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C. Subashini

PSGR Krishnammal College for Women

S. Logesh Kumar

Christ the King Engineering College

V. D. Nithya

Bannariamman Institute of Technology

N. Priyadharsini

`priyadharsinin@psgrkcw.ac.in`

PSGR Krishnammal College for Women

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Atmosphere-Controlled Aqueous Sodium-Ion Storage Kinetics in $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$

Cathode for Hybrid Capacitor

C.Subashini ^a, S. Logesh Kumar ^b, V.D. Nithya ^c, N. Priyadharsini ^{a*}

^a Department of Physics, GRG EVolve Hub, Centre of Excellence in Electric Vehicles Training and Research, PSGR Krishnammal College for Women, Coimbatore-641004, Tamil Nadu, India.

^b Department of Electronics and Communication Engineering, Christ the King Engineering College, Coimbatore-641104, Tamil Nadu, India.

^c Department of Physics, Bannariamman Institute of Technology, Sathyamangalam- 638401, Tamil Nadu, India.

ABSTRACT

Sodium-ion capacitors (SICs) are gaining prominence as high-performance energy storage systems since they combine the superior energy densities of batteries and the high-power densities/long cycle life of supercapacitors. The present study focuses on the development of such battery-type $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ cathode materials and investigates their redox kinetics and charge storage capacity. The influence of calcination atmospheric effect causes the morphological and electrochemical behaviour were analysed. The off-stoichiometric compound was synthesized via a facile combustion route, with calcination undergone under both ambient air and argon atmospheres. The structural analysis confirmed an anorthic-triclinic crystal structure where an octahedral Ni^{2+} framework provides favorable sites for Na^+ accommodation between P_2O_7 layers via polyhedral coordination. Material characterization using thermogravimetric/Differential thermal analysis (TG/DTA), X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), and Raman spectroscopy verified the phase purity and thermal stability of the materials. The morphology was studied using a Field-Emission Scanning Electron Microscope (FESEM). The electrochemical performance and transport kinetics of the $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ cathode were investigated using COMSOL Multiphysics. A numerical model was developed to evaluate the electrochemical behaviour within the electrode under operating conditions. The simulation results illustrated the charge-storage behaviour in $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ through 2D and 3D plots. The findings revealed the

suitability of $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ cathode for enhancing the efficiency and stability of the hybrid capacitor. The constructed $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2||\text{AC}$ hybrid capacitor using 1M NaOH electrolyte demonstrated exceptional performance. Specifically, the argon-calcined sample achieved a specific capacitance of 115 F g^{-1} , with maximum energy and power densities of 38 Wh kg^{-1} and 489 W kg^{-1} , respectively. The long-term durability was confirmed with over 86% capacitance retention after 2,000 cycles. These results highlight that the synthesized $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ material could be well utilized as a robust and efficient electrode for advanced sodium-based storage applications. The theoretical performance of the assembled sodium-ion capacitor was validated through numerical simulations with COMSOL Multiphysics.

Keywords: Sodium-ion capacitor; Combustion; off-stoichiometric; Calcination atmosphere; Cyclic stability.

Corresponding author

* Email ID: priyadharsinin@psgrkcw.ac.in (Dr. N. Priyadharsini)

1. INTRODUCTION

Population growth and technological development increase the call for reliable and sustainable energy storage systems (ESS).^[1] The global transition toward a decarbonized economy, coupled with the limited availability of conventional energy resources paves the way for electrochemical energy storage systems.^[1] Among the available technologies, secondary batteries and supercapacitors have emerged as indispensable components for portable electronics, electric vehicles (EVs), and grid-scale energy storage applications.^[1,2] Lithium-ion batteries (LIBs) have dominated the commercial energy storage market for decades, owing to their long-lasting cycle life, maximum energy density, as well as robust electrochemical performance.^[3] However, the uneven geographical distribution and gradual depletion of lithium resources, coupled with rising costs, have motivated the search for alternative battery systems.

In this context, sodium-ion-based devices have gained considerable attention.^[4] Sodium is characterized by its natural abundance, low cost, and widespread availability in the Earth's crust. The Na^+ ions possess a larger ionic radius 1.02 Å compared to Li^+ ions 0.76 Å. Appropriate material design strategies, such as expanding interlayer spacings or using open-framework structures, can enable efficient sodium storage via intercalation and surface redox processes.^[4,5] Collectively, these developments have improved both the viability and electrochemical efficiency of sodium-based devices, for future energy storage applications.^[5]

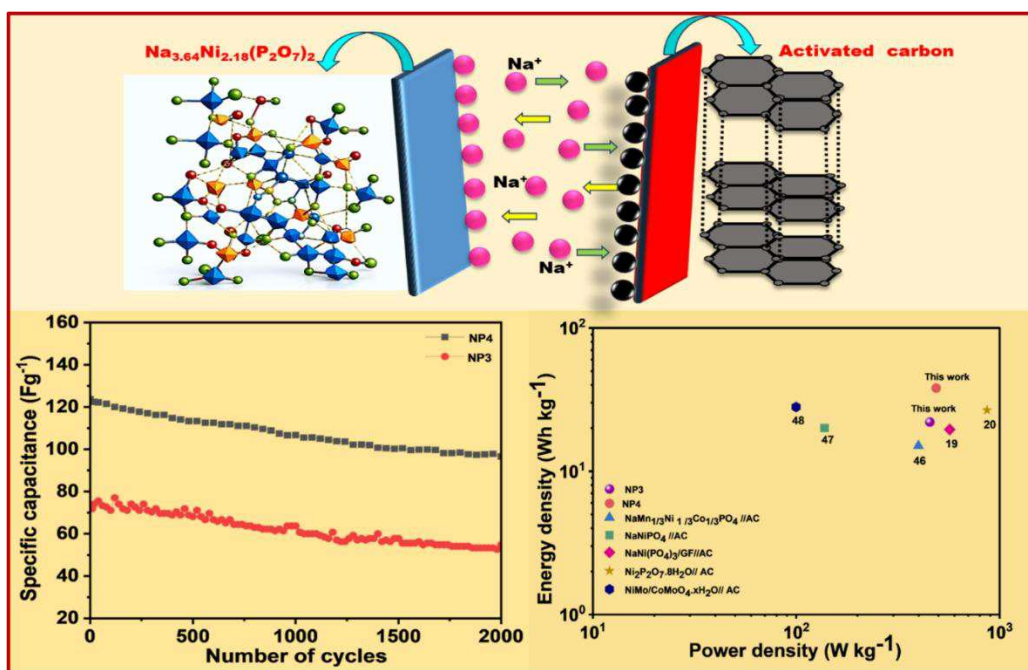
Sodium-ion batteries and sodium-ion capacitors represent promising candidates for next-generation systems.^[6] SICs, intends to sandwich the extraordinary properties of battery and capacitor in terms of energy and power densities.^[7] In recent years, electrode materials with open-framework structures have attracted increasing interest. Their interconnected channels and spacious cavities facilitate rapid ion diffusion and enhanced electrochemical activity.^[8] Particularly, the metal phosphate and pyrophosphate compounds have demonstrated excellent structural stability and tunable electrochemical properties, making them attractive for sodium-based energy storage applications.^[8,9]

Pyrophosphate-based materials containing $\text{P}_2\text{O}_7^{4-}$ groups have been widely investigated due to their robust covalent–ionic frameworks and strong affinity toward redox-active metal centers.^[10] The P-O-P bridge provides a stable environment that minimizes volume expansion during ion insertion/extraction. Several transition-metal-based pyrophosphates have been reported to exhibit promising performance in both aqueous and non-aqueous electrolytes.^[11, 12] However, many reported materials still suffer from limited energy density and sluggish charge-transfer kinetics.^[13] Consequently, the development of electrode materials with favorable structural features and improved transport properties remains essential.

Among transition-metal-based compounds, nickel-containing materials have received significant attention owing to their low cost, high elemental abundance, and excellent electrochemical stability.^[14] Nickel pyrophosphate $\text{Ni}_2\text{P}_2\text{O}_7$ possesses a three-dimensional framework composed of corner-sharing NiO_6 octahedra and P_2O_7 units, which enables pseudocapacitive behaviour associated with reversible $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox reactions.^[15] The monoclinic crystal structure provides interconnected diffusion pathways. Introducing sodium ions into this lattice to form sodium nickel pyrophosphate derivatives generates an alkali-ion sublattice and modifies the local electronic environment.^[16,17] This structural modification improves ionic conductivity and stabilizes the framework during repeated redox processes.^[18]

However, most previously reported nickel pyrophosphate systems exhibited a limited energy density and insufficient rate capability, highlighting the need for structurally optimized sodium-containing pyrophosphate frameworks.^[19,20] Consequently, sodium-containing nickel pyrophosphates are expected to serve as promising host materials for hybrid energy storage systems.^[21] Among them, off-stoichiometric electrode materials offer several advantages for electrochemical energy-storage applications due to the presence of intrinsic defects and mixed-valence states within the crystal framework.^[22] Deviation from ideal stoichiometry can generate cation vacancies, local lattice distortions, and defect sites, which provide additional ion-diffusion pathways and reduce ion migration barriers, thereby enhancing ionic conductivity.^[23, 24] To maintain charge neutrality, mixed oxidation states of transition-metal ions are often formed, facilitating electron hopping and improving electronic conductivity.^[25] Furthermore, the structurally flexible defect-rich framework can better accommodate repeated ion insertion/extraction during cycling, resulting in enhanced rate capability and long-term cycling stability.^[26] Therefore, off-stoichiometric modification has emerged as an effective approach for tailoring the structural and electrochemical characteristics of electrode materials, thereby enhancing their performance in advanced energy storage systems.^[27, 28]

In this work, the synthesis and electrochemical investigation of sodium nickel pyrophosphate, $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$, as a cathode for sodium-ion capacitor were studied. The compound was synthesized via a facile combustion method under ambient and argon atmospheres. The influence of synthesis atmosphere on the physical, morphological, and electrochemical properties was methodically examined. Electrochemical performance was evaluated using a three-electrode configuration in an aqueous electrolyte. Furthermore, a hybrid sodium-ion capacitor was assembled using $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ as the cathode and activated carbon as the anode. The graphical representation of the assembled device is shown in Scheme 1. The assembled device exhibits high energy and power densities over a wide operating voltage window, along with excellent cycling stability exceeding 2000 cycles. This study demonstrates the potential of sodium nickel pyrophosphate as a robust and efficient electrode material for advanced sodium-based energy storage systems. Even though, several nickel phosphate and pyrophosphate materials have been investigated for sodium-ion storage, studies on off-stoichiometric sodium nickel pyrophosphates and the influence of calcination atmosphere on their electrochemical behavior remains limited. In particular, understanding the relationship between atmosphere-induced structural modification, Ni valence states, and sodium-ion transport kinetics is still deficient. Therefore, this work focuses on the synthesis of off-stoichiometric $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ under ambient and argon atmospheres and systematically correlates the structural, surface electronic, and electrochemical properties for aqueous sodium-ion capacitor applications. Furthermore, the suitability of $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ cathode for enhancing the efficiency and stability of hybrid capacitor was investigated using COMSOL Multiphysics.



Scheme 1: Graphical representation of assembled $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2 // \text{AC}$ aqueous sodium-ion hybrid capacitor.

2. Experimental Materials and Methods

2.1. Materials

Nickel nitrate tetrahydrate ($\text{Ni}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$) (Himedia, > 98.9%, USA), sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) (Merck; > 98.90%, Germany), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) (Merck; > 98%, Germany) were used for synthesizing the compound. Activated carbon of commercial grade (AC) (Sigma Aldrich, > 99.90%, USA), N-methyl-2-pyrrolidone (NMP) (Alfa Aesar > 99.90%, USA), polyvinylidene difluoride (PVDF, Alfa-Aesar > 99.90%, USA) were used for cell preparation. All these chemicals were made into solution using deionised water.

2.2. Combustion synthesis of $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ material

The off-stoichiometric $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ compound was synthesized via a facile solution combustion route. This method was chosen for its ability to produce highly crystalline, homogeneous powders with high surface areas at relatively low temperatures. For the synthesis

of $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$, a stoichiometric amount of the starting materials, such as sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$), and citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) were taken and dissolved in deionized water individually. Herein, the citric acid was used as a fuel. The aqueous citric acid (2.26g) was added dropwise to the mixture containing $\text{Ni}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ to attain a homogeneous precursor solution. Then, the mixture was stirred uniformly at 500 rpm at 80°C . The solution underwent decomposition and dehydration, forming a transparent green gel, which was then combusted at around 400°C to yield black powder. The pristine black powder (NP1) was ground and calcined at various temperatures. NP1 calcined at 500°C and 700°C for 5 hours under atmospheric conditions was labelled as NP2 and NP3, respectively. Additionally, NP1 was calcined at 700°C for 5 hours under an argon atmosphere, and the resultant sample was labelled as NP4. Further elevation of the calcination temperature resulted in the material melting.

2.3 Material characterization techniques

The crystallization temperature and thermal stability of the compound were confirmed through Thermogravimetric and Differential Thermal Analysis (TG/DTA). The phase purity and crystalline structure were identified using X-ray Diffraction (XRD). The local bonding environment and functional groups were examined using FTIR and Raman spectroscopy, with a focus on the P_2O_7 stretching and P-O-P bending vibrational modes. Field-Emission Scanning Electron Microscopy (FESEM) was employed to elucidate the morphological features and grain size distribution. The presence of surface elemental and its valence state composition of the sample was carried out by X-ray photoelectron spectroscopy (XPS). The electrochemical and transport kinetics of $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ cathode was investigated using COMSOL Multiphysics.

2.4. Electrode preparation

The electrochemical behaviour of the synthesized $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ was evaluated by preparing a working electrode. The active material (80 wt.%) was homogeneously blended with conductive carbon black (15 wt.%) and the solvent polyvinylidene difluoride (PVDF, 5 wt.%), which served as the polymeric binder. This mixture was processed into a fine black powder, to which a few drops of N-methyl-2-pyrrolidone (NMP) were added to achieve a fine black slurry. The resulting electroactive slurry (1 mg) was precisely casted onto a 1 cm² stainless-steel (SS) foil substrate. To ensure complete solvent removal and robust adhesion of the active layer, the electrodes were dried overnight at 80°C in a stabilized hot-air oven. The electrochemical behaviour of $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ cathode was primarily investigated by three-electrode configuration in an aqueous 1M NaOH electrolyte. In this setup, a platinum (Pt) wire served as the counter electrode, while a standardized Hg/HgO electrode was utilized as the reference electrode to ensure precise potential control. To assess the practical applicability of the material for sodium-ion storage, a full hybrid cell assembly was constructed. This two-electrode system comprised of synthesized $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ as the cathode and AC as the anode. A glass microfiber separator was employed to prevent electrical shorting while maintaining efficient ionic transport through the 1 M NaOH electrolyte. Comprehensive electrochemical analyses, including cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS), were conducted using a Biologic SP-150 (Germany) electrochemical workstation. The CV analysis recorded over various scan rates elucidates the charge storage kinetics and redox reversibility. The specific capacitance and the evaluation of energy and power densities were performed using GCD analysis. Furthermore, the EIS analysis was performed across a broad frequency range of 10MHz to 1MHz at room temperature. This systematic approach provides a holistic view of the material's ability to maintain high-rate capability and structural integrity over repeated cycling.

3. RESULTS AND DISCUSSIONS

3.1 Structural and morphological studies

The TG/DTA analysis was performed to examine the thermal stability, structural phase transition, and crystallization temperature of the pristine NP1 sample, ensuring complete conversion of the precursor to the desired $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ compound. In Fig. 1(a), two distinct weight losses are evident as the temperature increases. An overall weight loss of 15% is observed from room temperature to 900°C. The initial weight loss, approximately 5.9%, occurs between 0 and 300 °C and is attributed to the decomposition of volatile compounds and to the presence of physisorbed water molecules in the sample. Around 300-350°C, the sample underwent the exothermic decomposition of nitrate precursors versus fuel.^[29] The subsequent weight loss of 6.2% occurs in the temperature range of 400-750 °C, with the effective crystallization temperature identified as 500 -700 °C. Beyond 750°C, complete sample decomposition takes place. Apart from the DTA profile reveals a distinct, sharp endothermic reaction, excluding water molecules, confirming the formation of a stable metal oxide. Beyond 500°C, the weight loss is attributed to a sharp, reversible endothermic phase transition. Eventually, the compound possesses robust thermal stability.^[30]

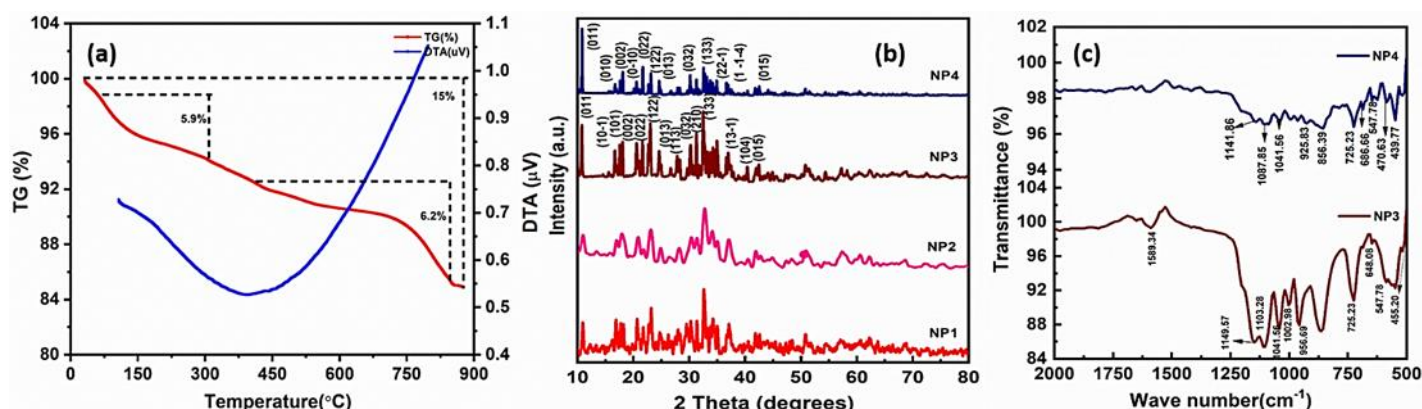


Figure 1: (a) TG/DTA curve of NP1 sample, (b) XRD spectra of $\text{Na}_2\text{NiP}_2\text{O}_7$ samples at different temperatures, (c) FTIR pattern of NP3 and NP4 samples

Fig. 1(b) shows comparative XRD spectra of the prepared materials at different calcination temperatures. NP1 shows the XRD spectrum of the pristine material. NP2 shows the XRD pattern of the prepared materials calcined at 500°C for 5 hours. The XRD patterns of NP3 and NP4 showed the profiles formed at 700°C for 5 hours under air and argon atmospheres, respectively. The XRD pattern of NP1 showed the presence of impurities due to excess nitrate precursors. Then, the XRD pattern of NP2 illustrated the formation of $\text{Na}_4\text{Ni}_7\text{P}_6\text{O}_{24}$ compound. It showed that a temperature of 500°C is insufficient to fully decompose the nitrate and phosphate precursors, resulting in an incomplete solid-state reaction and the formation of an intermediate $\text{Na}_4\text{Ni}_7\text{P}_6\text{O}_{24}$ phase. The limited thermal energy restricts the diffusion and crystallization, preventing the condensation of phosphate units into a stable pyrophosphate (P_2O_7) structure. The desired compound $\text{Na}_{3.16}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ was achieved at a calcination temperature of 700°C (5 hours) in an air (ambient) atmosphere. Furthermore, the calcination was repeated at 700°C for 5 hours under an argon atmosphere, yielding the $\text{Na}_{3.16}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ compound. Calcination under an argon atmosphere prevents Ni oxidation and stabilizes the phase, resulting in improved purity and structural integrity. After 700°C, partial melting of the material occurred, which disrupted the pyrophosphate framework due to thermal instability.

The XRD pattern of both compounds (NP3 and NP4) matched well with the ICDD card no. 98-020-1760, exhibiting an anorthic-triclinic crystal structure. The space group is P_1 , and the cell volume is $559.68 \times 10^6 \text{ \AA}^3$. The corresponding lattice parameters are $a=6.35 \text{ \AA}$, $b=9.35 \text{ \AA}$, $c=10.88 \text{ \AA}$, and $\alpha=64$, $\beta=85$, $\gamma=73$. The crystallite size (D) of the synthesized material was calculated by Scherer formula (equation (1)) using the values of full width half maximum (β), Bragg angle (θ) and wavelength of X-ray (λ).^[31]

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

The crystallite sizes of the NP3 and NP4 samples were calculated to be 52 nm and 43 nm, respectively. The crystallite size determines the surface area, ion diffusion length, and structural stability of electrode materials, which altogether determine their electrochemical behavior. Smaller crystallites lead to more grain boundaries and defects, which can increase charge-transfer resistance or electrolyte decomposition.^[32]

The FTIR spectra of NP3 and NP4 shows predominant stretching and bending mode associated with P-O and Ni-O vibrations respectively (Fig. 1 (c)). Even though both NP3 and NP4 exhibit similar vibration modes, there is a slight shift in their transmittance peak observed. This slight peak shift and improved vibrations observed for NP4 indicate reduced lattice distortion in NP4 when compared to NP3. Next, the asymmetric stretching mode of P-O is appeared around 1041 cm^{-1} 1087 cm^{-1} for NP3 and NP4 respectively. Additionally the symmetrical stretching mode of P-O bond occurs between 950-920 cm^{-1} attributes to $(\text{PO}_3)^{2-}$ group ^[33] Furthermore, the peaks at 770 cm^{-1} and 779 cm^{-1} corresponds to P-O-P bond. The splitting of peaks around 725.23 cm^{-1} and 725 cm^{-1} indicates the stretching of P-O-P and condensation of $[\text{PO}_4]_3$ tetrahedra to $[\text{P}_2\text{O}_7]$. The peaks at $\sim 686 \text{ cm}^{-1}$ and $\sim 683 \text{ cm}^{-1}$ was identified to be PO_3 groups.^[34] The bending vibration of Ni-O bond was identified at 547 cm^{-1} for NP3 and 490 cm^{-1} for NP4. The stretching modes of Ni-O bond was detected for both NP3 and NP4 at 439 cm^{-1} and 417 cm^{-1} respectively.^[35] Additionally, the NP3 and NP4 exhibited an asymmetric and symmetric stretching vibrations of P-O-P which is a characteristic of P_2O_7 group.^[35] The presence of well-defined P-O-P, PO_3 and Ni-O-P framework validate the formation of a stable pyrophosphate framework which could be beneficial for reversible Na^+ insertion/extraction during electrochemical cycling.

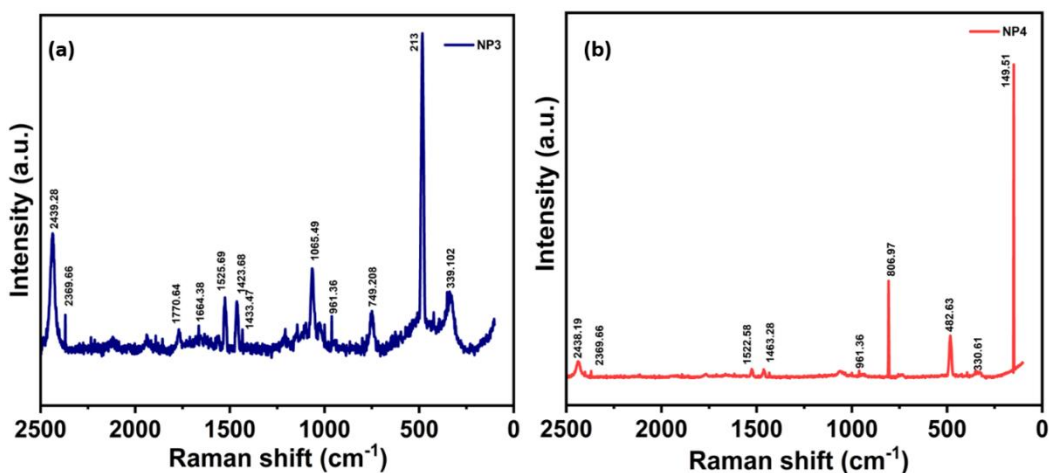


Figure 2: Raman analysis of (a) NP3 and (b)NP4 samples

The Raman spectra of NP3 and NP4, presented in Fig. 2(a) and (b), provide valuable information regarding the vibrational characteristics of the pyrophosphate framework. A strong Raman band centered at approximately 961 cm^{-1} is attributed to the symmetric stretching vibration of the P–O–P bridge in the P_2O_7 polyanion. Another distinct band located near 482 cm^{-1} originates from the bending vibration of the P–O–P linkage. The prominent peaks observed at around 1065 cm^{-1} for NP3 and 1052 cm^{-1} for NP4 correspond to the asymmetric stretching vibrations of the phosphate tetrahedra (PO_4), whereas the band near 570 cm^{-1} is associated with the bending vibration of the phosphate group. These vibrational features agree well with those reported for nickel-based pyrophosphate materials in the literature.^[36,37] Additional Raman bands appearing near 1522 cm^{-1} and 806 cm^{-1} further confirm the presence of P–O stretching and bridging P–O–P vibrational modes characteristic of the pyrophosphate network.^[37] The band around $330\text{--}340\text{ cm}^{-1}$ is assigned to lattice vibrations involving Ni–O and O–Ni–O bonds, indicating the coordination of nickel within the octahedral oxygen environment.^[38] The presence of these characteristic vibrational modes verifies the formation of the interconnected P_2O_7 framework in both samples. Compared with NP3, NP4 exhibits refined peak shifts and broader Raman bands, suggesting the introduction of local lattice distortions and defect sites after argon-assisted calcination. Such structural modifications can

improve charge transport for electrochemical reactions. Moreover, the pyrophosphate framework together with the Ni–O coordination promotes reversible $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox processes and enhance Na^+ diffusion during repeated charge–discharge cycles, thereby contributing to the superior electrochemical performance of NP4.

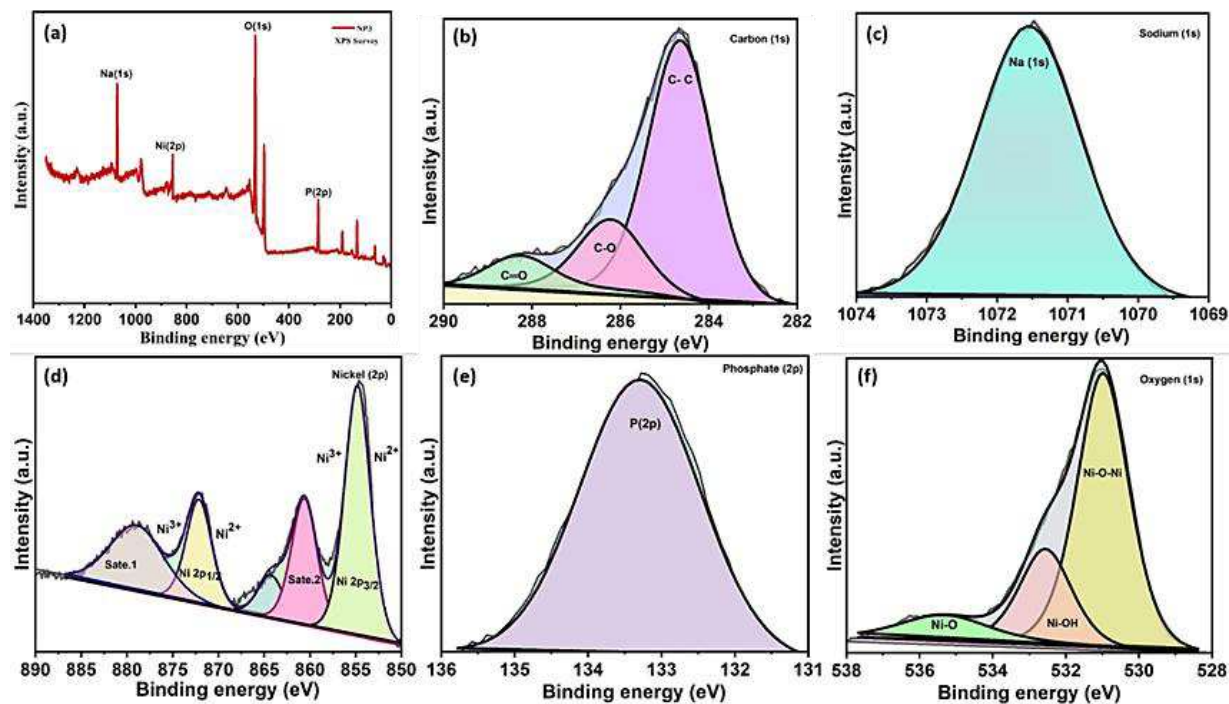


Figure 3: XPS spectra of NP3 (a) survey spectrum, (b) carbon, (c) sodium, (d) Nickel, (e) phosphate, and (f) oxygen.

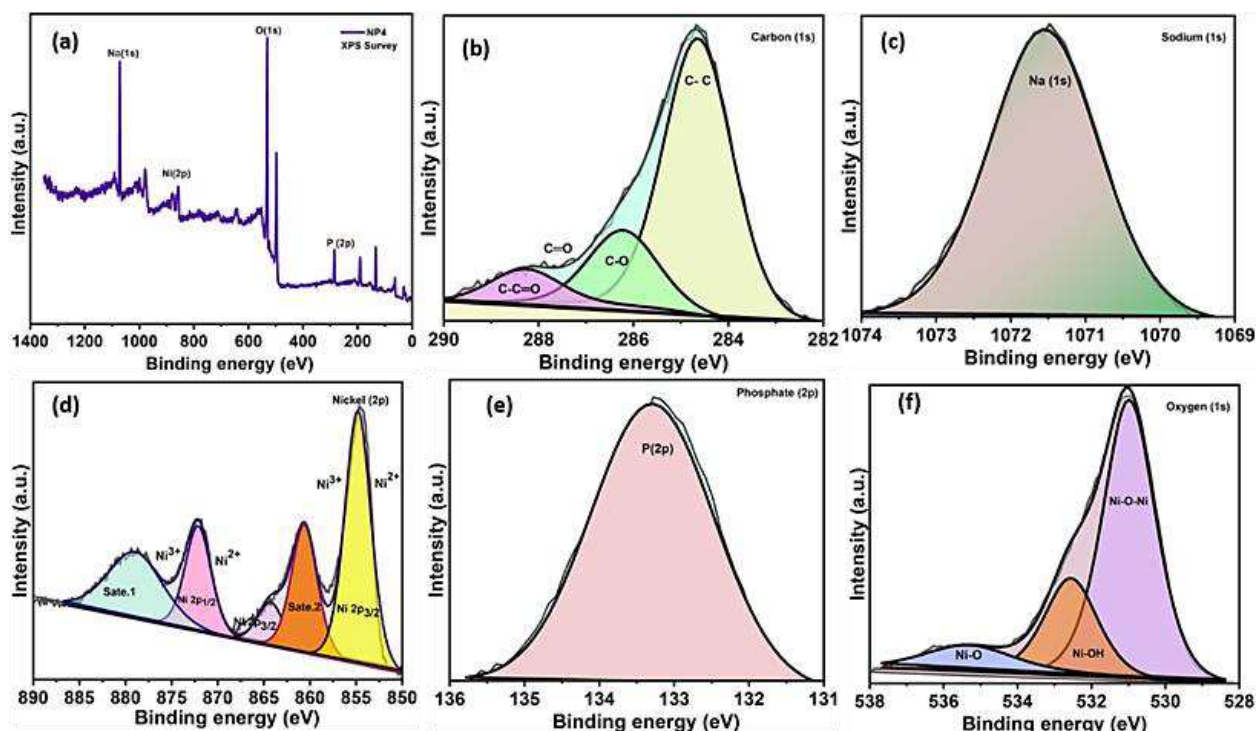


Figure 4: XPS spectra of NP4 (a) survey spectrum, (b) carbon, (c) sodium, (d) Nickel, (e) phosphate, and (f) oxygen

The elemental composition and oxidation states of NP3 and NP4 were identified from XPS analysis. The corresponding survey spectrum and core level spectra of NP3 and NP4 is provided in Fig. 3 and Fig. 4. The XPS spectrum confirmed the presence of carbon (C), sodium (Na), Nickel (Ni), phosphate (P), and oxygen (O) in NP3 and NP4 samples, respectively. The absence of any foreign elements confirmed the formation of pure $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ materials. From the survey spectrum of NP3 sample (Fig. 3(a)), the valence states of Na (1s), Ni (2p), P (1s), and O (2p) was confirmed. The high-resolution XPS spectra of Ni 2p consist of doublet peaks at 782.23 eV and 797.82 eV, that corresponds to Ni 2p_{1/2} and Ni 2p_{3/2} (Fig. 3d) that substantiates the presence of Ni³⁺ in NP3 and NP4 compounds.^[39, 40] There is a slight positive shift visualized in the Ni 2p binding energies that can be attributed to reduced electron density around the Ni ions, arising from strong metal–oxygen bonding. Most importantly, the presence of a shake-up satellite peak at about 785 and 804 eV for NP3 and NP4, indicates the oxidation state of Ni²⁺.^[41] Compared with untreated material, the argon-treated material showed a relatively larger integrated peak area associated with Ni²⁺ accompanied by reduced contribution

from Ni^{3+} species. The increased $\text{Ni}^{2+}/\text{Ni}^{3+}$ ratio in the argon-calcined sample reflects the formation of an oxygen-deficient environment. The co-existence of Ni^{2+} and Ni^{3+} can facilitate electron hopping between the two oxidation states, thereby improving the electronic conductivity and charge-transfer characteristics of the material. The high-resolution O 1s spectrum shows lattice oxygen species and surface-adsorbed oxygen species at 531 eV, suggesting the presence of O-Ni bond. The spectra also revealed the presence of sodium (Na) 1s peak at 1071.36 eV and characteristic C-C peak at 281.8 eV.^[41] The prominent peak noticed in Fig. 3(e) at 133.42 eV corresponds to P 2p that indicates the presence of P-O-P forming a P_2O_7 group.^[42] It is observed from XPS analysis that both NP3 and NP4 possess similar valence states for Na (1s), Ni (2p), P (1s), and O (2p) with a slight shift in peak value. The improved electrochemical behavior of argon-treated material is likely to be associated with optimized Ni valence states and defect-induced oxygen vacancies, which can enhance electronic conductivity and facilitate Na^+ diffusion.

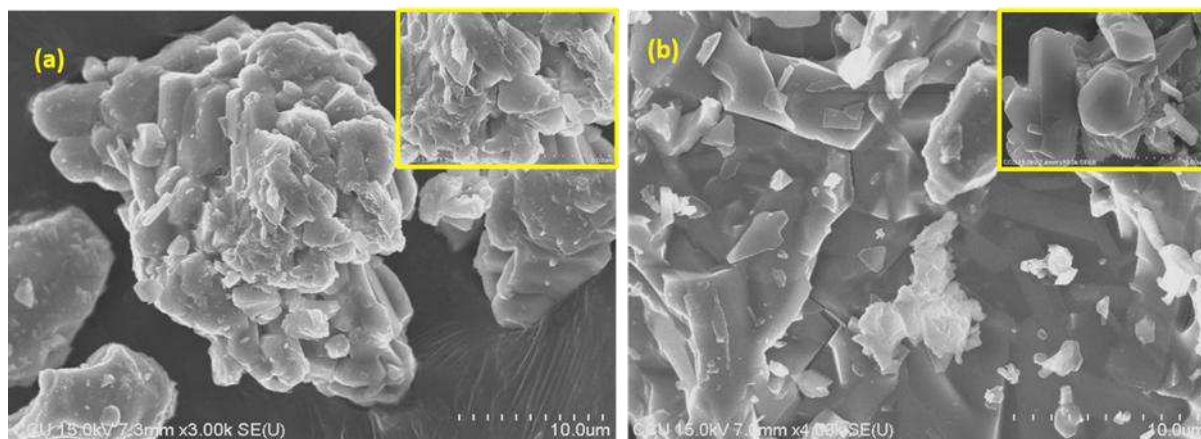


Figure 5: FE-SEM micrographs of (a) NP3 and (b) NP4 samples at 10 μm range with corresponding inset images at a 5 μm range

The surface morphology of $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ was examined using high-resolution FE-SEM analysis, as shown in Fig. 5. The micrographs illustrate the morphological features of NP3 and NP4. Fig. 5(a) reveals that NP3 exhibits an irregular plate-like structure composed of

stacked sheet layers as observed at the 10 μm range. The particles appear bulky and agglomerated, likely due to particle fusion during combustion synthesis. The anorthic crystal structure of NP3, characterized by non-uniform lattice parameters, may contribute to this morphology, as observed in the inset of Fig. 5(a), which is magnified to a 5 μm scale. In contrast, Fig. 5(b) shows that NP4 displays a more uniform particle distribution, with elongated flakes and disc-like features observed at the edges and corners, which formed upon further calcination. This improvement in morphology can be attributed to synthesis under an argon atmosphere, which minimizes interaction with ambient air during calcination. The inset of Fig. 5(b) shows the stacked plate-like morphology of NP4 samples at 5 μm . During the electrochemical process, this morphology facilitates Na^+ ion transport and electrolyte penetration into the voids and open spaces. The stacked plate-like morphology provides interconnected ion transport pathways and a larger electrochemically active interface, thereby facilitating faster Faradaic reactions and improved charge storage kinetics.

4. ELECTROCHEMICAL CHARACTERIZATION:

The electrochemical performance of the $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ cathodes, synthesized under ambient (NP3) and argon (NP4) atmospheres, was systematically investigated to elucidate the influence and understand the role of calcination atmosphere on charge storage characteristics mechanism. Systematic evaluation was conducted using cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) in a three-electrode configuration. An aqueous 1 M NaOH electrolyte was selected for these studies, leveraging its high ionic conductivity and low internal resistance, which facilitate rapid Na^+ mobility and enhance the evaluation of battery-type Faradaic processes.

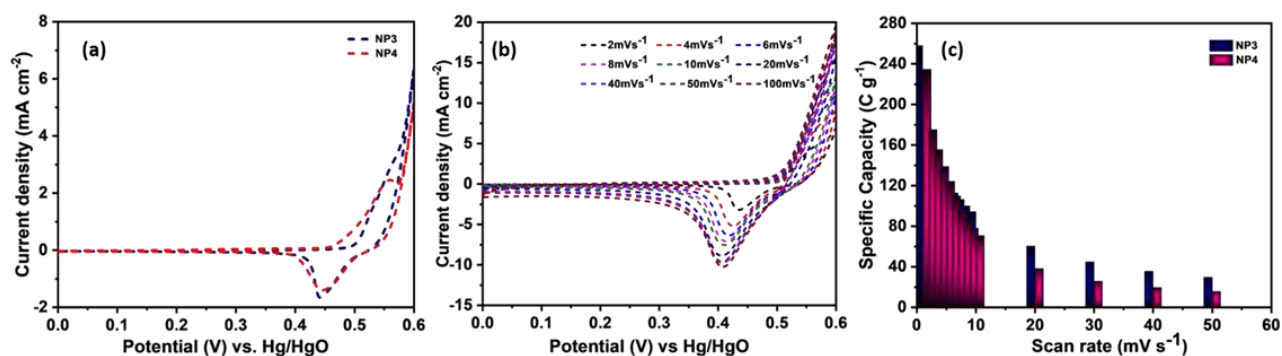


Figure 6: (a) Comparative CV analysis of NP3 and NP4; (b) CV curve of NP4 at different scan rates; (c) specific capacity comparison of NP3 and NP4 for different scan rates

Fig. 6(a) shows the comparative CV profiles of the NP3 and NP4 electrodes in 1 M NaOH at 2 mV s⁻¹. Compared with NP3, NP4 exhibits a higher current response and a larger voltammetric area, indicating improved electrochemical performance. The observed anodic/cathodic peaks at approximately 0.14/0.47 V and 0.04/0.48 V correspond to the Ni²⁺/Ni³⁺ and Ni³⁺/Ni⁴⁺ redox transitions, respectively. While both samples exhibit similar redox positions, the sharper, more symmetric peaks of NP4 suggest superior redox reversibility and reduced polarization compared to NP3. This highlights the critical role of argon calcination in stabilizing the electroactive Ni–O–P framework and minimizing defect-induced charge trapping that can arise under ambient conditions. The redox peaks observed in the CV curves demonstrate the battery-type electrochemical behaviour of the electrodes, where charge storage is dominated by reversible Faradaic reactions.^[31] The 3D architecture of Na_{3.64}Ni_{2.18}(P₂O₇)₂ enables Na⁺ diffusion and maximizes the number of electrochemically active sites during cycling. The tunnel-like structure of Ni and a pair of P₂O₇⁴⁻ ionic sites, with Na⁺ at the center, in NP3 cathodes provides a more surface area.

Fig. 6(b) shows the CV curve of the NP4 electrode measured at scan rates ranging from 2 and 100 mV s⁻¹ within a 0–0.5 V potential window. Increasing the scan rate the current response enhances proportionally while retaining the characteristic redox features.^[41] At higher

scan rates, the gradual shift and broadening of the redox peaks arise from diffusion controlled and electrode polarization confirming the dominant Faradaic charge-storage mechanism and favourable kinetics of the NP4 electrode. The redox reversibility of $\text{Ni}^{2+}/\text{Ni}^{3+}$ transition governs the charge storage mechanism, accompanied by electron transfer during Na^+ intercalation and deintercalation as follows,

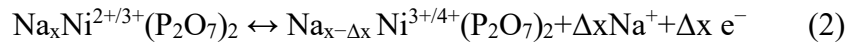


Fig.6(c) shows the comparative bar graph of specific capacity of NP3 and NP4 cathodes at the various scan rates. The specific capacity (C) was calculated based on the equation 3.

$$C = \frac{\int i(E)dE}{2mv} \quad (3)$$

where $\int i(E)dE$ represents the integrated area of the CV curve, m (g) is the mass of the active material loaded on the electrode, and v (mV s^{-1}) is the scan rate.^[31] The NP4 electrode delivers specific capacities of 186, 130, 95, 30, and 16 C g^{-1} at scan rates of 2, 5, 10, 50, and 100 mV s^{-1} , respectively, whereas the corresponding values for NP3 are 175, 124, 71, 15, and 8 C g^{-1} . At all scan rates, NP4 exhibits superior charge-storage performance compared to NP3, indicating improved electrochemical activity. For both electrodes, the specific capacity decreases with increasing scan rate, which is due to the limited diffusion of OH^- ions into the interior of the electrode and the reduced availability of active sites for Faradaic reactions at higher polarization rates.^[39,40, 41]

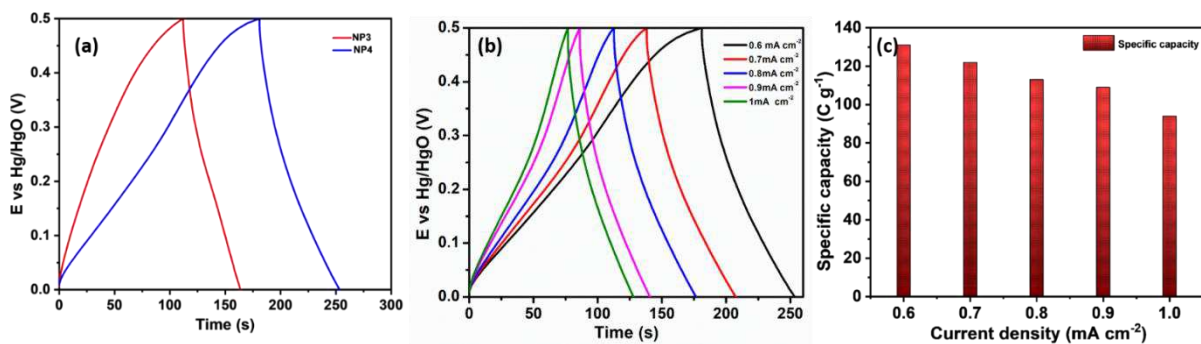


Figure 7: (a) Comparative GCD analysis of NP3 and NP4 compounds, (b) GCD analysis of NP4 at various current densities, (c) comparative analysis of specific capacity versus various current densities of NP3 and NP4

The galvanostatic charge–discharge (GCD) behaviour of the NP3 and NP4 electrodes was evaluated within a potential window of 0–0.5 V at different current densities. Fig. 7(a) compares the GCD profiles of both electrodes at 1 mA cm⁻² current rate. The charge–discharge curves exhibit distinct voltage plateaus, confirming that the charge storage is governed by Faradaic redox reactions. Compared with NP3, the NP4 electrode shows a more uniform and reversible charge–discharge profile, suggesting enhanced reaction kinetics and lower internal resistance resulting from argon-assisted calcination. Fig. 7(b) presents the GCD curves of the NP4 electrode recorded at current densities ranging from 0.6 to 1 mA cm⁻². As the applied current density increases, the discharge time decreases because of the reduced charge–discharge duration that limits Na⁺ ion intercalation/deintercalation within the active material. The specific capacity C (C g⁻¹) can be calculated by,

$$C = \frac{i \times \Delta t}{m} \quad (4)$$

where i denote the discharge current (A), Δt represents the discharge time (s), and m is the mass of the active material (g). The specific capacities obtained from the GCD profiles for the NP4 electrode at different current densities are represented in Fig. 7(c). The specific capacity of NP4 at 0.6, 0.7, 0.8, 0.9, 1 mA cm⁻¹ is found to be 147,138, 126, 103,95 C g⁻¹ respectively, while the specific capacity of NP3 at 0.6, 0.7, 0.8, 0.9, 1 mA cm⁻¹ is found to be 82, 73,55,19, 15 C g⁻¹ respectively. The three-dimensional heterostructure enables efficient electron transport and rapid Na⁺ ion diffusion, thereby accelerating Faradaic reaction kinetics. The improved charge-transfer behavior is well supported by CV and GCD results, explaining the enhanced rate capability and higher specific capacitance of the NP3 and NP4 electrodes. Based on the

electrochemical performance obtained from the three-electrode measurements, asymmetric hybrid devices were constructed using NP3 and NP4 electrodes to further evaluate their device-level performance.

4.1. Electrochemical performance of fabricated NP3 and NP4 hybrid sodium-ion capacitor

To demonstrate the practicability of the electrode materials, hybrid sodium-ion capacitor (SIC) devices were fabricated using NP3 and NP4 as the cathodes and AC as the anode. A glass microfiber separator was soaked in 1 M NaOH served as the electrode-electrolyte separator. The mass loading of the positive and negative electrodes was optimized based on the charge balance relationship ($q^+ = q^-$) to ensure balanced electrochemical performance. The electrode mass ratio was determined using the following equation:

$$\frac{M_+}{M_-} = \frac{Q_{sep-}}{C_{sep+}\Delta E_+} \quad (5)$$

where M_+ and M_- are the active material mass (g) on the positive and negative electrode respectively, C_{sep+} is the specific charge capacity of the positive electrode and ΔE_+ (V) denotes its operating potential window.^[44] Using the charge balance equation, the optimal mass ratio of the positive to negative electrode in the assembled hybrid capacitor was calculated to be 1.2.

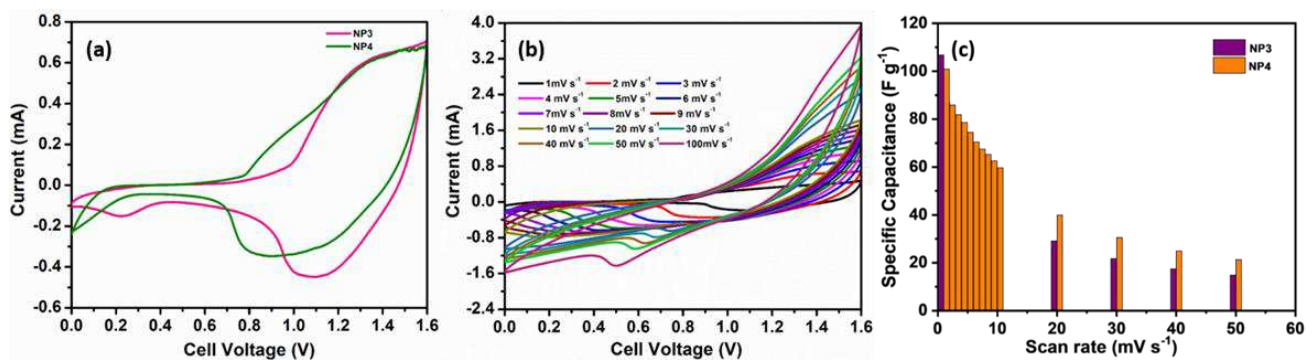


Figure 8: (a) CV curves of the fabricated hybrid cells, NP3 and NP4, at scan rates, (b) CV curves of NP4 at various scan rates, and (c) Comparative graph of specific capacitance with scan rate curves of NP3 and NP4 hybrid sodium ion capacitor

The electrochemical performance of the assembled hybrid sodium-ion capacitor (SIC) devices, NP3||AC and NP4||AC, was evaluated over an operating voltage window of 0–1.5 V. Fig. 8(b) compares the cyclic voltammograms of both devices recorded at a scan rate of 2 mV s⁻¹. Among the two configurations, NP4||AC exhibits a larger enclosed CV area and higher current response, indicating enhanced charge storage capability. The improved electrochemical performance is attributed to the favourable crystal structure of the Ni-based pyrophosphate framework, where interconnected NiO₆ octahedra and P₂O₇⁴⁻ polyanions provide stable Na⁺ diffusion pathways. The three-dimensional framework facilitates rapid ion transport and reversible Faradaic reactions, contributing to the superior capacitive behaviour of the NP4||AC device. The superior electrochemical response of NP4||AC is due to the tunneled pyrophosphate framework, where Na⁺ ions occupy multiple crystallographic sites and migrate efficiently through interconnected channels. In contrast, the NP3||AC device, although electrochemically active, exhibits a relatively higher polarization due to surface oxidation and less efficient ion diffusion resulting from ambient atmospheric processing. The specific capacitance versus scan rate plotted in Fig. 8(c). The specific capacitance is evaluated by

$$C_{sc} = \frac{i \int v dt}{2m v \Delta V} \quad (6)$$

where I is current, m (g) is the mass of active materials, and ΔV (V) is the potential window, v is the scan rate.^[44] The specific capacitance of the NP4||AC whole cell at 2, 10, 50, and 100 mV s⁻¹ is 115, 91, 18, and 12 F g⁻¹, respectively. The specific capacitance of NP3||AC whole cell at 2, 10, 50, and 100 mV s⁻¹ is 109, 63, 22, and 10 F g⁻¹, respectively. The diffusion coefficient (D) is an important parameter that determines the rate of ion transport within the

electrode material and directly influences electrochemical performance and reversibility. The Na^+ diffusion coefficient (D) was calculated using the Randles–Sevcik equation from the CV response at different scan rates. The equation is given as

$$D = \left[\frac{i_p}{2.69 \times 10^5 \cdot n^2 \cdot A \cdot C \cdot \nu^{1/2}} \right]^{1/2} \quad (7)$$

Where i_p (A) denotes the peak current, n is the number of electrons transferred during the redox reaction, A (cm^2) is the area of the electrode, C (mol cm^{-3}) is the concentration of Na^+ ions, D ($\text{cm}^2 \text{ s}^{-1}$) represents the Na^+ diffusion coefficient, ν (V s^{-1}) is the scan rate. The obtained D values indicate that the NP4 electrode exhibits higher ionic diffusivity compared to NP3. The higher cathodic diffusion coefficient for NP4 ($6.0 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) suggests that it provides faster Na^+ ion transport and enhanced electrochemical kinetics during the reduction process. This can be attributed to a more open microstructure and a more accessible surface area, which facilitate electrolyte penetration and charge transference at the electrode-electrolyte interface. On the other hand, NP3 shows relatively lower diffusion coefficients for both cathodic ($5.16 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) and anodic ($2.76 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) processes. This implies comparatively sluggish ion mobility, likely due to a denser morphology or limited pore connectivity that restricts ion diffusion pathways.

Hence, both materials exhibit smaller D values during the anodic scan than during the cathodic scan, indicating asymmetric ion transport behavior—pseudocapacitive or intercalation-type materials, in which the oxidation process involves slower charge compensation or partial structural rearrangement. The higher Na^+ diffusion coefficient is obtained for the NP4 electrode indicates faster ion transport kinetics and electrochemical reversibility compared to NP3. The improved diffusion behaviour facilitates more efficient Na^+ insertion/extraction during the redox process, leads to greater utilization of electroactive sites. These findings demonstrate that argon-assisted calcination (NP4) promotes Na^+ diffusion

within the electrode. The higher diffusion coefficient of NP4 confirms improved Na^+ transport kinetics and enhanced electrochemical reversibility compared to NP3.

The cyclic voltammograms of NP3 and NP4 recorded at 1 mV s^{-1} exhibit clear redox peaks corresponding to $\text{Ni}^{2+}/\text{Ni}^{3+}$ transition coupled with Na^+ intercalation and de-intercalation within the pyrophosphate lattice. During the cathodic scan, Na^+ ions are inserted into the host structure with the reduction of Ni^{3+} to Ni^{2+} , while the anodic sweep involves ion extraction and oxidation of Ni^{2+} back to Ni^{3+} . NP3 shows sharper, more symmetric peaks and a smaller potential separation than NP4, indicating faster charge transfer and enhanced reversibility. The higher cathodic diffusion coefficient of NP3 ($6.0 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) compared with NP4 ($5.16 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) confirms an improved Na^+ transport through its more open and conductive microstructure.

The lower anodic diffusion coefficients of $1.66 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ for NP3 and $2.76 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ for NP4 reflect slower Na^+ extraction and the kinetic asymmetry typical of diffusion-controlled redox systems. NP4's broader anodic peak further suggests higher polarization and restricted ion motion. These observations imply that NP3 enables smoother Na^+ insertion/extraction via a more flexible Ni–O–P framework, resulting in superior electrochemical reversibility and rate capability. Thus, the Ni redox activity in NP3 is more efficient, making it an efficient electrode for improved performance sodium-ion energy-storage devices.

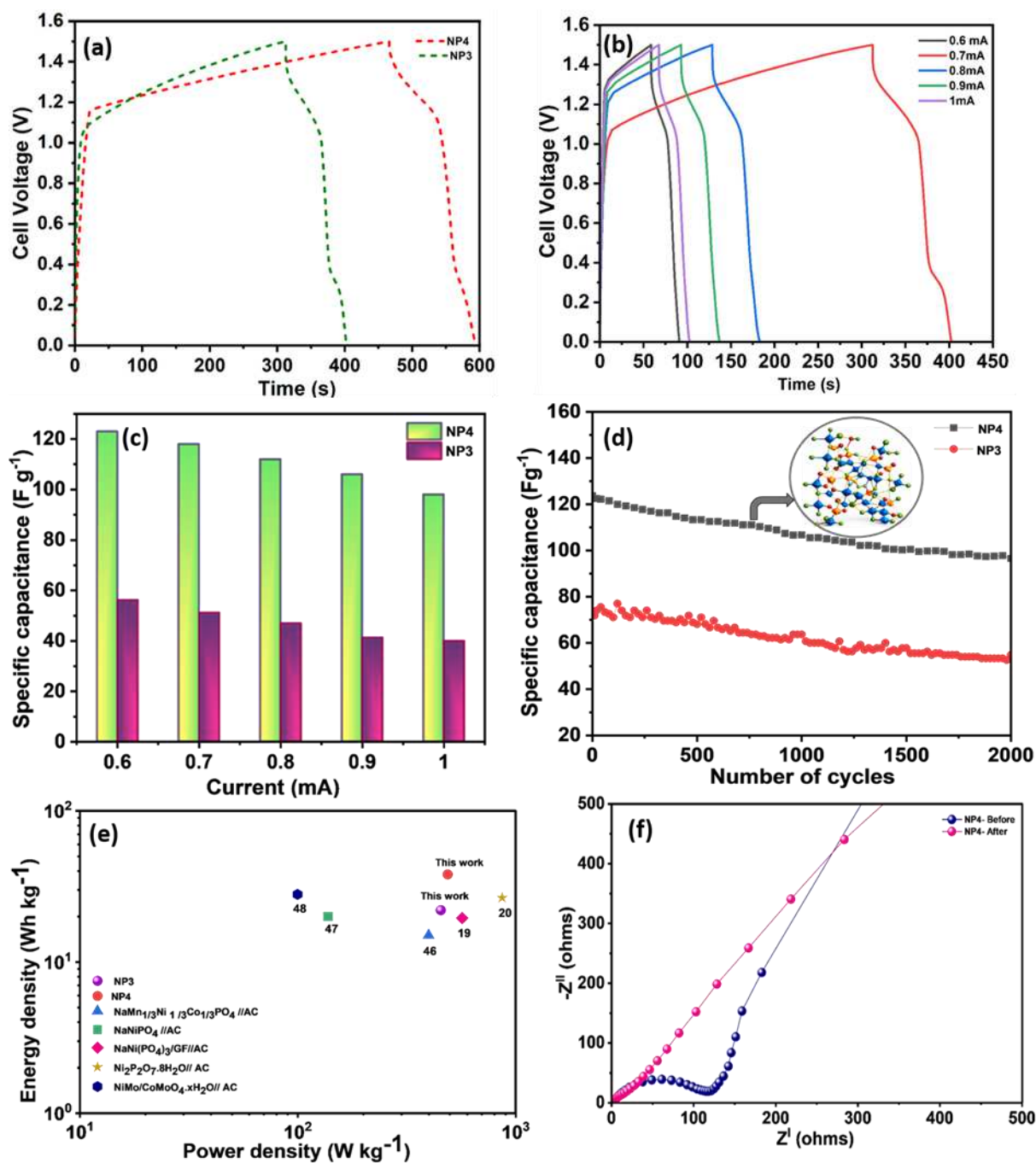


Figure 9: (a) Galvanostatic charge-discharge of NP3 and NP4; (b) GCD curve of NP4 at different current densities; (c) comparative analysis of specific capacitance of NP3 and NP4; (d) Cycling stability of NP3 and NP4, (e) Ragone plot; (f) EIS analysis of NP4 before and after cycling experiments.

Fig. 9(a) compares the galvanostatic charge–discharge (GCD) profiles of the NP3||AC and NP4||AC hybrid sodium-ion capacitor devices. Both devices exhibit non-linear charge–discharge characteristics with distinct voltage plateaus, confirming that the charge-storage process is predominantly governed by reversible Faradaic redox reactions rather than electric double-layer capacitance (EDLC). During charging and discharging, Na⁺ ions undergo reversible inter/deintercalation at the NP3/NP4 cathode, while charge neutrality is maintained by the movement of OH[−] ions in the 1 M NaOH electrolyte. Compared with NP3||AC, the NP4||AC device exhibits a more symmetric charge–discharge profile with reduced polarization. Fig. 9(b) presents the GCD curves of the NP4||AC device recorded at current densities ranging from 0.6 to 1.0 mA. The fabricated hybrid device yields high energy density (E) and power density (P), which were calculated using the following equations.

$$E = \frac{\int v dt}{m \times 3.6} \quad (8)$$

$$P = \frac{E \times 3600}{\Delta t} \quad (9)$$

where E, P, m, C, and Δt (s) represent energy density (Wh kg^{−1}), power density (W kg^{−1}), total mass of the electrode (g), specific capacitance (F g^{−1}), and the discharge time (s), respectively [31]. The electrochemical performance of the assembled hybrid devices was further assessed in terms of energy density, power density, and cycling stability. The NP4||AC device delivers a maximum energy density of 38 Wh kg^{−1} at a power density of 489 W kg^{−1}, together with a specific capacitance of 124 F g^{−1} at 1 mA. In comparison, the NP3||AC device achieves an energy density of 22 Wh kg^{−1}, at the power density of 455 W kg^{−1}, and a specific capacitance of 83 F g^{−1} under the same current density, demonstrating the superior charge-storage capability of the NP4 device. The long-term cycling performance of both hybrid cells was evaluated over 2000 charge–discharge cycles at 0.6 mA, and the corresponding results are presented in Fig. 9(d). Both devices exhibit stable operation within a 1.5 V potential window with minimal

capacity degradation throughout the cycling test. The NP4||AC device retains 86% of its initial capacitance after 2000 cycles, whereas NP3||AC maintains 82% retention under identical conditions. The improved cycling stability of the NP4-based device is attributed to its enhanced Na^+ diffusion kinetics and the robust pyrophosphate framework.

Fig. 9(e) presents a Ragone plot of the hybrid device performance in this work, comparing energy and power densities with those reported in the literature. Compared with previously reported sodium-ion hybrid capacitor systems such as $\text{NaMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{PO}_4//\text{AC}$ (15 Wh kg^{-1}), $\text{NaNiPO}_4//\text{AC}$ (20 Wh kg^{-1}), and $\text{Ni}_2\text{P}_2\text{O}_7 \cdot 8\text{H}_2\text{O}//\text{AC}$ (26.6 Wh kg^{-1}), the present $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2 //\text{AC}$ device delivers an improved energy density of 38 Wh kg^{-1} while maintaining good cycling stability. The improved performance can be attributed to the off-stoichiometric pyrophosphate framework, enhanced Na^+ diffusion pathways, and improved charge-transfer kinetics induced by argon-assisted calcination. The $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2 //\text{AC}$ hybrid device delivered the highest energy and power densities of 38 Wh kg^{-1} and 455 W kg^{-1} , respectively, over an extended cell voltage range. The structural stability of $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ shows minimal volume change compared to NaNiPO_4 which has narrower channels. Table 1 shows a comparison of the electrochemical performance metrics of the NP4||AC device with those reported for related sodium-ion capacitor systems in the recent literature, demonstrating its competitive energy density, power density, and operating voltage. ^[46-48, 19, 20]

Table I: Comparison of energy and power densities with reported sodium-ion capacitors

Hybrid Cell	Energy density (Wh kg^{-1})	Power density (W kg^{-1})	Electrolyte	Ref.
$\text{NaMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{PO}_4 //\text{AC}$	15	400	NaOH	46
$\text{NaNiPO}_4 //\text{AC}$	20	138	NaOH	47
$\text{NaNi}(\text{PO}_4)_3/\text{GF} //\text{AC}$	19.5	570	NaNO_3	19
$\text{Ni}_2\text{P}_2\text{O}_7 \cdot 8\text{H}_2\text{O} // \text{AC}$	26.6	870	KOH	20
$\text{NiMo}/\text{CoMoO}_4 \cdot x\text{H}_2\text{O} // \text{AC}$	28	100	NaOH	48
$\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2 //\text{AC}$	38	489	NaOH	Proposed

The interfacial kinetics and charge-transport mechanisms were further elucidated using Electrochemical Impedance Spectroscopy (EIS). Fig. 9(f) illustrates the Nyquist plots for both NP3 and NP4 electrodes before and after the stability test. In the high-frequency region, the spectra display a characteristic semicircle representing the charge-transfer resistance (R_{CT}), while in the low-frequency region, the impedance is nearly linear Warburg (W). This linear trend, particularly prominent at the negative AC electrode-electrolyte interface, signifies ideal capacitive behaviour.

To quantify the resistive components, the spectra were fitted to an equivalent circuit (Fig. 9, inset) comprising solution resistance (R_s), surface resistance, and charge-transfer resistance (R_{CT}) associated with the Faradaic transitions. The NP4 electrode (argon-calcined) demonstrates a significantly lower (R_{CT}) and a steeper Warburg slope compared to the ambient-calcined NP3. This indicates accelerated Na^+ diffusion and enhanced electrode-electrolyte interactions, facilitated by the superior surface chemistry and conductive pathways formed during inert-atmosphere processing. Post-cycling analysis after 2,000 cycles revealed a marginal increase in impedance for both samples, attributed to gradual sluggishness in ion mobility. However, NP4 maintained superior ionic transport and electrochemical reversibility, evidenced by higher calculated diffusion coefficients. Conversely, NP3 exhibited slower Na^+ mobility, likely due to its denser morphology and the presence of surface oxides formed under ambient conditions. Consequently, the NP4 || AC hybrid device demonstrates an extraordinary diffusion gradient and optimized electrical conductivity, ensuring superior rate capability and energy density.

5. SIMULATION CHARACTERISTICS

In the Sodium-Ion Hybrid Capacitor (SIHC) simulation, this window contains all essential components required to define and solve the electrochemical system, including

geometry creation, material assignment, physics interfaces, meshing, study settings, and result visualization. The model builder window in COMSOL Multiphysics acts as the central workspace where the complete simulation model is organized in a hierarchical tree structure. The global definitions section is used to define model parameters and material properties, while the Component section contains the 3D geometry of the capacitor structure, such as the (AC)anode, $(\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2)$ cathode, (polypropylene) separator, (1M NaOH) electrolyte, and (SS) current collectors. The geometry is then associated with appropriate material domains and physical conditions. The design parameters, such as electrode thickness ($1 \times 1 \text{ cm}^2$), electrolyte concentration (1 M NaOH), diffusion coefficient ($5.16 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$), operating voltage (1.5V), and temperature are defined. Fig. 10 represents the simulation window of the assembled sodium ion hybrid capacitor.

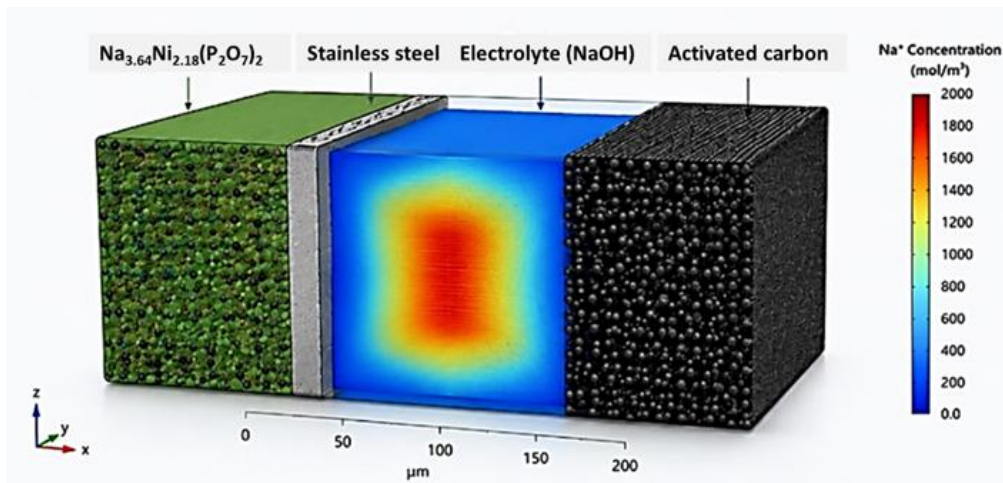


Figure 10: Simulation window of the assembled sodium ion hybrid capacitor

The Physics Interfaces section plays a major role in describing the electrochemical behaviour of the hybrid SIC. In this model, the Electrochemistry (ec) interface governs charge conservation and electrode reaction kinetics. The Charge Conservation feature computes the distribution of electric potential, while the Electrode Reaction nodes describe the electrochemical reactions occurring at between the electrodes. The Transport of Diluted

Species (tds) interface models the movement of (Na^+) within the electrolyte. It solves the diffusion equations governing ion transport and concentration distribution during charging and discharging. This interface enables the prediction of concentration gradients and ion depletion regions inside the capacitor.

The mesh section discretizes the model geometry into finite elements for numerical computation, whereas the study node defines the type of analysis, such as time-dependent transient simulation. Finer meshes are employed near electrode–electrolyte interfaces where electrochemical reactions and concentration gradients are most significant. Finally, the results section provides post-processing tools including 2D/3D plot groups, tables, datasets, and derived values for analyzing sodium-ion (Na^+) concentration, voltage distribution, current density, and overall capacitor performance. From Fig. 11 (a), the results portray similar results on the 2D plot groups - the graph of number of cycles vs specific capacitance and number of cycles vs specific capacitance. The theoretical specific capacitance remains in good agreement with the experimental value, with only minor deviations that can be attributed to idealized assumptions in the numerical model, such as homogeneous electrode properties, uniform ion diffusion, and negligible side reactions. This close agreement validates the accuracy and reliability of the developed simulation model.

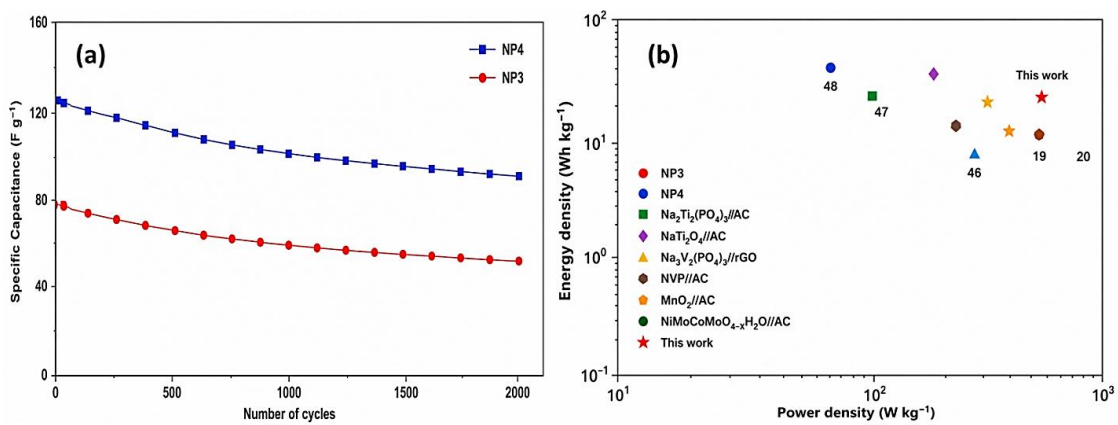


Figure 11: Theoretical performance of the simulated sodium-ion hybrid capacitor:

(a) Specific capacitance as a function of the number of cycles, and (b) Ragone plot.

The Study node specifies the type of analysis to be performed. For sodium-ion hybrid capacitors, a Time-Dependent Study is commonly selected to simulate transient charging and discharging behaviour. The solver calculates the temporal variation of electric potential, current density, ion concentration, and reaction rates throughout the simulation period. Fig. 11(b) shows the Ragone plot of the theoretically simulated results compared with previously reported values for the sodium-ion capacitor. Compared with earlier sodium-ion capacitors, the simulated device demonstrates competitive energy density while maintaining high power capability, indicating efficient Na^+ transport kinetics and low internal resistance. The slight differences between the simulated and reported values arise primarily from variations in electrode composition, electrolyte properties, operating voltage window, and electrode architecture employed in different studies. Nevertheless, the overall agreement confirms that the numerical model successfully captures the essential electrochemical behaviour of the device and can be used as a reliable tool for predicting capacitor performance under various operating conditions.

Overall, the Model Builder window provides a structured, integrated environment that enables comprehensive Multiphysics simulation of sodium-ion hybrid capacitors by combining electrochemistry, ion transport, electrical conduction, meshing, numerical solution, and post-processing in a single workflow. The close correlation among theoretical predictions, experimental observations, and prior literature demonstrates the effectiveness of the simulation approach in optimizing electrode materials and guiding the design of high-performance sodium-ion hybrid capacitors.

6. CONCLUSION

This work emphasizes the production of a battery-type cathode for sodium-ion capacitor application to enhance the redox reaction mechanism. The current study emphasizes the strategic development of a battery-type cathode, specifically off-stoichiometric $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$, optimized for improved performance sodium-ion capacitor (SIC) applications. The compound was prepared through a solution-combustion process and subsequently calcined under ambient and argon atmospheres. X-ray diffraction (XRD) patterns confirmed the phase purity and identified the material as having an anorthic crystal structure, which provides a robust framework for sodium-ion transport. The local bonding environment was scrutinized via Fourier-transform infrared (FTIR) spectroscopy, which revealed characteristic stretching and bending modes of P-O and P-O-P vibrational units, confirming the integrity of the pyrophosphate backbone. Furthermore, the thermal evolution and crystallization kinetics were established using thermogravimetric and differential thermal analysis (TG/DTA), identifying the precise temperature required for structural stabilization and the removal of organic precursors. The electrochemical evaluation of the single-electrode system demonstrated a significant Faradaic response, yielding a high specific capacity of 234 C g^{-1} . This performance is primarily attributed to the reversible $\text{Ni}^{3+}/\text{Ni}^{2+}$ redox transitions occurring within the P_2O_7 framework. To evaluate practical utility, a hybrid sodium-ion capacitor was assembled by pairing the $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ cathode with a commercially available activated carbon (AC) anode in a 1 M NaOH electrolyte. The full cell delivered a notable energy density of 38 Wh kg^{-1} while maintaining a peak power density of 489 W kg^{-1} across a wide 1.5 V operating window. The long-term durability of the device was assessed through extensive galvanostatic charge/discharge (GCD) cycling. The $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2 \parallel \text{AC}$ system exhibited remarkable stability, retaining 86% of its initial capacity over 2000 continuous cycles. This high retention rate underscores the structural resilience of the cathode

during repeated Na^+ insertion and extraction. The present work demonstrates that atmosphere-controlled synthesis can effectively tune the structural ordering, surface electronic states, and Na^+ diffusion behavior of off-stoichiometric sodium nickel pyrophosphates for enhanced aqueous sodium-ion capacitor performance. Considering these advantages, $\text{Na}_{3.64}\text{Ni}_{2.18}(\text{P}_2\text{O}_7)_2$ emerges as a capable cathode material for hybrid aqueous sodium-ion capacitors.

Authorship contribution statement

C. Subashini: Writing – original draft, Methodology, Data curation, Formal analysis. V. D. Nithya: Validation, Formal analysis. S. Logesh Kumar: Writing – original draft, Methodology, Data curation. N. Priyadharsini: Validation, Methodology, Resources, Supervision, Writing-review & editing.

Data availability

The research data and materials of this study are available from the corresponding author, on reasonable request.

Declaration of competing interest

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

REFERENCES:

1. T. H. Hong, J. D. Kim, W. Kang, Y. H. Lee, C. Jo, J. T. Lee, Operational strategy for multiredox-reaction electrodes for long-lifespan Na-ion hybrid capacitors. *Chem. Eng. J.* **475**, 146132 (2023). <https://doi.org/10.1016/j.cej.2023.146132>
2. R. Zhao, K. Wang, W. Li, Y. Yuan, X. Tang, J. Hu, H. Fan, K. Chen, W. Song, Y. Jiang, X. Guo, High recoverable energy storage density and efficiency achieved in doped NaNbO_3 ceramics via a composition design strategy for a pulsed power capacitor. *Chem. Eng. J.* **495**, 153421 (2024). <https://doi.org/10.1016/j.cej.2024.153421>

3. P. Cai, K. Zou, X. Deng, B. Wang, M. Zheng, L. Li, H. Hou, G. Zou, X. Ji, Comprehensive understanding of sodium-ion capacitors: definition, mechanisms, configurations, materials, key technologies, and future developments. *Adv. Energy Mat.* **11(16)**, 2003804 (2021). <https://doi.org/10.1002/aenm.202003804>
4. G. Z. Chen, Supercapacitor and supercapattery as emerging electrochemical energy stores. *Inter. Mater. Rev.* **62(4)**, 173-202 (2017). <http://dx.doi.org/10.1080/09506608.2016.1240914>
5. M. Yassine, D. Fabris, Performance of commercially available supercapacitors. *Energies* **10(9)**, 1340 (2017). <https://doi.org/10.3390/en10091340>
6. D. Karimi, H. Behi, J. Van Mierlo, M. Berecibar, A comprehensive review of lithium-ion capacitor technology: Theory, development, modeling, thermal management systems, and applications. *Molecules* **27(10)**, 3119 (2022). <https://doi.org/10.3390/molecules27103119>
7. H. Su, S. Jaffer, H. Yu, Transition metal oxides for sodium-ion batteries. *Energy storage Mater.* **5**, 116-131 (2016). <http://dx.doi.org/10.1016/j.ensm.2016.06.005>
8. M. Keller, D. Buchholz, S. Passerini, Layered Na-ion cathodes with outstanding performance resulting from the synergetic effect of mixed P- and O- type phases. *Adv. Energy Mater.* **6(3)** 1501555 (2016). <https://doi.org/10.1002/aenm.201501555>
9. R. Jia, G. Shen, D. Chen, Recent progress and future prospects of sodium-ion capacitors. *Sci. China Mater.* **63** 185-206 (2020). <https://doi.org/10.1007/s40843-019-1188-x>
10. Y. Niu, Y. Zhang, M. Xu, A review on pyrophosphate framework cathode materials for sodium-ion batteries. *J. Mater. Chem. A* **7(25)** 15006-15025 (2019). <https://doi.org/10.1039/C9TA04274A>
11. V. Aravindan, M. Ulaganathan, S. Madhavi, Research progress in Na-ion capacitors. *J Mater Chem A* **4(20)**, 7538-7548 (2016). <https://doi.org/10.1039/C6TA02478E>
12. Y. Zhang, J. Jiang, Y. An, L. Wu, H. Dou, J. Zhang, Y. Zhang, S. Wu, M. Dong, X. Zhang, Z. Guo, Sodium-ion capacitors: materials, mechanism, and challenges. *Chem. Sus. Chem.* **13(10)**, 2522-2539 (2020). <http://dx.doi.org/10.1002/cssc.201903440>

13. Z. Khan, B. Senthilkumar, S. Lim, R. Shanker, Y. Kim, H Ko. Redox-Additive-Enhanced High Capacitance Supercapacitors Based on $\text{Co}_2\text{P}_2\text{O}_7$ Nanosheets Adv. Mater. Interfaces **4**, 1700059 (2017) <http://dx.doi.org/10.1002/admi.201700059>
14. P. Barpanda, T. Ye, M. Avdeev, S.C. Chung, A.Yamada, A new polymorph of $\text{Na}_2\text{MnP}_2\text{O}_7$ as a 3.6 V cathode material for sodium-ion batteries. J. Mater. Chem. A, **1(13)**, 4194-4197 (2013). <https://doi.org/10.1039/C3TA10210F>
15. S. J. Marje, P. K. Katkar, B. Kale, A.C.Lokhande, C.D. Lokhande, U.M.Patil, Effect of phosphate variation on morphology and electrocatalytic activity (OER) of hydrous nickel pyrophosphate thin films. J. Alloys Compd. **779**, 49-58 (2019). <https://doi.org/10.1016/j.jallcom.2018.11.213>
16. Y. You, A.Manthiram, Progress in high-voltage cathode materials for rechargeable sodium-ion batteries. Adv. Energy Mater. **8(2)**, 1701785 (2018). <https://doi.org/10.1002/aenm.201701785>
17. S. Surendran, A. Sivanantham, S. Shanmugam, U.Sim, R.K.Selvan, $\text{Ni}_2\text{P}_2\text{O}_7$ microsheets as efficient Bi-functional electrocatalysts for water splitting application. Sustainable Energy & Fuels **3(9)**, 2435-2446 (2019). <https://doi.org/10.1039/C9SE00265K>
18. B. Senthilkumar, Z. Khan, S. Park, K. Kim, H. Ko, Y. Kim, Highly porous graphitic carbon and $\text{Ni}_2\text{P}_2\text{O}_7$ for a high-performance aqueous hybrid supercapacitor. J. Mater. Chem. A **3(43)** 21553-61 (2015). <https://doi.org/10.1039/C5TA04737D>
19. A. A. Mirghni, K.O. Oyedotun, O. Olaniyan, B. A. Mahmoud, N. F. Sylla, N. Manyala, Electrochemical analysis of Na–Ni bimetallic phosphate electrodes for supercapacitor applications. RSC Adv. **9(43)** 25012-25021 (2019). <https://doi.org/10.1039/C9RA04487F>
20. S. J. Marje, P. K. Katkar, S. S. Pujari, S.A.Khalate, A.C. Lokhande, U.M.Patil, Regulated micro-leaf-like nickel pyrophosphate as a cathode electrode for an asymmetric supercapacitor. Syn. Metals **259**, 116224 (2020). <https://doi.org/10.1016/j.synthmet.2019.116224>
21. M. M. Sundaram, D.R.Mitchell, Dispersion of Ni^{2+} ions via acetate precursor in the preparation of NaNiPO_4 nanoparticles: effect of acetate vs. nitrate on the capacitive energy storage properties. Dalton Transactions **46(40)**, 13704-13713 (2017). <https://doi.org/10.1039/C7DT02444D>

22. N. Zhang, C. Chen, Y. Chen, G. Chen, C. Liao, B. Liang, J. Zhang, A. Li, B. Yang, , Z. Zheng, X. Liu, $\text{Ni}_2\text{P}_2\text{O}_7$ nanoarrays with decorated C_3N_4 nanosheets as efficient electrode for supercapacitors. *ACS Appl. Energy Mater.* **1(5)**, 2016-2023 (2018). <https://doi.org/10.1021/acsaem.8b00114>
23. Y. Zhou, C. Liu, X. Li, L. Sun, D. Wu, J. Li, P. Huo, H. Wang, Chemical precipitation synthesis of porous $\text{Ni}_2\text{P}_2\text{O}_7$ nanowires for supercapacitor. *J. Alloys Compd.* **790**, 36-41 (2019). <https://doi.org/10.1016/j.jallcom.2019.03.192>
24. H. Chevulamaddi, K. Venkateswara Rao. Electrochemical behaviour of ultrasonic probe assisted nickel pyrophosphate ($\text{Ni}_2\text{P}_2\text{O}_7$) nanosheets for supercapacitor applications. *Inorganic Chem. Comm.* **163**, 112310 (2024). <https://doi.org/10.1016/j.inoche.2024.112310>
25. H.J.Song, H.Yoon, B. Ju, D.W. Kim, Sodium nickel pyrophosphate as a novel oxygen evolution electrocatalyst in alkaline medium. *J. Am. Ceram. Soc.*, **103(9)**, 4748-4753 (2020). <https://doi.org/10.1111/jace.17195>
26. D. Kim, J. Kang, B. Yan, K. D. Seong, Y. Piao, Ambient temperature synthesis of iron-doped porous nickel pyrophosphate nanoparticles with long-term chemical stability for high-performance oxygen evolution reaction catalysis and supercapacitors. *ACS Sus. Chem. Eng.* **8(7)**, 2843-2853 (2020). <https://doi.org/10.1021/acssuschemeng.9b06920>
27. H. Li, Z. Zhang, M. Xu, W. Bao, Y. Lai, K. Zhang, J. Li, Triclinic off-stoichiometric $\text{Na}_{3.12}\text{Mn}_{2.44}(\text{P}_2\text{O}_7)_2/\text{C}$ cathode materials for high-energy/power sodium-ion batteries. *ACS Appl. Mater. Inter.* **10(29)**, 24564-24572 (2018). <https://doi.org/10.1021/acsami.8b07577>
28. A.R. Nath, K.K. Garlapati, A. Yatheendran, N. Sandhyarani,. Asymmetrical supercapacitor fabricated using sodium nickel phosphate and transition metal-carbon nitride nanocomposite as electrodes. *Energy & Fuels*, **36(22)**, 13882-13893 (2022). <https://doi.org/10.1021/acs.energyfuels.2c02089>
29. B. Senthilkumar, G. Ananya, S. Ramaprabhu,. Synthesis of carbon coated nano- $\text{Na}_4\text{Ni}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ as a novel cathode material for hybrid supercapacitors. *Electrochim. Acta*, **169**, 447-455 (2015). <http://dx.doi.org/10.1016/j.electacta.2015.04.088>
30. G. S. Gopalakrishna, M. J. Mahesh, K. Ashamanjari, Magnetic and thermal characterization of $\text{Na}_2\text{NiP}_2\text{O}_7$ crystals. *Ind. J. Physics*, **80**, 293-296 (2006).

31. C. Subashini, R. Sivasubramanian, M. M. Sundaram, N.Priyadharsini, The evolution of allotropic forms of $\text{Na}_2\text{CoP}_2\text{O}_7$ electrode and its role in future hybrid energy storage. *J Energy Storage* **130**, 117390 (2025). <https://doi.org/10.1016/j.est.2025.117390>
32. G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors. *Chem. Soc. Rev.* **41(2)**, 797-828 (2012). <https://doi.org/10.1039/C1CS15060J>
33. P. Barpanda, J.Lu, T.Ye, M.Kajiyama, S.C.Chung, N.Yabuuchi, S.Komaba, A.Yamada, A layer-structured $\text{Na}_2\text{CoP}_2\text{O}_7$ pyrophosphate cathode for sodium-ion batteries. *RSC Adv.* **3(12)**, 3857-3860 (2013). <https://doi.org/10.1039/C3RA23026K>
34. Z. Wei, Q. Wang, M. Qu, H. Zhang, Rational design of nanosheet array-like layered-double-hydroxide-derived NiCo_2O_4 in situ grown on reduced-graphene-oxide-coated nickel foam for high-performance solid-state supercapacitors. *ACS Appl. Mater. Inter.* **16(15)** 18734-18744 (2024). <https://doi.org/10.1021/acsami.3c17839>
35. S. D. Dhas, P. S. Maldar, M.D.Patil, M.R.Waikar, R.G.Sonkawade, S.K.Chakarvarti, S.K.Shinde, D.Y.Kim, A.V. Moholkar, Probing the electrochemical properties of NiMn_2O_4 nanoparticles as prominent electrode materials for supercapacitor applications. *Materials Science and Engineering: B*, **271**, 115298 (2021). <https://doi.org/10.1016/j.mseb.2021.115298>
36. M. Liu, Z. Qu, D. Yin, X. Chen, Y. Zhang, Y. Guo, D. Xiao, Cobalt– iron pyrophosphate porous nanosheets as highly active electrocatalysts for the oxygen evolution reaction. *Chem Electro Chem.*, **5(1)**, 36-43 (2018). <http://dx.doi.org/10.1002/celc.201700956>
37. N. Priyadharsini, R. K. Selvan, Nano-sheet-like KNiPO_4 as a positive electrode material for aqueous hybrid supercapacitors. *Electrochim. Acta*, **246**, 963-970 (2017). <http://dx.doi.org/10.1016/j.electacta.2017.06.100>
38. S. El Arni, M. Hadouchi, A. Assani, M. Saadi, M. El Marssi, A. Lahmar, L. El Ammari, Structural and magnetic investigations of the novel pyrophosphate $\text{Na}_7\text{Ni}_3\text{Fe}(\text{P}_2\text{O}_7)_4$ *Magnetochem.* **9(7)**, 162 (2023). <https://doi.org/10.3390/magnetochemistry9070162>
39. Z. Ali Sheikh, D. Vikraman, M. Faizan, H. Kim, S.F. Aftab, S. Shaikh, K.W. Nam, J. Jung, S. Hussain, D.K.Kim,. Formulation of hierarchical nanowire-structured CoNiO_2 and

MoS₂/CoNiO₂ hybrid composite electrodes for supercapacitor applications. *ACS Appl. Mater. Interfaces*, **16**(8), 10104-10115 (2024). <https://doi.org/10.1021/acsami.3c17201>

40. S. Deshagani, D. Maity, A. Das, M. Deepa, NiMoO₄@ NiMnCo₂O₄ heterostructure: a poly (3, 4-propylenedioxythiophene) composite-based supercapacitor powers an electrochromic device. *ACS Appl. Mater. Inter.* **13**(29), 34518-34532 (2021). <https://doi.org/10.1021/acsami.1c07064>
41. M. Liu, J. Li, W. Han, L. Kang, Simple synthesis of novel phosphate electrode materials with unique microstructure and enhanced supercapacitive properties. *J. Energy Chem.* **25**(4), 601-608 (2016). <http://dx.doi.org/10.1016/j.jechem.2016.03.002>
42. V. Kumar, R. Aepuru, A. Faizal, H.S. Panda, Elucidating the pseudocapacitive mechanism of ternary Co-Ni-B electrodes—Towards miniaturization and superior electrochemical performance for building outmatched supercapacitors. *Electrochim. Acta*, **409**, 140003 (2022). <https://doi.org/10.1016/j.electacta.2022.140003>
43. S.S. Rabbani, H. Mustafa, A. Zafar, S. Javaid, M.A. Bakar, A. Nisar, Y. Liu, S. Karim, H. Sun, S. Hussain, Z.Zafar, Nickel foam supported hierarchical NiCo₂S₄@NiFe LDH heterostructures as highly efficient electrode for long cycling stability supercapacitor. *Electrochim. Acta*, **446**, 142098 (2023). <https://doi.org/10.1016/j.electacta.2023.142098>
44. N. Priyadharsini, Surendran, B.Senthilkumar, L.Vasylechko, R.K.Selvan, Synthesis and electrochemical performances of γ -KCoPO₄ nanocrystals as promising electrode for aqueous Supercapatteries. *ChemElectroChem*, **6**(2), 369-377 (2019). <https://doi.org/10.1002/celec.201801440>
45. A. Chowdhury, S. Biswas, A. Dhar, P. S. Burada, A. Chandra, Stable Na-ion supercapacitor under non-ambient conditions using maricite-NaMnPO₄ nanoparticles. *J Power Sources*, **516**, 230679 (2021). <https://doi.org/10.1016/j.jpowsour.2021.230679>
46. M. Minakshi, D. Meyrick, D. Appadoo. Maricite (NaMn_{1/3}Ni_{1/3}Co_{1/3}PO₄)/activated carbon: hybrid capacitor. *Energy & Fuels*, **27**(6), 3516-3522 (2013). <https://doi.org/10.1021/ef400333s>
47. B. Senthilkumar, K.V. Sankar, L. Vasylechko, Y.S. Lee, R.K.Selvan, Synthesis and electrochemical performances of maricite NaMPO₄ (M= Ni, Co, Mn) electrodes for hybrid

supercapacitors. RSC Advances, **4(95)**, 53192-53200 (2014).
<https://doi.org/10.1021/ef400333s>.

48. B.Senthilkumar, D.Meyrick, Y.S.Lee, R.K.Selvan, Synthesis and improved electrochemical performances of nano β -NiMoO₄-CoMoO₄·xH₂O composites for asymmetric supercapacitors. RSC Advances, **3(37)**, 16542-16548 (2013).
<https://doi.org/10.1039/C3RA43021A>