and

discharge curve increases significantly with higher C-rates, suggesting sluggish Na^+ diffusion kinetics as well as limited intrinsic electronic conductivity.[12] However, comparison with NFMP@NC helps identify the dominant limitation. The N-doped carbon coating substantially suppresses polarization and enhances the rate capability, indicating that improving electronic conductivity has the most significant impact on reducing overpotential during fast cycling. The conductive carbon network provides efficient electron pathways, ensuring more uniform electrochemical reactions across the electrode and thereby alleviating the major electronic bottleneck in pristine NFMP.[23] Once electronic pathways are enhanced, the remaining polarization at high C-rates can be mainly attributed to intrinsic Na^+ diffusion within the NFMP lattice. Therefore, although both processes influence the overall polarization, the marked reduction achieved through carbon coating clearly shows that poor electronic conductivity is the primary rate-limiting factor in the pristine material. Although the $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox couple contributes additional electrochemical activity and enhances the sodium-storage capacity, the formation of Mn^{3+} may induce Jahn-Teller distortion, leading to local lattice strain and potential structural instability. In addition, prolonged exposure of Mn^{3+} -containing materials to the electrolyte may promote transition-metal dissolution. Despite these potential limitations, the excellent cycling stability and retention of the alluaudite framework observed in the present study suggest that the structure can effectively accommodate the redox-induced lattice changes. Furthermore, the N-doped carbon coating may contribute to maintaining interfacial stability by reducing direct contact between the active material and electrolyte.

Furthermore, the rate capability performance illustrated in **Figure 4.7 (c)** highlights the advantage of the N-doped carbon coating in enhancing performance. Both materials follow the typical trend of decreasing specific capacity with increasing C-rates. Specifically, NFMP delivers 58.7, 54.1, 36.6, 26.0, and 17.4 mAh/g at 0.1C, 0.2C, 0.5C, 1C, and 2C, respectively.

On the other hand, the specific capacity of NFMP@NC is 77.1, 75.8, 53.7, 33.7, and 23.2 mAh/g at 0.1C, 0.2C, 0.5C, 1C, and 2C, respectively.

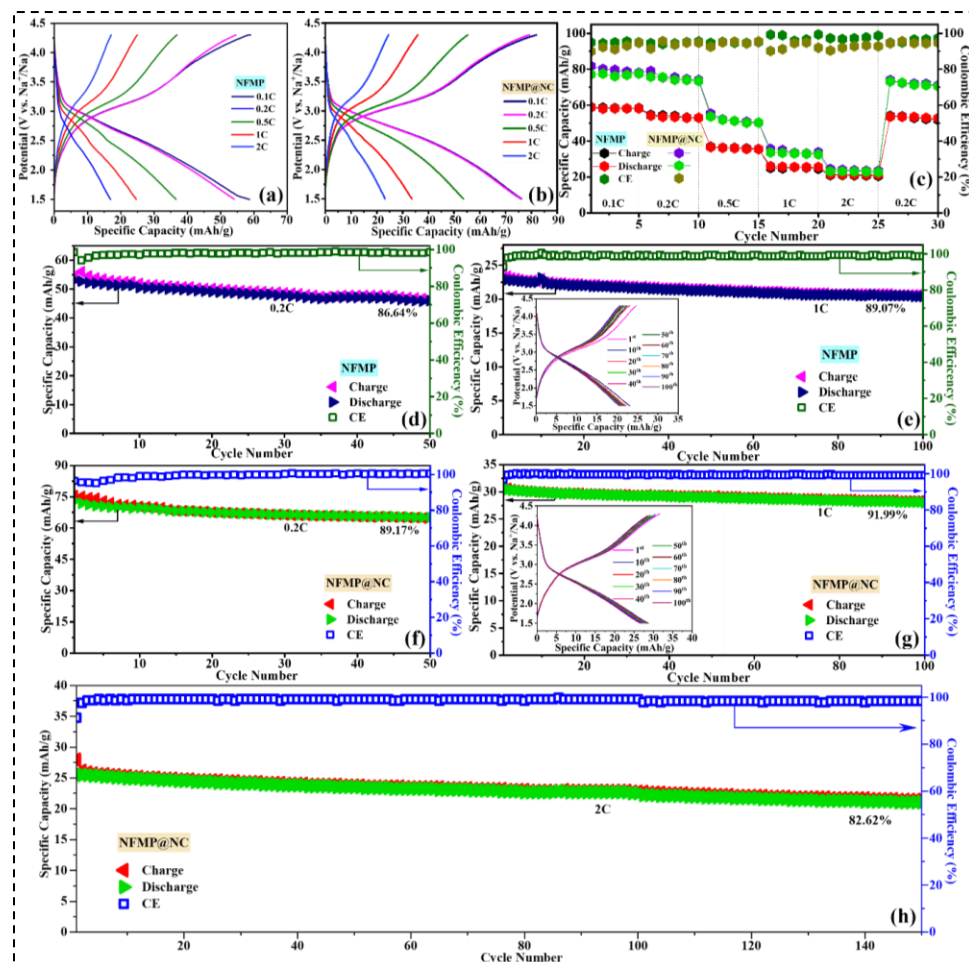


Figure 4.7 GCD profile of (a) NFMP, (b) NFMP@NC at different C-rates, (c) rate capability of NFMP and NFMP@NC, Cyclic stability of NFMP (d) at 0.2 C for 50 cycles, (e) at 1C for 100 cycles (Inset: corresponding GCD profile), Cyclic stability of NFMP@NC (f) at 0.2C for 50 cycles, and (g) at 1C for 100 cycles (Inset: corresponding GCD profile), (h) at 2C for 150 cycles.

Upon reverting the current to 0.2C, both materials demonstrate excellent capacity recovery, implying good structural stability and reversibility. The more pronounced capacity retention in NFMP@NC at elevated C-rates underscores its faster charge transport kinetics, originating from (i) an

interconnected conductive carbon framework reducing charge-transfer resistance, and (ii) heteroatom (N)-induced defect sites that facilitate Na⁺ adsorption and diffusion.[15] These synergistic effects collectively enhance the rate capability and electrochemical kinetics of NFMP@NC compared to pristine NFMP.

NFMP suffers from a rapid decline in specific capacity with increasing current density, reflecting the intrinsic kinetic limitations of pristine NFMP. Conversely, NFMP@NC retains a considerably larger fraction of its capacity compared to NFMP under high current conditions and recovers its initial capacity when the current is reduced. At 2C, the charge-discharge profiles exhibit less-defined voltage plateaus, which are characteristic of polyanionic cathode materials under rapid Na⁺ insertion/extraction. The increased polarization and diffusion limitations at elevated rates result in a broadened or sloping plateau, indicating a shift from distinct two-phase behavior to more solid-solution-like kinetics. This rate-induced polarization behavior results in the smoother curves observed at 2C. To further evaluate the cycling stability, the GCD was carried out for 50 and 100 cycles at 0.2C and 1C, NFMP demonstrated 86.64% and 89.07% respectively (**Figure 4.7 (d & e)**). Meanwhile, NFMP@NC retained 89.17% and 91.99% after 50 and 100 cycles at 0.2C and, 1C respectively (**Figure 4.7 (f & g)**). To further evaluate the long-term cycling stability under high-rate conditions, additional measurements were performed at 2C for 150 cycles. As shown in **figure 4.7 (h)**, the NFMP@NC electrode exhibits stable capacity retention of 82.62% after 150 cycles, maintaining a consistent discharge capacity with minimal degradation. The CE remains close to 100%, indicating highly reversible Na⁺ insertion/extraction and a stable electrode-electrolyte interface. These results, together with the earlier cycling data at 0.2C and 1C, confirm that the N-doped carbon coating significantly enhances the structural stability and rate capability of the NFMP electrode during prolonged high-rate operation. This enhancement in rate capability and stability originates from the conductive carbon shell,

which shortens the charge transport pathways, and N heteroatoms, which introduce additional active sites and improve charge transfer dynamics. Consequently, the NFMP@NC exhibits minimal voltage hysteresis and higher reversible capacities across all tested C-rates, highlighting the beneficial impact of N-doped carbon on the electrochemical performance.

Table 4.2 Comparison of the electrochemical performance of NFMP@NC with previously reported derivatives.

Composition	Voltage Window	Average potential	Specific Capacity, C-rate	Retention, Cycle Number	Ref.
$\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$	1.5-4.5V vs Li/Li ⁺	3V	107 mAh/g, 5 mA/g	99.1%, 115@20 mA/g	[13]
$\text{Na}_2\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$	1.5-4.5V vs Li/Li ⁺	2.8V	70 mAh/g, C/15	99%, 50@C/5	[41]
$\text{Na}_2\text{Ni}_2\text{Fe}(\text{PO}_4)_3$	1.4-4.5V vs Na/Na ⁺	2.3V	63.2 mAh/g, C/10	85%, 30@C/10	[8]
NFMP	1.5-4.3V vs Na/Na ⁺	2.95V	58.7 mAh/g, 0.1C	89.07, 100@1C	This work
NFMP@NC	1.5-4.3V vs Na/Na ⁺	2.95V	77.1 mAh/g, 0.1C	91.99%, 100@1C	This work

Table 4.2 compares the electrochemical performance of the present work with previously reported alluaudite phosphate derivatives. Karegeya *et al.* reported $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ as a cathode for LIBs, delivering a specific capacity of 107 mAh/g at 5 mA/g within a voltage window of 1.5-4.5 V.[13] Similarly, $\text{Na}_2\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$, also evaluated as a LIB cathode, exhibited a specific capacity of 70 mAh/g at C/15 with 99% capacity retention after 50 cycles at C/5. These performances are attributed to the redox activity of the Fe²⁺/Fe³⁺ and Mn²⁺/Mn³⁺ couples. The relatively high

capacities achieved in the LIB system can be explained by the facile de/intercalation of Li^+ ions and their faster diffusion kinetics, owing to the smaller ionic radius of Li^+ (0.76 Å). Consequently, the average operational voltage of these LIB systems falls in the range of 2.8–3.0 V.[41] In comparison, $\text{Na}_2\text{Ni}_2\text{Fe}(\text{PO}_4)_3$, investigated as a cathode for SIBs, delivered a specific capacity of 63.2 mAh/g at C/10 with 85% retention after 30 cycles at C/5, operating at an average voltage of 2.3 V.[8] The present study evaluates NFMP and NFMP@NC as cathodes for SIBs within the voltage range of 1.5–4.3 V. Pristine NFMP exhibited a capacity of 58.7 mAh/g at 0.1C with 89.07% retention after 100 cycles at 1C, whereas NFMP@NC achieved an enhanced capacity of 77.1 mAh/g at 0.1C with 91.99% retention after 100 cycles at 1C. The lower electrochemical performance observed in SIBs compared to LIBs is primarily due to the larger ionic radius of Na^+ (1.02 Å), which induces sluggish diffusion kinetics and limits full utilization of redox-active sites. Nevertheless, the nitrogen-doped carbon coating in NFMP@NC effectively alleviates these drawbacks by enhancing charge transfer, reducing interfacial resistance, and introducing additional defect sites for surface Na^+ storage, thereby improving the overall electrochemical performance and yielding an average operational voltage of ~2.95 V. Importantly, this work represents the first demonstration of NFMP-based compositions as cathodes for SIBs, thereby establishing NFMP@NC as promising candidates for next-generation sodium-ion energy storage systems.

4.3.2.2 CV Analysis

The electrochemical properties and corresponding charge storage mechanisms of NFMP and NFMP@NC are systematically evaluated and compared to study the effect of surface engineering on sodium storage. Cyclic voltammetry (CV) was performed within a potential range of 1.5–4.3V for both materials as cathodes in SIBs. **Figure 4.8 (a) and (b)** depict the CV profile of NFMP and NFMP@NC, respectively, at 1, 2, 3, and 5 mV/s with pronounced peaks associated with $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$

couples. Notably, NFMP@NC exhibits a higher current response across all scan rates compared to pristine material, which is attributed to improved electrical conductivity and faster charge transfer resulting from the N-doped carbon coating.[42]

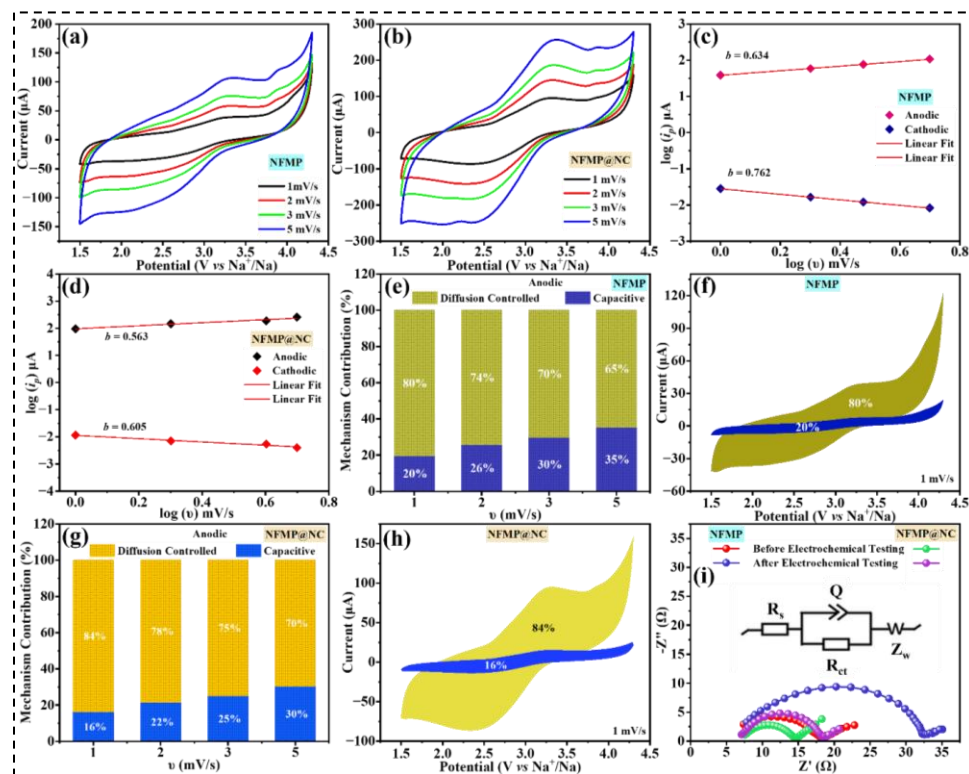


Figure 4.8 CV plot of (a) NFMP, (b) NFMP@NC at various scan rates from 1-5 mV/s, plot of $\log(v)$ vs $\log(ip)$ for (c) NFMP, (d) NFMP@NC, (e) mechanism contribution of NFMP at all scan rates, (f) CV plot of mechanism contribution at 1 mV/s in NFMP, (g) mechanism contribution of NFMP@NC at all scan rates, (h) CV plot of mechanism contribution at 1 mV/s in NFMP@NC, (i) Nyquist plot of NFMP and NFMP@NC before and after electrochemical testing (Inset: Equivalent electrochemical circuit)

To quantitatively assess the charge storage mechanism, the power law relationship was employed as shown in equation (2.6).[26] For NFMP, the b value (0.634 for anodic, 0.762 for cathodic) indicates a mixed charge storage mechanism with a considerable pseudocapacitive contribution. On

the other hand, lower b -values (0.563 for anodic and 0.605 for cathodic) for NFMP@NC indicate that the surface modification favors a considerably diffusion-controlled mechanism (**Figure 4.8 (c,d)**). This can be attributed to the structural and interfacial modifications induced by the conformal N-doped carbon layer.[26] The coating masks the NFMP surface, decreasing the density of exposed defect sites and surface redox-active centers that typically contribute to pseudocapacitive Na^+ storage. Additionally, the carbonization process passivates residual surface functional groups, yielding a smoother interface and thereby suppressing rapid surface-controlled kinetics. Concurrently, the improved electronic conductivity imparted by N-doping facilitates deeper Na^+ insertion into the bulk lattice, enhancing the relative contribution of diffusion-dominated intercalation. As a result of these combined effects, the NFMP@NC electrode displays b -values that more clearly reflect diffusion-controlled behavior. Further, the mechanism contributions were analyzed using Dunn's method as per equation (2.8).[43] The values of k_1 and k_2 were determined from the slope and intercept of the plot of $i_p/v^{0.5}$ vs $v^{0.5}$, as shown in **Figures 4.9 (a) and (c)**. In the case of NFMP, the contribution from the diffusion-controlled mechanism decreases from 80% at 1 mV/s to 65% at 5 mV/s at higher scan rates, indicating facile Na^+ surface adsorption and desorption, as well as rapid redox activity, enabled by the open framework of alluaudite phosphate as depicted in **Figure 4.8 (e)**. In contrast, NFMP@NC exhibits a predominantly diffusion-controlled mechanism, reducing from 84% at 1 mV/s to 70% at 5 mV/s as shown in **Figure 4.8 (g)**. This highlights the benefit of carbon coating in electrochemical kinetics, which sustains bulk Na^+ transport and moderate surface storage, making the material highly suitable for fast-charging and discharging applications. The lower capacitive contribution of NFMP@NC compared to pristine NFMP, as shown in **Figure 4.8 (e, g)** and **Figure 4.9 (b, d)**, arises from the N-doped carbon coating covering the NFMP surface.

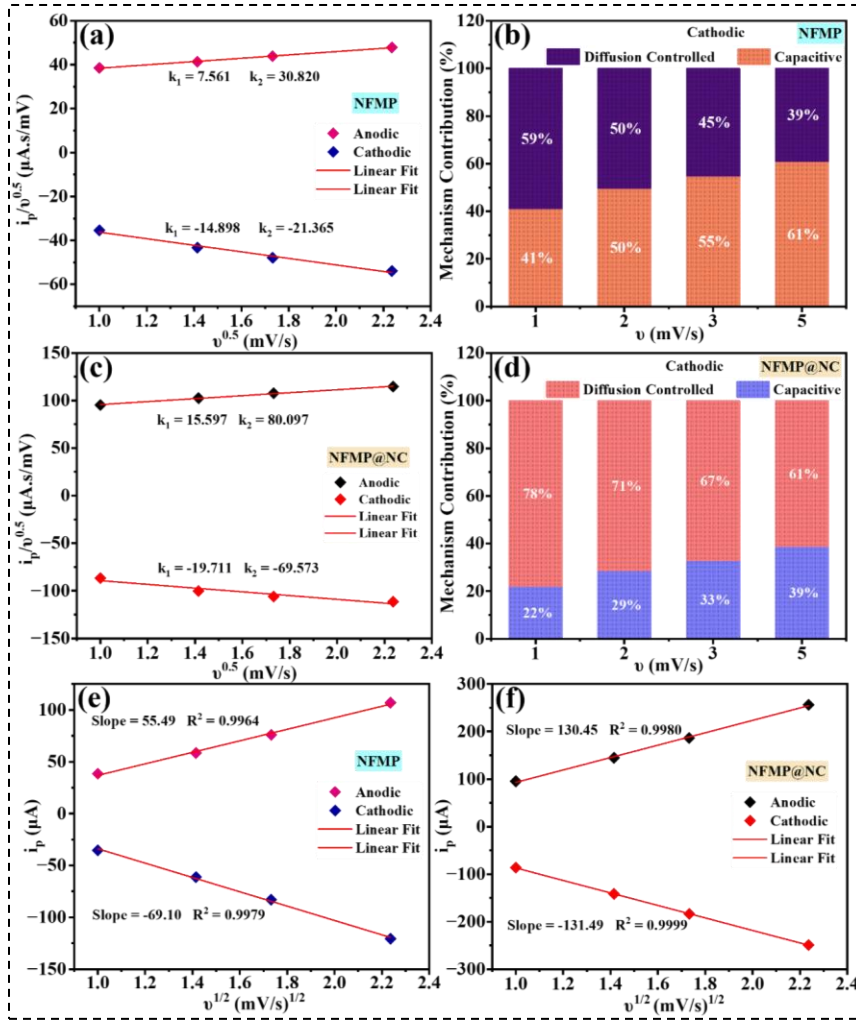


Figure 4.9 (a) Plot of $v^{0.5}$ vs $i_p/v^{0.5}$, (b) mechanism contribution for cathodic peak of NFMP, (c) Plot of $v^{0.5}$ vs $i_p/v^{0.5}$, (d) mechanism contribution for cathodic peak of NFMP@NC, Plot of $v^{0.5}$ vs i_p for (e) NFMP, and (f) NFMP@NC.

This surface coverage reduces the number of accessible defect sites and redox-active centers that normally enable fast pseudocapacitive Na^+ storage. At the same time, the carbon coating enhances electronic conductivity, promoting deeper Na^+ intercalation into the bulk.[25] As a result, the overall Na^+ storage shifts from being surface-dominated to more diffusion-controlled, explaining the observed reduction in the capacitive fraction for NFMP@NC. **Figure 4.8 (f & h)** represents the spatial distribution of the current distribution at 1mV/s for NFMP and NFMP@NC,

respectively. This indicates that bulk diffusion is dominant at low scan rates for both materials (80% for NFMP and 84% for NFMP@NC). This property is related to the sufficient duration available for deep Na⁺ insertion into the electrode material at a low scan rate. The carbon layer in NFMP@NC further improves ion accessibility and mitigates polarization losses.

Table 4.3 D_{Na^+} while charging and discharging process of NFMP and NFMP@NC

Composition	D_{Na^+} Charging (cm ² /s)	D_{Na^+} Discharging (cm ² /s)
NFMP	2.9332×10^{-10}	4.5486×10^{-10}
NFMP@NC	16.2108×10^{-10}	16.4703×10^{-10}

The diffusion coefficient (D_{Na^+}) was calculated from the CV data using the Randles–Ševčík equation (2.5).[44] Here, F is the Faraday constant (96485 C/mol), A is the working electrode surface area, D_{Na^+} is the diffusion coefficient, n is the number of electrons transferred during the redox process, C is the concentration, R is the gas constant (8.31 J/K.mol), and T is the temperature (K). For both materials, C is approximately 0.006 mol/cm³, A is 2.01 cm², and n is 1. **Figures 4.9 (e) and (f)** presents the linear relationship between i_p and $v^{0.5}$, from which the slope was obtained and subsequently used in the above equation. For NFMP, the anodic and cathodic slopes were 55.49 and -69.10, respectively, while for NFMP@NC, the corresponding slopes were significantly higher, 130.45 and -131.49. These higher slope values directly translate into higher sodium-ion diffusion coefficients for NFMP@NC compared to NFMP. According to the equation and these values, the D_{Na^+} for both samples while charging and discharging are summarized in **Table 4.3**. Notably, NFMP@NC exhibits enhanced diffusion kinetics, with nearly identical values for charging (16.2108×10^{-10} cm²/s) and discharging (16.4703×10^{-10} cm²/s). This close agreement highlights the excellent reversibility of Na⁺ transport in NFMP@NC, indicating that surface engineering via nitrogen-doped carbon

coating facilitates faster and more stable ion diffusion compared to pristine NFMP.[45]

4.3.2.3 EIS Analysis

Table 4.4 Fitted EIS parameters of NFMP and NFMP@NC.

Composition		R_s (Ω)	R_{ct} (Ω)
NFMP	Before	7.370	15.303
	After	7.806	29.211
NFMP@NC	Before	7.595	11.591
	After	7.108	15.446

To further probe the interfacial charge transfer properties of materials, EIS is performed. **Figure 4.8 (i)** depicts the Nyquist plot for both materials before and after electrochemical testing, and fitted with the equivalent electrochemical circuit shown in the inset. It displays one semicircle in the high-frequency region and the Warburg line in the low-frequency region for each Nyquist plot. The fitted parameters are tabulated in **Table 4.4**. NFMP@NC exhibits a smaller semicircle with a lower charge-transfer resistance (R_{ct}) of 11.591 Ω than NFMP, ensuring rapid electron conduction prior to electrochemical testing. After prolonged cycling, both NFMP and NFMP@NC exhibit an increase in R_{ct} , which is commonly observed in polyanionic phosphate electrodes. After electrochemical testing, the R_{ct} value increases slightly to 15.446 Ω for NFMP@NC compared to 29.211 Ω for NFMP. This increase can be attributed to interfacial modifications that develop during repeated Na^+ insertion/extraction. Continuous electrolyte decomposition results in the formation and gradual thickening of the solid-electrolyte interphase (SEI), along with surface by-products that partially block active sites and impede Na^+ transport across the electrode/electrolyte interface.[34,46] Moreover, repeated structural relaxation and minor surface reconstruction of the NFMP particles may further reduce the number of electrochemically accessible regions. These combined effects diminish interfacial charge-

transfer kinetics, thereby increasing R_{ct} after cycling. Notably, NFMP@NC exhibits a slight increase in R_{ct} , indicating improved interfacial stability compared to NFMP. The N-doped carbon shell not only ensures rapid electron conduction but also stabilizes the electrode-electrolyte interface, thereby reducing energy barriers for Na^+ transfer and enhancing the reversibility of redox reactions over prolonged cycling.[47]

4.3.3 Post electrochemical analysis

Overall, the enhanced electrochemical performance of NFMP@NC is closely associated with its structural modifications. XRD and Rietveld analyses confirmed lattice expansion caused by carbon coating-induced strain, while HRTEM revealed a uniform N-doped carbon layer ensuring particle connectivity. These structural features improve electronic conductivity and Na^+ diffusion, leading to superior capacity retention and rate capability compared to pristine NFMP. These modifications underpin the superior rate capability and cycling stability of the material, making it a promising phosphate-based cathode for advanced SIBs.

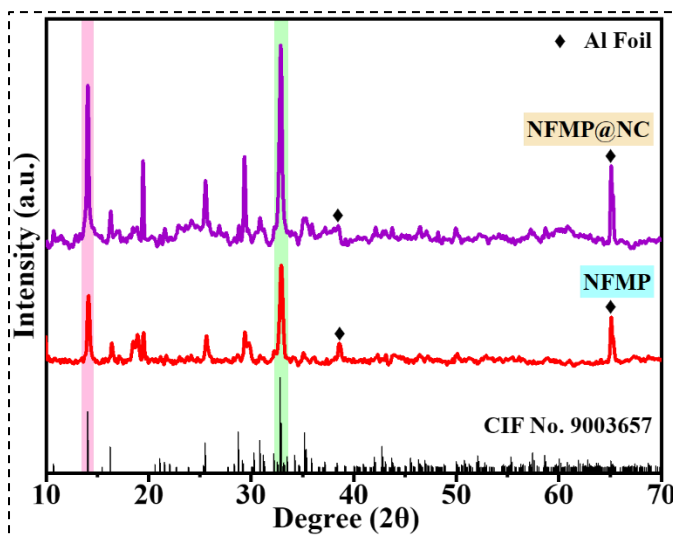


Figure 4.10 Ex-situ XRD patterns of NFMP and NFMP@NC.

Furthermore, ex-situ analysis was performed to examine the structural and morphological stability of the materials after electrochemical

testing. The cells were disassembled in a glove box, washed with the carbonate solvent to remove electrolyte residue, and dried for 2 hours at 100°C. Then used for further physicochemical testing. **Figure 4.10** presents ex-situ XRD patterns, confirming the phase stability of both samples even after electrochemical analysis. All diffraction peaks are matching with the standard data (CIF No. 9003657), along with the minor peaks of the Al foil. This indicates good structural reversibility and phase stability of the phosphate framework during repeated Na⁺ extraction/insertion. The peak around 19-20° may be attributed to the presence of crystalline α -phase PVDF binder in the electrode composite. The slight broadening of the diffraction peaks in the NFMP@NC material is attributed to the presence of an amorphous N-doped carbon coating.

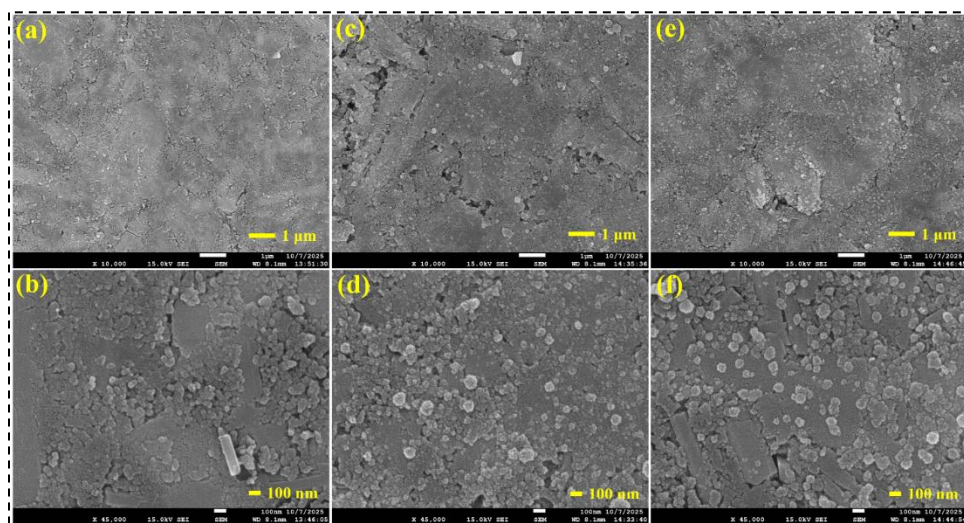


Figure 4.11 FESEM images of (a & b) pristine NFMP before electrochemical testing, (c & d) pristine NFMP, and (e & f) NFMP@NC post-electrochemical testing.

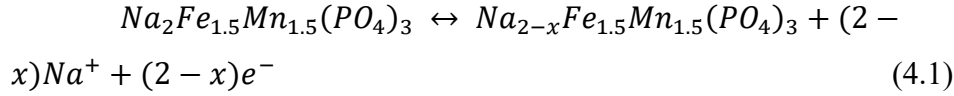
Nevertheless, the primary diffraction peaks remain at the same positions of 2θ positions, which proves that the phase transformation did not take place as a result of the carbon modification. **Figure 4.11** provides the information about the morphological changes of the electrodes before and after an electrochemical test. The bare NFMP electrode has smooth and

compact surface as indicated in **Figures 4.11 (a) and (b)**. It has a low apparent porosity and this may limit the entry of electrolytes and the diffusion pathway of Na^+ . Following the electrochemical analysis, NFMP electrode (**Figures 4.11 (c) and (d)**) surface turns rough with microfissures and fragmented areas, which shows mechanical stress and alteration of volume as a result of the repeated insertion and extraction of Na^+ ions. The SEI film is also associated with the formation of the granular layer, and is formed as a result of the electrolyte breakdown during the cycling process. Such structural degradation implies the instability of the pristine NFMP electrode and may lead to performance degradation throughout the long cycles. Conversely, the NFMP@NC electrode has a homogenous surface with few cracks, despite taking the electrochemical analysis as illustrated in **Figures 4.11 (e) and (f)**. The NFMP particles are still connected and encircled with a fine and conductive carbon layer. This is due to the fact that the introduction of N into the carbon layer gives a continuous conductive network which not only improves the transport of electrons but also gives the layer a protective layer to avoid the changes of the volume with excessive SEI formation.[40] Overall, the N-doped carbon layer enhances the electrode durability. Whereas the pristine NFMP does show significant surface degeneration after cycling, the NFMP@NC electrode does not, as the carbon coating serves to stabilize the surface, increase conductivity, retain the phosphate framework, and have the capability of deinserting and inserting Na^+ reversibly during prolonged cycling.

4.3.4 Sodium storage mechanism

The sodium storage in NFMP@NC, acting as a cathode in a half-cell configuration, is governed by the reversible insertion and extraction of Na^+ ions associated with the redox transitions of Fe and Mn within the phosphate framework. During charging, the Fe^{2+} and Mn^{2+} ions become oxidized to Fe^{3+} and Mn^{3+} respectively as Na^+ is deintercalated out of the host structure and moves to the sodium metal anode releasing electrons to the external circuit. This process is reversed during discharge, and Fe^{3+} and

Mn^{3+} are reduced to Fe^{2+} and Mn^{2+} , respectively, as Na^+ intercalate into the host structure and are reduced by the external circuit.[21] The overall reaction mechanism can be written as follows in equation (4.1):



The N-doped carbon coating plays a crucial role in enhancing this sodium-storage behavior. The N-doped carbon coating enhances the electrochemical performance of NFMP@NC through multiple mechanisms. First, it improves electronic conductivity, facilitating faster charge transfer at the electrode-electrolyte interface.[47] Second, nitrogen heteroatoms in pyrrolic, pyridinic, and graphitic forms introduce defects and active sites within the carbon layer, providing favorable adsorption sites and additional pathways that aid Na^+ transport.[25] Third, the coating enhances interfacial contact with the electrolyte, thereby reducing polarization and charge-transfer resistance, as confirmed by EIS measurements. Collectively, these effects enhance the overall ion and electron transport, promote both surface-controlled and bulk diffusion-controlled Na^+ storage, and result in higher capacity, improved rate performance, and enhanced cycling stability compared to pristine NFMP. Thus, the combination of the phosphate framework and the N-doped carbon coating enables efficient and reversible Na^+ storage in NFMP@NC.

Importantly, the structural and morphological stability observed in the ex-situ analyses supports this mechanistic interpretation. Ex-situ XRD confirms that the alluaudite framework of NFMP and NFMP@NC remains intact after cycling, with no phase transformation, while FESEM reveals that pristine NFMP undergoes severe surface deterioration and crack formation after cycling. In contrast, NFMP@NC retains a more uniform, interconnected morphology due to the mechanically robust N-doped carbon coating, which buffers volume changes, suppresses excessive SEI

formation, and maintains intimate particle contact. This structural stability ensures more reversible Na^+ insertion and extraction, directly contributing to the superior electrochemical performance of NFMP@NC.

Overall, this study indicates that an N-doped carbon coating on NFMP improves the electrochemical properties through an increase in surface area, mesoporosity and electronic conductivity, so that it can increase the transport of Na^+ and stabilize the redox activity of Fe/Mn. Although the mesoporous architecture and N-doped carbon coating contribute to enhanced electrochemical performance and structural stability, their ability to suppress Mn^{3+} -induced Jahn-Teller distortion or prevent manganese dissolution was not directly investigated in the present study. Nevertheless, the preserved alluaudite framework and improved post-cycling morphology suggest that these structural features help mitigate degradation processes associated with repeated Na^+ insertion/extraction. NFMP@NC has improved specific capacity, rate capability, and retention of capacity, making it an attractive cathode to use in SIBs. Nonetheless, further developments are necessary to achieve a higher capacity and long-term cycling stability of practical full cells. These findings demonstrate the possibilities of heteroatom-doped carbon engineering in developing phosphate-based cathodes for next-generation SIBs.

4.4 Conclusions

Herein, NFMP and NFMP@NC were successfully synthesized to explore their potential as a cathode material for SIBs. Notably, NFMP@NC exhibited improved physicochemical properties, along with confirmation of N introduction into the carbon layer. Moreover, this material exhibited significant improvements in electrochemical behavior, specifically in terms of specific capacity, rate capability, and cycling stability, which is superior to that of pristine NFMP. This is attributed to the synergistic effect of the presence of a heteroatom in the N in the carbon layer, which enhances electronic conductivity, offers defect locations where the Na^+ can be stored

and ensures structural stability during cycling. Ex-situ XRD and FESEM analyses after electrochemical cycling confirmed the preservation of the crystal framework without detectable phase decomposition, indicating good structural stability during repeated Na⁺ insertion/extraction. Moreover, the presence of Fe²⁺/Fe³⁺ and Mn²⁺/Mn³⁺ redox activity ensures multi-electron transfer, which is facilitated by the presence of surface-engineered mesoporous architecture, promoting rapid ion transport. Importantly, this work presents the first report of heteroatom-introduced, surface-engineered NFMP alluaudite phosphate as a cathode material for SIBs, thereby bridging the knowledge gap and establishing its viability as a cost-effective and durable alternative to conventional cathode materials. This study highlights the significance of heteroatom-introduced carbon surface engineering in the development of phosphate-based compounds, which represents a promising avenue for safe, high-performance, and sustainable SIBs.

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Heteroatom Doping Strategy for Enhanced Sodium-Ion Storage in $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ Anode

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Heteroatom Doping Strategy for Enhanced Sodium-Ion Storage in $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$

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Sodium-ion batteries (SIBs) are promising and cost-effective substitutes for lithium-ion batteries for large-scale energy storage. Hence, exploring novel anode materials is crucial to developing sustainable SIBs. Herein, a nitrogen and sulfur co-doped carbon layer wrapped alluaudite $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ (NFMP@SNC) with uniform 3D urchin-like morphology is successfully synthesized via a simple hydrothermal technique. For the first time, this study examines their electrochemical properties as an anode for SIBs. The N, S-doped carbon layer forms a conductive network that enhances electron transport, facilitates Na^+ diffusion, and prevents particle aggregation and side reactions. As a result, NFMP@SNC displays an irreversible capacity of 774.52 mAh g^{-1} and a reversible capacity of 253.40 mAh g^{-1} at 0.05C, retaining 61.2% of its theoretical capacity (414 mAh g^{-1}). Furthermore, it shows an excellent rate capability of 71.76% at 0.1C (25 cycles) and retention of 48.49% at 0.2C (100 cycles). Additionally, density functional theory (DFT) calculations are conducted to evaluate the electronic band structure, density of states, charge density distribution, and Na^+ diffusion energy barriers of pristine NFMP, providing fundamental insights into its electrochemical behavior. With a low average voltage of ≈ 0.7 V, NFMP@SNC emerges as a promising intercalation-type anode material enabled by 3D architecture and N,S co-doping for high-performance SIBs.

1. Introduction

Environmental issues continue to drive the energy sector toward clean and eco-friendly power sources, including wind, solar, and tidal energy. However, the lack of large-scale and efficient energy storage technologies^[1] limits the widespread adoption of these

renewable sources.^[2-6] Lithium-ion batteries (LIBs) have evolved as the standard among existing storage technologies due to their superior energy density, reliability, and longevity, making them suitable for portable electronics and grid-scale applications. Nevertheless, the limited and localized availability of Li raw materials results in the high cost of LIBs, constraining their scalability for large-scale energy storage systems. Consequently, research efforts have increasingly turned toward sodium-ion batteries (SIBs), which share similar electrochemical principles and operational mechanisms with LIBs but leverage abundant and low-cost sodium resources. The charging and discharging process in LIBs and SIBs involves the intercalation and deintercalation of ions within the active electrode materials, facilitating energy storage. Further development of SIB technologies requires engineering durable electrode materials that can efficiently host sodium ions reversibly.^[7-9] To date, considerable progress has been made in identifying suitable positive electrodes with promising sodium storage

performance,^[10-12] but investigating high-performance negative electrodes with such stable and high-capacity performance is limited and quite challenging.

Several negative electrodes for SIBs have been rapidly explored, including hard carbon, transition metal-based electrodes, phosphates, alloy materials, and titanium materials.^[13-15] Among

In this chapter, a nitrogen and sulfur co-doped carbon layer wrapped alluaudite $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ (NFMP@SNC) with uniform 3D urchin-like morphology is successfully synthesized via a simple

hydrothermal technique. For the first time, this study examines their electrochemical properties as an anode for SIBs. The N, S-doped carbon layer forms a conductive network that enhances electron transport, facilitates Na^+ diffusion, and prevents particle aggregation and side reactions. As a result, NFMP@SNC displays an irreversible capacity of 774.52 mAh/g and a reversible capacity of 253.40 mAh/g at 0.05C, retaining 61.2% of its theoretical capacity (414 mAh/g). Furthermore, it shows an excellent rate capability of 69.6% at 0.1C (25 cycles) and retention of 48.49% at 0.2C (100 cycles). Additionally, density functional theory (DFT) calculations were conducted to evaluate the electronic band structure, density of states, charge density distribution, and Na^+ diffusion energy barriers of pristine NFMP, providing fundamental insights into its electrochemical behavior. With an low average voltage of ~ 0.7 V, NFMP@SNC emerges as a promising intercalation-type anode enabled by 3D architecture and N,S co-doping for high-performance SIBs.

4.5 Introduction

As discussed in Chapter 1, polyanion-type materials enable reversible sodium dissociation due to their 3D stable framework.[48] The rapid ionic diffusion coefficient, reduced Na^+ migration barrier, and superior sodium storage performance of polyanionic phosphate electrodes, along with their excellent structural and chemical stability, as well as a substantial discharge capacity, have recently prompted research into them.[49] Among them, $\text{NaTi}_2(\text{PO}_4)_3$ is a potential anode for SIBs, offering excellent sodium storage and structural robustness.[50,51] However, its high operating voltage ($\sim 1.5\text{--}2.1$ V vs Na/Na^+) limits energy density, making it less suitable for practical anode applications.[52] This prohibits using $\text{NaTi}_2(\text{PO}_4)_3$ as anode in SIBs for practical application. Some studies have explored $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$ in symmetric SIBs, reporting reversible capacities of ~ 150 mAh/g and ~ 60 mAh/g, respectively, though both face challenges such as unclear storage mechanisms[53] and electrode polarization leading to capacity fading.[54] Beyond these materials, alluaudite phosphates have gained much interest due to their tunable structural chemistry as well as ability to accommodate a variety of transition elements. The general formula of alluaudite compound is $\text{X}(2)\text{X}(1)\text{M}(1)\text{M}(2)_2(\text{PO}_4)_3$ where monovalent or divalent cations (e.g. Na, Li, K) occupy X(2) and X(1) sites while M(2), M(1) can accommodate bivalent as well as trivalent cations.[55,56] The compositional versatility results in tuning the electrochemical properties, making these materials promising electrodes for energy storage applications. Durio[57] and Richardson[58] were the first to study the electrochemical properties of alluaudite-type materials, highlighting their potential as electrode materials for LIBs. Since then, several iron-based alluaudite compounds have been explored for their promising electrochemical performance. These materials have attracted interest in improving both LIBs and SIBs, with most being investigated as positive electrode materials for LIBs. However, solid-state synthesis features limited morphology and composition control than wet

chemistry approaches.[59] More recently, Boschini *et al.* reported $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ by solvothermal method as a negative electrode for LIBs. It demonstrated a reversible specific capacity of 340 mAh/g at 50 mA/g within a voltage range of 0.03-3V.[60,61] Despite these advancements, the low electrical conductivity of Fe-based phosphate materials remains challenging.[62] To overcome this, researchers have explored various strategies, such as surface coatings and conductive composites, to improve their electrochemical performance in both LIBs and SIBs.

As a result, many strategies have been used to mitigate this issue by improving diffusion kinetics, including carbon coating, morphology control, nanostructuring, heteroatom doping and others.[63,64] Till now, the heteroatom doping (P, N, B, F, and S) in the carbon matrix has been verified as an efficient way to enrich the electronic conductivity and serve additional active sites to advance the specific capacity of the electrode without increment in the specific surface area to achieve lower initial coulombic efficiency (ICE).[65,66] Since N functions as an electron donor as a dopant, N doping is the most popular technique to enhance electrical conductivity and electron/ Na^+ transfer kinetics.[67,68] Also, S doping helps provide additional active sites for Na^+ and extra capacity. C-S-C bonds at the carbon skeleton edge can enlarge the interplanar distance of the carbon layer. Furthermore, introducing the C-S-C bond lessens the damage to the conjugated pi bonds, contributing to the higher conductivity. Further, N, S dual doping in the carbon layer has proved to be better ion storage performance than solo-doping due to the synergistic effect.[69]

In the present work, N and S dual-doped carbon-coated NFMP (NFMP@SNC) was synthesized via a hydrothermal process followed by pyrolysis. During high-temperature pyrolysis, urea and thiourea form an S, N-doped carbon layer, enhancing the NFMP coating, though this approach has not been reported yet. This is the first time that the structure, morphology, and electrochemical performance of the modified NFMP

anode have been thoroughly examined. Various characterisation techniques have uncovered how the S, N-doped carbon coating affects the electrochemical reaction kinetics of the anode materials. Incorporating urea and thiourea enhances the rate capability and cycle performance of NFMP by creating more defects and active sites in the carbon layer, which speeds up the migration of electrons and Na ions.

4.6 Experimental Section

4.6.1 Materials Synthesis

Chapter 2 outlines the experimental methodology employed in this work, including the selection of precursor chemicals, synthesis procedures, slurry preparation, and electrode fabrication for the NFMP and its heteroatom-derived derivatives as an anode material. Using a hydrothermal synthesis route, a series of NFMP anode materials was prepared by varying the heteroatom, and their physicochemical properties were subsequently analyzed using several advanced characterization techniques.

4.6.2 Coin cell fabrication

For electrochemical studies, a CR2032-type sodium half-cell configuration was assembled in an inert glovebox. A 1 M NaClO₄ electrolyte dissolved in a 1:1 volume ratio of EC and DMC is used. The electrochemical behavior of the anode was examined through CV, GCD, and EIS.

4.7 Results and Discussions

The NFMP and its derivatives were synthesized using the hydrothermal method followed by the pyrolysis process, as represented in **Figure 2.3**. This synthesis of NFMP involves several steps of complex chemical reactions, as illustrated in **Figure 4.12**. Under the condition of 200°C, ions separate from FeC₂O₄·2H₂O as Fe²⁺ and MnCO₃ as Mn²⁺ in DI water. Also, NaH₂PO₄ releases PO₄³⁻ and NaNO₃ releases Na⁺. The

nucleation starts with crystal growth due to the high temperature and pressure inside the autoclave. In particle-mediated growth, once primary nanoparticles aggregate to produce a mesoparticle, the excess metallic atoms and ions in the solution adhere to the mesoparticle, leading to overgrowth. So, during nucleation, aggregation of metal precursors first forms a meatball-like structure called a microparticle. The PO_4^{3-} ions from the precursor solution, along with the remaining free metal ions (Fe^{2+} , Mn^{2+}) and Na^+ , adhere to the surface of the microparticle, promoting further growth and the formation of an overgrown structure. These intermediates start to nucleate and gradually convert into a 3D structure under hydrothermal conditions. The thermal breakdown of oxalate and carbonate ions (from $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and MnCO_3) liberates CO_2 and perhaps H_2O , facilitating the precipitation and crystallization process while promoting the development of channels that enhance the 3D morphology.

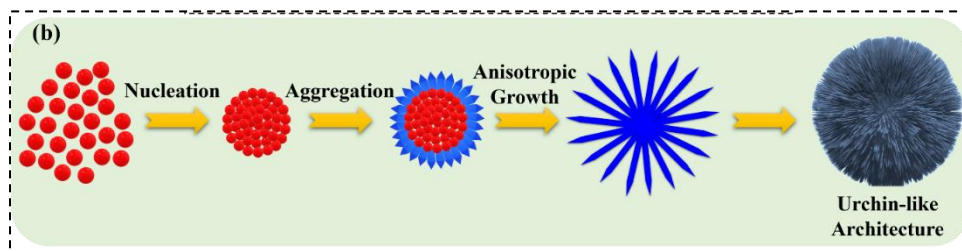


Figure 4.12 Schematic representation of the growth mechanism of the urchin-like architecture of NFMP.

This environment promotes fast nucleation and anisotropic development, most likely due to certain crystallographic orientations that result in outward radiating, branching structures typical of urchin-like morphologies.[70] During the crystallization of 3D NFMP, the overall process produces CO_2 and NO_2 gasses. By diffusing into the lattice and charge-balancing the phosphate framework with $\text{Fe}^{3+/2+}$ and Mn^{2+} ions, the extra Na^+ ions from the precursor solution stabilize the structure. This stabilization is crucial to obtain the stoichiometric NFMP composition. The spikes of the urchin-like

structure develop to alleviate surface energy and raise the surface area volume ratio.

4.7.1 Physicochemical characterization

4.7.1.1 Structural Analysis

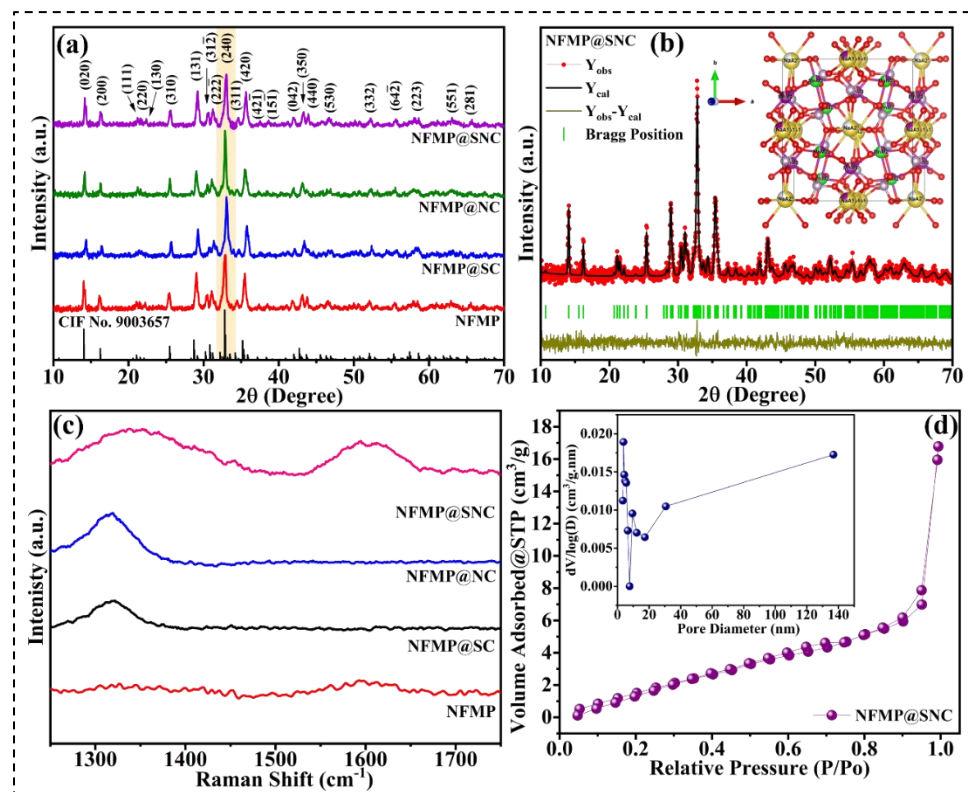


Figure 4.13 (a) Combined XRD patterns of NFMP, NFMP@SC, NFMP@NC, NFMP@SNC, (b) Rietveld refinement of NFMP@SNC (Inset: crystal structure of NFMP), (c) Combined Raman patterns of NFMP, NFMP@SC, NFMP@NC, NFMP@SNC, (d) N_2 adsorption-desorption analysis of NFMP@SNC (Inset: BJH pore size distribution)

The XRD patterns, determined FWHM, and crystallite size provide valuable insights into the microstructural properties of all samples and their implications for sodium storage application. All samples display a well-defined crystal structure, with diffraction peaks closely aligning with the CIF File No. 9003657 for the monoclinic phase shown in **Figure 4.13 (a)**. [71] This observation indicates that further incorporation of C, N, and S

does not affect the crystallinity or phase structure of the NFMP derivatives. Notably, the increased peak intensity observed overall in NFMP@NC and NFMP@SNC relative to NFMP and NFMP@SC suggests enhanced crystallinity, which may contribute to improved structural stability. For a deeper understanding of structural parameters, the XRD pattern of NFMP@SNC was refined using FullProf software based on CIF File No. 9003657, as shown in **Figure 4.13 (b)**. The lattice parameters are $a=12.009 \pm 0.005 \text{ \AA}$, $b=12.612 \pm 0.008 \text{ \AA}$, $c= 6.452 \pm 0.006 \text{ \AA}$, and $\beta=114.272^\circ$ which agreed with the standard data. Furthermore, the inset shows the corresponding crystal structure visualized using the Vesta Software.

Furthermore, a closer inspection of the FWHM values shows variations among the samples, as tabulated in **Table 4.5**. The FWHM is determined from the XRD peak corresponding to the (240) reflection, as it is one of the most intense and well-defined peaks in the diffraction pattern of all samples. The FWHM was extracted using Gaussian peak fitting in the XRD analysis software. The crystallite size was then estimated using the Scherrer equation (2.1)[72]. It is worth noting that the average crystallite sizes of these samples, ranging from approximately 27 to 31 nm, also play a key role in determining the balance between ionic diffusion and electrical conductivity. The NFMP sample has the highest FWHM (0.3683) and the smallest crystallite size of 23.48 nm, indicating a smaller crystalline domain. In contrast, NFMP@SC, NFMP@NC, and NFMP@SNC exhibit smaller FWHM values and larger crystallite sizes, with NFMP@NC showing the largest crystallite size (39.94 nm) due to its relatively low FWHM (0.2164). From a sodium-ion storage perspective, smaller crystallite sizes, as observed in NFMP, generally provide shorter diffusion paths for sodium ions, facilitating faster intercalation and deintercalation processes.[73–75] However, excessively small crystallite sizes may introduce more grain boundaries, impeding electronic conductivity.[76] The carbon-coated samples, particularly NFMP@SC and NFMP@SNC, achieve a balance between moderate crystallite sizes (27.79 nm and 31.42

nm, respectively) and enhanced conductivity due to the carbon coating. This combination will improve sodium-ion diffusion kinetics, rate capability, and cycling stability. NFMP@NC, with the largest crystallite size (39.94 nm), may exhibit better structural stability but could suffer from slightly reduced sodium-ion mobility due to longer diffusion paths. Overall, an optimal crystallite size plays a critical role; if the crystallite size is very small, then it can lead to a higher number of interfacial traps, resulting in increased grain boundary resistance. In contrast, large crystallites extend Na⁺ diffusion paths, hindering ionic transport. A moderate crystallite size, as observed in this study, offers a beneficial compromise - minimizing charge transfer resistance while maintaining adequate diffusion pathways. This favourable structure-property relationship may contribute significantly to enhancing the electrochemical behaviour of the NFMP derivatives. These findings emphasize the significance of simultaneously optimizing crystallite size and FWHM, in conjunction with the advantageous effects of carbon coatings, to improve sodium-ion storage capabilities.

Table 4.5 FWHM and crystallite size of all samples.

Sample	2 θ (°)	FWHM (°)	Crystallite Size
NFMP	33.093	0.368	23.48 nm
NFMP@SC	33.033	0.311	27.79 nm
NFMP@NC	32.849	0.216	39.94 nm
NFMP@NSC	33.329	0.275	31.42 nm

4.7.1.2 Thermogravimetric analysis

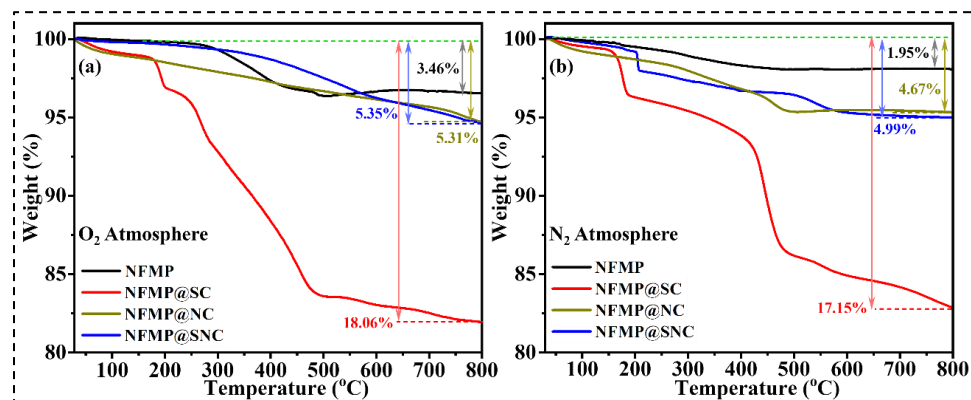


Figure 4.14 TGA analysis of all samples under (a) O₂ atmosphere, and (b) N₂ atmosphere.

Furthermore, TGA analysis was conducted on all samples to evaluate their thermal stability and to provide additional insight into the decomposition behaviour. The results, summarised in **Figure 4.14**, provide insights into the decomposition behaviour and support the observed structural stability. The thermal stability of the synthesized materials, essential to energy storage applications, was evaluated by utilizing TGA under both oxidative (O₂) and inert (N₂) atmospheres, as shown in **Figure 4.14**. Under O₂ atmosphere (**Figure 4.14 (a)**), pristine NFMP exhibits weight loss of 3.46% up to 800 °C, attributed to desorption of surface-bound moisture or residual hydroxyl groups. In contrast, NFMP@SC shows a significant total weight loss of 18.06%, indicating the higher weight loss derived from thiourea. This multi-step decomposition includes: moisture evaporation at ~150 °C, degradation of sulfur-containing functional groups (thiols, sulfoxides) in the 200-400°C range, and oxidation of sulfones and carbon backbones at higher temperatures. Furthermore, NFMP@NC and NFMP@SNC show more modest weight losses of 5.31% and 5.35%, respectively, suggesting thinner carbon layers. The slightly higher loss in NFMP@SNC compared to NFMP@NC implies a higher carbon content due to dual doping with N and S.[67,77] Moreover, TGA conducted in N₂ atmosphere, as shown in **Figure 4.14 (b)**, provides insights into the

pyrolytic stability. Pristine NFMP shows minimal weight loss of 1.95% up to 800°C, ascribed to the physically adsorbed moisture and the hydroxyl group, confirming the thermal stability of the material and the absence of any carbonaceous layer. In contrast, NFMP@SC exhibit a total three-step weight loss of 17.15%, following a decomposition pattern similar to that in O₂ atmosphere. Furthermore, NFMP@NC and NFMP@SNC show improved thermal stability, with total weight loss of 4.67% and 4.99%, respectively, up to 800°C, indicating improved structural integrity due to N and N-S co-doping. This stability may arise from the incorporation of N species, such as graphitic-N, pyridinic-N, which enhance the thermal resistance of the carbon matrix. The slightly higher loss in NFMP@SNC suggests S doping introduces minor additional decomposition, possibly stabilized by N. These observations confirm that NFMP@NSC, with its superior thermal resilience, is the most promising candidate for SIB applications requiring robust thermal stability, followed by NFMP@NC, highlighting the critical role of heteroatom-doped carbon coatings. Moreover, the CHNS-O supports these findings, with measured carbon contents of 2.1%, 6.34%, 4.14%, and 5.37% for NFMP, NFMP@SC, NFMP@NC, and NFMP@SNC, respectively. The higher carbon content in NFMP@SC correlates with its significant weight loss in both O₂ and N₂ atmospheres. Conversely, NFMP@NC and NFMP@SNC exhibit moderate carbon contents, reflecting thinner N and N-S co-doped carbon layers, respectively. Overall, the CHNS-O and TGA results consistently confirm the successful and tunable carbon incorporation across the synthesized materials.

4.7.1.3 Raman analysis

The Raman spectra depicted in **Figure 4.15 (c)** provide key insights into the structural nature of the carbon coatings in the doped NFMP composites. In the case of NFMP@SC and NFMP@NC, the spectra exhibit a prominent D band but absent G band. This is due to S and N doping in the

carbon layer, which can introduce significant structural disruptions suppressing the formation of well-ordered sp^2 -hybridized domains needed for the G band to appear.[69] The D band corresponds to the A_{1g} vibration mode of disordered sp^2 carbon atoms, typically associated with structural defects, edges, or amorphous domains. The highly disordered carbon coating can provide a large number of active sodium-ion adsorption and diffusion sites with many defects. However, a lower electronic conductivity could limit the rate performance and overall charge transfer during electrochemical reactions due to the absence of a graphitic structure, which is indicated by the absence of the G band. The NFMP@SNC sample, on the other hand, clearly exhibits both the D and G bands. In addition to the disordered structure, the appearance of the G band suggests the presence of ordered graphitic carbon domains. The synergistic effect of simultaneous S and N co-doping is linked to this unique behaviour. By enabling the rearrangement of carbon atoms into sp^2 -rich domains and preserving a sufficient number of defects advantageous for sodium storage, dual doping has been demonstrated to promote partial graphitization. Additionally, co-doping may improve the formation of conductive graphitic structures by stabilising intermediate carbon species during thermal breakdown. Under specific circumstances, S is known to catalyse the formation of graphitic domains, which helps co-doped samples develop the G band. These structural variations in the carbon matrix directly impact electrochemical performance. Because of their high defect density, the disordered carbon coatings in NFMP@SC and NFMP@NC offer a large number of active sites for Na^+ adsorption and diffusion, which is advantageous for capacity. However, electronic conductivity is limited by the absence of graphitic content, which also increases charge transfer resistance and limits rate capability. The balanced carbon structure of NFMP@SNC, on the other hand, includes both graphitic and defect-rich domains, providing enhanced electrical conductivity while maintaining a large number of ion transport pathways. Better electrochemical performance could result from dual

doping, which facilitates more rapid electron movement and less polarization. NFMP@SNC offers a better combination of high capacity, rate performance, and cycling stability than NFMP@SC and NFMP@NC, making it more effective for electrochemical applications due to its dual effect of enhanced conductivity and sufficient defect density. Therefore, the interaction of doping elements and their impact on the carbon framework during synthesis is what causes the structural variations.

4.7.1.4 N₂ Adsorption-desorption isotherm

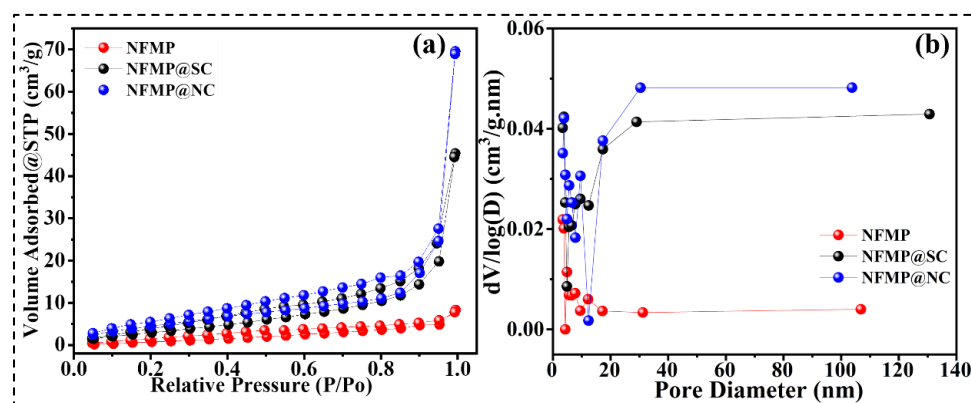


Figure 4.15 (a) N₂ adsorption-desorption isotherm, and (b) BJH pore size distribution of NFMP, NFMP@SC and NFMP@NC.

The BET N₂ adsorption-desorption analysis, as depicted in **Figure 4.14 (d)** and **Figure 4.15** revealed the specific surface areas of the electrode materials as follows: NFMP (8.751 m²/g), NFMP@SC (16.393 m²/g), NFMP@NC (21.684 m²/g), and NFMP@NSC (29.144 m²/g). The significantly enhanced surface areas observed for NFMP@SC, NFMP@NC, and NFMP@NSC compared to pristine NFMP are attributed to introducing heteroatoms into the carbon matrix, which increases porosity and generates active sites essential for sodium-ion storage.[78] The carbon coating forms during pyrolysis, where sucrose carbonizes to create a porous matrix around the NFMP particles. NFMP@SC gains additional surface area due to S atoms disrupting the carbon lattice during carbonization, introducing structural defects and additional pores. However, these S-

induced defects may not contribute uniformly to sodium-ion storage, as their electrochemical activity can vary. In the case of NFMP@NC, N doping through urea decomposition ($\text{CO}(\text{NH}_2)_2 \rightarrow \text{NH}_3 + \text{HCNO}$) releases gases at high temperatures, which expand the carbon network and substantially boost the surface area of the material. N also introduces functional groups that enhance sodium ion interaction, creating more effective sites for electrochemical activity. The combined S and N doping in NFMP@NSC further optimizes surface area by establishing a synergistic, spatially organized structure within the carbon layer. With regard to its fundamental alluaudite-type framework, a three-dimensional interconnected network of $[\text{PO}_4]$ tetrahedra and $[\text{Fe}/\text{MnO}_6]$ octahedra, all samples maintain a relatively low specific surface area regardless of these improvements. This well-ordered structure ensures excellent structural stability, but developing high-surface-area morphologies is inherently constrained. Additionally, as high-temperature treatment encourages grain growth and particle densification, the hydrothermal synthesis followed by pyrolysis produces well-crystallized particles with low porosity. Microporous structures are further explained by the Barrett–Joyner–Halenda (BJH) pore diameter distributions, which show larger pores of 3.821 nm and 3.805 nm for NFMP@NC and NFMP@NSC, respectively, and pore sizes of 3.399 nm for NFMP and 3.397 nm for NFMP@SC. Effective sodium-ion transport and storage are provided with feasible by these mesopores, which promote optimal electrolyte access and assure wide contact with the active component.[79]

4.7.1.5 Surface morphology analysis

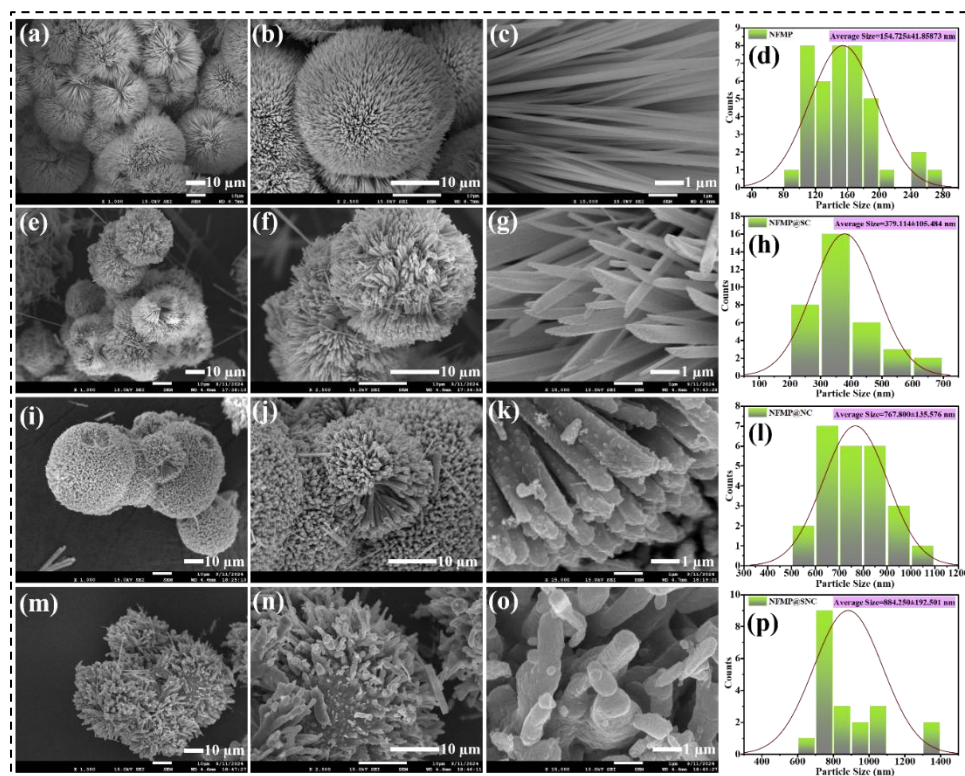


Figure 4.16 FESEM images of (a-c) NFMP, (e-g) NFMP@SC, (i-k) NFMP@NC, (m-o) NFMP@SNC, Particle size distribution plot of (d) NFMP, (h) NFMP@SC, (l) NFMP@NC, and (p) NFMP@SNC.

The FESEM images show the morphology of NFMP and its composites, providing insights into the effect of different dopants and carbon coatings on the material structure. Also, the microrod thickness distribution for the NFMP samples, as seen in the FESEM images in **Figure 4.16**, is quantitatively represented in the provided graph. The pristine NFMP exhibits a well-defined urchin-like morphology shown in **Figure 4.16 (a-c)**, characterized by radially aligned microrods of thickness approximately 154.725 ± 41.858 nm (**Figure 4.16 (d)**), forming undoped dense spherical assemblies. This structure is indicative of controlled crystal growth during the hydrothermal synthesis process. In the NFMP@SC sample, S and carbon are introduced through thiourea and sucrose. The S doping leads to surface modification and slight broadening of the rods, as observed from the FESEM images in **Figure 4.16 (e-g)**, where tiny dots are visible on the

tips of the rods. The average rod thickness increases to around 379.11 ± 105.484 nm (**Figure 4.16 (h)**). Furthermore, incorporating N into the carbon coating results in a more substantial coating, enhancing the structural integrity and thickening the nanorods of NFMP@NC. The FESEM images in **Figure 4.16 (i-k)** confirm this observation with a smoother, more robust microrod appearance. The average thickness of NFMP@NC, N-doped carbon coated with urea and sucrose, rises significantly to approximately 767.800 ± 135.576 nm, as plotted in **Figure 4.16 (l)**. The NFMP@SNC sample, co-doped with N and S using urea, thiourea, and sucrose, shows a more compact and densely coated urchin-like morphology, with thickened microrods suggesting enhanced surface interaction and material growth due to the combined dopants (**Figure 4.16 (m-o)**). The particle size distribution shown in **Figure 4.16 (p)** gives the most significant average microrod thickness, around 884.250 ± 192.501 nm. The co-doping synergistically enhances the carbon coating and the overall particle thickness. The thermal analysis observed that co-doping strengthens the structural framework, producing a more resilient and thermally stable material. These structural changes are critical to boost electrochemical performance and thermal stability in SIB applications.

4.7.1.6 Structural analysis: HRTEM

The coating thickness and crystallinity of all samples were investigated using HRTEM analysis, providing valuable insights into their structural properties. The TEM image of NFMP presented in **Figure 4.18 (a)** reveals that the NFMP particles have smooth surfaces with a notable interplanar distance of 0.281 nm related to the (240) plane. According **Figure 4.18 (c-f)**, and **Figures 4.17 (a)**, the particles of NFMP@SC, NFMP@NC and NFMP@SNC are effectively wrapped by carbon layer. This layer, generated through the carbonization of sucrose and incorporated with exotic atoms, exhibits interplanar distances of ~ 0.259 nm, corresponding to the (420) plane. The presence of carbon coating effectively mitigates the agglomeration of particles during thermal

processing. In addition, it improves electronic contact between particles, thereby reducing the resistance at the particle interfaces, resulting in improved overall material performance. Moreover, incorporating N and S introduces active defects and nucleation sites on the carbon layer. This strategic doping is conducive to suppressing the crystalline growth of NFMP particles, allowing for more controlled and efficient structural development.

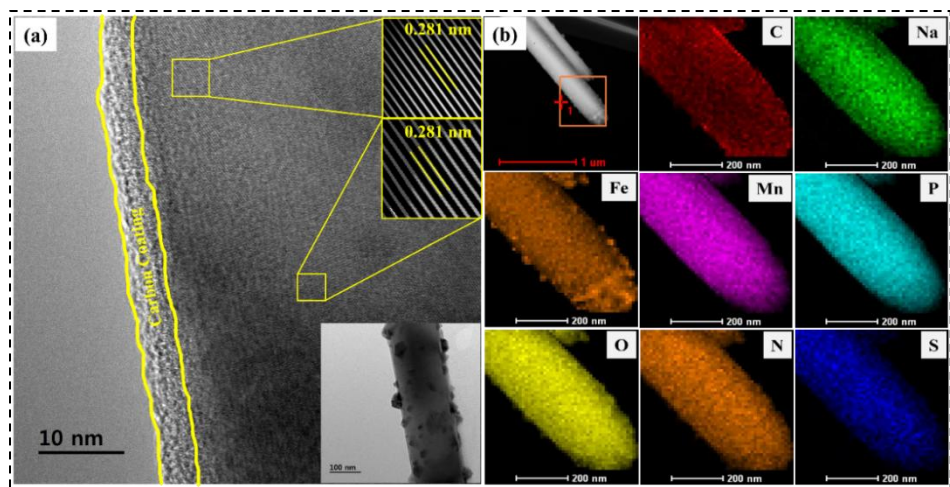


Figure 4.17 (a) TEM and HRTEM image of NFMP@SNC, (b) EDS elemental mapping of C, Na, Fe, Mn, P, O, N, S in NFMP@SNC

Moreover, the NFMP@SNC particles are integrated within a thin carbon matrix, forming the 3D porous structure that promotes efficient Na^+ diffusion and enhances electronic conductivity, both critical for optimal functionality. The HRTEM image of NFMP@SNC illustrates that the ~ 5 nm integrated carbon layer uniformly coats the NFMP particles, as evidenced in **Figure 4.17 (a)**. This core-shell structure not only improves the stability of the particles but also enhances their overall electrochemical performance. Additionally, **Figure 4.17 (b)** confirms the uniform distribution of elements Na, Fe, Mn, P, O, C, N, and S within micro rods of NFMP@SNC, further underscoring the well-integrated and balanced composition that characterizes this advanced material.

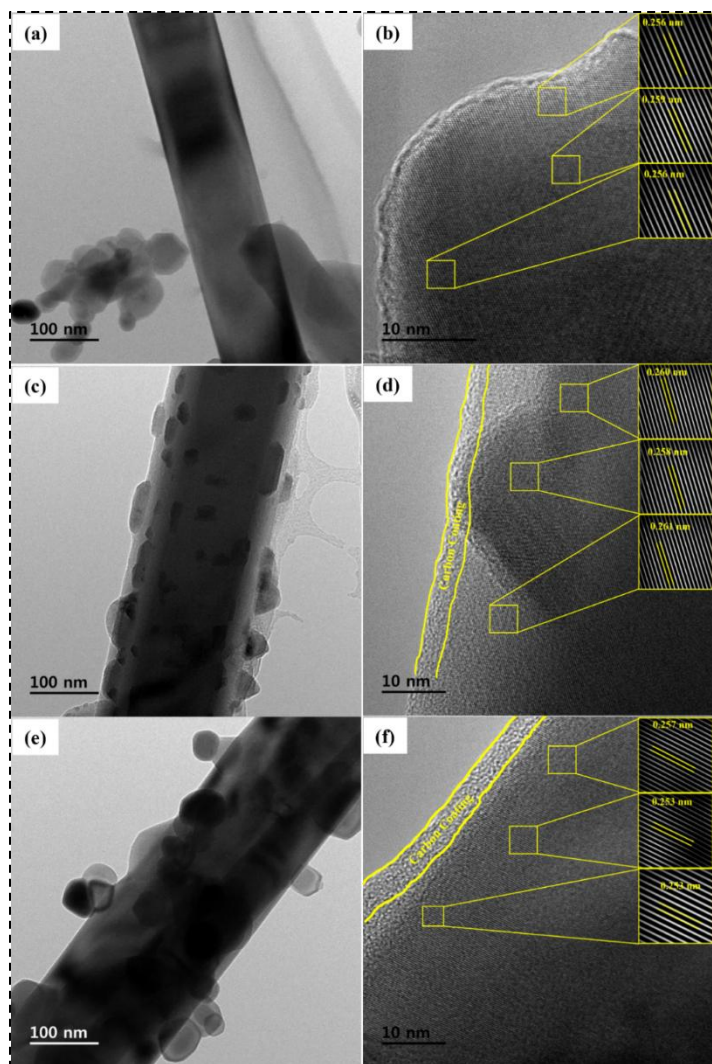


Figure 4.18 (a) TEM, (b) HRTEM analysis of NFMP, (c) TEM, (d) HRTEM analysis of NFMP@SC, (e) TEM, (f) HRTEM analysis of NFMP@NC.

4.7.1.7 Chemical Analysis

XPS analysis was performed to study the electronic structure and elemental composition of the NFMP and composites. The survey spectra of all the samples are given in **Figure 4.19 (a)**, and it verifies the presence of Na, Fe, Mn, P, O, C, S, and N. The high-resolution C 1s spectrum presented in **Figure 4.19 (b)** is deconvoluted into three distinct peaks at 284.6, 285.7, and 288.8 eV, corresponding to C–C, C–O and C=O bonds, respectively for NFMP. In NFMP@SC, NFMP@NC and NFMP@SNC, a noticeable shift

in C-O binding energy towards higher value is observed, which is attributed to changes in the local electronic environment of carbon due to the incorporation of heteroatoms. This incorporation happens when precursors like urea and thiourea undergo high-temperature pyrolysis, releasing reactive species that contain N and S and chemically integrating into the carbon framework. By introducing structural defects and altering the electronic structure of carbon coating, these heteroatoms improve their electrical conductivity and increase the number of electrochemically active sites. In the case of NFMP@SNC, the C 1s spectrum exhibits an even more pronounced shift in binding energy, particularly for the C–N and C–S bonds, suggesting stronger interactions or higher dopant concentrations. Higher electron-withdrawing effects triggered on by the incorporation of heteroatoms are reflected in the higher binding energies; these effects are also associated with better charge delocalization and increased electronic conductivity. Since the synergistic effects of S and N co-doping not only improve ionic/electronic transport but also encourage more effective Na⁺ storage, this could aid in improving the electrochemical performance.

As shown in **Figure 4.19 (e)**, the N 1s spectrum of NFMP@SNC is deconvoluted into pyridinic N, pyrrolic N and graphitic N, at 398.6, 400.8 and 402.5 eV. The large amount of pyridinic and pyrrolic N are more dominant than graphitic N, revealing the abundant extrinsic defect in the pyrolytic carbon. The pyridinic-N is located at one corner of the carbon hexagon ring, and pyrrolic-N forms a pentagonal ring with the carbon atoms that provide a pair of lone electrons to the primary material, leading to the appearance of atomic vacancy as well as dangling bonds. The graphitic-N replaces one C atom from the hexagon ring as shown in **Figure 4.19 (g)**. These three bonds can boost the electronic conductivity of the carbon matrix. The pyrrole and pyridine N affect the carbon skeleton and escalate the number of defects and active sites on its surface. This leads to the increased electrochemical active sites for transporting electrons and sodium ions.[80] Peaks at 164.1, 167.1, and 171.6 eV are seen in the deconvolution

of S 2p (**Figure 4.19 (f)**). The latter peak is associated with the C-SO_x-C group, but the first two peaks are associated with the S-C-S covalent thiourea bond with 2p_{3/2} and 2p_{1/2}, confirming the S doping into the carbon matrix.[81]

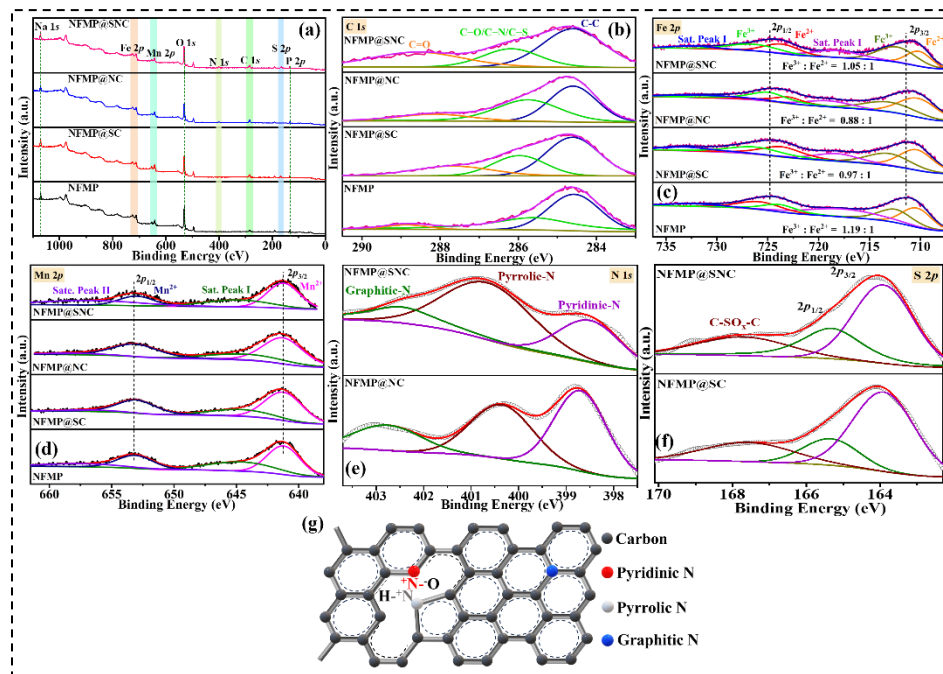


Figure 4.19 (a) XPS survey scan, (b) High-resolution XPS spectra of C 1s, (c) Fe 2p, (d) Mn 2p of NFMP, NFMP@SC, NFMP@NC, NFMP@SNC, (e) High-resolution XPS spectra of N 1s of NFMP@NC and NFMP@SNC, (f) High-resolution XPS spectra of S 2p of NFMP@SC and NFMP@SNC, (g) Schematic illustration of three types of bonding configurations of N atoms within N-doped carbon.

In the high-resolution depicted in **Figure 4.19 (c)**, the Fe 2p spectrum of NFMP exhibits two peaks at 711.35 and 724.8 eV, corresponding to Fe 2p_{3/2} and 2p_{1/2}, respectively. Both doublets show the existence of mixed-state Fe²⁺ and Fe³⁺ in the material. The presence of the Fe³⁺ is further confirmed by the satellite peaks at 717.6 and 732.4 eV. The introduction of the S in NFMP@SC, N in NFMP@NC and both in NFMP@SNC exhibited a negative shift in the core Fe 2p spectrum

compared to the pristine NFMP. It shows that the surface modification of the material influences the local chemical states of Fe^{2+} and Fe^{3+} , where the ratio of $\text{Fe}^{3+}:\text{Fe}^{2+}$ is given in **Figure 4.19 (c)**. The influence of different surface modifications is reflected in the variations in the $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio among the samples. The $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio of 1.19:1 in Pristine NFMP shows a more Fe^{3+} state, which could be connected to slower charge transfer kinetics and increased polarisation. NFMP@SC and NFMP@NC with ratios of 0.97:1 and 0.88:1, respectively, show a comparatively higher Fe^{2+} content, which can improve sodium-ion diffusion and electronic conductivity. With a $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio of 1.05:1, NFMP@SNC shows a more balanced redox state, which may help to enhance electrochemical reversibility. These variations in the $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio show how surface modifications affect the electronic structure and charge storage mechanisms of NFMP. They further demonstrate the impact of adjusting Fe oxidation states on the overall battery performance and sodium storage behaviour.[82] Furthermore, the XPS of Mn 2*p* of NFMP depicted in **Figure 4.19 (d)** shows the two peaks at 641.3 and 653.2 eV attributed to the $2p_{3/2}$ and $2p_{1/2}$. It shows the presence of Mn^{2+} in all the materials with satellite peaks at 644.9 and 657.8 eV. Structurally, the incorporation of Mn^{2+} helps to reduce lattice strain and minimize structural distortion due to its slightly larger ionic radius (0.81 Å) compared to Fe^{2+} (0.78 Å).[83] This may ensure better mechanical integrity of the alluaudite framework, preventing excessive volume expansion during Na^+ insertion/extraction and thereby improving the long-term cycling stability.

4.7.2 Electrochemical characterizations

4.7.2.1 GCD analysis

To study the influence of heteroatom doping in carbon on their electrochemical properties, the electrochemical properties of all samples as an anode were evaluated by testing a sequence of half-cells, the electrochemical performance of NFMP, MFMP@SC, NFMP@NC and NFMP@SNC were performed by charge-discharge curve, rate performance

and CV analysis. The GCD profiles of all the heteroatom-doped carbon-coated samples were carried out to analyze their rate capability and stability further. **Figure 4.20 (a)** compares the GCD profiles for the initial cycle of all four samples at a constant 0.05C, likely to demonstrate the influence of different heteroatom dopants on the electrochemical property. The NFMP@SNC with N and S co-doping shows higher specific discharge capacity among all the samples, which is 774.552 mAh/g at 0.05C, suggesting the enhanced sodium-ion storage facilitated by the S and N co-doping. The plots show the stable behaviour indicating the impact of carbon doping on improving the electronic/ionic diffusion. The corresponding specific discharge capacities of NFMP, NFMP@SC and NFMP@NC are 568.238, 591.8 and 603.784 mAh/g, respectively.

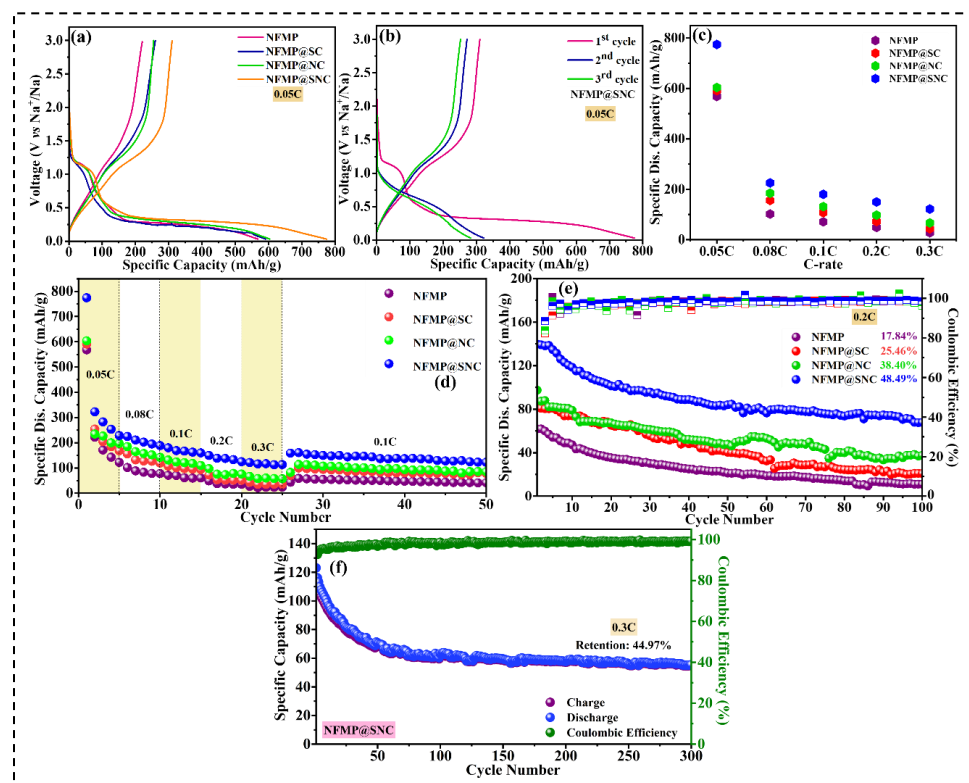


Figure 4.20 (a) Initial three charge/discharge profiles of NFMP@SNC 0.05 C, (b) Initial charge/discharge profile, (c) Specific capacity at various scan rates, (d) Rate capability plot, (e) Cyclic stability performance at 0.2C of NFMP, NFMP@SC, NFMP@NC and NFMP@SNC, (f) Cyclic Stability performance at 0.3C of NFMP@SNC.

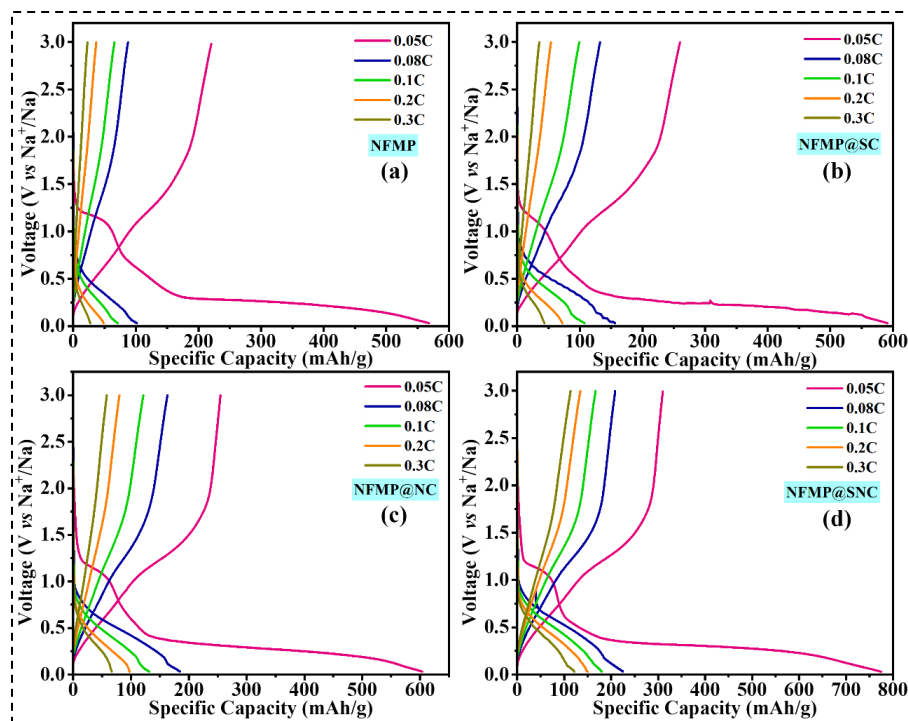


Figure 4.21 GCD profile at different scan rates for (a) NFMP, (b) NFMP@SC, (c) NFMP@NC, and (d) NFMP@SNC.

Further, **Figure 4.20 (b)** shows the first three GCD cycles of the NFMP@SNC at 0.05C, showing the highest capacity stabilizing over the subsequent cycles. The initial high specific capacity is attributed to forming a solid electrolyte interface (SEI) and activating redox sites with unavoidable electrochemical polarisation. The gradual shift in the curves shows typical behaviour in SIB electrodes with the initial stabilization phase of the electrode material. The first-cycle discharge and charge capacities of NFMP@SNC were 310.29 and 774.57 mAh/g, respectively, corresponding to an ICE of 40.06%. The observed irreversible capacity loss during the initial cycle is attributed primarily to SEI formation and other interfacial side reactions occurring on the high-surface-area porous electrode. **Figure 4.20 (c)** depicts the specific capacity of the first cycle at various C-rates for all samples, revealing a consistent trend of decreasing specific capacity with increasing C-rate observed across all samples. This behavior is ascribed to the limited time available for sodium-ion intercalation and deintercalation

at higher C-rates, which hinders the efficient utilization of the active material. Furthermore, the GCD profiles for all samples performed at various C-rates are depicted in **Figure 4.21**.

Further, **Figure 4.20 (d)** illustrates the rate capability of all the samples analyzed at various C-rates, increasing from 0.05C to 0.3C. Generally, the specific capacity decreases with the increasing current rates for all the samples, showing stable but distinct capacities at each current rate. Notably, the NFMP@SNC shows the higher capacity at each current rate among all the samples. In contrast to the relatively modest electrochemical performance of NFMP, NFMP@SC, and NVP@NC, NFMP@NSC offers the highest capacity and enhanced rate capability with a superior discharge capacity of 774.522, 225.162, 179.928, 149.59 and 121.534 mAh/g at 0.05C, 0.08C, 0.1C, 0.2C, and 0.3C, respectively. Again, when the current rate is reversed back to 0.1C, the 71.76% capacity is retained after 25 cycles with the lowest polarisation with increasing current rates. The NFMP electrodes exhibit the lowest capacity in rate capability tests, confirming that heteroatom doping can greatly elevate the electrochemical performance of NFMP-based electrodes. **Figure 4.20 (e)** represents the cycling performance of the NFMP-based samples at 0.2C over extended cycles. The NFMP@NC and NFMP@SNC show superior cycling stability with minimal capacity fading over the testing period compared to NFMP and NFMP@SC, showing the beneficial impact of S and N doping in the carbon layer of the samples. The cycling stability of the NFMP shows lower capacity retention with capacity fading, highlighting the importance of surface modifications in enhancing electrochemical performance. Additionally, NFMP@SC shows improved stability compared to the NFMP but could not perform as well as NFMP@NC and NFMP@SNC. Moreover, extended cycling stability of NFMP@SNC is conducted for 300 cycles at 0.3C to evaluate the long-term stability of the anode material, as shown in **Figure 4.20 (f)**. The data reveals that NFMP@SNC retains 41.9% of its initial capacity after 300 cycles,

indicating its ability to sustain prolonged electrochemical cycling. The minimal degradation in Coulombic efficiency, which remains close to 100% throughout the cycling process, suggests highly reversible sodium-ion intercalation/extraction with negligible side reactions or electrolyte decomposition. This observed cycling stability is attributed to the synergistic effects of N and S doping, which enhance electronic conductivity, stabilize the electrode structure, and facilitate better electrode-electrolyte interaction. The presence of heteroatoms in the carbon matrix introduces defects and functional groups, as confirmed via XPS analysis, that act as active sites for Na-ion storage while also preventing severe structural collapse upon repeated cycling.

Table 4.6 Comparative table of the phosphate anode materials used in SIBs.

Material	Voltage (V)	Synthesis method	Morphology	Initial Specific Capacity (mAh/g)	Retention (%) / C-rate/Cycle number	Ref.
C@NaTi ₂ (PO ₄) ₃	0.01-3.0	Traditional Stöber method	Nanospheres	256.1, 20 mA/g	85.4%/20C/10000	[84]
NaTi ₂ (PO ₄) ₃ @C	0.01–3.0	Hydrothermal	Nanocubes	225, 0.05 A/g	84.3%/1A/g/1000	[51]
Na _{1.5} V _{0.5} Nb _{1.5} (PO ₄) ₃	1.0-3.0	Solid-state	Microcubes	140, 0.1C	89%/5C/500	[85]
NaSn ₂ (PO ₄) ₃	0.005–3.0	modified Pechini method	Nanorods	266, 500 mA/g	52.2%/500 mA/g/100	[86]
Na ₃ MnTi(PO ₄) ₃ /C-N	1.5-2.5	Sol-gel	-	54.2, 0.05C	93.2%/2C/350	[87]
Na ₃ Co _{0.5} Mn _{0.5} Ti(PO ₄) ₃	1.5-3.0	Sol-gel	worm-like microparticles	51, 0.1C	80%/0.2C/100	[88]
Na ₂ Co ₂ Fe(PO ₄) ₃	0.03-3.0	solid state reaction	-	110, 10 mA/g	-	[89]
NaCrNb(PO ₄) ₃ /C	0.8–3.0	Sol-gel Pechini-type polymer	Submicron particles	171, 0.1C	82.6%/1C/300	[90]

complex technique						
Na₂Fe_{1.5}Mn_{1.5}(P O₄)₃@SNC	0.03-3.0	Hydrothermal	3D Urchin- like	774, 0.05C	44.9%/0.3C/ 300	This work

The impact of morphology, synthesis techniques, and heteroatom doping on the electrochemical performance of phosphate-based SIB materials is shown in **Table 4.6**. Among these materials, C@NaTi₂(PO₄)₃ (256.1 mAh/g) and NaSn₂(PO₄)₃ (266 mAh/g) demonstrated the highest capacities due to their advantageous nanostructures. Additionally, over 10,000 cycles, C@NaTi₂(PO₄)₃ retained 85.4%, underscoring the significance of carbon coating and nanoscale design. In contrast to larger structures like NaCrNb(PO₄)₃/C (171 mAh/g) and Na_{1.5}V_{0.5}Nb_{1.5}(PO₄)₃ (140 mAh/g), which offered moderate capacity but better cycling, NaTi₂(PO₄)₃@C (nanocubes) delivered 225 mAh/g with good stability. NaSn₂(PO₄)₃ exhibited significant fading in spite of its high initial capacity. Materials with lower capacities, such as Na₃MnTi(PO₄)₃/C-N and Na₃Co_{0.5}Mn_{0.5}Ti(PO₄)₃, exhibited good stability. The novel NFMP@SNC, developed in this work, achieved the highest capacity of 774 mAh/g at 0.05C, owing to S/N co-doping, which enhances electronic conductivity and ion diffusion. Additionally, its unique 3D urchin-like morphology, formed through hydrothermal synthesis, further improved performance by achieving a high surface area and short diffusion paths. However, it retained only 44.9% after 300 cycles at 0.3C, indicating that while the architecture supports high initial capacity, improvements in structural stability are needed for long-term cycling. These comparisons highlight that heteroatom doping, advanced morphologies, and optimised synthesis are critical for achieving high-performance SIB electrodes.

4.3.2.2 CV Analysis

The CV profiles represented in **Figure 4.22 (a)** of all samples at a sweep rate of 0.2 mV s⁻¹ over the voltage range of 0 to 3 V vs. Na/Na⁺

display characteristic redox peaks attributed to the redox activities of Fe and Mn ions.

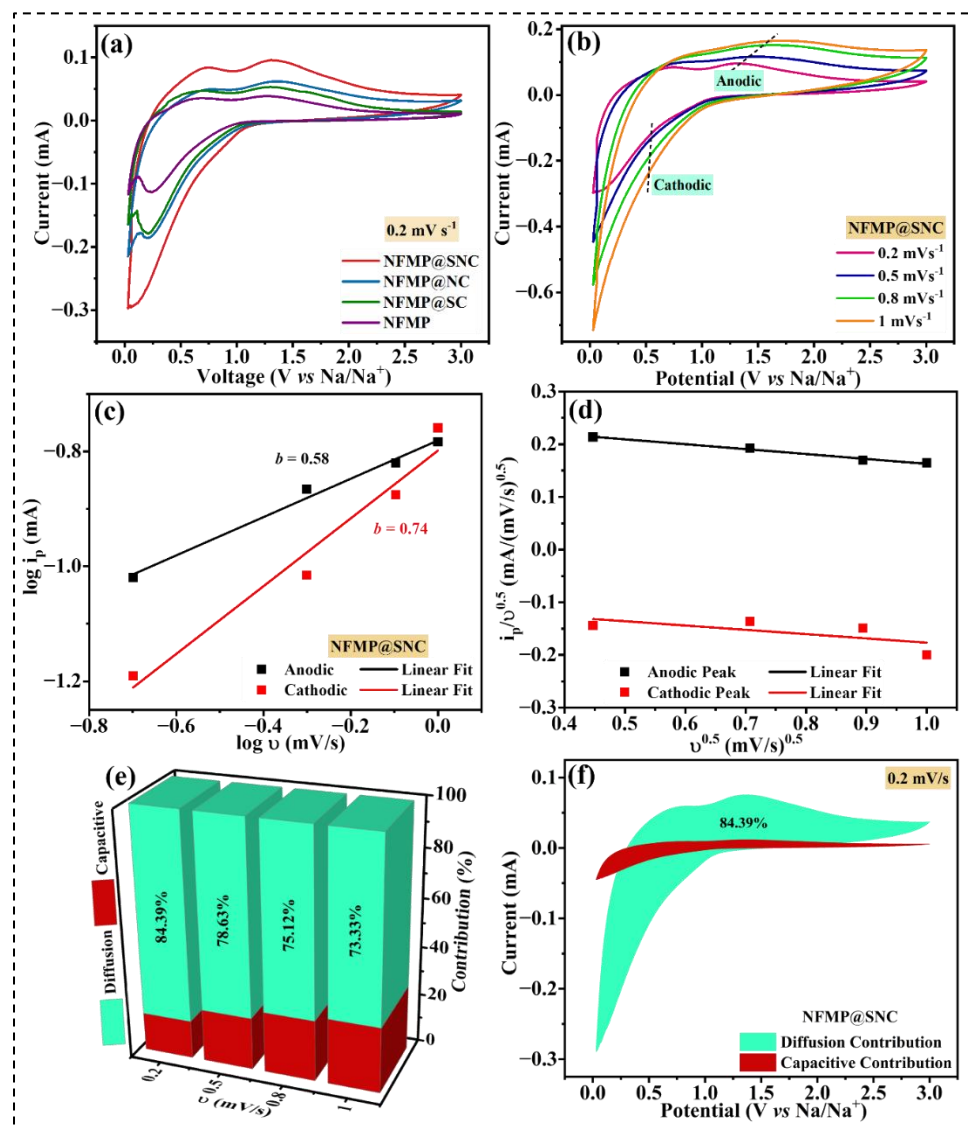


Figure 4.22 (a) CV profile of all four samples recorded at 0.2 mV s⁻¹, (b) CV profile of NFMP@SNC at various scan rates, (c) Plot of log i_p vs log v , (d) Plot of log $i_p/v^{0.5}$ vs $v^{0.5}$, (e) Sodium storage contribution ratio of capacitive and diffusion-controlled capacities of NFMP@SNC at various scan rates, (f) CV curves of NFMP@SNC with the capacitive and diffusion-controlled currents at 0.2 mV s⁻¹.

In these materials, the electrochemical processes are mainly governed by the Fe²⁺/Fe³⁺ and Mn²⁺/Mn³⁺ redox couples, essential for sodium-ion

intercalation and deintercalation. The anodic peaks observed around 0.5 V and the corresponding cathodic peaks around 0.2 V in the CV profiles are associated with the reversible $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox reaction, where Fe^{2+} ions are oxidized to Fe^{3+} during charging (anodic scan) and reduced back to Fe^{2+} during discharging (cathodic scan). The $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox activity, generally observed at higher potentials, contributes to the secondary redox reactions, enhancing the overall capacity of the material. However, due to partial activation, the Mn redox peaks are less prominent than those of Fe, resulting in the primary focus on the Fe redox activity in these materials.

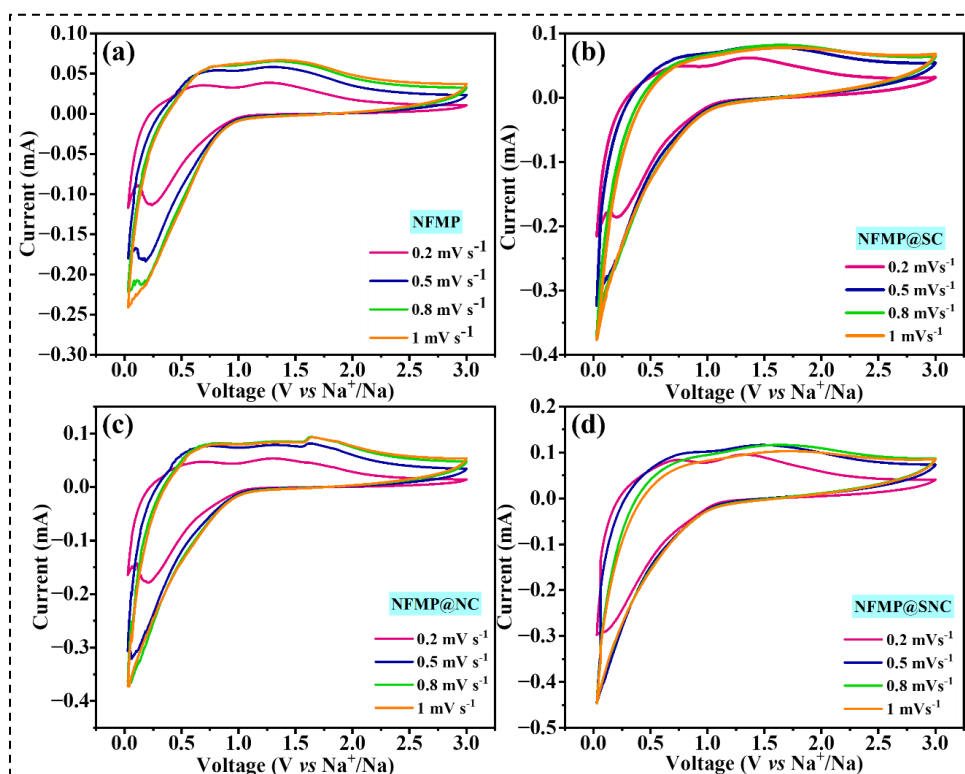


Figure 4.23 CV profile at different scan rates for (a) NFMP, (b) NFMP@SC, (c) NFMP@NC, and (d) NFMP@SNC.

Although Mn^{2+} partially contribute to redox reactions, its presence indirectly optimizes the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple by modifying the local electronic environment.[82] This results in improved electrochemical reversibility and more efficient charge storage. Additionally, the presence of Mn makes the NFMP structure more stable, as Mn^{2+} helps to balance the crystal structure and minimize Jahn-Teller distortions.[83] This improved

stability prevents the framework from breaking down over long-term cycling, thereby enhancing the durability and performance of the material in SIBs.

The CV profiles for all sample at various scan rates are shown in **Figure 4.23**. The CV profiles reveal that NFMP@NC and NFMP@SNC exhibit sharper, more intense redox peaks than the pristine NFMP and NFMP@SC. This improvement is ascribed to the improved electrical conductivity and ionic diffusion pathways facilitated by N in NFMP@NC and dual N-S doping in NFMP@SNC. N doping introduces additional active sites and improves the electronic structure, enhancing charge transfer kinetics for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox process. In NFMP@SNC, S doping further amplifies this effect by modifying the surface chemistry, creating additional defects and active sites that promote faster sodium-ion transport. The shape of the CV curves also supports these observations. Both NFMP@NC and NFMP@SNC exhibit a particular shape at higher voltages, indicating enhanced capacitive behaviour, which supplements the faradaic redox processes. This capacitive contribution and sharp redox peaks suggest an improved sodium storage mechanism involving bulk intercalation (associated with Fe and Mn redox activities) and surface adsorption. Among the samples, NFMP@SNC demonstrates the highest current response and most distinct redox peaks, implying that dual doping with N and S is particularly effective in activating both Fe and Mn redox centres, thereby maximizing capacity and reversibility. Moreover, the presence of Mn^{2+} also works synergistically with the N and S co-doped carbon layer, which provides an interconnected conductive network, ensuring efficient electron transport and minimizing internal resistance. NFMP@SC, on the other hand, shows intermediate behaviour, with S doping alone providing some benefits but not as significantly as N doping. These findings underscore the synergistic effect of dual heteroatom doping on the electrochemical performance of NFMP, rendering NFMP@SNC a promising material for SIBs.

The charge storage kinetics of NFMP@SNC were investigated quantitatively through CV. CV measurements were recorded at sweep rates varying from 0.2 to 1 mV/s (**Figure 4.22 (b)**). The relationship between the scan rates and respective current peaks is analyzed using the following power law[81] equation (2.6). The calculated b values for the anodic and cathodic peaks were found to be 0.58 and 0.74, respectively, as shown in **Figure 4.22 (c)**. These b values indicate that the charge storage mechanism involves both diffusion-controlled and capacitive processes.[91] Furthermore, the current response was deconvoluted into capacitive and diffusion-controlled contributions using equation (2.8).[81]

The values of k_1 and k_2 are determined from the linear fitting of the graph of $v^{0.5}$ vs $i_p/v^{0.5}$, as represented in **Figure 4.22 (d)**. Furthermore, the relative mechanism contribution is calculated exclusively for the anodic peaks. The contributions of these mechanisms at different scan rates are presented in **Figure 4.22 (e)**. NFMP@SNC exhibits a diffusion-controlled contribution of 84.39% at 0.2 mV/s, gradually decreasing to 73.33% at higher scan rates. This trend aligns with the CV profiles of NFMP@SNC at varying scan rates. The green-shaded region in the CV curve at 0.2 mV/s shown in **Figure 4.22 (f)** highlights the diffusion-controlled mechanism, while the brown-shaded region corresponds to the capacitive mechanism. These results confirm that the sodium storage process in NFMP@SNC is predominantly diffusion-controlled, with a capacitive contribution. Overall, the mixed storage mechanism can be attributed to the porous urchin-like architecture of NFMP@SNC, which features a high specific surface area. This structure provides abundant active sites for Na^+ intercalation and adsorption while simultaneously reducing ion diffusion pathways, achieving excellent rate capability and long cycling performance.

4.3.2.3 EIS analysis

This section determines the sodium ion diffusion parameters using the graphical interpretation of AC impedance spectra and the Nyquist plot. **Figure 4.24 (a & b)** depicts the Nyquist plot of all the NFMP composite

electrodes analyzed at OCV before and after stability testing. Each plot represents the semicircle in the high-to-medium frequency region with a linear portion in the low-frequency region, which is fitted using an equivalent electrochemical circuit. The semicircle on the Z' axis of the plot related to the combination of charge transfer resistance (R_{ct}), indicating the ease of the Na^+ sodiation and desodiation and SEI layer impedance (R_{SEI}). Samples with a smaller semicircle suggest lower charge transfer resistance and better conductivity.[92] The linear region at low frequencies is linked to the Na^+ diffusion in the anode material. The R_{ct} values of all the electrodes are tabulated in **Table 4.7**.

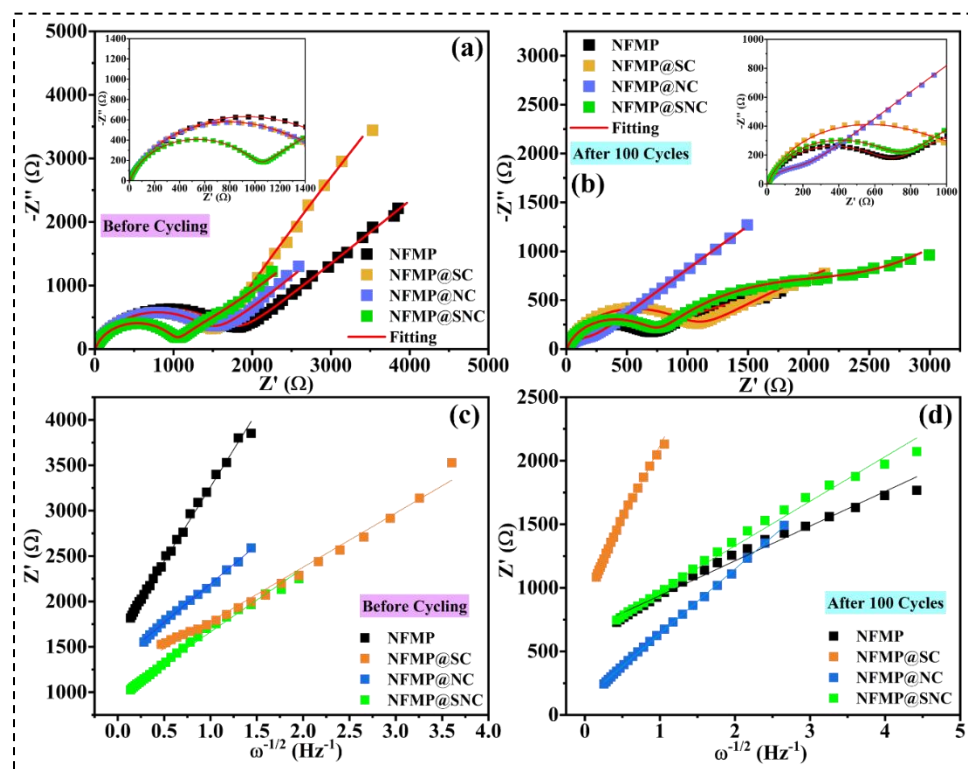


Figure 4.24 Nyquist plots of all samples (a) before and (b) after stability testing, Plot of Z' vs $\omega^{-1/2}$ for all samples (c) before and (d) after stability testing.

The lower R_{ct} of NFMP@SNC, which is 615.1 Ω , is related to the S, N doped carbon structure, which has additional defects and active sites

that enhance the electronic conductivity and facilitate the transport of Na^+ . This shows that the R_{ct} values decrease with the heteroatom doping showing increasing Na^+ intercalation, which increases from NFMP@SC and NFMP@NC to NFMP@SNC due to the irreversible SEI layer formation. Further, to reveal the kinetics of the electrode process, the Na^+ diffusion coefficient of all the electrodes was calculated from the relationship shown by equation (4.2)[69] in the low-frequency region.

$$Z' \propto \sigma \omega^{-1/2} \quad (4.2)$$

The linear relationship between Z' and $\omega^{-1/2}$ is represented in **Figure 4.24 (c & d)**, where the sloping line at low frequencies is attributed to the Warburg impedance, which is related to the diffusion of Na^+ within the bulk of the electrode material. Samples with a steeper slope in this region have higher diffusion coefficients, calculated from the Warburg region slope. The Na^+ diffusion coefficients were calculated using the following equation (2.13).[69] At OCV, the estimated Warburg factors for NFMP, NFMP@SC, NFMP@NC and NFMP@SNC samples are 1640.878, 701.255, 853.761 and 597.521, respectively. Thus, the corresponding Na^+ diffusion coefficients (D_{Na^+}) are calculated using the equation mentioned above are 3.734×10^{-18} , 1.308×10^{-17} , 1.801×10^{-17} , and $7.209 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$, respectively.

Further, the study reveals that surface engineering is crucial in Na^+ diffusion. Notably, the D_{Na^+} slightly increases with the cycle due to the electrochemical activation while charging-discharging. The improved electrochemical performance of NFMP@SNC and NFMP@NC can be attributed to the higher D_{Na^+} and the shorter pathways for sodium ion transfer. This observation aligns with the charge and discharge results. The NFMP@SNC and NFMP@NC samples with more significant D_{Na^+} have higher capacity when charged, discharged at higher rates, and possess better rate performance. This is because cycling can sometimes induce microstructural changes, such as slight increases in porosity or cracks in the

electrode material. These changes can create additional pathways or channels, enhancing ion diffusion through the material.

Table 4.7 EIS parameters for all NFMP samples fitted with electrochemical circuit before and after stability testing.

	Before Cycling				After 100 Cycles			
	NFMP	NFMP@ SC	NFMP@ NC	NFMP@ SNC	NFMP	NFMP@ @SC	NFMP@ NC	NFMP @SNC
Rs (Ω)	4.736	3.145	11.13	7.63	4.583	4.328	4.014	6.849
R_{SEI} (Ω)	581	469.7	407	476.7	376.9	459.4	83.13	454.6
R_{ct} (Ω)	1 205	1178.8	793.4	615.1	408	854.93	161.9	654
Q1 ($F s^{-1}$)	1.652×10^{-6}	6.275×10^{-6}	1.92×10^{-6}	3.108×10^{-6}	7.984×10^{-6}	6.754×10^{-6}	8.088×10^{-6}	4.473×10^{-6}
Q2 ($F s^{-1}$)	5.623×10^{-6}	0.3884×10^{-3}	3.568×10^{-6}	0.4047×10^{-3}	0.672×10^{-3}	0.1764×10^{-3}	29.86×10^{-6}	0.2996×10^{-3}
W (Ωs^{-2})	959.2	3 720	1 253	799.1	196.6	944.3	2 112	299.3
σ	1640.878 ± 20.479	701.255 ± 12.945	853.761 ± 11.484	597.521 ± 14.465	273.231 ± 7.409	1181.0 64 $\pm$ 20.485	510.577 ± 2.348	351.17 6 $\pm$ 7.196
D_{Na+} ($cm^2 s^{-1}$)	3.734×10^{-18}	1.308×10^{-17}	1.801×10^{-17}	7.209×10^{-17}	1.346×10^{-17}	1.845×10^{-17}	5.037×10^{-17}	5.217×10^{-17}

4.3.3 Post-electrochemical analysis

The FESEM analysis of all sample electrodes pre- and post-electrochemical battery testing is essential for the comprehensive understanding of the behaviour of the materials under operational conditions, providing significant insights into the relationship between electrode microstructure and overall battery performance. After stability testing, all cells were disassembled inside the glovebox, and the composite electrodes were retrieved and rinsed with EC/DMC solvent to eliminate any remaining electrolyte. Subsequently, the electrodes were vacuum-dried and prepared for further analysis. **Figure 4.25 (a-d)** shows the FESEM images of the surface morphology of NFMP, NFMP@SC, NFMP@NC and NFMP@SNC before the battery testing. **Figure 4.25 (a)** reveals the pristine

NFMP with its characteristic rough and irregular particle morphology, while **Figure 4.25 (b and c)** exhibit comparatively compact surface morphology due to the S and N coating, respectively.

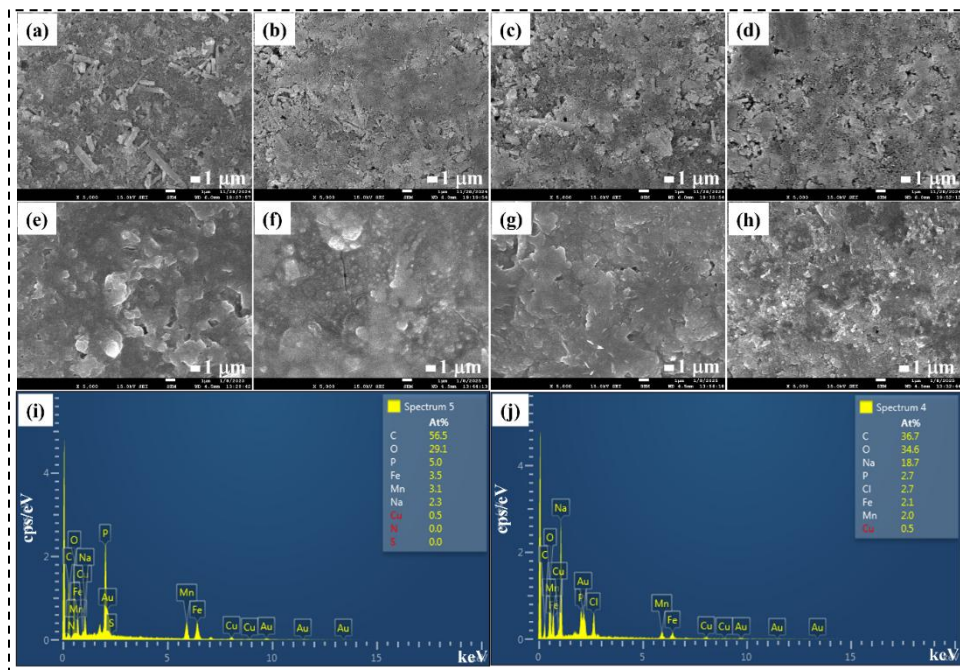


Figure 4.25 FESEM images of NFMP, NFMP@SC, NFMP@NC and NFMP@SNC (a-d) pre-electrochemical testing and (e-h) post-electrochemical testing, respectively. EDX analysis of NFMP@SNC (i) pre-electrochemical and (j) post-electrochemical testing.

Furthermore, NFMP@SNC (**Figure 4.25 (d)**) highlights a combined effect of N and S doping, resulting in a smoother and denser surface morphology. This surface morphology of all samples, where the spaces between particles are crucial for accommodating the electrolyte, can facilitate Na-ion diffusion.[93,94] After cyclic stability testing, the morphological changes highlight the impact of long-term cycling on the structural integrity of the materials. **Figure 4.25 (e)** shows that pristine NFMP exhibits severe structural degradation, with increased porosity and particle detachment, whereas NFMP@SC, NFMP@NC, and NFMP@SNC retain more stable morphologies as depicted in **Figure 4.25 (f-h)**, respectively.

NFMP@SNC, in particular, demonstrates the least degradation, maintaining a uniform and coherent surface, which suggests improved structural stability due to the synergistic effects of S and N doping. Furthermore, the EDX spectra in **Figure 4.25 (i and j)** provide quantitative elemental compositions before and after cycling for NFMP@SNC. Initially, the material shows high carbon and oxygen content with minor contributions from Na, P, Fe, and Mn, reflecting the addition of conductive additives. After cycling, the decrease in carbon content and a slight increase in oxygen signify partial oxidation or electrolyte interaction, while consistent Na, P, Fe, and Mn levels confirm structural retention of the underlying material. Additionally, increased Na indicates the complex reaction between the electrode material and NaClO₄ electrolyte. The S content before and after cycling is negligible, emphasizing its role in doping rather than as a significant compositional element.

4.4 Plausible Charge Storage Mechanism

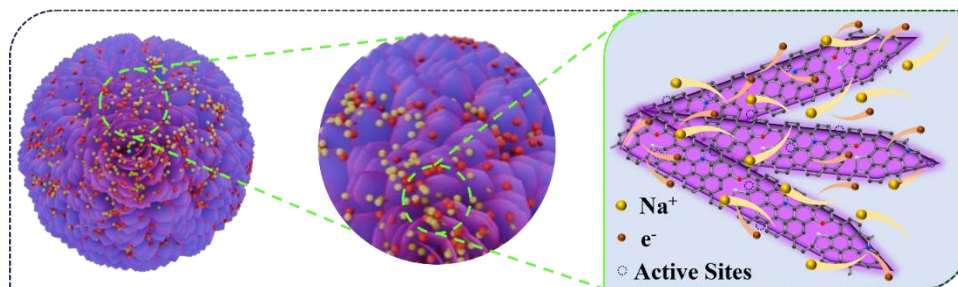
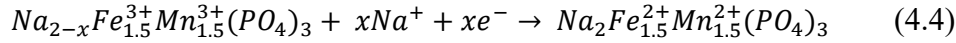
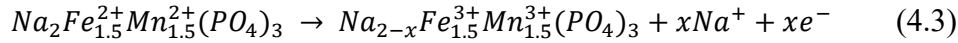


Figure 4.26 Illustration of charge storage mechanism in NFMP@SNC.

The Alluaudite framework of NFMP provides a stable 3D network of FeO₆/MnO₆ octahedra and PO₄ tetrahedra, which are bonded through covalent interactions, enabling structural integrity and rapid Na⁺ diffusion through its large interstitial sites.[95] While, the Na⁺ storage mechanism of the phosphate material for SIBs is explained by in-situ XRD analysis for anode materials such as Na_{1.5}V_{0.5}Nb_{1.5}(PO₄)₃ and Na₃V₂(PO₄)₃. [85,96] The 3D urchin-like morphology of NFMP also plays a crucial role in the charge storage mechanism, as illustrated in **Figure 4.26**. This unique architecture

has radially aligned structures that help provide a high surface area, enabling sufficient active sites for Na^+ intercalation and deintercalation. The porous interconnected structure allows efficient electrolyte penetration, facilitating rapid ion diffusion and reduced diffusion pathways. Moreover, the radial alignment ensures the direct and low-resistance pathways for electron transport to the current collector, improving the conductivity of the NFMP and maintaining structural integrity, as evidenced by EIS analysis. Further, NFMP shows the mixed electrochemical redox activities of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and partial $\text{Mn}^{2+}/\text{Mn}^{3+}$, which are responsible for the increased capacity of NFMP. The corresponding reactions while discharging and charging can be written as **eq. (6)** and **eq. (7)**:



Moreover, this architecture synergizes intercalation-dominated ion storage with pseudo-capacitive contributions, balancing high capacity and fast kinetics as determined from the CV and GCD analysis. In NFMP@SNC, the doped carbon coating improves the electrical conductivity of the low-conductive phosphate framework. Additionally, N doping increases the electron density and active sites on the carbon surface, and S doping introduces defects in the carbon lattice, further enhancing charge transfer kinetics. Also, this coating layer acts as a protective layer, enhancing structural integrity and contributing to additional pseudo-capacitive mechanisms. Overall, the combination of these features enables N, S-doped carbon-coated NFMP to deliver improved capacity, superior rate capability, and long-term cycling stability, making it a highly efficient anode material for SIBs.

4.5 Theoretical study

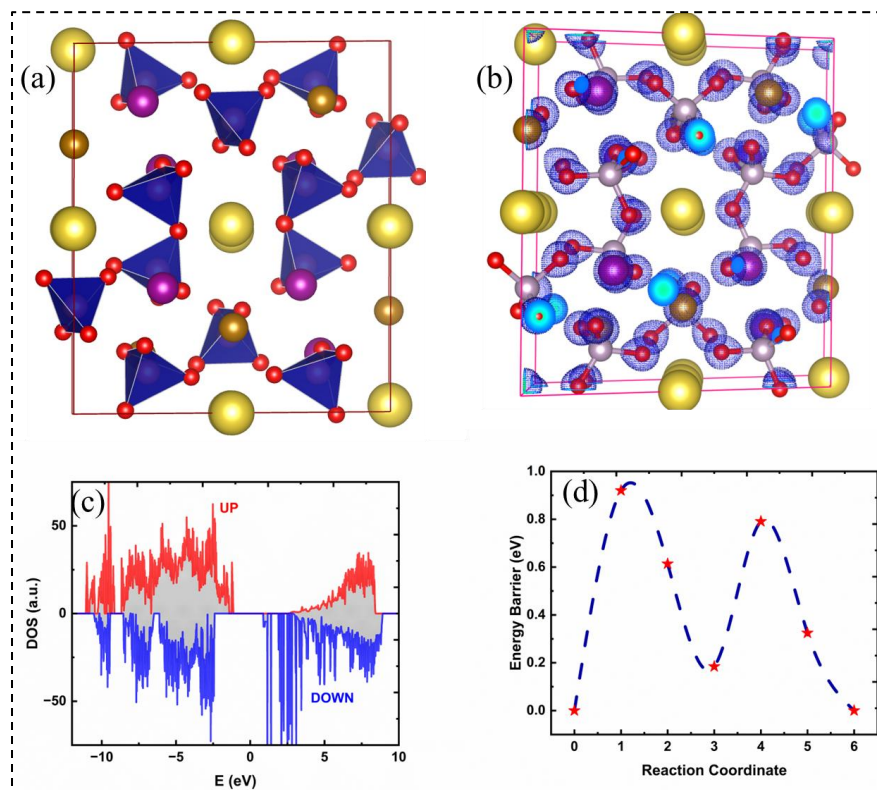


Figure 4.27 (a) Crystal structure of NFMP, (b) Representation of charge density distribution in NFMP, (c) DOSs and, (d) Na^+ diffusion energy profile with calculated migration barriers for NFMP.

Density functional theory (DFT) calculations were performed to gain further insight into the structural and electronic properties of NFMP, including charge density distribution, density of states (DOSs), and Na-ion migration energy barriers. **Figure 4.27 (a)** depicts the optimised crystal structure of NFMP, with lattice parameters $a = 11.920 \text{ \AA}$, $b = 12.611 \text{ \AA}$, and $c = 6.638 \text{ \AA}$, and with angles $\alpha = 90.16^\circ$, $\beta = 114.80^\circ$, and $\gamma = 89.4927^\circ$. A close agreement between our simulations and experimentally observed lattice parameters confirms the accuracy of the computational model employed to represent the NFMP structure. A uniform charge density distribution is observed in NFMP, as illustrated in **Figure 4.27 (b)**. This uniformity accounts for the observed stable electrochemical performance, as it facilitates consistent Na ion diffusion, balanced redox activity of Fe

and Mn centres, and reduced internal resistance, each contributing to enhanced electrical conductivity and long-term cycling stability. Further, we evaluated the DOSs, as shown in **Figure 4.27 (c)**. A narrow band gap of approximately 1.8 eV is observed in NFMP, which contributes to enhanced electrical conductivity and supports favorable electrochemical performance. Lastly, we evaluated the diffusion pathway and corresponding energy barrier, as shown in **Figure 4.28** and **Figure 4.27 (d)**, respectively. A migration energy barrier of approximately 0.9 eV was found for Na-ion diffusion. This value is in close agreement with that reported for a similar material, where a barrier of 0.77 eV was observed.[97]

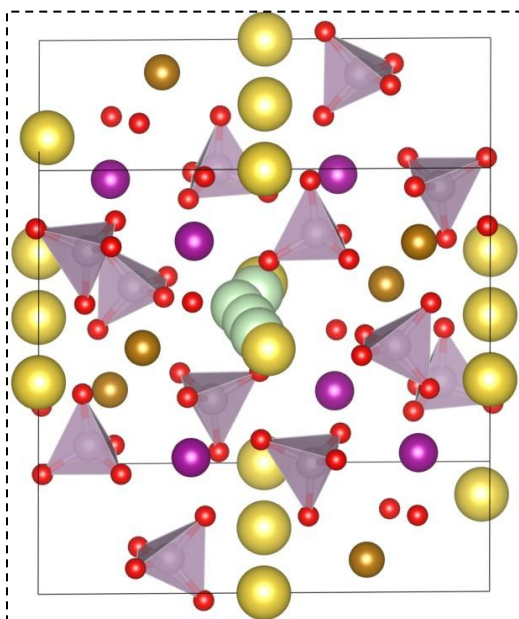


Figure 4.28 Na⁺ ion migration pathway in NFMP.

4.6 Conclusions

In summary, NFMP@SNC with an urchin-like morphology is successfully synthesized via the hydrothermal method. The pyrolysis of urea and thiourea generated volatile species that facilitated the formation of a porous structure while simultaneously introducing N and S dopants into the carbon layer. These dopants induced defects and active sites in the carbon coating, enhancing the electrical conductivity of the material,

accelerating charge transfer, and improving Na⁺ diffusion between the electrode and electrolyte. Further, Raman and XPS data analyses confirmed that N doping created additional defects and active sites, while S doping introduced sulfur-containing functional groups that modified the electronic structure and surface chemistry of the carbon matrix, collectively promoting sodium-ion transport. The NFMP@SNC electrode exhibited exceptional electrochemical performance when used as an anode material for SIBs for the first time. Notably, it delivered a specific 774.55 mAh/g capacity at 0.05C with remarkable rate capability. Additionally, it demonstrated a cyclic stability of 48.49% over 100 cycles at 0.2C. EIS analysis revealed a superior D_{Na^+} of 7.209×10^{-17} cm²/s for NFMP@SNC, surpassing other composites studied in this chapter. Moreover, DFT calculations provided insight into the electronic structure and ion transport by analyzing the band structure, DOS, charge density distribution, and Na⁺ diffusion energy barriers of NFMP. These theoretical results support the experimental observations. Overall, this work offers an efficient and cost-effective strategy for the in-situ formation of conductive, heteroatom-doped carbon layers on electrode materials. The theoretical and experimental findings provide a pathway for advancing anode materials for SIBs and other next-generation secondary batteries. Moreover, the heteroatom-doping approach demonstrated here can be extended to other anode materials, further advancing SIB technology and supporting the development of sustainable energy storage systems.

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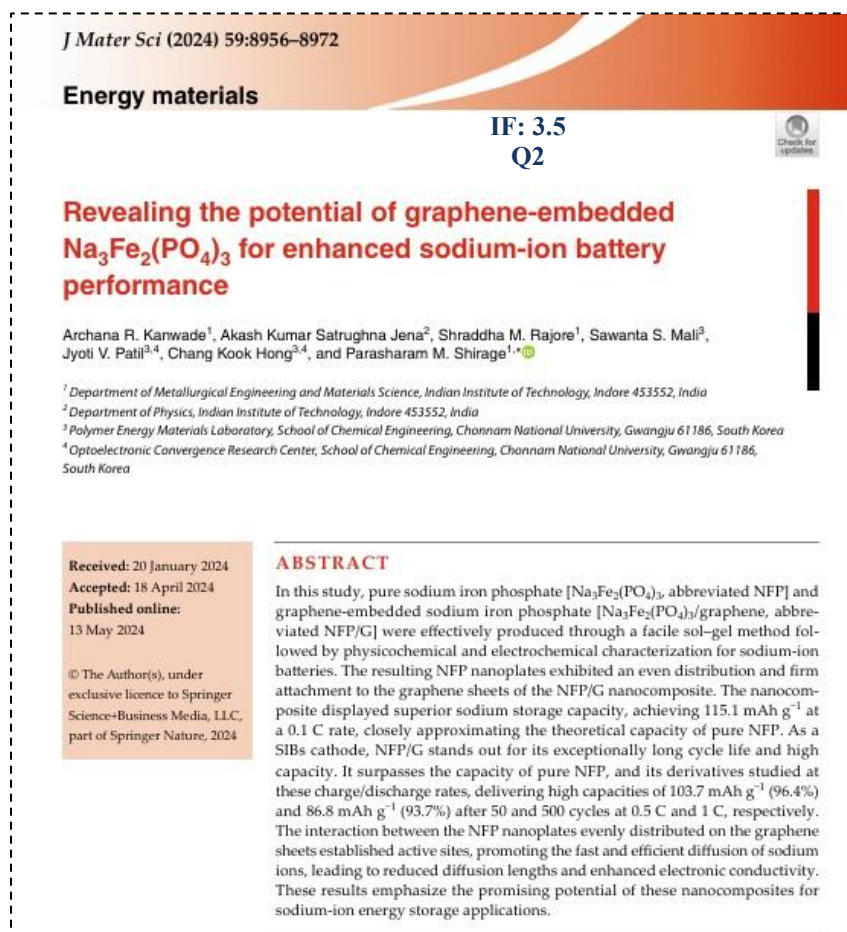
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Chapter 5

Graphene-Embedded $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ for Enhanced Sodium-Ion Battery Performance



In Chapter 4, vanadium is completely replaced by Fe and Mn in combination with heteroatom engineering. Although the resulting material

demonstrated dual functionality as both cathode and anode, its cathodic performance exhibited relatively low capacity, indicating the need for further enhancement. To address this limitation, this chapter focuses on developing a fully Fe-based system, where V is entirely substituted with Fe, along with the formation of a graphene-based composite to improve electrochemical performance. In this chapter, pure $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ (NFP) and graphene-embedded $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ (NFP/G) were effectively produced through a facile sol-gel method, followed by physicochemical and electrochemical characterization for SIBs. The resulting NFP nanoplates exhibited an even distribution and firm attachment to the graphene sheets of the NFP/G nanocomposite. The nanocomposite displayed superior sodium storage capacity, achieving 115.1 mAh g^{-1} at 0.1 C rate, closely approximating the theoretical capacity of pure NFP. It surpasses the capacity of pure NFP, and its derivatives studied at these charge/discharge rates, delivering high capacities of 103.7 mAh g^{-1} (96.4%) and 86.8 mAh g^{-1} (97.6%) after 50 and 500 cycles at 0.5C and 1C , respectively. The interaction between the NFP nanoplates evenly distributed on the graphene sheets established active sites, promoting the fast and efficient diffusion of sodium ions, leading to reduced diffusion lengths and enhanced electronic conductivity. These results emphasize the promising potential of these nanocomposites for sodium-ion energy storage applications.

5.1 Introduction

As discussed in Chapter 1, iron phosphates are considered the least hazardous materials to be utilized in SIBs because of their composition, which includes abundant and ecologically inert components[1]. As SIB cathode materials, FePO_4 , NaFeP_2O_7 , NaFePO_4 , and other conventional iron-based phosphate cathode materials have all been thoroughly researched[2–6]. The high theoretical capacity, thermodynamic stability, and affordability of olivine NaFePO_4 set it apart from the competition. Since the Na^+ ions are much larger than the Li^+ ions, producing olivine- NaFePO_4 using conventional solid-state reaction methods is difficult and results in structural changes to maricite- NaFePO_4 with inactive Na^+ ions. Unfortunately, the large maricite NaFePO_4 is not electrochemically active because it does not have appropriate cationic transport channels [26,27]. The $\text{Na}_2\text{FePO}_4\text{F}$ lattice's F^- anions substantially increase the ionicity in strong covalent connections, causing an inductive action that stabilizes the $\text{Fe}^{2+}/\text{Fe}^{3+}$ state and raising energy density and reduction-oxidation potentials. The ion exchange synthesis of $\text{Na}_2\text{FePO}_4\text{F}$ was described in detail by Ellis and colleagues [28]. This compound has interesting electrochemical characteristics, which are especially beneficial for Na^+ migration and mobility. This results in increased stability and longer cycle life [28]. However, its slow kinetic reaction kinetics and electrical conductivity make it unsuitable for use in batteries [29]. In 2013, Barpanda et al. presented $\text{Na}_2\text{FeP}_2\text{O}_7$, which functions as a cathode material in SIBs with a high working potential of 3.1V and no volumetric impact. It is distinguished by bigger pyrophosphate ligands and correspondingly larger pores [30]. However, because of the high pyrophosphate element, it has a low theoretical capacity of 90 mAh g^{-1} , which obviously limits its applicability for energy storage. In addition, as electrode materials for SIBs, Sodium Super-Ionic Conductor (NASICON) compounds with the formula $\text{Na}_3\text{MM}'(\text{PO}_4)_3$ (where M and M' are transition elements) have demonstrated outstanding electrochemical properties, conductivity, and

thermal stability[7–9]. In the 3D framework of NASICON materials, the linked channels generated by the corners of the MO_6 octahedron and PO_4 tetrahedron enable the efficient and reversible insertion and extraction of Na^+ ions. Owing to their unusual transport behaviour and ability to function as solid electrolytes in electrochemical devices, these materials have drawn enormous interest, and current research is still examining their capabilities[10–12].

$\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ (hereafter will be referred as NFP) has a higher ion channel radius of 6.487 Å and is a unique NASICON-like substance reported by Masquelier *et al.* The crystal structure model of NFP was ideal for Na^+ insertion and deinsertion because of its outstanding structural stability and low manufacturing costs, making it an attractive cathode material for industrial applications. By developing an NFP cathode for an SIB, Liu *et al.* attained a specific discharge capacity of 61 mAh g⁻¹ at 1C[13]. Qiu *et al.* studied the use of NFP as an anode for an aqueous SIB and reported that NFP performed satisfactorily in terms of rate and cycle stability[14]. These investigations showed that NFP can insert Na^+ reversibly, but NFP possesses low electrical and ionic conductivity, leading to limited cyclic performance and decreased capacity retention.

Recently, various methods for synthesis and processing, such as reducing the particle size, introducing foreign atoms such as K and Mn, and applying carbon coatings, have been investigated to overcome these limitations[15–17]. Among the carbon coating materials, graphene nanosheets, characterized by a single-atom-thick honeycomb carbon lattice, are widely recognized as the most effective conductive additive for hybrid nanostructured electrodes. This recognition is due to their exceptional electronic conductivity, impressive structural flexibility, and extensive surface area. Numerous electrode materials, including WO_3 [18], $\text{Fe}(\text{PO}_3)_2$ [19], and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ [19], have been enriched with graphene nanosheets, improving the cycle stability and rate performance. By adding

a conductive carbon layer to NFP, Rajagopalan *et al.* could activate the $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox reaction, which increased the capacity to 109 mAh g^{-1} [17]. This difference was attributed to the high conductivity and 3D conductive network of carbon. To the best of our knowledge, no research has been performed on NFP/G composites or their electrochemical characteristics. As a result, simple NFP/G nanocomposites with outstanding extended cycling performance at high rates should be studied.

Herein, a facile and cost-effective synthetic approach was used, and an extensive electrochemical evaluation of the composite was performed to demonstrate the viability of NFP/G as a feasible cathode material for SIBs based on an organic electrolyte solution. The 3D network of graphene and NFP primary nanoparticles interlaces in this composite, allowing quick electron migration and Na^+ diffusion across the nanoplate secondary particles, ensuring its high specific capacity and outstanding cycling stability.

5.2 Experimental section

5.2.1 Materials synthesis

The experimental procedures for selecting precursor chemicals, determining the synthesis strategy, preparing the slurry, and fabricating the NFP/G cathode material were described in Chapter 2. In this study, NFP and NFP/G cathode materials were synthesized using the sol-gel method, and the influence of graphene on the structural and electrochemical properties of the material was investigated. The synthesized samples were systematically characterized using several advanced physicochemical techniques to analyze their structural, morphological, and compositional features.

5.2.2 Coin cell fabrication

For electrochemical evaluation, a CR2032-type sodium half-cell configuration was assembled in a nitrogen-filled glove box. 1 M NaClO₄ dissolved in a 1:1 volume ratio of EC and PC was used as the electrolyte. After cell assembly, the electrochemical performance was evaluated through CV, EIS, and GCD.

5.3 Results and Discussions

5.3.1 Physicochemical characterizations

5.3.1.1 Thermogravimetric analysis

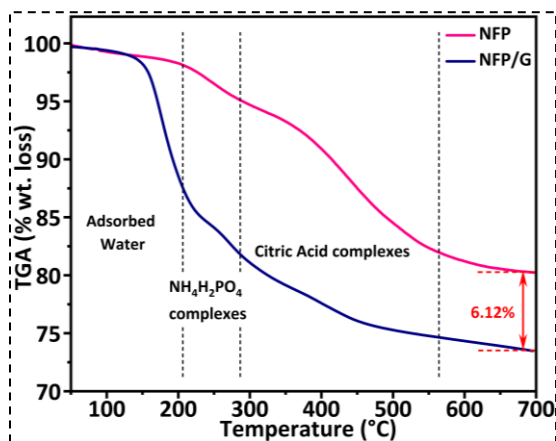


Figure 5.1 TGA curves of NFP and NFP/G.

The thermal characterization of the precursor samples of NFP and NFP/G is illustrated in the **Figure 5.1**. Notably, the weight loss exhibits a three-stage process in both samples. The first stage involves the evaporation of absorbed water, occurring below 206 °C. Subsequently, between 206°C and 286°C, thermal decomposition of ammonium dihydrogen phosphate complexes initiates the formation of NFP in both samples. As the temperature rises further, up to 563°C, citric acid decomposes completely. Citric acid is nearly completely decomposed at around 480°C, which can be explained by the high amount of oxygen in NFP, which can be released as CO or CO₂ due to reduction reactions [44]. The mass loss occurring from 480°C to 563°C is attributed to the decomposition of oxygen-containing groups and carbon oxidation from graphene in NFP/G [45]. Beyond 563°C, the weight remains stable. Consequently, the annealing temperature was

optimized at 600°C to achieve the particular morphology of the NFP particles. Based on the total weight loss of NFP/G composites, the weight ratio of graphene in the composites is determined to be 6.12 wt% [46].

5.3.1.2 Structural analysis: XRD

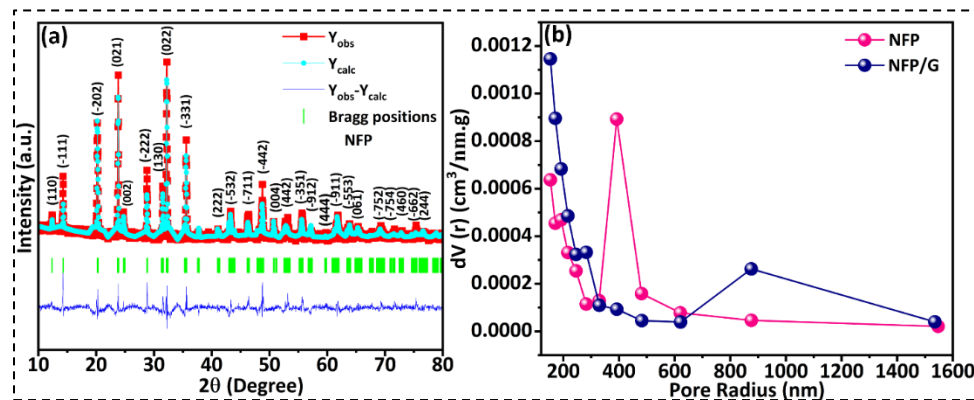


Figure 5.2 (a) Rietveld refinement of NFP. **(b)** pore size distribution of NFP and NFP/G by BJH method.

The XRD patterns for both the NFP and NFP/G nanocomposites are depicted in **Figure 5.3 (a)**. The presence of prominent peaks in these XRD patterns confirms the crystalline nature of both materials, as they primarily exhibit monoclinic crystal structure with the space group C2/c. Notably, there are no observable diffraction peaks related to impurities, and all the identified peaks are in excellent agreement with the characteristics of pure NFP (JCPDS No. 45-0319). The crystal lattice parameters for NFP were precisely determined using the FullProof Suite software tool (**Figure 5.2 (a)**). The calculated lattice parameters are $a = 15.070 \pm 0.007$ Å, $b = 8.740 \pm 0.005$ Å, $c = 8.724 \pm 0.009$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 125.1 \pm 0.1^\circ$, and these values closely match previously reported data for NFP[3439]. In the composite sample, no peaks associated with graphene were found. This difference might be due to the minimal quantity of graphene in the NFP crystal structure.

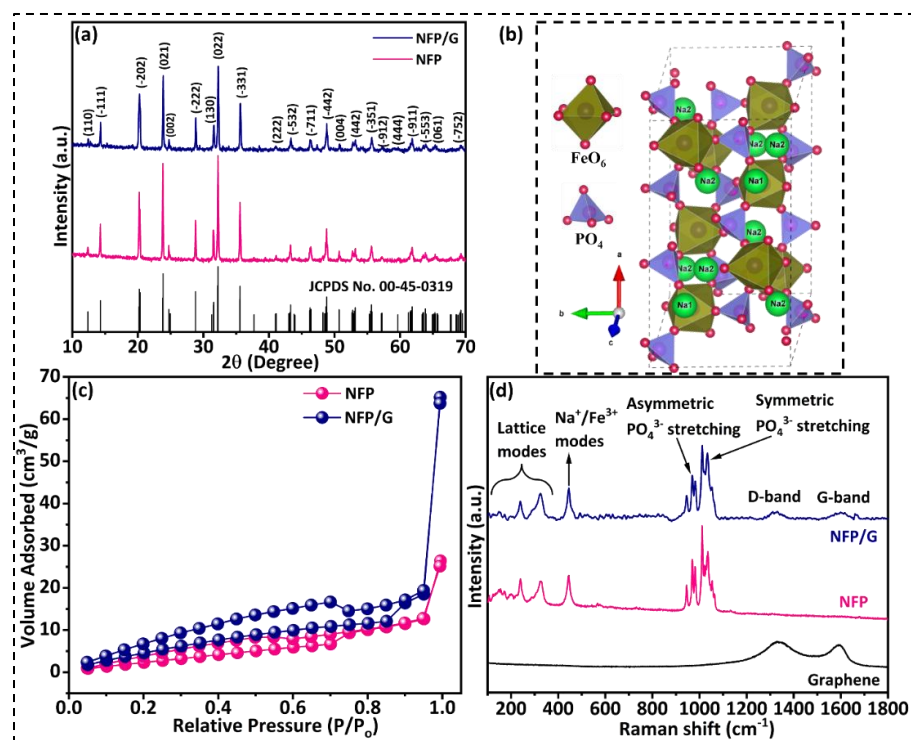


Figure 5.3 (a) XRD patterns of NFP and NFP/G. (b) Schematic of the crystal structure of NFP. (c) BET adsorption/desorption isotherm plot. (d) Raman spectra of pure graphene, NFP and the NFP/G composite.

A detailed visualization of the crystal structure of NFP, presented in **Figure 5.3 (b)** and generated using VESTA software, elucidates its composition. It comprises interconnected FeO₆ octahedra and PO₄ tetrahedra, sharing corners and forming an intricate three-dimensional network. Specifically, the FeO₆ octahedra are linked through shared edges within NFP, generating dimers that combine to form two-dimensional layers. These layers are further interconnected via PO₄ tetrahedra to construct a robust three-dimensional framework, with the stability of the crystal structure maintained through P-O and Fe-O bonds. An essential feature of the structure of NFP is the deliberate positioning of Na⁺ ions within the framework channels. A thorough comprehension of the crystal arrangement of NFP is imperative for acquiring insights into its characteristics, providing valuable insights into the spatial distribution of atoms and ions within the substance. This understanding has substantial implications for the

functionality of NFP across various applications, especially in the context of SIBs.

5.3.1.3 N₂ adsorption-desorption isotherm

The surface area of the prepared samples was determined using BET N₂ adsorption-desorption isotherms within the relative pressure range of 0.0 to 1.0, as illustrated in **Figure 5.3 (c)**. The determined surface areas for NFP and NFP/G were 27.8 and 38.6 m²/g, respectively. Compared to that of pure NFP, the surface area of NFP/G increased due to the presence of graphene nanosheets alongside smaller NFP particles. **Figure 5.2 (b)** shows the pore size distributions of NFP and NFP/G, which were analysed using the Barrett–Joyner–Halenda (BJH) method. Most pores in NFP measure less than 391.9 nm, whereas in NFP/G, the majority measure approximately 282.4 nm. Graphene nanosheets are the principal factor responsible for the formation of these pores. This porous structure creates more accessible pathways for electrolyte penetration, and a reasonably sized BET surface area guarantees effective contact between the electrode material and the electrolyte.

5.3.1.4 Raman analysis

Figure 5.3 (d) shows the Raman spectra of the prepared samples. Notably, distinct peaks are observed, each corresponding to specific vibrational modes, which provide valuable insights into the structural composition of the materials. The obtained data reveal characteristic lattice modes at 149 cm⁻¹ and a broader range extending from 220 to 400 cm⁻¹, reflecting the inherent vibrational characteristics of the lattice structure in both materials. Furthermore, prominent features are evident in the 300 to 450 cm⁻¹ range, corresponding to alkali-metal cage modes, specifically Na⁺/Fe³⁺, which further illuminate the unique vibrational properties of these materials. Symmetric PO₄³⁻ vibrations are distinguishable at 1010 cm⁻¹ and 1030 cm⁻¹, while asymmetric PO₄³⁻ vibrations manifest at 970 cm⁻¹ and 990

cm⁻¹. These observations offer valuable insights into the structural integrity and chemical interactions of this material, particularly concerning the phosphate groups associated with the PO₄³⁻ species in both NFP and NFP/G[480]. Additionally, the presence of graphene in NFP/G is unambiguously confirmed by the discernible D and G bands. The Raman shift in D band observed for NFP/G at 1330.51 cm⁻¹ may be ascribed to the defects in graphitic structure which is appears by converting sp² carbon to the sp³ carbon. The upshift Raman wavenumber of G band at 1599.05 cm⁻¹ is attributed to the in-plane vibration of C-C bond from sp² orbital of stacked graphene layers. This characteristic highlights the successful incorporation of graphene sheets within the composite framework[41,42,49,50].

5.3.1.5 Surface morphology analysis

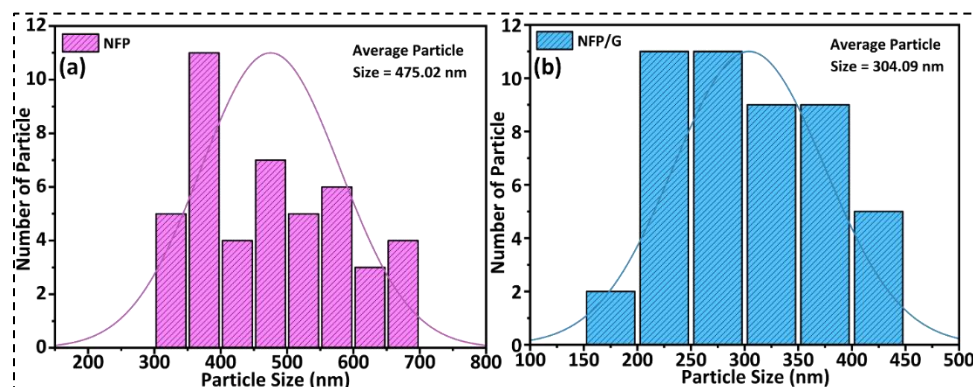


Figure 5.4 The average particle size distribution of (a) NFP and (b) NFP/G particles.

FESEM images of the NFP and NFP/G cathodes are depicted in **Figure 5.5**. These images reveal that the material is characterized by a compact, homogeneous plate-like morphology, exhibiting well-defined and regular crystalline features indicative of a highly organized crystal structure. **Figure 5.5 (d)** shows the morphology of graphene and **Figure 5.5 (e)** demonstrates that the NFP/G composites consist of plate-like structures with agglomeration. It is evident that the NFP/G particles are densely agglomerated nanoparticles. This can be ascribed to the graphene wrapping,

which effectively inhibits the grain growth of the NFP plates. When the electrolyte penetrates the cathode material, it interacts with the nanoparticles, which have a high surface area, leading to an increased contact area with the electrolyte. The particle size distributions of both materials are presented in **Figure 5.4**. The average particle size of NFP is 475.02 nm, whereas that of NFP/G is 304.09 nm. The reduced nanoparticle size of NFP/G shortens the diffusion paths for electrons and sodium ions, resulting in a significant improvement in the sodium-ion diffusion of the cathode material. The graphene sheets successfully form an efficient conducting network, bridging and intimately connecting the active NFP particles.

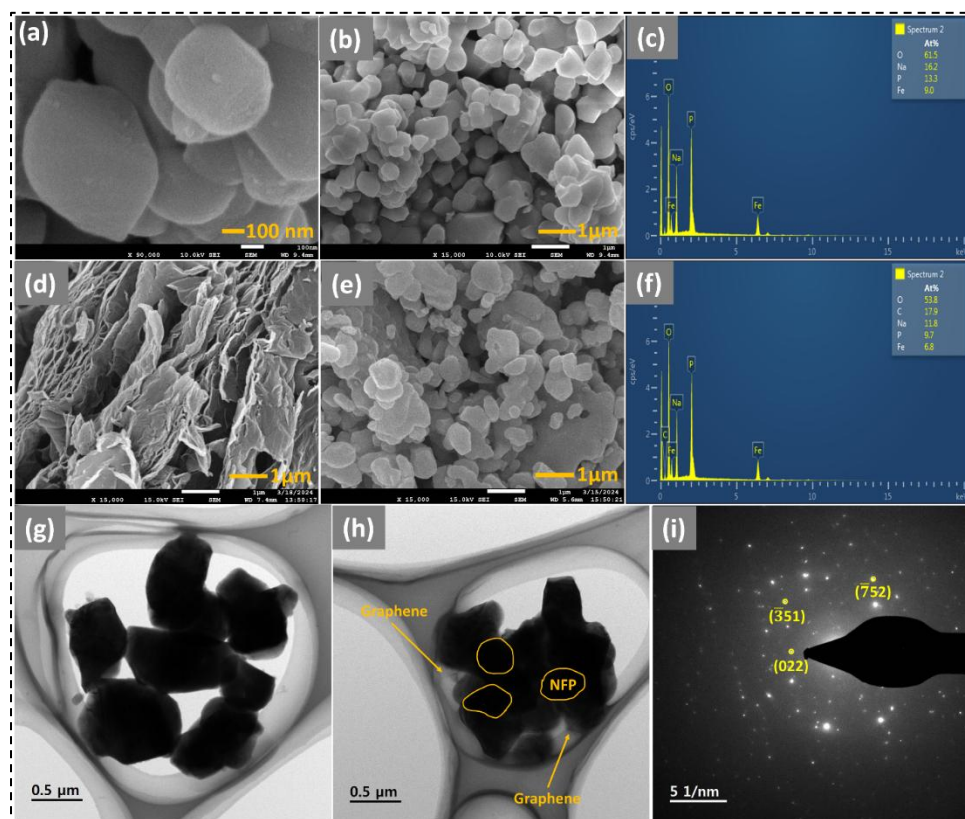


Figure 5.5 (a,b) FESEM images and c EDAX spectra of NFP. (d,e) FESEM images, (f) EDAX spectra of NFP/G. TEM images of (g) NFP, (h) NFP/G and i SAED pattern of NFP/G.

Figure 5.5 (e) also indicates that the graphene sheets surrounding the NFP particles possess a highly graphitic nature, contributing to the desirable electrochemical properties of the material. Further elemental analysis, as shown in **Figure 5.5 (c,f)**, reveals the appropriate composition of Na, Fe, P, and O across the surface of the NFP and NFP/G with carbon. This even distribution further enhances the electrochemical performance of the cathode material.

5.3.1.6 Structural analysis: HRTEM

Figure 5.5 (g,h) depicts the HRTEM image of the synthesized NFP and NFP/G samples respectively. The NFP/G particles have an agglomerated and heterogeneous appearance compared to NFP with average size of the particles measures approximately 393.25 nm, which is in line with the FESEM-observed particle size distribution. The NFP particles in **Figure 5.5 (h)** are represented by darker patches in the HRTEM image, and they are bound together by a light grey graphene network that was generated during the calcination process from graphene sheets. In **Figure 5.5 (i)**, the indexed SAED pattern of the NFP/G sample is presented. This outcome demonstrates polycrystalline properties, aligning well with the XRD findings. Furthermore, these HRTEM images of NFP/G offer additional indication of the effective growth of NFP particles on graphene surfaces. The existence of this graphene network around nanoparticles not only allows for faster ion/electron transport, but it also inhibits nanoparticle development over extended charge/discharge cycles.

5.3.1.7 Chemical analysis

XPS analysis provides valuable insights into the chemical composition and oxidation states of both NFP and NFP/G, survey spectra is presented in **Figure 5.6 (a)**. The existence of Na, Fe, P, O, and C within the materials is confirmed by **Figure 5.6 (a,b)**. Within the C 1s spectrum (**Figure 5.6 (c)**) of NFP, three distinct peaks are observed: C - C at

approximately 284.6 eV, C - O at about 286.15 eV, and O - C = O at around 288.45 eV, contributing 56.93%, 30.68%, and 12.39%, respectively, to the total C 1s integrated intensity. Conversely, three peaks in NFP/G attributed to C = C at about 283.22 eV, C - C at about 284.6 eV, and C - O at about 287.01 eV were observed, contributing 21.49, 58.95, and 19.55% to the total C 1s integrated intensity, respectively as shown in **Figure 5.6 (d)**. These findings indicate a limited presence of oxygen functional groups on the surface and suggest the presence of sp^2 C = C in the material, suggesting the incorporation of graphene in the NFP/G composite [4351].

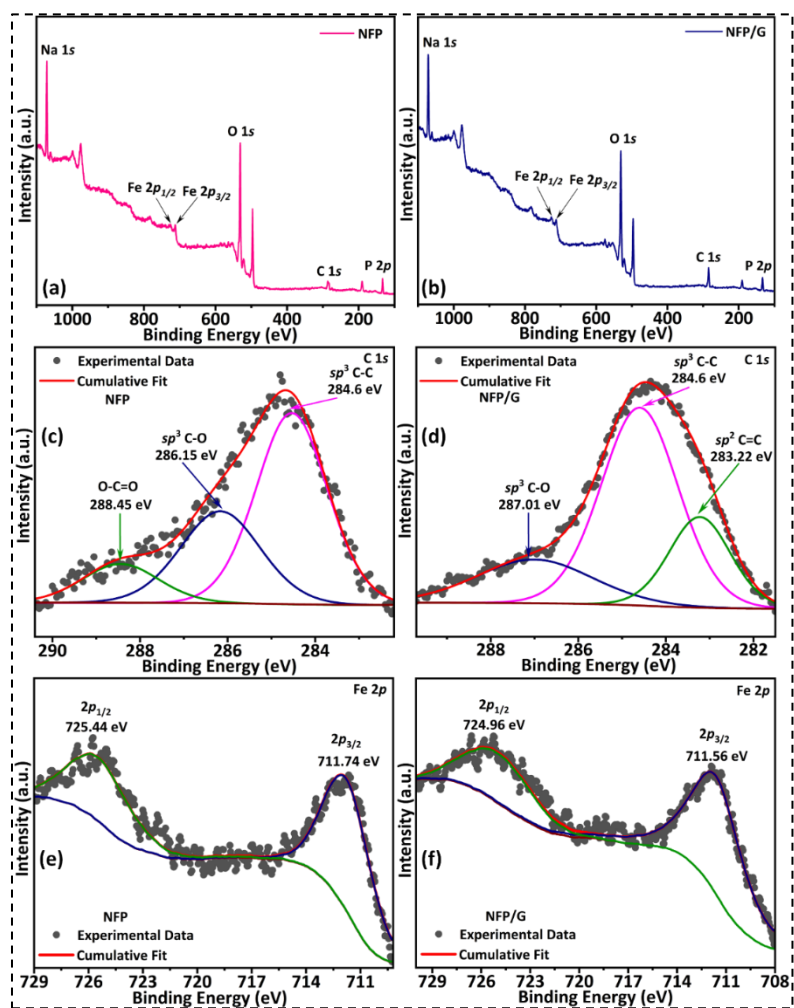


Figure 5.6 XPS spectra of the NFP: (a) survey scan, (c) C 1s spectrum, (e) Fe 2p spectrum and NFP/G composite: (b) survey scan, (d) C 1s spectrum, (f) Fe 2p spectrum.

Figure 5.6 (e) displays the XPS spectra of the Fe 2*p* signals from both NFP and the NFP/G composite, showing two discernible peaks. The Fe 2*p*_{3/2} peak at 711.74 eV constitutes 54.77% of the total Fe 2*p* integrated intensity, with a spin-orbit splitting (ΔBE) of 13.7 eV, while the Fe 2*p*_{1/2} peak at 725.44 eV accounts for 45.23% of the total Fe 2*p* integrated intensity, suggesting the formation of NFP. The core-level spectra of Fe 2*p* depicted in **Figure 5.6 (f)** exhibit two principal peaks at 711.56 eV for Fe 2*p*_{3/2} (contributing 54.27%) and 724.96 eV for Fe 2*p*_{1/2} (contributing 45.73%), with a spin-orbit splitting (ΔBE) of 13.4 eV, consistent with literature values indicating the presence of Fe³⁺ in NFP/G [51,52]. In summary, the presence and respective roles of Na, Fe, P, O, and C, in addition to their oxidation states, significantly influence the electrochemical characteristics of NFP/G, making it a viable candidate for SIBs.

5.3.2 Electrochemical Characterizations

5.3.2.1 CV Analysis

The electrochemical characteristics of both the NFP and NFP/G materials for SIBs were comprehensively evaluated through CV, GCD, stability, and EIS analyses. Notably, open-circuit voltage (OCV) measurements yielded values of 2.543 V for NFP and 2.676 V for NFP/G, underscoring their potential for high-performance electrochemical systems. **Figure 5.8 (a,b)** prominently illustrates the CV curves for NFP and NFP/G, which were precisely recorded across a range of scan rates spanning from 0.1 to 5 mV/s within the potential window of 1.5-4 V. A noteworthy observation is the consistent manifestation of a distinct redox pair behaviour at each scan rate for both materials. When analysing the CV curve recorded at 0.1 mV/s for both NFP and NFP/G, it becomes evident that a distinct redox pair predominates the electrochemical response, as depicted in **Figure 5.7 (a)**. Specifically, the redox couple, involving the Fe³⁺/Fe²⁺ transition, exhibited well-defined anodic and corresponding cathodic peaks, occurring at approximately 2.677 V and 2.382 V, respectively, for NFP and

at 2.687 V and 2.389 V, respectively, for NFP/G. Significantly, the close agreement in the redox potential deviation between the anodic and cathodic peaks for both NFP and NFP/G underscores the remarkable electrochemical reversibility exhibited by these materials.

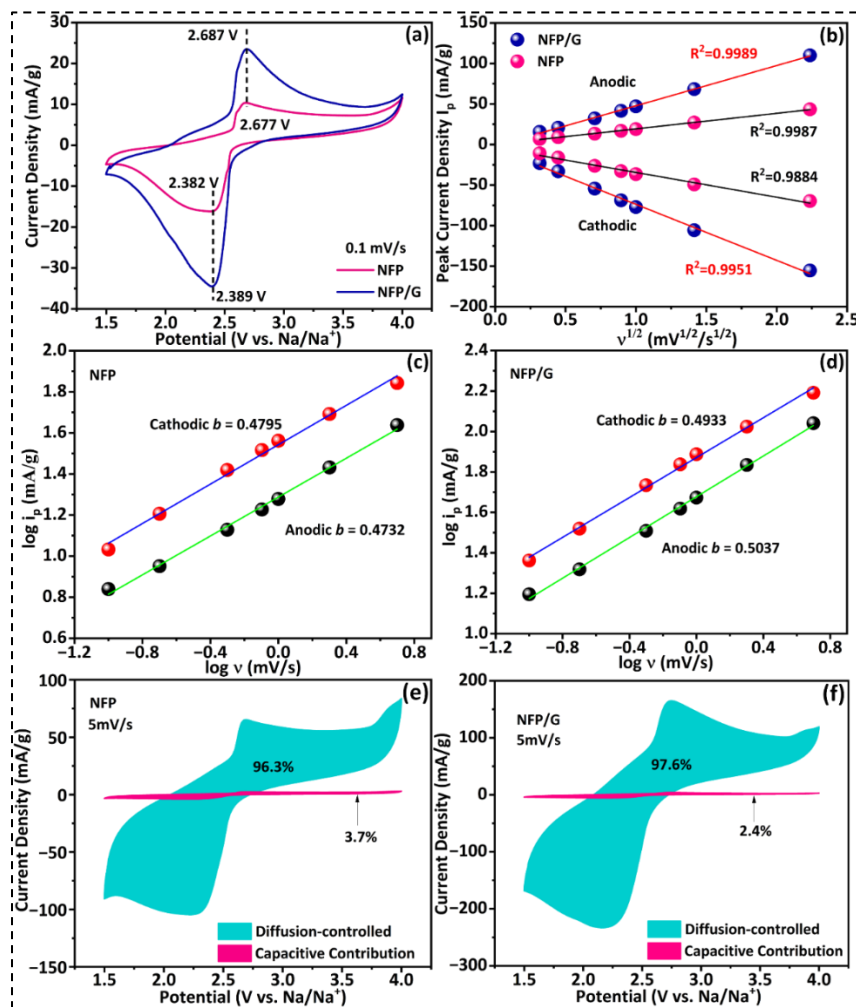


Figure 5.7 Electrochemical kinetic behavior of NFP and NFP/G. (a) Cyclic voltammogram measured at a scan rate of 0.1 mV/s. (b) Plot of I_p versus $v^{1/2}$. (c, d) Plot of $\log I_p$ versus $\log v$. (e, f) capacitive and diffusion-controlled contribution to the charge storage at 5 mV/s for NFP and NFP/G, respectively.

Furthermore, it is pertinent to highlight that NFP/G demonstrated a notably greater peak intensity, indicative of an augmented discharge capacity, as

evidenced by the enlarged curve area in the CV analysis compared to that of pure NFP. This enhanced electrochemical property can be attributed to the establishment of a conductive network facilitated by the graphene sheets, which effectively stabilizes and reinforces the crystal structure of NFP. Consequently, these exceptional enhancements in electrochemical performance and uniformity of the CV curves underscore the rapid kinetics of the sodiation/desodiation processes and the outstanding electrochemical reversibility inherent in these materials.

Table 5.1 R^2 and the diffusion coefficient of Na^+ for anodic and cathodic processes for NFP and NFP/G.

	R^2	D_{Na^+} Anodic/Charging	D_{Na^+} Cathodic/Discharging	D_{Na^+} Average
NFP	0.9987	1.834×10^{-11}	4.662×10^{-11}	3.248×10^{-11}
	0.9884	$\text{cm}^2 \text{ s}^{-1}$	$\text{cm}^2 \text{ s}^{-1}$	$\text{cm}^2 \text{ s}^{-1}$
NFP/G	0.9989	1.228×10^{-10}	2.383×10^{-10}	1.805×10^{-10}
	0.9951	$\text{cm}^2 \text{ s}^{-1}$	$\text{cm}^2 \text{ s}^{-1}$	$\text{cm}^2 \text{ s}^{-1}$

The Na^+ diffusion coefficient (D_{Na^+}) was assessed adopting the CV method, employing the established Randles–Sévcik formula (equation 2.5). Figure 5b meticulously presents the comprehensive fitting information derived from the graphs of I_p versus $v^{1/2}$. The square root of the scan rate (values are tabulated) and the anodic and cathodic peak currents were shown to be linearly related for both NFP and NFP/G conclusively establishes the dominant role of diffusion control over both oxidative and reductive processes. The calculated D_{Na^+} values for NFP and NFP/G, as determined using equation (2.5), are provided in **Table 5.1**. Remarkably, NFP/G exhibited a D_{Na^+} of $1.228 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for the extraction process and $2.383 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for the insertion process, representing a substantial improvement compared to NFP. This notable enhancement in Na^+ de/intercalation kinetics can be attributed to the distinctive open 3D

NASICON structure, and the heightened electronic conductivity facilitated by the scaffolded graphene sheet.

To evaluate the diffusion-controlled and capacitive characteristics of the NFP and NFP/G cathodes, power-law and Dunn plots were generated[546]. The power-law equation relating $\log i_p$ to $\log v$ based on cyclic voltammetry (CV) data is described in equation (2.6). A value of b approaching 0.5 indicates a diffusion-controlled process, while a value near 1 suggests a capacitive process. **Figure 5.7 (c,d)** shows the linear regression of $\log i_p$ and $\log v$ at the redox peak potentials. For the NFP electrode, b is 0.48 and 0.47 for the cathodic and anodic peaks, respectively. For the NFP/G electrode, b is 0.49 and 0.5 for the cathodic and anodic peaks, respectively. These values suggest that the reaction mechanism involves diffusion as the dominant mechanism. Subsequently, equation (2.8) aids in quantifying the contribution of diffusion-controlled behaviour. The k_1 and k_2 values are determined from the slope and intercept of the $\vartheta^{0.5}$ vs. $i(V)/\vartheta^{0.5}$ plot. By evaluating k_1 and k_2 at various potentials and scan rates, the diffusion-controlled contributions of NFP and NFP/G can be assessed. **Figure 5.7 (e,f)** shows the contribution plot at a scan rate of 5 mV/s. Both electrodes exhibit clear diffusion-controlled contributions across various scan rates. The diffusion-controlled and capacitive contributions were quantified at different scan rates. Notably, with increasing scan rate, the diffusion-controlled contribution of both electrodes decreased, albeit at a slower rate (**Figure 5.8 (c,d)**). Even at a higher scan rate of 5 mV/s, NFP and NFP/G displayed diffusion-controlled contributions of 96.3% and 97.6%, respectively. Comprehensive analysis of the redox behaviour of NFP/G, characterized by a significant fraction of diffusion-controlled behaviour, further underscores its outstanding rate performance, indicating rapid redox reactions and rate-independent behaviour throughout the electrochemical process.

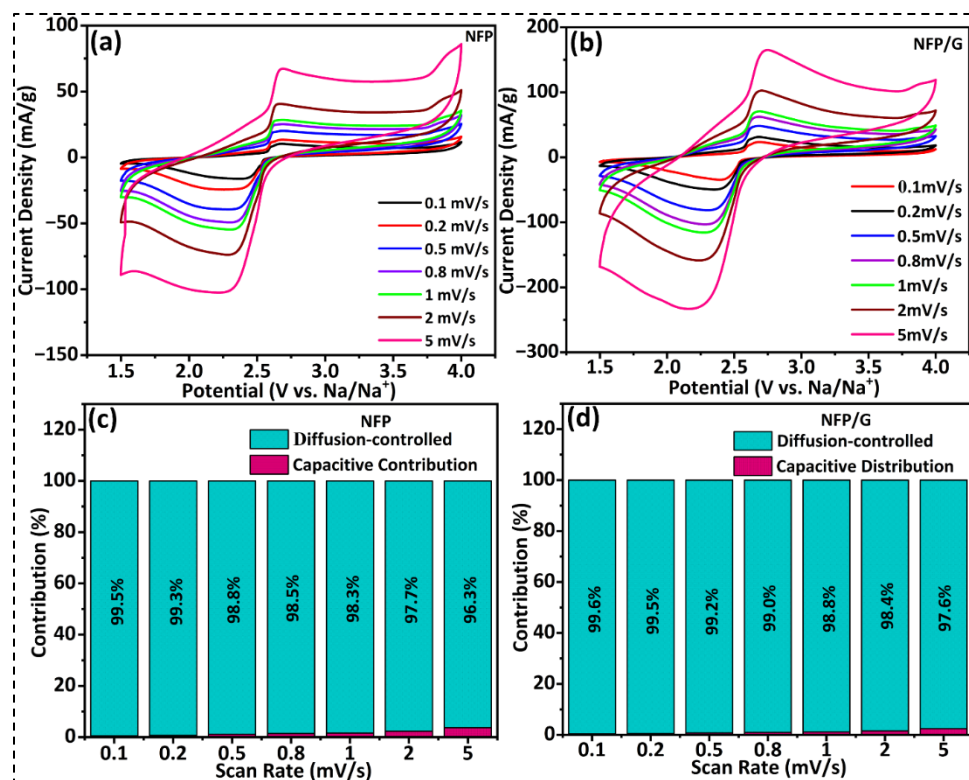


Figure 5.8 Cyclic Voltammogram measured at scan rate from 0.1 to 5 mV/s for (a) NFP, and (b) NFP/G. capacitive and diffusion-controlled contribution to the charge storage at various scan rates from 0.1 to 5 mV/s for (c) NFP, and (d) NFP/G respectively.

5.3.2.2 GCD Analysis

Within the voltage range of 1.5-4 V, the NFP and NFP/G samples served as cathode materials for cell fabrication, and their electrochemical performance was assessed through GCD experiments. As depicted in **Figure 5.9 (a)**, the initial GCD curves for NFP and NFP/G, recorded at a rate of 0.1 C at room temperature, revealed discharge capacities of 84.8 mAh g⁻¹ and 115.1 mAh g⁻¹, respectively. The discharge capacity of NFP/G closely approximated the theoretical capacity (115.3 mAh g⁻¹) of the NFP sample within this voltage window. This result can be attributed to the superior electron conductivity of NFP/G, which restricts the degree of graphitization in the graphene component compared to that of pure NFP. Both materials exhibited distinct discharge plateaus at approximately 2.5 V during the electrochemical reactions. Subsequent GCD analyses were

conducted at various C rates, ranging from 0.1C to 10C, as depicted in **Figure 5.10 (a,b)**. The results revealed reversible capacities for NFP and NFP/G at different rates, with values of 84.8, 71.8, 60.7, 40.9, 29.2, and 13.5 mAh g⁻¹ and 115.1, 108.8, 94.6, 70.7, 58.8, and 41.2 mAh g⁻¹ at 0.1, 0.5, 1, 2, 5, and 10C, respectively (**Figure 5.10 (b,d)**).

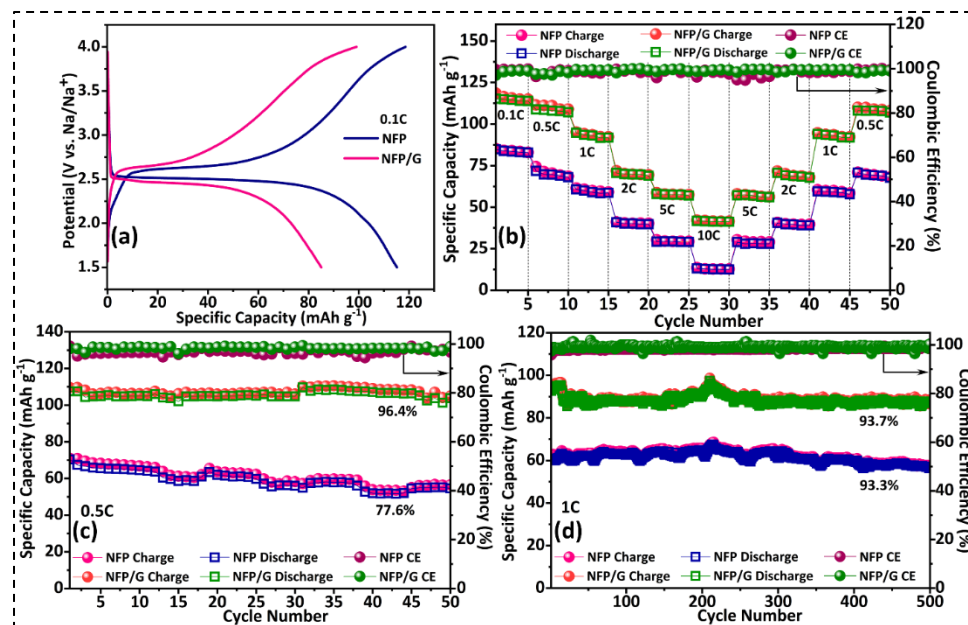


Figure 5.9 Electrochemical performances of NFP and NFP/G: (a) 1st galvanostatic charge-discharge profile at 0.1 C. (b) rate performance at various C-rates in comparison with those of NFP and NFP/G. (c) cycling performance at 0.5 C, and (d) at 1 C.

Notably, NFP/G exhibited an exceptional rate capability even at a reduced C rate of 0.5 C; it retained a discharge-specific capacity of 104.2 mAh g⁻¹, as depicted in **Figure 5.9 (b)**. These findings underscore the significant potential of graphene modification for enhancing the rate of sodium storage, rendering it a potential cathode material for SIBs. The coulombic efficiency remained consistently high, nearly 100%, throughout the cycling process. This stability is expected to have a positive impact on the cycling performance. **Figure 5.9 (c,d)** also illustrates the coulombic efficiency and charge/discharge specific capacity retention at 0.5C and 1C for both NFP and NFP/G. The cycling performances of both materials

within the potential range of 1.5–4 V, tested at a 0.5C rate, are presented in **Figure 5.9 (c)**. In the case of NFP, the discharge specific capacity at 0.5 C gradually decreases to 54.6 mAh g⁻¹ over 50 cycles, with a capacity retention of only 77.6% (**Figure 5.11 (a)**). This capacity decrease can be attributed to the inherent limitations of NFP. In contrast, incorporating graphene into the NFP/G composite contributes to enhanced structural stability during cycling, resulting in negligible capacity fading.

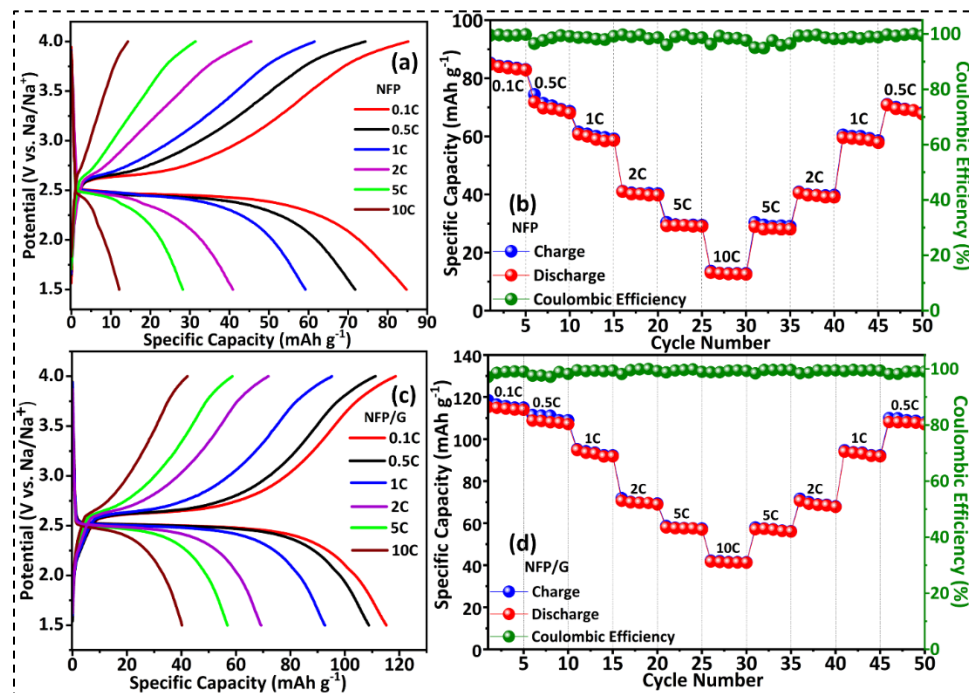


Figure 5.10 GCD profile at various C-rates from 0.1C to 10C and rate performance of (a, b) NFP and (c, d) NFP/G.

Notably, NFP/G demonstrated remarkable endurance, maintaining a capacity of 103.7 mAh g⁻¹ even after 50 cycles, equivalent to 96.4% of the initial capacity (**Figure 5.11 (d)**). Throughout all the cycles, NFP/G consistently exhibited a superior initial coulombic efficiency, maintaining it very close to 100% after 50 cycles. Furthermore, when subjected to more demanding conditions with a higher charge/discharge rate of 1C, NFP/G remains resilient, as depicted in **Figure 5.1 (c,d)**. It retains a discharge capacity of 86.8 mAh g⁻¹ after 500 cycles at this acceleration rate, with

corresponding capacity retention consistently above 93.7%, as demonstrated in **Figure 5.10 (d)**, which is superior to that of NFP.

From a comprehensive perspective, **Table 2** compares the capacity retention for NFP with that in previously reported literature. Most of the reported NFP materials were synthesized by solid-state reactions and exhibited good electrochemical performance. Rajagopalan *et al.* synthesized NFP-C by the solid-state method and reported a 96% capacity after 200 cycles at 1C. Remarkably, the exceptional cycling performance of NFP/G, particularly its capacity retention of 93.7% after more than 500 cycles at 1C, surpasses that of previously reported materials. This underscores the significance of these findings in the field.

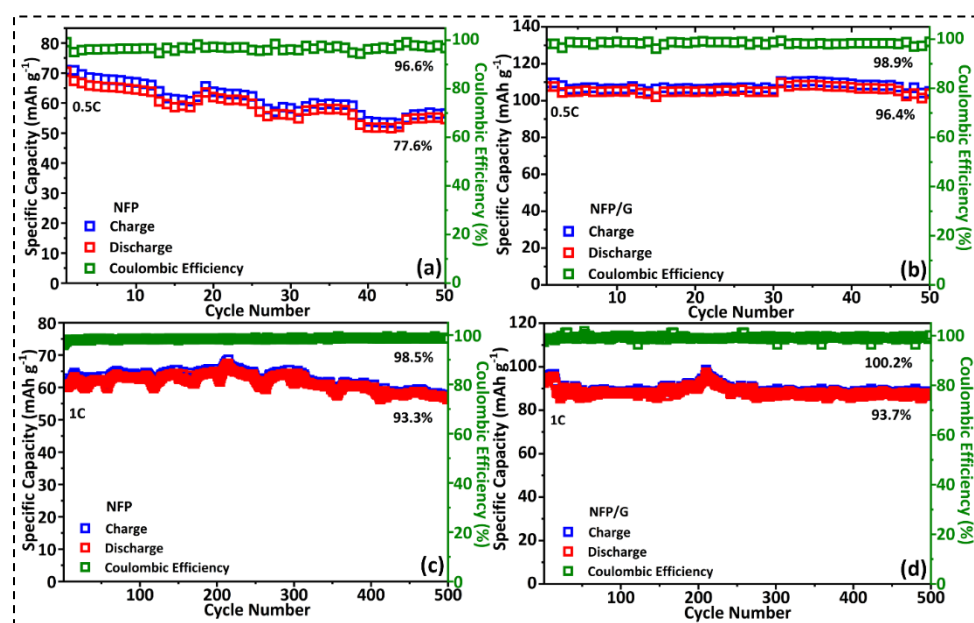


Figure 5.11 Cyclic performance and coulombic efficiency of (a) NFP and (b) NFP/G at 1C, respectively, (c) NFP, and (d) NFP/G at 0.5C, respectively.

Table 5.2 Comparisons of the electrochemical performances of this work and the previously reported NFP.

Material	Specific Capacity (mAh g⁻¹), 1C	Capacity Retention, Cycles, C-rate	Synthetic Method	Carbon Form	Voltage Range
NFP[394]	60, 1C	70.5%, 50, 1C	Sol-gel	NA	1.5-3.5 V
NFP[17]	61, 1C	80%, 200, 1C	Solid-state reaction	NA	1.5-4.2 V
NFP-C[17]	96, 1C	96%, 200, 1C	Solid-state reaction	Graphitic carbon	1.5-4.2 V
NFP[16]	30, 1C	-	Solid-state reaction	NA	1.5-4.5 V
NFP[26]	61, 1C	93.4%, 500, 1C	Coprecipitation	NA	1.5-3.5 V
NFP[27]	87.1, 1C	96%, 300, 1C	Spray drying method	NA	1.5-3.5 V
NFP This work	60.7, 1C	93.3%, 500, 1C	Sol-gel method	NA	1.5-4 V
NFP/G This work	94.7, 1C	97.6%, 200, 1C 93.7%, 500, 1C	Sol-gel method	Graphene	1.5-4 V
NFP/G This work	108.8, 0.5C	96.4%, 50, 0.5C	Sol-gel method	Graphene	1.5-4 V

5.3.2.3 EIS Analysis

EIS was conducted to study the kinetics of the two-electrode process. The Nyquist plots for both NFP and NFP/G are depicted in **Figure 5.12 (a)**. The corresponding electrochemical circuit model, represented in the inset, is fitted with a semicircle, effectively capturing the experimental results. The rapid transfer of sodium ions at the interface between the

surface electrode and the electrolyte (between active material and sodium metal) is responsible for the observed semicircles at higher and medium frequencies. The EIS spectra of NFP and NFP/G feature a single depressed semicircle in the high-frequency region and a straight line in the low-frequency region indicating Warburg impedance. For both materials, this semicircle can typically be attributed to a combination of the solution resistance (R_s), coating resistance (R_c) which is due to the roughness of the active material coating and charge transfer resistance (R_{ct}). R_s is associated with Na^+ migration through the solid-electrolyte interfacial layer, while R_{ct} represents the resistance between the cathode and electrolyte interface[459]. The impedance of NFP/G is lower than that of NFP, indicating faster Na intercalation on the surface of the NFP/G cathode, as illustrated in **Table 5.3**. Before GCD and stability tests, NFP exhibited a resistance of $6.69\ \Omega$ at the interface. Notably, based on the R_{ct} and R_s values, NFP/G demonstrated excellent ionic conductivity, as presented in **Table 5.3**, which was attributed to the introduction of graphene into NFP.

Table 5.3 The obtained values of the resistances and conductivities of NFP from EIS.

EIS parameters	NFP	NFP/G
$R_s\ (\Omega)$	6.69 ± 0.02	6.50 ± 0.01
$R_{ct}\ (\Omega)$	36.77 ± 0.03	16.06 ± 0.02
Conductivity, $\sigma\ (\text{S/cm})$	0.92×10^{-4}	1.75×10^{-4}

5.4 Possible mechanism of energy storage

Sodium ions readily interact with specific sites or channels within a crystal lattice of material, leading to intercalation where sodium ions insert themselves into interstitial spaces. This process allows for ion hopping, enabling sodium ions to traverse the crystal structure through established pathways such as channels or tunnels, promoting rapid sodium ion transport

between interstitial sites. Such movement constitutes sodium ion diffusion, aided by a conductive network within the lattice crystals that serves as diffusion channels, greatly enhancing sodium ion transport during charging and discharging processes, thus increasing the overall sodium storage capacity.

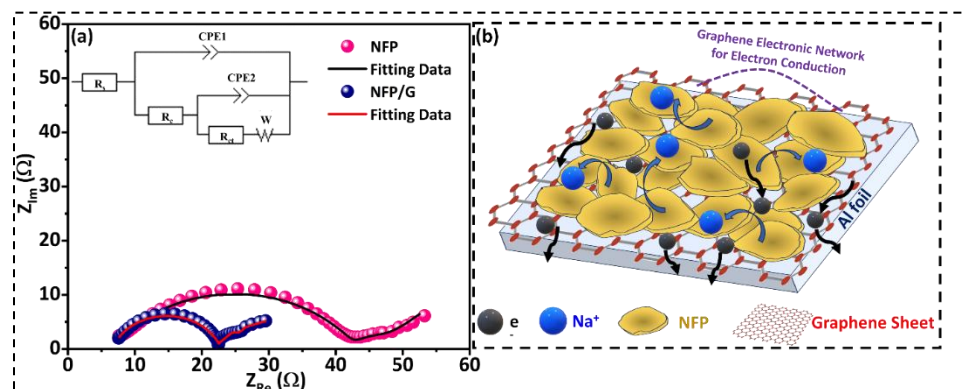
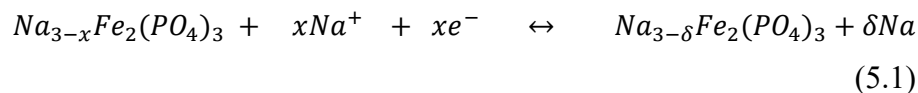


Figure 5.12 (a) Nyquist plots of NFP and NFP/G; the insert Figure shows the equivalent circuit for EIS data fitting. (b) Mechanism of the enhanced high-rate capacity and long cyclability of the NFP/G composite as an SIB cathode (the upwards blue arrow indicates deintercalation/extraction of Na ions from the cathode material to the other electrode, and the downwards black arrow indicates the transfer of electrons to the aluminum foil or external circuit).

Upon entering the NFP cathode material through diffusion, sodium ions undergo an electrochemical process, notably a reduction process where high oxidation state Fe ions (Fe^{3+}) are reduced to lower oxidation state Fe ions (Fe^{2+}). To maintain charge balance within the battery cell, Na^+ ions are concurrently intercalated into the crystal lattice of the cathode material.

Equation (4) outlines the reaction mechanism occurring during discharge cycles:



Here, ' δ ' corresponds to the number of sodium molecules lost at the anode side of the electrode-electrolyte interface during each cycle of charging/discharging. Ideally, the value for δ is proposed to be $\leq 5\%$ of the initial sodium content in the material of interest for each successive charge–discharge cycle. Similarly, the reverse process occurs during the charging process.

Several key factors influence the electrochemical performance of NFP. First, its plate-like shape reduces the sodium-ion diffusion length, shortens the electron transport length, and increases the surface area in contact with the electrolyte. Second, the expansion of the lattice spacing weakens the interaction between the intercalated sodium ions and the FeO interlayer, resulting in numerous sodium-ion storage sites and promoting rapid sodium-ion diffusion. These factors collectively contribute to the electrochemical properties of the NFP coin cell. The fundamental process for storing electrical charge in an NFP cathode material involves the intercalation and deintercalation of sodium ions (Na^+) within its crystal structure during charge and discharge cycles. Specifically, during battery discharge, Fe(III) undergoes reduction to Fe(II) as Na^+ are incorporated into the crystal lattice of the material. However, pure NFP exhibited slow kinetics, indicating inefficient sodium ion movement within the crystal lattice. This limitation leads to low-rate capabilities and suboptimal overall battery performance. The introduction of NFP nanoplates in combination with graphene nanosheets generates synergistic effects. The mechanism of the high rate capacity and long cyclability of the NFP/G composite is illustrated in **Figure 5.12 (b)**. The graphene nanosheet functions as a conductive scaffold, connecting and supporting the nanoplates and creating a substantial surface area where sodium ions can readily interact[29]. Because these nanoplates are interconnected, sodium ions can efficiently travel along their surfaces and move between them, significantly enhancing the diffusion process. Moreover, the interconnected nanoplates, along with the conductive graphene network, collaboratively reduce the barrier to

sodium-ion diffusion. This process facilitates the efficient flow of electrons, released or accepted during charge and discharge cycles by sodium ions, through the graphene nanosheet, thereby minimizing the risk of electron bottlenecks without a conductive framework. Efficient electron conduction is essential for rapid and reversible redox processes accompanying sodium ion insertion and extraction. The graphene network within NFP/G promotes this electron conduction, improving the charge/discharge kinetics and overall battery performance.

In summary, the outstanding rate performance of NFP/G can be attributed to two crucial factors. First, it arises from the reduced sodium ion transport distance within NFP particles. Second, the process is facilitated by graphene nanosheets that enable rapid electron conduction. This interpretation is substantiated by the results obtained from electrochemical impedance spectroscopy (EIS) measurements. Overall, the electrochemical performance of NFP/G surpasses that of the NFP half-cell. This improvement in the sodium-ion diffusion coefficient can be ascribed to the combined effects of the NFP nanoplates and graphene nanosheets. This structural combination provides a higher density of active sites for sodium-ion diffusion, resulting in superior specific discharge capacity and enhanced capacity retention.

5.5 Conclusions

In conclusion, a sol-gel technique was implemented to successfully synthesize a nanoplate-like NFP/G composite material with a 304.09 nm particle size. This composite even exhibited an NFP particle distribution on the graphene sheets and displayed an improved diffusion coefficient. During the first cycle, NFP/G achieves a nearly theoretical specific discharge capacity of 115.1 mAh g⁻¹ at 0.1 C, and it maintains a high capacity of 86.8 mAh g⁻¹ with an impressive 97.6% capacity retention rate over 200 cycles at 1 C, surpassing that of pure NFP under the same conditions. These remarkable outcomes are attributed to the reduced NFP

particle size in the composite and the excellent conductivity provided by graphene. Overall, these nanostructured NFP/G composites hold significant potential as cathode materials for SIBs.

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Chapter 6

Conclusions and Scope for Future Work

The main objective of this thesis was to design, synthesize, optimize, and systematically study high-performance cathode materials in SIBs and especially the polyanionic phosphate-based compounds. Through the sol-gel and hydrothermal synthesis methods, a series of polyanionic phosphate materials, $\text{Na}_3\text{VFe}(\text{PO}_4)_3$, $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3@NC$, $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3@SNC$, and $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$, were effectively synthesized and thoroughly compared as the cathode materials of SIB. Specific care was taken in the knowledge of the influences of compositional tuning, heteroatom doping, vanadium reduction, and compatibility of the electrolytes on the electrochemical behavior of the cathode materials. The electrodes produced were promising in terms of electrochemical properties such as high specific capacity, enhanced energy density, and high capacity retention even after extensive cycling, and thus show the potential to achieve viable use as SIBs. Furthermore, significant emphasis was placed on establishing correlations between the physicochemical characteristics and electrochemical activity of the materials, as well as the ability to be combined with various electrolytes. These studies were a useful contribution to the structure-performance relationship of the electrochemical performance of polyanionic phosphate cathodes.

Overall, the results of this thesis would not only help create promising cathode materials for SIBs but also enhance the basic understanding of strategies for designing materials for next-generation energy storage systems.

7.1 Brief Summary and Outcomes of the Thesis

Chapter 1 identifies the scientific and technological necessity of sustainable, cost-effective, electrochemical energy-storage systems and positions sodium-ion batteries as viable alternatives to lithium-ion systems for large-scale applications. It critically assesses SIB basics, working principles, key performance metrics, and major cathode categories (layered oxides, Prussian blue analogues, polyanionic structures), discussing the main structural peculiarities, their strengths, and their weaknesses for storing Na. Based on this, it presents important research gaps in cathode design (cost, structural stability, conductivity, interfacial behavior) and clearly states the aim, objective, and scope of the thesis, focused on Fe-based polyanionic phosphate electrodes and interfacial/surface engineering strategies.

Chapter 2 describes the experimental and computational toolbox adopted in the thesis, thereby providing a standard platform for understanding structure-property-performance relationships. It reports on controlled sol-gel and hydrothermal synthesis of $\text{Na}_3\text{FeV}(\text{PO}_4)_3$, heteroatom-doped $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$, and $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3/\text{graphene}$ composites, the fabrication of electrodes and the assembly of Na half-cells, and the entire suite of physicochemical (TGA, DTG, XRD, FESEM, EDS, HRTEM, Raman, FTIR, XPS, BET) and electrochemical (CV, GCD, EIS) along with DFT methods to study Na ion migration and electronic structure analysis to provide a correlation between experimental behaviour, atomistic Na diffusion pathways and interfacial chemistry.

Chapter 3 demonstrates that electrolyte selection and interfacial chemistry, which depend on the electrolyte, strongly influence the electrochemical performance of high-voltage $\text{Na}_3\text{FeV}(\text{PO}_4)_3$. With sol-gel-derived $\text{Na}_3\text{FeV}(\text{PO}_4)_3$, a detailed structural and surface analysis (XRD, XPS,

FESEM, HRTEM) and a combination of CV, GCD, and EIS studies are described. The structure and surface behavior under various carbonate-based electrolytes, and their effects on SEI formation, charge-transfer resistance, Na^+ diffusion coefficient, and capacity retention of 86.11% after 2000 cycles at 1C, are determined. With the aid of DFT, the chapter elucidates the migration patterns and interface reaction mechanisms of Na, which have led to design rules for optimizing the electrolyte in high-voltage polyanionic SIB cathodes.

Chapter 4 (Part A) demonstrates that heteroatomic (N) carbon coating on alluaudite $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ (NFMP) is an efficient measure to eliminate the inherent low conductivity of Fe-Mn alluaudites and can fasten Na kinetics. Hydrothermal growth and subsequent annealing produce NFMP and N-doped carbon-coated NFMP (NFMP@NC) with retained monoclinic alluaudite structure. However, it altered the lattice parameters, the mesoporous 3D urchin-like structure, a thin (approximately 3nm) conductive layer of C, and N-derived graphitic/pyridinic/pyrrolic species, which generate additional electronic pathways and Na active sites. Compared to pristine NFMP, NFMP@NC provides higher reversible capacity (approximately 77.1 mAh/g at 0.1C and 0.1C), greater rate capability, reduced charge-transfer resistance, higher Na diffusion coefficients, and higher capacity retention (at 0.1C, 83% and at 2C, 92%). **Part B** extends $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ chemistry to the negative electrode side and proves that N, S co-doped carbon-wrapped alluaudite $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ (NFMP@SNC) can function as a high-performance, low-voltage intercalation-type anode for SIBs. The hydrothermal-pyrolysis process produces 3D urchin-like particles with an adjustable, thin N/S doped, carbon coating, balanced crystallite size, increased surface area and porosity, and mixed disordered/graphitic carbon network as evidenced by XRD, TGA, CHNS-O, Raman, BET, FESEM, HRTEM, and XPS. NFMP@SNC demonstrates high reversible capacity (~ 253 mAh/g at 0.05C,

~61% of theoretical), high rate capability, and retention at 0.1C and 0.2C, with good cycling stability in a polyanionic phosphate anode. The DFT shows a reduced band gap, optimized Na diffusion barriers, and a favorable charge distribution, indicating that N, S co-doping is a promising approach to enhance Na storage kinetics and stability in polyanionic phosphate anodes.

Chapter 5 establishes that embedding $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ nanoplates into a 3D graphene network (NFP/G) markedly improves Na-storage kinetics, electrical transport, and long-term cyclability relative to pristine NFP. Monomeric NASICON-type NFP and NFP/G, having the same crystal structure but larger surface area, smaller particle size (~304 nm), well-dispersed nanoplates on graphene, and a percolating conductive carbon framework in NFP/G, are synthesized through sol-gel method as evidenced by XRD, BET, Raman, FESEM, HRTEM, and XPS. NFP/G exhibits almost theoretical capacity (115.1 mAh/g at 0.1C), excellent rate capability and exceptional cycling stability (~104 mAh/g with ~96% retention at 0.5C/50 cycles; ~86.8 mAh/g with ~94% retention at 1C/500 cycles), higher Na diffusion coefficients and reduced R_{ct} compared to NFP. This indicated that graphene-based conductive network engineering is a promising way to high-rate, long-lasting NASICON cathodes.

Overall, this thesis has the potential to clearly demonstrate how the engineering, synthesis, and optimization of Fe-based polyanionic phosphate cathode materials for SIBs can be achieved through compositional tuning and interfacial engineering. The results provide evidence on the strategic vanadium replacement (partial V to Fe replacement in $\text{Na}_3\text{FeV}(\text{PO}_4)_3$ with electrolyte optimization, and subsequently complete V-elimination by substituting with $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$ alluaudite), N, S-heteroatom-doped carbon coatings of improved conductivity with dual electrode functionality, and graphene-incorporated $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ networks can be useful in

improving sodium storage capabilities, rate and cycle performance. The outcomes of the thesis give valuable insights into structure-property-performance connections and open the pathway for future work on the development of low-cost, high-capacity, and long-cycle-life cathode materials for SIBs. These outcomes contribute to the development of secure, sustainable, and scalable SIB technologies as the next generation of future energy storage solutions, mainly in the integration of renewable energy, grid storage, and electric mobility.

7.2 Outlook and Future Prospects

The study in this thesis contributes to the development of SIBs, particularly in the development of cost-efficient Fe-based polyanionic phosphate cathode materials. By following a methodical design, synthesis, physicochemical, and electrochemical investigations of $\text{Na}_3\text{FeV}(\text{PO}_4)_3$, $\text{Na}_2\text{Fe}_{1.5}\text{Mn}_{1.5}(\text{PO}_4)_3$, and graphene-embedded $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ cathodes, the present research lays a solid foundation for future SIBs. The materials investigated had favorable characteristics such as good reversible capacity (approximately 115 mAh/g), high cycle stability (94 percent when used in 1 C 500 cycles), enhanced redox activity, rapid Na⁺ diffusion, and low interfacial resistance, which make them appropriate in sustainable, cost-effective, and safe battery technologies.

Although significant advancements have been made, future work could be focused on further investigating sophisticated material design methods, such as heterointerface engineering, lattice substitution with multiple transition metals, carbon-based coatings, and defect modulation to reduce irreversible phase transitions and stabilize electrode-electrolyte interfaces. The engineering of multicomponent TM phosphate systems, progressing from quaternary Fe-Mn-Cr-Ni compositions to high-entropy phosphates with 5+ transition metals, can enhance structural stability, electronic conductivity, and Na⁺-ion kinetics through synergistic redox

activity. In addition, the half-cell-based testing of these cathode materials should be conducted in a full cell configuration with optimized hard-carbon anodes, high voltage electrolytes, and stable separators in real-world applications. Simultaneously, scalability, cost-effectiveness, and eco-friendliness of the cathode synthesis should be prioritized. In addition, computational thermodynamic analyses can be used to accelerate the development of new high-entropy phosphate cathode materials by tracing complex structure-property-performance correlations.

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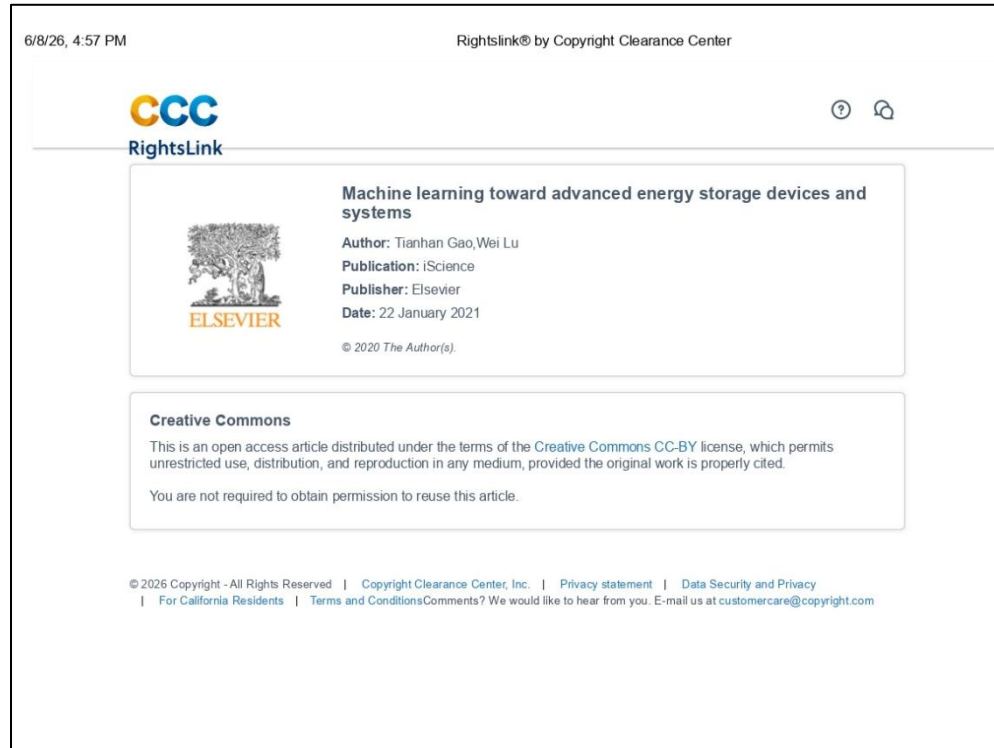


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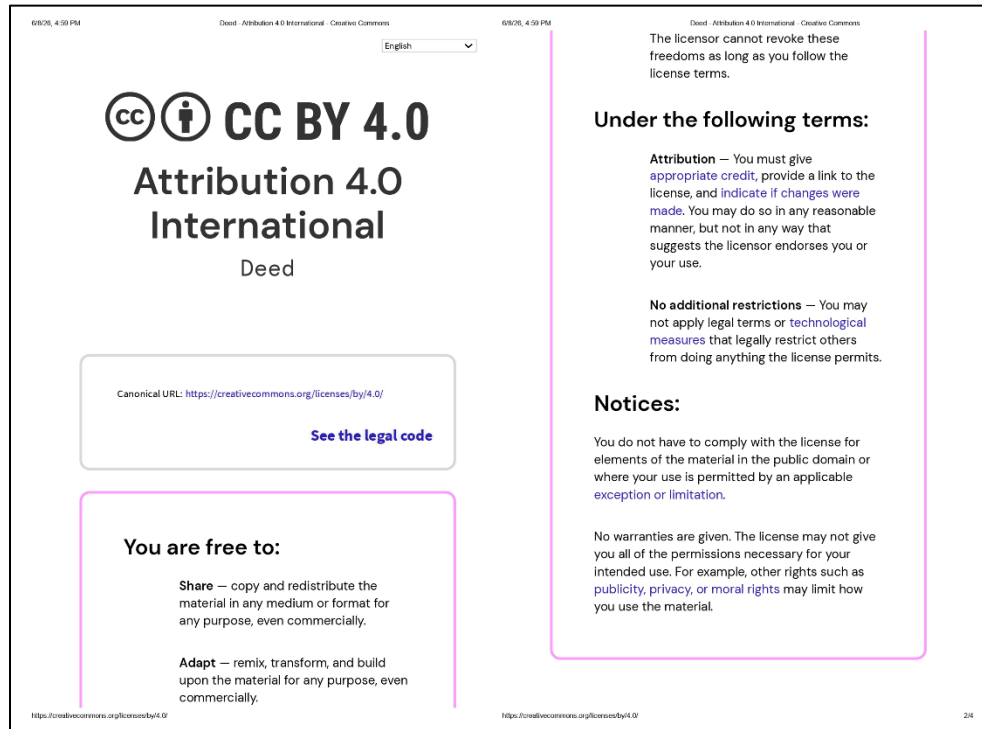


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Publication: ACS Nano

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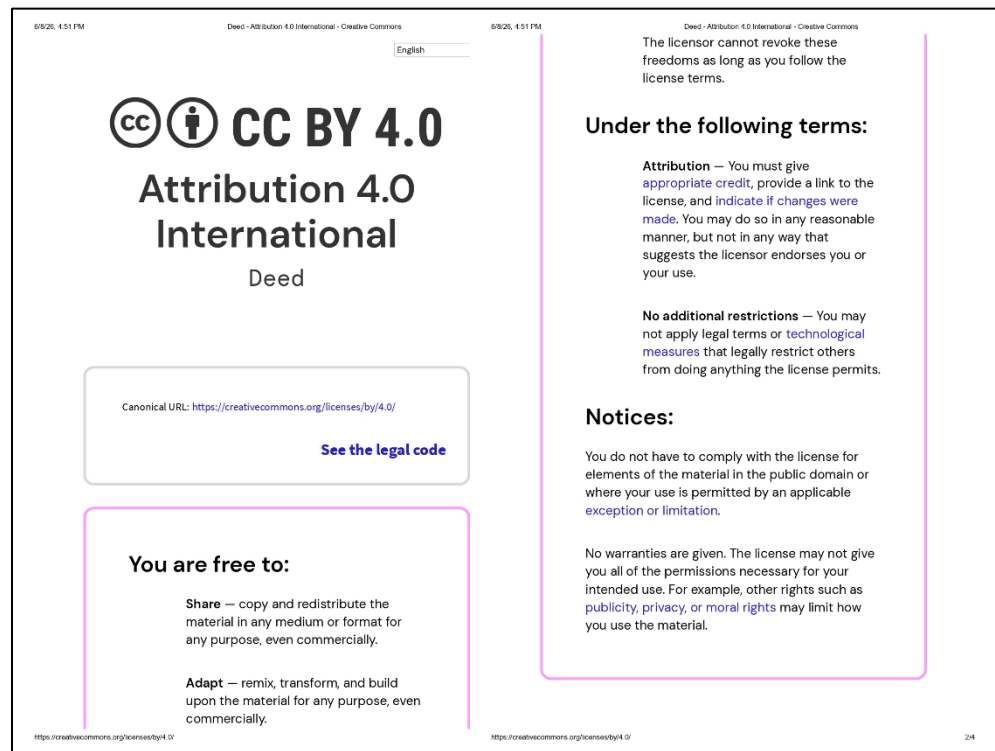


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