

Review article

Sodium vanadium phosphate cathodes for Na-ion batteries: Carbon modification strategies and electrolyte compatibility

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ABSTRACT

Sodium Vanadium Phosphate ($\text{Na}_3\text{V}_2(\text{PO}_4)_3$, (NVP)) is a promising cathode for sodium-ion batteries (SIBs) due to its stable Sodium Super Ionic Conductor (NASICON) structure, high operating voltage, and fast Na^+ diffusion. However, its inherently low electronic conductivity limits rate performance and cycling stability. Carbon modification effectively mitigates these challenges by enhancing the electronic conductivity of NVP particles, improving ion movement, and reducing charge transfer resistance. This review systematically analyzes major carbon-modification strategies, such as in-situ carbon coating, integration of carbon nanostructures, heteroatom-doped carbon, and composite architectures, and their influence on the electrochemical performance of NVP cathodes. Special emphasis is given to how carbon coating thickness and morphology affect conductivity, ion transport, and interface stability of the NVP cathode. Furthermore, the interplay between carbon modification and electrolyte compatibility is examined to clarify their combined role in solid electrolyte interface (SEI) and cathode electrolyte interface (CEI) formation and long-term stability. Finally, the review highlights existing challenges and future directions toward optimizing carbon-modified NVP cathodes for next-generation sodium ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) have revolutionized portable electronics and electric vehicles due to their high energy density, long cycle life, and compact design [1–3]. However, the growing demand for lithium, cobalt, and nickel materials that are costly, scarce, and concentrated in geopolitically sensitive regions has raised concerns over long-term sustainability, cost, and supply security. These challenges, especially in regions such as the European Union, have prompted the search for safer, more sustainable battery technologies and improved material systems [4–6].

Sodium-ion batteries have emerged as a promising alternative, benefiting from the natural abundance, low cost, and wide availability of sodium [7,8]. Sharing a similar working principle with LIBs, SIBs are well-suited for large-scale energy storage applications, particularly in

grid systems. Nevertheless, SIBs typically exhibit lower energy density because the larger ionic radius of Na^+ (1.02 Å) leads to slower ion diffusion and potential structural strain in host materials [9–11]. To overcome these limitations, research has focused on developing suitable electrode materials capable of reversible sodium storage with high capacity and structural stability.

The performance of SIBs strongly relies on the intrinsic properties of the cathode and anode materials [12–15]. Ideal anode materials for sodium-ion batteries should be lightweight, conductive, cost-effective, and capable of storing sodium ions efficiently with stable cycling performance [16]. Hard carbon has proven to be one of the most promising anode materials owing to its disordered structure and wide interlayer spacing, which promote efficient sodium-ion storage and good reversibility [17].

Cathode materials, which determine the battery's energy density,

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operating voltage, and cycling stability, are equally important. Ideal cathodes for SIBs should provide structural robustness, facilitate efficient sodium-ion diffusion, and deliver high capacity to achieve competitive energy density. Cathode materials for sodium-ion batteries are generally classified into three categories: layered oxides, Prussian blue analogs (PBAs), and polyanionic compounds [18–21]. While layered oxides and PBAs offer certain advantages, such as high energy density and fast ion diffusion, they often face issues related to structural stability and moisture sensitivity [22–24]. Polyanionic compounds, on the other hand, are known for their strong covalent bonding frameworks, which provide excellent structural robustness, thermal stability, and stable voltage profiles [25]. A comparison of specific capacity versus voltage for various cathode systems is shown in Fig. 1.

Among polyanionic materials, sodium vanadium phosphate has attracted particular interest because of its favorable electrochemical and structural properties [26]. NVP features a NASICON-type framework that enables fast sodium-ion diffusion, high ionic conductivity, and excellent structural stability. It delivers an operating voltage of approximately 3.4 V (Vs. Na/Na⁺) and a theoretical capacity of 117 mAhg⁻¹, making it suitable for high-energy applications. The robust phosphate groups within its structure enhance thermal stability and ensure reversible Na⁺ interactions during cycling [27–31].

Despite these advantages, pristine NVP suffers from low intrinsic electronic conductivity and relatively large particle size, which limit charge and ion transport, resulting in polarization and reduced rate performance [33,34]. Surface instability during cycling can also cause side reactions and the formation of insulating layers, lowering Coulombic efficiency and long-term stability. Moreover, slight structural distortions during repeated Na⁺ insertion and extraction can lead to gradual capacity fading. These limitations have motivated extensive efforts to modify NVP to improve its conductivity, structural integrity, and electrochemical performance [34].

Several strategies have been developed to address these challenges, including particle size reduction, element doping, structural tuning, and carbon-based modification. Among these, carbon modification has proven to be the most effective approach. It enhances electronic conductivity, stabilizes the structure, and facilitates sodium-ion transport while reducing charge-transfer resistance. As a result, carbon-modified NVP materials exhibit improved rate capability and cycling stability [35–37]. Different carbon modification techniques have been explored, such as in-situ carbon coating using organic precursors, formation of carbon composites with materials like graphene (GN), carbon nanotubes

(CNTs), and carbon nanofibers (CNFs), carbon quantum dots (CQDs), and heteroatom-doped carbon coating. These approaches create conductive networks, mitigate surface degradation, and enhance electrochemical activity, thereby improving the overall performance of NVP cathodes [37–39].

In addition to electrode design, electrolyte selection plays a key role in achieving optimal battery performance and safety [40,41]. Organic liquid electrolytes, especially carbonate-based systems containing sodium salts such as NaClO₄ or NaPF₆, are commonly used because of their high ionic conductivity and compatibility with carbon-coated NVP cathodes. Other systems, including ionic liquids, gel polymers, and solid-state electrolytes, are being actively investigated for their thermal stability, non-flammability, and potential to improve interfacial stability [42–46]. The interaction between electrolytes and carbon-modified NVP cathodes is discussed in detail in Chapter 5 of this review.

This review aims to provide a comprehensive overview of carbon modification strategies for Na₃V₂(PO₄)₃ cathodes in sodium-ion batteries, while also examining their compatibility with various electrolytes. It focuses on how various carbon architectures, such as coatings, composites, and doped frameworks, improve structural stability, electronic conductivity, and interfacial behavior. The effect of carbon content, morphology, and heteroatom incorporation on electrochemical performance is analyzed in detail. Finally, the review highlights current challenges, including the optimization of carbon content and electrolyte compatibility, and also discusses future research directions toward developing high-performance, commercially viable NVP-based cathodes for next-generation sodium-ion batteries.

2. Crystal structure and electrochemical performance of NVP

2.1. Crystal structure of NVP

Na₃V₂(PO₄)₃ crystallizes in a rhombohedral lattice (space group R3⁻c) with hexagonal parameters $a = b = 8.74$ Å and $c = 21.84$ Å, forming a stable NASICON framework renowned for its structural robustness and high sodium-ion mobility (Fig. 2a). The 3D network consists of corner-sharing VO₆ octahedra and PO₄ tetrahedra, producing a rigid, lantern-like motif along the c-axis that ensures high mechanical stability and minimal volumetric change (~8.26 %) during cycling. The large interstitial voids within this framework facilitate efficient Na⁺ conduction, contributing to the material's reversibility and long-term stability [47–49].

Within the NVP structure, two distinct sodium-ion sites exist: Na₁ (6b sites, sixfold coordinated) and Na₂ (18e sites, eightfold coordinated). Due to the weaker Na₂–O bonding compared to Na₁–O, Na⁺ ions at Na₂ sites are more easily extracted and inserted, enabling faster ion transport. Occupancy factors of 0.843 and 0.719 at Na₁ and Na₂, respectively, indicate a stronger equilibrium affinity for Na₁ sites. The strong polyanionic backbone and limited volume change collectively enhance the cycling stability and lifespan of NVP electrodes [49,50]. First-principles and DFT studies have revealed three major sodium migration pathways (Fig. 2b): Pathway 1 (x-direction, 0.0904 eV), Pathway 2 (y-direction, 0.1177 eV), and Pathway 3 (curved path bypassing octahedra and tetrahedra, ~2.438 eV). The low barriers in Pathways 1 and 2 support rapid sodium-ion diffusion, while the much higher barrier along the z-direction (>200 eV) underscores the anisotropic nature of Na⁺ mobility [51]. Sodium-ion transport predominantly occurs via Na₂ site hopping, as direct Na₁, Na₂ migration is energetically unfavorable (activation barrier ~36.1 kcal/mol). The efficient Na⁺ migration along specific crystallographic directions, combined with NVP's highly ordered structure and robust framework, underpins its excellent electrochemical kinetics, stable voltage profile, and superior cycle life in sodium-ion batteries [52].

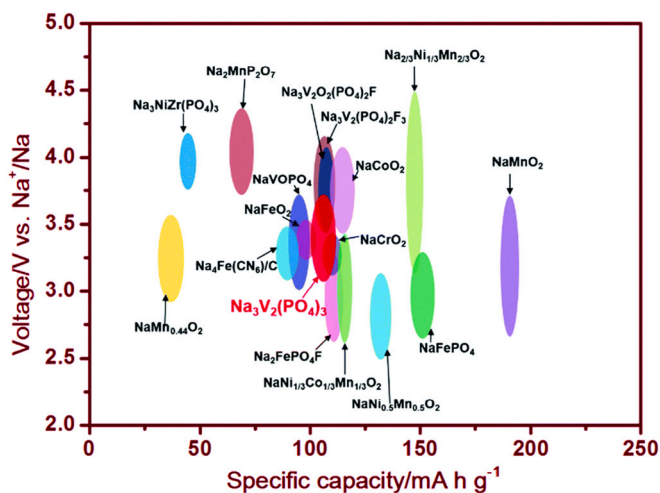


Fig. 1. Cathode materials for Na-ion batteries (specific capacity versus voltage).

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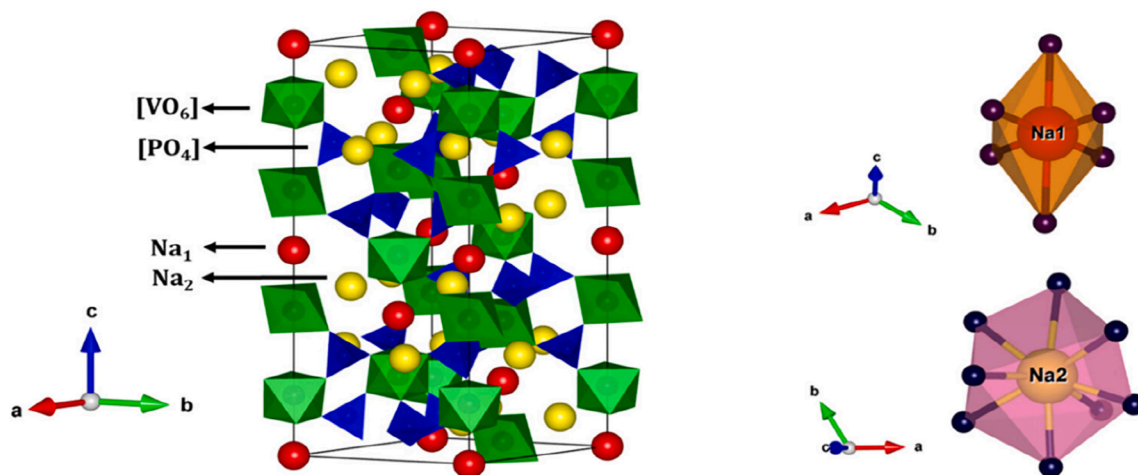
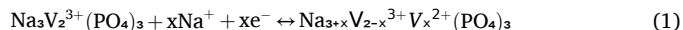


Fig. 2. (a) Crystal structure of NVP and (b) polyhedral view of Na1 and Na2 sites. (Reproduced with permission from [53] Copyright 2022 American Chemical Society.)

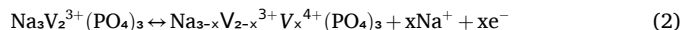
2.2. Electrochemical performance of NVP

The electrochemical performance of Na₃V₂(PO₄)₃ is largely decided by its capacity, rate capability, and cycle stability, as shown in Fig. 3 [54]. Two distinct redox pairs in Na₃V₂(PO₄)₃: a higher-voltage plateau at ~3.4 V (V³⁺/V⁴⁺) and a lower-voltage plateau at ~1.6 V (V²⁺/V³⁺). The 3.4 V plateau corresponds to the reversible extraction/insertion of two Na⁺ ions from/into the Na₂ sites, driving a two-phase transition between Na₃V₂(PO₄)₃ and NaV₂(PO₄)₃, with a theoretical capacity of 117.6 mAhg⁻¹. The 1.6 V plateau reflects the reduction of V³⁺ to V²⁺ via insertion of one additional Na⁺, forming Na₄V₂(PO₄)₃ (58.8 mAhg⁻¹), limited by the NASICON framework's Na⁺ occupancy [55]. It is challenging to reach this full theoretical value because of inherent material limitations. In practice, NVP composites possess an initial capacity of about 72.5 mAhg⁻¹ at a 1C rate that slowly decreases to about 65.6 mAhg⁻¹ after 100 cycles. Furthermore, at the lower voltage plateau, a second sodium ion could be inserted into the Na₂ site, adding capacity of 58.8 mAhg⁻¹. The special structural flexibility of NVP enables it to be applied both as a cathode and an anode in sodium-ion batteries, thus rendering it a versatile tool to apply in energy storage [56]. The underlying electrochemical reactions governing NVP's charge and discharge processes can be represented as shown in the below eqs. [57].

Anode reaction:



Cathode reaction:



An additional reduction peak near 3.2 V, linked to sodium migration from Na₁ to Na₂ sites, appears initially but diminishes with cycling without significantly impacting capacity retention. The sodium-ion diffusion coefficients (DNa⁺) are calculated as ~4.05 × 10⁻¹¹ cm² s⁻¹ (anodic) and ~4.10 × 10⁻¹¹ cm² s⁻¹ (cathodic), indicating relatively moderate ion mobility that affects rate performance. To further enhance capacity and energy density, strategies have been proposed to extend the vanadium oxidation state to V⁵⁺, enabling a reversible V⁴⁺/V⁵⁺ redox couple and involving more sodium ions during cycling.

3. Carbon modification strategies for enhancing NVP performance

To overcome the intrinsic limitations of Na₃V₂(PO₄)₃ and enhance its electrochemical performance, various modification strategies have been developed. Among these, carbon modification has emerged as the most effective and widely adopted approach. Coating NVP with conductive carbon materials or integrating carbon-based additives such as

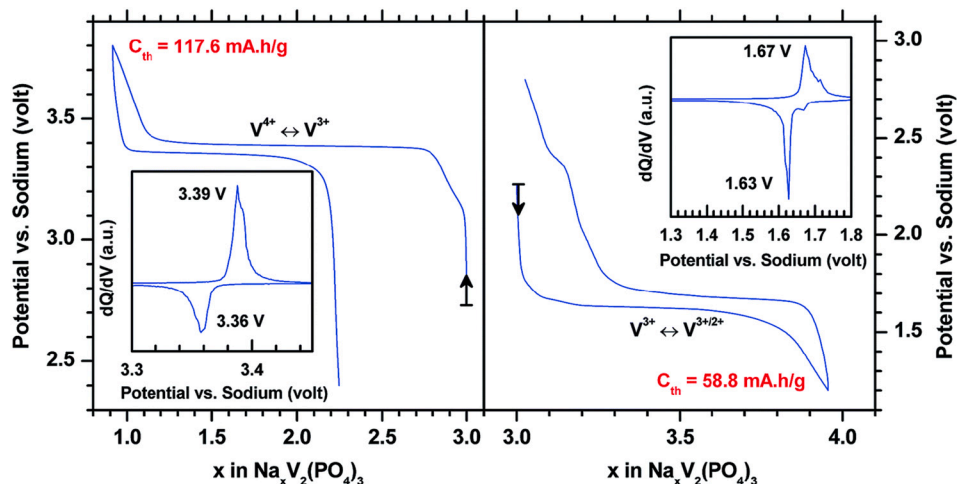


Fig. 3. Galvanostatic charge/discharge profiles of Na₃V₂(PO₄)₃ electrodes showing V³⁺/V⁴⁺ (left) and V²⁺/V³⁺ (right) redox plateaus. (Reproduced with permission from [54] copyright 2015 Royal Society of Chemistry.)

graphene, carbon nanotubes, carbon nano fibers, or carbon quantum dots noticeably enhances its electronic conductivity and facilitates sodium-ion transport. Furthermore, heteroatom doping can promote Na^+ mobility and improve the structural stability of the electrode [58]. Complementary techniques, such as nano-structuring, morphology control (e.g., Particle size reduction and porosity introduction), surface engineering, and electrolyte optimization, also contribute to improving ion diffusion kinetics and long-term cycling stability. Nonetheless, among these diverse strategies, carbon-based modifications continue to stand out for their proven ability to effectively address the intrinsic electronic conductivity limitations of NVP [59].

3.1. In-situ carbon coating

Carbon coating remains one of the most effective strategies to enhance the electrochemical performance of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ Cathodes. The inherently low electronic conductivity of NVP limits its performance at high current densities in sodium-ion batteries [60]. To overcome this, various organic precursors such as citric acid, glucose, sucrose, pitch, and oxalic acid have been employed to generate in situ carbon layers during synthesis. These compounds decompose under thermal treatments, forming uniform, conductive carbon films on the NVP surface [61–63]. Such coatings enhance electronic conductivity, provide mechanical buffering to accommodate volumetric changes during cycling, and stabilize the electrode-electrolyte interface, thereby improving Na^+ transport, structural integrity, and cycling stability. The molecular structure and decomposition behavior of the precursor critically influence the morphology, thickness, and conductivity of the resulting carbon layer, making careful precursor selection essential for optimal electrochemical performance [64].

Li et al. [65] systematically evaluated citric acid as a carbon source, demonstrating its dual role as a chelating agent and carbon provider (Fig. 4a). Citric acid enhanced precursor homogeneity and up on calcination generated a thin, uniform carbon coating ($\sim 3\text{--}5\text{ nm}$) on NVP particles while inducing a porous structure. The optimized CR125%-NVP (citric acid with the overdose coefficient of 125 %) composite exhibited a high initial capacity of 116.2 mAhg^{-1} at 0.1C and retained 88.9% capacity after 500 cycles at 10C (Fig. 4b). The synergistic effect

of the porous architecture and continuous carbon network facilitated rapid Na^+ diffusion, reduced charge-transfer resistance, and enhanced electronic pathways. Building on this approach, Chen et al. [66] employed a V-MOF template combined with citric acid as a secondary carbon source to construct a core-shell spherical NVP/C architecture. The resulting NVP-0.01 M ($400\text{ ml ethanol}/0.01\text{ M}$) composite achieved 115.1 mAhg^{-1} at 0.1C , 92.2 mAhg^{-1} at 30C , and 91.3% retention after 500 cycles (Fig. 4c, d), illustrating that citric acid can reinforce conductive networks and control particle growth when integrated with MOF templates.

Glucose has also proven to be an effective, low-cost, and environmentally friendly precursor. Li et al. [67] synthesized 3D porous NVP/C composites via the sol-gel combustion method with different glucose content ($0\text{--}15\text{ wt}\%$), showing that the glucose content directly controlled carbon layer thickness and connectivity. The NVP/C-G10% (glucose 10%) composite, with $4.21\text{ wt}\%$ carbon, delivered 118 mAhg^{-1} at 0.2C and 81.5% capacity retention after 1000 cycles at 10C (Fig. 4e, f). Under or overcoating reduced performance by either limiting conductivity or hindering Na^+ diffusion, highlighting the importance of precise carbon optimization.

Jiang et al. [68] investigated sucrose as a carbon precursor to form an integrated carbon scaffold around hydrothermally synthesized NVP nano fibers ($\sim 30\text{ nm}$). The C8 sample ($6.95\text{ wt}\%$ carbon) exhibited 114 mAhg^{-1} at 0.2C and 76 mAhg^{-1} at 40C , maintaining a high 99.9% capacity after 10,000 cycles at 20C . The dual-function sucrose-derived scaffold not only provided conductive pathways but also physically constrained the NVP Fibers, preventing structural degradation, which demonstrates how carbon architecture can fundamentally enhance mechanical and electrochemical stability.

Pitch, a low-cost industrial by-product, has also been used effectively as a carbon source. Ding et al. [69] showed that an optimal $13.1\text{ wt}\%$ pitch-derived carbon coating improved electronic conductivity while maintaining facile Na^+ transport. The NVP/C-2($13\text{ wt}\%$) composite delivered 108.2 mAhg^{-1} at 0.2C , retained 90.5 mAhg^{-1} at 10C , and showed virtually no capacity fading over 1000 cycles, demonstrating pitch's potential as a scalable and cost-effective solution for high-performance NVP cathodes.

Finally, oxalic acid has been highlighted as a dual-function precursor

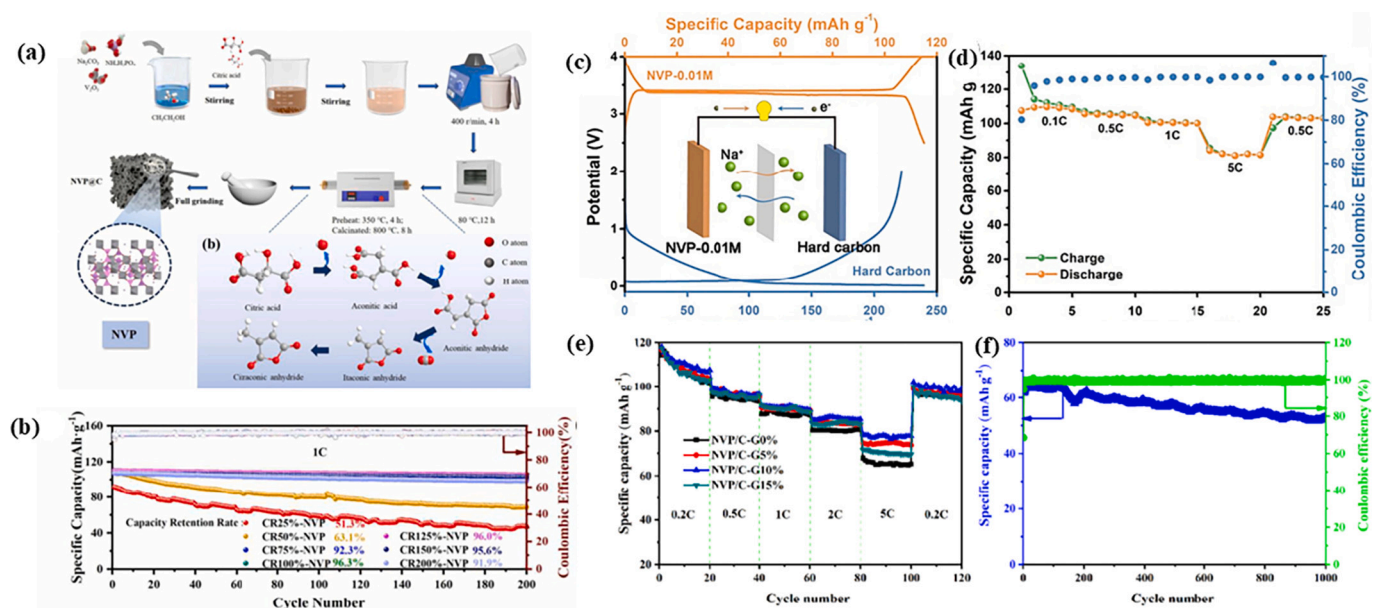


Fig. 4. (a) Schematic synthesis route and carbon reduction mechanism of NVP@C using citric acid. (b) Cycling stability of NVP with different citric acid excess coefficients. Reproduced with permission from [65] copyright 2024 Elsevier. (c) Charge-discharge curves of NVP-0.01 M half-cells and NVP-0.01 M/HC full cell, and (d) its rate performance. Reproduced with permission from [66] Copyright 2023 Elsevier. (e) Rate capability of NVP/C-G_x(glucose) composites ($x = 0\text{--}15\%$) and (f) long-term cycling of NVP/C-G10% at 10C . Reproduced with permission from [67] copyright 2020 Elsevier.

and chelating agent. Zhang et al. [70] used oxalic acid to produce a thin (~3 nm), conformal carbon layer on NVP nanoparticles via Sol-gel synthesis. This coating enhanced electronic conductivity and combined with nano-scale particle size, shortened Na^+ diffusion paths. The resulting NVP/C composite exhibited remarkably high-rate performance in aqueous electrolytes, delivering 94.5 mAhg^{-1} at 10C, 90 mAhg^{-1} at 15C, and 71.1 mAhg^{-1} at 20C, demonstrating the ability of in situ oxalic-acid derived carbon to unlock high-power operation in safe, low-cost systems.

Collectively, these studies illustrate that the choice of organic precursors profoundly influences carbon layer thickness, morphology, and particle architecture, which in turn determines electronic conductivity, Na^+ ion transport, and cycling stability. Citric acid offers uniform coatings and synergistic effects with MOF templates, glucose provides tunable porosity for 3D networks, sucrose forms mechanically confining scaffolds, pitch provides a low-cost conductive layer, and oxalic acid simultaneously chelates and produces ultra-thin carbon shells. Thus, in situ carbon coating with optimized organic precursors remains a cornerstone strategy for advancing the performance of NVP cathodes in sodium-ion batteries. (See Tables 1 and 2.)

3.2. Ex-situ (pre-formed) carbon integration

Pre-formed carbon materials such as carbon nanotubes, graphene, carbon black, carbon nanofibers, and quantum carbon materials are key to improving the electrochemical performance of NVP cathodes by physical integration rather than chemical bonding in the crystalline matrix. They are not integrated within the NVP lattice but rather create conductive networks with external contacts that bridge NVP particles and enable more efficient electron transport within the electrode [67]. Unlike in-situ carbon materials coated by decomposition of organic precursors, pre-formed carbon materials maintain their intrinsic morphology-tubular, fibrous, or sheet-like-and act like efficient highways for electrons within the matrix of the cathode [81]. This improves charge transfer and diffusion by preventing internal resistance and enabling better electrical connection of the active material particles. Pre-formed carbon materials also offer structural reinforcement, preventing volume expansion and structural degradation upon cycling. Integration by ex-situ or hybrid routes like ball milling, ultrasonication, or hydrothermal mixing offers free-tuning of the composite structure and makes pre-formed carbon materials a promising technique to enhance the efficiency and lifespan of NVP-based Na-ion batteries [82,83]. The following sections provide a detailed overview of various pre-formed carbon materials, highlighting their individual structural characteristics, integration methods, and specific contributions to enhancing the electrochemical performance of NVP cathodes.

3.2.1. Carbon nanotubes

Carbon nanotubes have emerged as one of the most effective pre-

formed carbon materials for enhancing the electrochemical performance of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes in sodium-ion batteries, owing to their outstanding electrical conductivity, mechanical strength, and unique one-dimensional (1D) tubular structure. CNTs are typically categorized as single-walled carbon nanotubes (SWCNTs), comprising a single rolled graphene sheet that offers superior electron mobility, and multi-walled carbon nanotubes (MWCNTs), consisting of multiple concentric graphene layers that provide enhanced structural robustness. Their 1D conductive pathways facilitate rapid and Directional electron transport, directly addressing the intrinsic low electronic conductivity of pristine NVP and improving charge transport kinetics [84,85].

In NVP cathodes, CNTs establish an interconnected conductive framework that not only accelerates charge-transfer reactions but also promotes more efficient Na^+ ion diffusion throughout the electrode. Their mechanical flexibility further acts as a buffer against volume changes during cycling, preserving electrode integrity and mitigating particle fracture or detachment. Among the notable advances, Pan et al. [86] synthesized an NVP/C@CNT (Fig. 5a) composite using a low-temperature solid-state ball milling approach, where amorphous carbon coating and CNT wrapping were simultaneously employed to generate a dual-carbon conductive architecture. The CNTs effectively suppressed particle growth, reducing the NVP particle size to approximately 100 nm, thereby shortening Na^+ diffusion paths. This synergistic structure enabled the composite to deliver a capacity of 114.5 mAhg^{-1} at 0.1C and maintain 93.3 mAhg^{-1} even at 20C, with a remarkable 99.5 % capacity retention after 2710 cycles (Fig. 5b, c). Additionally, the full-cell configuration using a Sn_3P_4 @C anode achieved 100.8 mAhg^{-1} at 1C, confirming the suitability of CNT-modified NVP for High-rate, long-duration SIB applications.

Similarly, Kadam et al. [85] demonstrated that incorporating an optimal amount of MWCNTs (0.5 wt%) (FNV-2) into NVP through a solid-state process produced a well-connected three-dimensional (3D) conductive network (Fig. 5d). This Network effectively prevented particle agglomeration, yielding smaller particles with larger active surface areas and improved Na^+ diffusion. The resulting composite exhibited a high reversible capacity of 110 mAhg^{-1} at 0.1C, an excellent rate capability of 97 mAhg^{-1} at 10C, and outstanding stability with 98.66 % retention after 600 cycles at 2C and 97.2 % after 2000 cycles at 10C (Fig. 5e). Electrochemical impedance spectroscopy further confirmed its superior charge-transfer characteristics with a low resistance of 418.65Ω , while full-cell testing with hard carbon anode delivered 103 mAhg^{-1} at C/20, confirming excellent electrode compatibility and interfacial stability.

Collectively, these studies demonstrate that CNT integration, whether through single or multi-walled architecture, plays a pivotal role in enhancing both the electronic and ionic transport of NVP cathodes. The dual function of CNTs as conductive highways and mechanical stabilizers ensures efficient charge transfer, mitigates electrode degradation, and extends cycling longevity. These synergistic enhancements

Table 1
Electrochemical performance of carbon-modified $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes prepared via various synthesis methods and organic carbon precursors.

Material	Method	Carbon Content (wt%)	Carbon Precursor (Formula)	Discharge Capacity (mAhg^{-1} @ C-rate)	Capacity Retention (% @cycles /C-rate)	ref
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Solid phase carbothermal reduction	17.0	Polyethylene glycol-2000 (PEG-2000; $\text{C}_2\text{H}_4\text{O}_n$)	103.9 @ 0.5C	89.89 @ 340 / 0.5C	[71]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Spray drying	8.4	Lactose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)	108 @ 0.15C	97.6 @ 225 / 0.15C	[72]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Pre-reduction and calcination	4.07	Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)	106 @ 0.5C	90 @ 50 / 20 mAhg^{-1}	[73]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Pyrolysis reduction	10.73	Acetylene (C_2H_2)	118 @ 0.05C	90.0 @ 300 / 1C	[74]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Pyrolysis reduction	6.5	Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$)	98 @ 0.1 A $\cdot \text{g}^{-1}$	74.0 @ 450 / 0.4 A $\cdot \text{g}^{-1}$	[75]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Hydrothermal-assisted sol-gel	12.5	Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) + PEG-400 ($\text{C}_4\text{H}_8\text{O}_n$)	104.3 @ 0.5C	96.1 @ 700 / 5C	[76]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Rheological phase reaction	7.6	Citric acid ($\text{C}_6\text{H}_8\text{O}_7$)	110 @ 1C	99.8 @ 500 / 1C	[77]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Sol-gel synthesis	–	Citric acid ($\text{C}_6\text{H}_8\text{O}_7$)	115.7 @ 1C	92.9 % @ 500 cycles / 1C	[78]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Sol-gel synthesis	–	Citric acid ($\text{C}_6\text{H}_8\text{O}_7$)	112.3 @ 0.1C	92.7 % @ 200 cycles / 2C	[79]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	solid-state	10.53 %	Span 80 ($\text{C}_{24}\text{H}_{44}\text{O}_6$)	114.2 @ 0.5C	87.3 % @ 1000 cycles / 1C	[80]

Table 2Electrochemical performance of carbon modified heteroatom doped $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ -based cathode materials.

Material	Method	Modification-Strategy	Discharge Capacity (mAhg^{-1} @ C-rate)	Capacity Retention (%@ cycles /C-rate)	Ref
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{rGO}$	Sol-gel	Flake-shaped NVP embedded in rGO network	112 @ 0.5C	71.0@10,000/30C	[121]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{rGO}$	Spray drying	Porous hollow spheres coated with rGO	116 @ 1C	94.0@400/1C	[122]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{rGO}$	Spray drying	3D porous graphene framework with amorphous carbon	115 @ 0.2C	81.0@3000/5C	[123]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{rGO}$	Spray drying	rGO sheets and amorphous carbon coating	102.2 @ 0.2C	95.5@100/10C	[124]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{rGO}$	Hydrothermal + freeze drying	NVP nanocrystals confined between rGO layers	118 @ 0.5C	98.0@100/ 1C	[125]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{rGO}-\text{CB}$	Electrophoretic deposition (EPD)	NVP uniformly distributed in rGO-carbon black matrix	87 @ 0.1 A·g ⁻¹	84.0@250/0.1 A·g ⁻¹	[126]
Graphene-wrapped $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Hydrothermal-assisted sol-gel	Carbon coating combined with graphene wrapping	106.5 @ 0.1C	99.4@10/0.2C	[127]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{graphene}$	Sol-gel + solid-state reaction	NVP nanoparticles anchored on graphene sheets	90.6 @ 0.2C	93.0@100/ 1C	[128]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}@-\text{N}-\text{graphene}$	Hydrothermal + sol-gel	Nitrogen-doped graphene wrapping with carbon coating	115.2@0.1C	82.8@1000/15C	[129]
NVP@C/N-GA	Precursor infiltration + post-heating	3D porous nitrogen-doped graphene aerogel	74.1@100C	84@12,000/20C	[130]
NVP/C@CNTs	Sol-gel	Carbon-coated NVP embedded in carbon nanotube (CNT) matrix	98.7 @ 0.1C	81.0@500/ 2C	[131]
NVP/NC@CNTs	Sol-gel	Nitrogen-doped dual carbon coating with CNTs	106.5@0.1C	98.9@2000/20C	[132]
$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{C}/\text{CNTs}$	Solvothermal	Carbon coating with 3D CNTs	114@0.2C	100@200/0.2C	[133]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}@-\text{NC}$	Hydrothermal-assisted sol-gel	Nitrogen-doped carbon coating	106.82@0.2C	83@1000/5C	[134]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{N-doped carbon}$	Sol-gel	Nitrogen-doped carbon coating	109.2@1C	72.9@8000/50C	[135]
NC15@NVP	Sol-gel	Nitrogen-doped carbon coating	114.9@0.2C	92.1@ 400/1C	[136]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}@-\text{N}$	Sol-gel	Nitrogen doping with carbon coating	69.5@0.1C	96.1@500/2C	[137]
NVP@NSC	Solid-state	Nitrogen and sulfur dual-doped carbon coating	113@1C	82.1@5000/50C	[138]
MWCNTs-NVP/C	Hydrothermal-assisted sol-gel	Core-shell NVP/C embedded in multi-walled CNT network	109.3@ 0.1C	93.9@500/10C	[139]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{MWCNTs}$	Sol-gel	NVP nanoparticles embedded in porous microspheres with MWCNT matrix	112.8@0.2C	90.0@ 400/ 1C	[140]
NVP/C/MWCNT	Sol-gel synthesis	MWCNT-pierced carbon structure	111.6@1C	–	[141]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{rGO}-\text{CNTs}$	Freeze drying	Chemically bonded NVP with rGO-CNT hybrid conductive network	105@1C	91.3@500/1C	[142]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}/\text{CNF}$	Simple casting method	Porous microspheres with interwoven CNFs	116.1@0.2C	90@500/1C	[143]
NVPC@CNF	Sol-gel synthesis	CNF network with glucose-derived carbon coating	51.1@10C	99.9@3000	[92]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanorods	Electrospinning	One-dimensional nanorod structure with uniform carbon coating	116.9@0.05C	97.9@50/0.1C	[144]

make CNT modification a highly effective and industrially viable strategy for advancing the performance and durability of NVP-based sodium ion battery cathodes.

3.2.2. Graphene and reduced graphene oxide (rGO)

Graphene and reduced graphene oxide are two-dimensional carbon nanostructures with exceptional electrical conductivity, high surface area, and mechanical flexibility. Their planar sheet-like structure enables the formation of large-area conductive networks that facilitate rapid electron transport and maintain electrode stability during Na^+ insertion/extraction. In addition, the oxygen-containing functional groups on rGO provide anchoring sites for NVP particles, preventing agglomeration and mitigating volume expansion during cycling [87].

Liu et al. [83] demonstrated the baseline benefits of rGO in constructing fragmented NVP@rGO (NVP@FG) composite. Here, NVP nanoparticles were homogeneously distributed on rGO sheets, forming a 3D conductive network that simultaneously enhanced electron transport and Na^+ diffusion (Fig. 6a). Compared to pristine NVP@C, the NVP@FG composite exhibited a tenfold higher Na^+ diffusion coefficient and lower charge-transfer resistance (358.7 Ω vs. 671.6 Ω). The electrochemical performance was remarkable, with 114.5 mAhg^{-1} at 0.2C and 97.5 % capacity retention over 1800 cycles at 10C (Fig. 6b), establishing the fundamental advantage of rGO as a conductive scaffold.

Building on this concept, Xu et al. [88] further leveraged rGO as a morphology-directing agent to fabricate porous NVP/rGO hollow

spheres (NVP/rGO HSs). In this design, rGO not only formed continuous conductive skin but also guided the formation of hollow spheres, which enhanced specific surface area and facilitated electrolyte infiltration. This architecture reduced Na^+ diffusion pathways, reflected in a diffusion coefficient and order of magnitude higher than pristine NVP. Consequently, the NVP/rGO HSs cathode delivered 98.5 mAhg^{-1} at an ultra-high rate of 20C and retained 73.1 mAhg^{-1} after 1000 cycles at 10C, demonstrating that morphology control via rGO integration can further amplify the benefits observed in basic rGO networks.

Cheng et al. [89] explored rGO incorporation in a blended $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$. $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{C}$ (B@rGO) cathode, emphasizing functional improvements beyond morphology. The rGO created a continuous conductive framework that suppressed particle aggregation, enhanced reaction kinetics, and facilitated pseudocapacitive behavior. Compared to the NVP@FG or hollow sphere designs, B@rGO highlighted rGO's role in accelerating surface-controlled charge storage, delivering 85.9 mAhg^{-1} even at 30C and retaining 81.6 % capacity after 200 cycles. This study illustrates that rGO's benefits extend to blended systems and high-power applications, where enhanced kinetics and rate performance are critical.

Finally, Ananthavel et al. [90] demonstrated the dual role of rGO in engineering flake-shaped NVP@C (rGO-NVP@C) cathodes by using sol-gel synthesis (Fig. 6c). The 2D rGO sheets guided the formation of flake-like morphology, shortened ion diffusion pathways, and increased specific surface area to 92.6 m^2/g . Coupled with the highly conductive rGO network, this design achieved the highest electrochemical performance

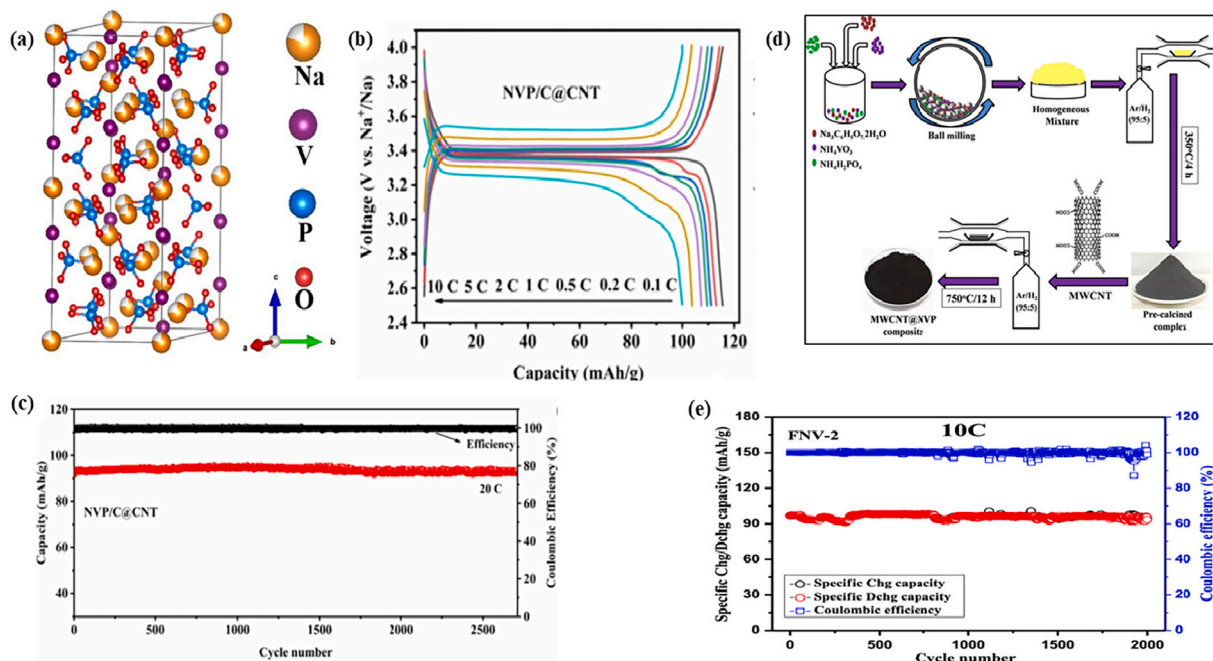


Fig. 5. (a) Schematic structure of the NVP/C@CNT. (b) discharge/charge curves at different current densities. (c) ultralong-life cycling performance at 20C. Reproduced with permission from [86] Copyright 2024 Elsevier. (d) Synthesis process of the MWCNT@NVP composite. (e) Cycling stability of the FNV-2 composite at 10C and Current rate over 2000 cycles. Reproduced with permission from [85] Copyright 2023 American Chemical Society.

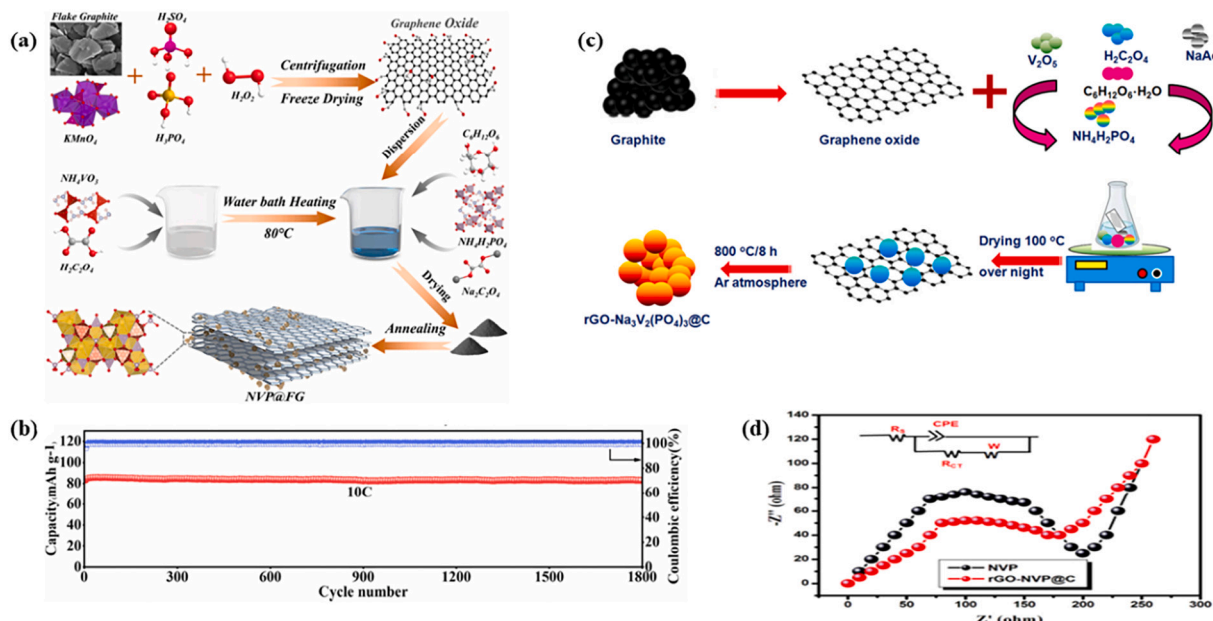


Fig. 6. (a) Schematic illustration of the synthesis process for NVP@FG samples. (b) Cyclability of NVP@FG at 10C. Reproduced with permission from [83] Copyright 2025 Elsevier. (c) Schematic representation of the synthesis process of rGO-NVP@C. (d) Nyquist plots and the equivalent circuit of NVP and rGO-NVP@C. Reproduced with permission from [90] Copyright 2023 Springer.

among the discussed studies, with 142.2 mAh⁻¹ at 0.2C and 95.5 % capacity retention over 100 cycles. Electrochemical impedance spectroscopy confirmed reduced charge-transfer resistance (52 Ω) (Fig. 6d) and higher Na⁺ diffusion, emphasizing that rGO can simultaneously enhance conductivity and structurally optimize NVP for superior rate capability and cycling stability.

Collectively, these studies demonstrate the multifaceted role of rGO in NVP cathodes from forming fundamental 3D conductive networks to guiding advanced morphologies and promoting capacitive kinetics in

blended systems. By carefully tailoring the rGO integration strategy, whether as a scaffold morphology director or conductivity enhancer, researchers can simultaneously improve electron transport, ion diffusion, structural integrity, and high-rate performance, underscoring rGO as a pivotal component in next-generation sodium ion battery cathodes.

3.2.3. Carbon nanofibers

Carbon nanofibers are one-dimensional carbon nanostructures with long, continuous fibers and high aspect ratios. They form highly

conductive, networked architectures that not only ensure efficient electron transport but also provide structural reinforcement, which is particularly beneficial for NVP cathodes with limited intrinsic conductivity and sensitivity to volume changes during Na^+ insertion/extraction. Meligrana et al. [91] developed a self-standing NVP/CNF cathode by supporting NVP on an electrospun CNF nonwoven fabric. The scalable fabrication involved electrospinning a flexible CNF mat, followed by dip-coating and filtration to load NVP onto the 3D porous scaffold. This architecture created an interconnected conductive network that enhanced electronic transport, leading to well-defined redox peaks with small voltage separation (55 mV), stable cycling over 200 cycles at 1.5C, and excellent reaction kinetics (Fig. 7b, c). The design eliminated the need for metallic current collectors or extra conductive additives, demonstrating a low-cost and practical approach for high-energy density sodium-ion battery cathodes.

Building on this, Jink et al. [92] integrated CNFs with a carbon-coated NVP composite (NVPC@CNFs) to create a high mass loading cathode ($\sim 8.5 \text{ mg cm}^{-2}$). Using a sonication-assisted sol-gel method (Fig. 7a), they achieved a uniform CNF network embedded within NVP/C particles, which significantly enhanced electronic conduction and reduced interfacial charge-transfer resistance. The resulting cathode exhibited exceptional rate capability (51.1 mAhg^{-1} at 10C and 82.3 mAhg^{-1} at 100C) and outstanding long-term cyclability (coulombic efficiency $> 99.9\%$ over 3000 cycles) in an ionic liquid electrolyte (Na/IL/NVPC@CNFs) (Fig. 7d, e).

Together, these studies underscore that CNF incorporation not only improves electronic and ionic transport but also provides mechanical resilience, enabling high-rate performance and long-term stability. They demonstrate that the choice of CNF architecture, self-standing mats versus embedded high-mass loading networks, can be tailored to meet specific practical requirements, bridging fundamental material design with scalable sodium ion battery applications.

3.2.4. Quantum carbon materials

Quantum carbon materials, including graphene quantum dots (GQD) and carbon quantum dots, are emerging as highly effective additives to enhance the electrochemical performance of NVP cathodes in sodium-ion batteries. These zero-dimensional carbon nanostructures, typically below 10 nm in diameter, exhibit unique properties such as quantum confinement, high specific surface area, and tunable surface functionalities, enabling intimate interaction with NVP at the nanoscale [93].

GQDs, as nanoscale graphene fragments, promote ion accessibility, reduce charge-transfer resistance, and boost pseudocapacitive behavior, thereby facilitating rapid Na^+ transport and improving cycling stability [94]. Deng et al. [95] demonstrated this by synthesizing carbon-coated, graphene quantum dots shielded $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}$ nano cuboids (NVOPF@C) via a solvothermal method. The GQDs prevented particle agglomeration, enhanced electronic and ionic conductivity, and provided additional Na^+ storage sites. This synergistic effect yielded a high reversible capacity of 70 mAhg^{-1} at an ultra-high rate of 45C and 81 % capacity retention after 2000 cycles (Fig. 8a, b), highlighting the critical role of GQDs in enabling high-power, long-cycle sodium-ion storage.

Building on this concept, Liu et al. [96] employed carbon quantum dots to modify NVPF hierarchical microspheres via a one-step solvothermal method followed by annealing. The CQDs acted as “designer additives” guiding the morphology from micro cuboids to compact microspheres, which improved Na^+ diffusion kinetics and electronic conductivity. The optimized NVPF@CQD cathode exhibited remarkable rate capability, delivering 105.1 mAhg^{-1} at 20C and maintaining 90.2 % capacity retention over 6000 cycles at 30C (Fig. 8d, e). Full-cell tests with hard carbon anodes confirmed enhanced voltage stability and cycling performance, demonstrating how CQDs can tailor microstructure while boosting electrochemical functionality. Further advancing the field, Huang et al. [97] introduced a trace carbon dot (NCDs) strategy using only 0.76 wt% to refine particle size, improve electrical conductivity, and optimize the cathode-electrolyte interface in NVP (Fig. 8c). The carbon dot promoted the formation of a thin, stable NaF-

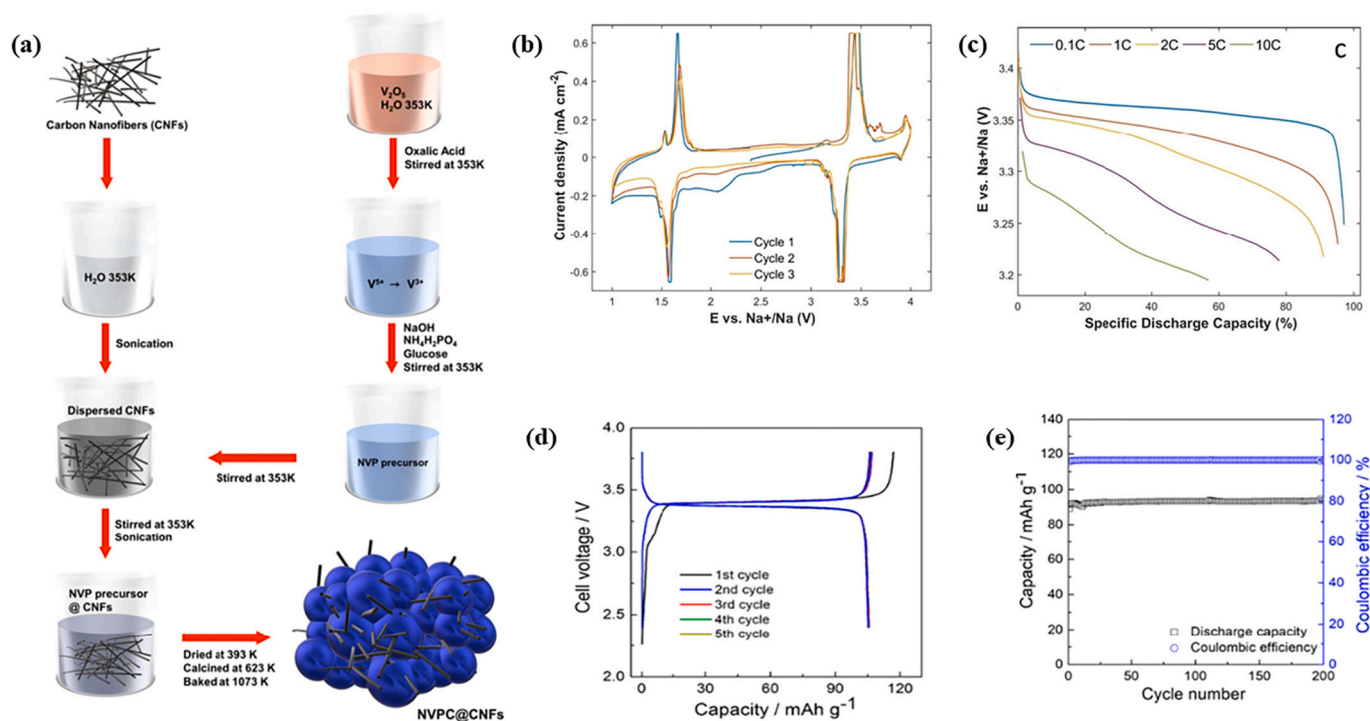


Fig. 7. (a) Schematic illustration of the synthesis process for NVP@CNFs (b) CV at 0.1 mV s^{-1} of the NVP/CNF cathode in the 1–4 V vs. Na^+/Na potential range. (c) potential vs. discharge specific capacity profiles at different C-rates. (d) Charge-discharge curves at 0.1C and (e) cycling properties of the Na/IL/NVPC@CNFs cell at 298 K and 2C. (b,c).

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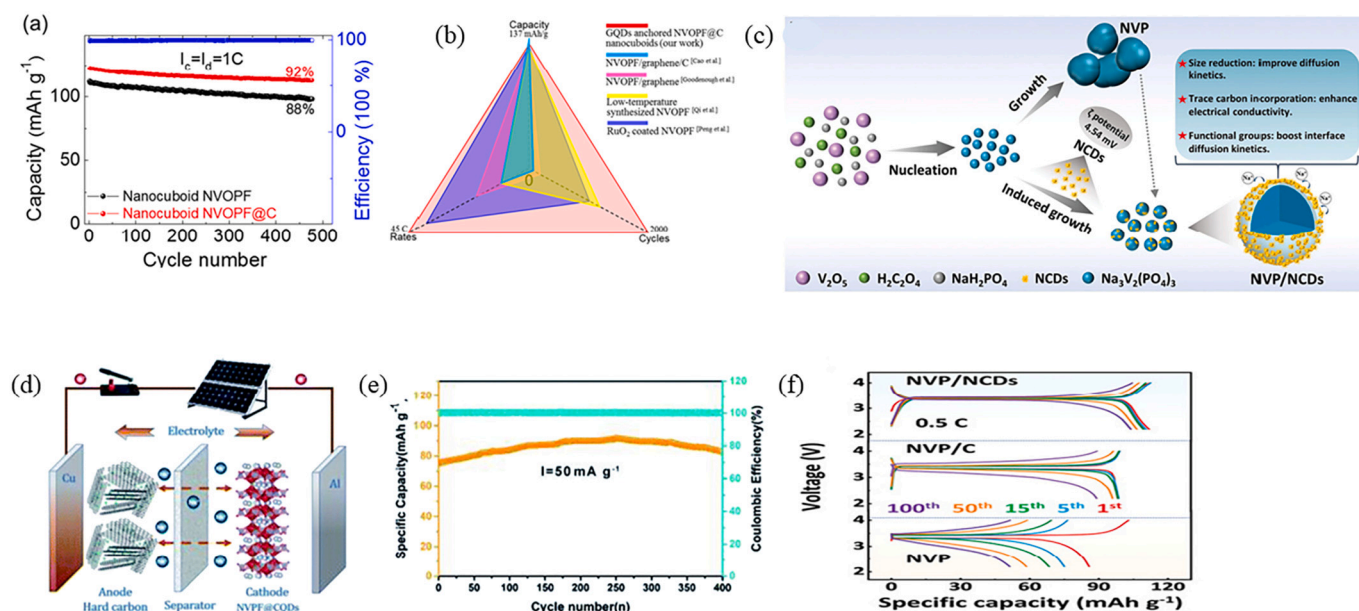


Fig. 8. (a) Low rate cycling performance of both NVPF and NVPF@C electrodes. (b) performance comparison with other reported sodium-vanadium fluorophosphates. Reproduced with permission from [95] copyright 2016 Elsevier (c) Illustration of optimization mechanism for carbon dot incorporation on NVP (d) Schematic illustration of the full-cell configuration (NVPF@CQD//hard carbon). (e) Cycling performance and coulombic efficiency of the NVPF@CQD//hard carbon cell at a current density of 500 mA g⁻¹ over 400 cycles. Reproduced with permission from [96] copyright 2020 Royal Society of Chemistry. (f) CV profiles under different rates. (c,f) Reproduced with permission from [97] copyright 2024 Wiley-VCH.

rich CEI layer, accelerating interfacial Na⁺ diffusion. As a result, the NVP/NCDs cathode achieved ultrahigh rate capability with 98.4 % capacity retention over 20,000 cycles and high voltage at 0.5C (Fig. 8f). Full-cell configurations paired with Hard carbon anodes reached high energy densities (368.7 Whkg⁻¹) and maintained 250.8 Whkg⁻¹ under fast-charging conditions. This work highlights that even trace amounts of carbon dots can drastically enhance charge-transfer kinetics, interfacial stability, and overall performance.

Collectively, these studies demonstrated that the synergy of nano-scale carbon dots, whether GQDs, CQDs, or NCDs, provides an effective approach to simultaneously improve electronic conductivity, structural robustness, ionic transport, and interfacial stability, establishing quantum carbon modification as a powerful route to next-generation high-power, long-life sodium-ion battery cathodes.

3.3. Composite carbon systems

Composite carbon systems represent an advanced strategy to enhance the electrochemical performance of Na₃V₂(PO₄)₃ cathodes by combining in-situ pyrolyzed carbon coatings with pre-formed carbon nanostructures, such as carbon nanotubes, reduced graphene oxide, and graphene. This hybrid approach leverages the unique advantages of each carbon type: pyrolytic carbon provides uniform surface coverage, improved electronic contact, and mechanical adhesion, while pre-formed carbons establish extended conductive networks, mitigate particle aggregation, and buffer volume changes during cycling, collectively enhancing rate capability and long-term stability [98].

Al-Marri et al. [99] demonstrated this concept by synthesizing a Na₃V₂(PO₄)₂F₃@C/rGO (NVPF@C/rGO) composite via a facile hydro/solvothermal method. In this system, 40–50 nm NVPF nanoparticles were coated with pyrolytic carbon and embedded within a conductive rGO network. The resulting architecture promoted rapid electron transfer, facilitated ion diffusion, and accommodated volumetric changes during cycling. Electrochemical testing revealed a high reversible capacity of 130 mAhg⁻¹ at 0.5C, outstanding cycling stability with 99 % retention over 500 cycles, and a maintained capacity of 115 mAhg⁻¹ at 10C. These results highlighted the synergistic effect of

combining carbon coating with rGO integration, where the rGO network extended conductivity beyond the local particle surfaces and reinforced structural integrity.

Building on this approach, Chen et al. [100] developed a more complex ternary carbon framework by integrating pyrolytic carbon, CNTs, and graphene with NVP particles (NVP@C/GN/CNTs). This NVP@C/GN/CNTs composite created a robust three-dimensional conductive network that simultaneously enhanced electronic conductivity and Na⁺ diffusion kinetics without altering the NASICON structure, as illustrated in Fig. 9. The material exhibited remarkable performance, retaining 92 mAhg⁻¹ after 800 cycles at 10C with only 10.6 % capacity decay, and sustaining 73.6 mAhg⁻¹ at an ultrahigh rate of 20C. In full-cell tests paired with a hard carbon anode, it maintained 93.6 % capacity after 100 cycles at 1C. The study underscores that multi-dimensional carbon networks, which combine the conformal coating of pyrolytic carbon with the extended conductive pathways of CNTs and graphene, provide a synergistic enhancement of charge transfer, structural stability, and high-rate performance.

Together, these works illustrate that composite carbon architectures offer a powerful approach to overcome the intrinsic conductivity limitations and structural fragility of NVP cathodes. By carefully selecting and integrating carbon types, researchers can construct multi-functional networks that maximize electronic transport, maintain electrode integrity, and unlock high-rate, long-life performance in sodium-ion batteries.

3.4. Heteroatom-doped carbon coating

Heteroatom doping within carbonaceous coatings has emerged as an important technique to enhance the electrochemical performance of Na₃V₂(PO₄)₃ cathodes. By introducing elements such as nitrogen (N), sulfur (S), fluorine (F), and boron (B) into the carbon matrix, the electronic structure of the coating can be tuned to improve conductivity, increase active sites, and enhance ion transport. These heteroatoms not only contribute to better electron mobility but also strengthen the interaction between the carbon layer and the NVP surface, thereby improving structural stability during cycling [101].

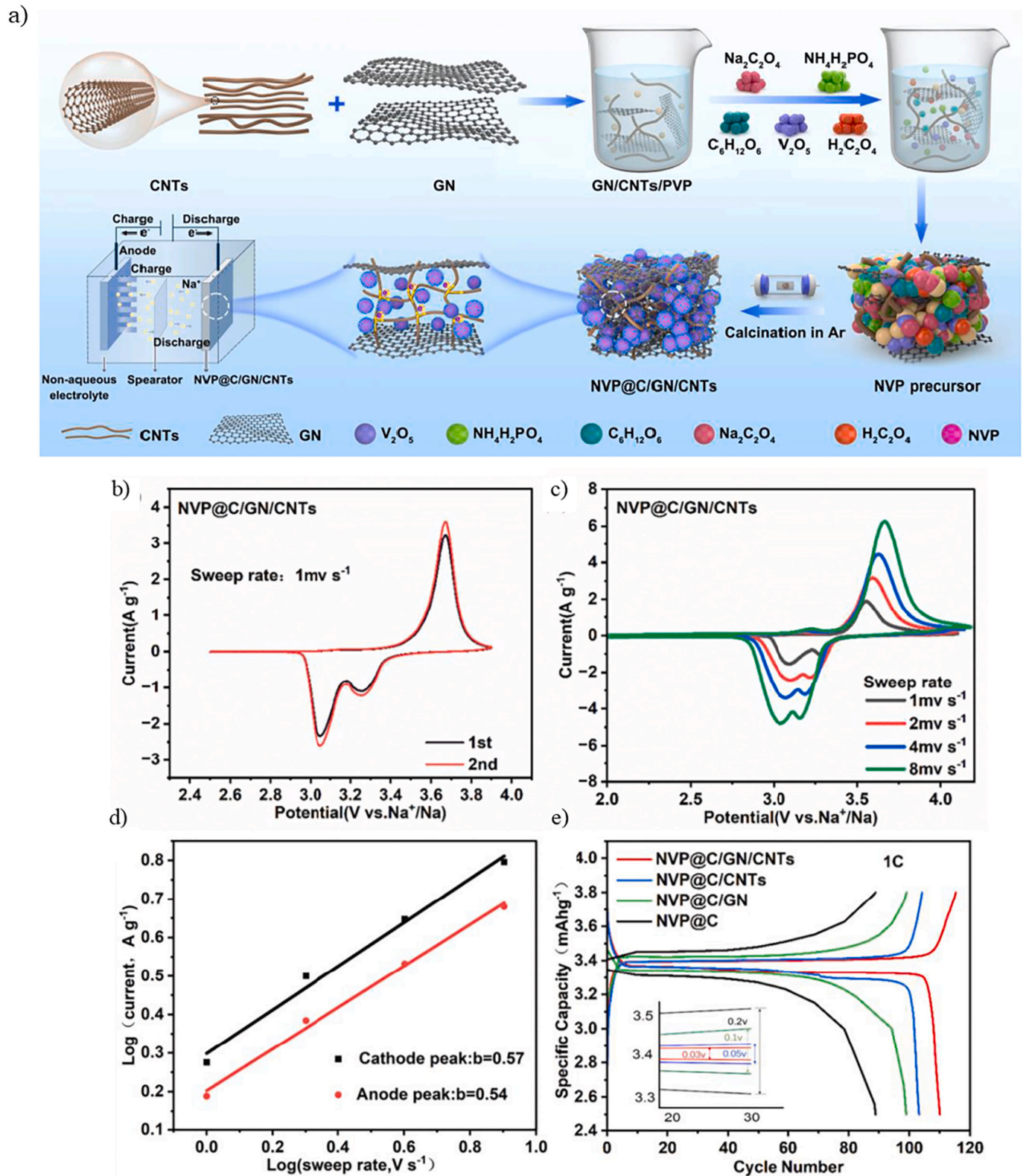


Fig. 9. (a) Process flow diagram for the synthesis of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}/\text{GN}/\text{CNTs}$ composite. (b) CV curve of $\text{NVP}/\text{C}/\text{GN}/\text{CNTs}$ at a scan rate of 1 mV s^{-1} . (c) CV curves of $\text{NVP}/\text{C}/\text{GN}/\text{CNTs}$ at different scan rates ranging from 1 to 8 mV s^{-1} . (d) $\text{Log}(\text{scan rate})$ versus $\text{log}(\text{peak current})$ plot to determine the b -values of the cathodic and anodic peaks of $\text{NVP}/\text{C}/\text{GN}/\text{CNTs}$. (e) Charge-discharge curves of NVP/C , $\text{NVP}/\text{C}/\text{GN}$, $\text{NVP}/\text{C}/\text{CNTs}$, and $\text{NVP}/\text{C}/\text{GN}/\text{CNTs}$ at 1C after 50 cycles. (Reproduced with permission from [100] Copyright 2025 Elsevier.)

Nitrogen doping is particularly effective, as it introduces lone-pair electrons and defect sites within the carbon matrix, promoting higher charge transfer rates and improving electrolyte wettability. For example, Xiao et al. [102] synthesized N-doped carbon-coated NVP (NVP/CN) using folic acid as a carbon and nitrogen source. The optimal NVP/CN-2 composite, containing 3.3 wt% N-doped carbon with a uniform ~ 2 nm coating, exhibited a high-rate capability of 91 mAhg^{-1} at 20C and maintained full capacity over 3000 cycles at 10C. Similarly, Qian et al. [103] employed polyethyleneimine (PEI) to create an N-doped porous carbon framework, achieving improved electronic conductivity, numerous active sites, and enhanced Na^+ adsorption and diffusion. The optimized 3 wt% PEI composite delivered 116.6 mAhg^{-1} at 0.1C and retained 74.6 mAhg^{-1} after 1000 cycles at 20C, while also mitigating volume changes and improving thermal stability.

Sulfur doping is a crucial method for improving the structural and electrochemical properties of NVP materials. As a result of their greater atomic size relative to carbon or nitrogen, sulfur atoms enlarge the interlayer spacing, which in turn favors faster Na^+ diffusion and improves rate performance. Furthermore, sulfur introduction creates defect sites and improves redox activity. When combined with nitrogen doping in a co-doping approach, the created synergistic effect dramatically improves both conductivity and structural stability. Yanjun et al. [104] employed thiourea as a nitrogen and sulfur bifunctional precursor in the synthesis of a carbon-coated NVP composite (NVP/C@N, S). The NVP/C@N, S-10 % sample showed exceptional performance with a high capacity of 123.15 mAhg^{-1} at a 0.1C rate and excellent durability over 20,000 cycles at a 60C rate, with a negligible capacity loss of merely 0.0017 % per cycle. Coral-like porous architecture, derived from pyrolysis of thiourea, facilitated electrolyte infiltration and accepted volume change, while the formation of C–S–V bonds served as a key factor for inhibiting vanadium dissolution.

Boron doping, though relatively less explored, has shown remarkable promise. When incorporated into the carbon framework or substituted at the phosphorus site, boron improves graphitization, enhances electronic conductivity, and reinforces structural integrity. Hong et al. [105] investigated boron substitution in $\text{Na}_3\text{V}_2(\text{P}_{2-x}\text{B}_x\text{O}_8)\text{O}_2\text{F}$, achieving significantly reduced bandgap energy and enhanced electron delocalization within the BO_4 tetrahedra. The optimized B-doped sample (NVP_{1.90}B_{0.10}OF) demonstrated an 11-fold increase in Na^+ diffusivity and excellent rate performance, maintaining 95.9 % capacity after 1000 cycles at 10C. A thin carbon coating worked in synergy with the boron dopants to further reduce charge-transfer resistance and improve ion kinetics. Full-cell tests paired with a Se–C anode achieved high energy and power densities with long-term stability.

Fluorine doping further complements these advancements by enhancing surface stability, ionic conductivity, and operating voltage. Due to its high electronegativity, fluorine facilitates the formation of a NaF-rich solid electrolyte interphase SEI, which protects the cathode surface and minimizes side reactions. Moreover, F-doping increases the inductive effect within the phosphate framework, raising the working voltage. Chen et al. [106] investigated F-doping combined with vanadium-defect engineering in NVP/C, which reduced particle size, shortened diffusion paths, and promoted the formation of Na_3PO_4 and NaVO_2 by-products that facilitated rapid Na^+ migration. The F0.1-NV1.98P/C sample exhibited a high discharge capacity of 116.9 mAh g^{-1} at 0.1C and retained 89.3 % after 100 cycles at 1C.

Beyond these extensively studied elements, phosphorus (P) and oxygen (O) doping are emerging as promising methods for fine-tuning the electronic structure and lattice dynamics of NVP-based materials. These dopants offer opportunities to further optimize ionic conductivity, enhance redox kinetics, and improve structural robustness under high-rate and long-life cycling conditions. Their integration into future design strategies could significantly broaden the material development landscape for next-generation sodium-ion battery cathodes [107].

In summary, heteroatom doping, particularly when combined with conductive carbon matrices, offers a highly tunable and effective

strategy for enhancing the electrochemical performance of NVP cathodes. The type, concentration, and distribution of dopants must be carefully optimized to maximize benefits such as improved electronic conductivity, enhanced Na^+ transport, and increased density of electrochemically active sites while avoiding potential drawbacks [108]. One of the most challenging aspects associated with heteroatom doping in carbon-modified NVP cathodes is the severe reduction in initial columbic efficiency (ICE), along with structural disorder and instability introduced by excessive defect formation. Bai et al. [109] clearly demonstrate this limitation in their experimental work, reporting an extremely low ICE of 42.9 % for S, N co-doped materials. They attribute this efficiency to extensive irreversible sodium consumption during solid electrolyte interphase formation on highly defective doped surfaces. Their results also reveal a delicate balance in dopant interactions, where increasing sulfur content disrupts favorable nitrogen configurations and shifts the storage mechanism toward diffusion-controlled processes at the cost of beneficial surface-capacitive contributions. Complementing these experimental observations, Yuan et al. [110] provide a systematic review outlining broader, fundamental limitations of hetero atom doping in carbon-based electrodes. They emphasize that increased defect density and enlarged surface area significantly intensify parasitic reactions. Further reducing the ICE—a trend consistently seen across doped carbon systems. Additionally, they highlight that the underlying sodium-storage mechanisms in doped carbons remain ambiguous and sometimes controversial, limiting rational design and optimization. In a broader context, hetero-atom doping introduces additional challenges, particularly when dopant levels are not carefully controlled. For example, Excessive fluorine or defect introduction can induce phase instability or surface degradation during prolonged cycling, compromising long-term performance [111]. Similarly, boron incorporation requires precise control, as inappropriate concentration may reduce electronic conductivity or lead to the formation of inactive phases [112]. High Nitrogen content can result in structural disorder, uneven carbon coatings, or diminished mechanical integrity, highlighting the necessity of optimized doping levels [113]. Collectively, these considerations underscore that while heteroatom doping can dramatically improve NVP cathode performance, achieving the full benefits relies on the precise control of dopant type and amount, enabling high-rate capability, long-term cycling stability, and robust structural integrity.

To fully utilize the advantage of heteroatom doping while minimizing associated drawbacks, it is essential to implement strategies that ensure precise dopant control and suppression of dopant-induced side reactions. Such control can be achieved by selecting molecular precursors with predictable decomposition pathways, optimizing the carbonization temperature to regulate dopant bonding states, and adjusting precursor to NVP ratios to prevent excessive defect formation [110,114]. Building on that, recent studies provide practical demonstrations of how precursor engineering and controlled doping environments can refine dopant incorporation and enhance electrochemical performance. Yao et al. [115] employed an ionic liquid precursor with a well-defined decomposition pathway to form an ultrathin, uniform N-doped carbon coating. By systematically tuning the ionic liquid content, they achieved precise control over nitrogen concentration and bonding configurations, maximizing the formation of pyridinic and pyrrolic nitrogen while avoiding excessive structural disorder. This optimized dopant distribution facilitated faster Na^+ transport and significantly improved high-rate capability, illustrating how targeted precursor selection and thermal regulation can yield beneficial heteroatom incorporation in NVP. Similarly, Li et al. [116] demonstrated the utility of a decoupled two-step doping strategy, in which glucose first generated a stable carbon matrix before urea introduced Nitrogen under a controlled H_2/Ar atmosphere. Carefully adjusting the urea to precursor ratio enabled the author to identify an optimal doping level that improved electronic conductivity and Na^+ diffusion without producing an overly resistive carbon overlayer. Their results emphasize the necessity of balancing dopant concentration to avoid both insufficient and excessive

doping while promoting favorable nitrogen bonding states that stabilize the electrode interface and enhance long-term cycling.

In parallel, mitigating dopant-induced side reactions requires minimizing surface defects and controlling the reactivity of doped sites. Approaches such as applying a uniform, moderately thick carbon coating, conducting post-annealing to heal disordered carbon domains, and using electrolyte additives help suppress parasitic reactions and improve initial coulombic efficiency [117–119]. Complementing these measures, controlled fluorine doping can further stabilize interfacial behavior. A study by Yang et al. [120] further reinforces the critical role of controlled fluorine incorporation in stabilizing interfacial behavior. Their work demonstrates that precise F-doping effectively regulates SEI formation while mitigating the side reactions commonly associated with hetero-atom doping. By optimizing the F-doping level to an intermediate ratio (2:1 mass ratio of tetrafluoro terephthalic acid to hard carbon), the electrode delivered a high reversible capacity of 434.53 mAhg⁻¹ at 20 mAhg⁻¹ and an excellent rate capability of 141 mAhg⁻¹ at 400 mAhg⁻¹. The fluorine incorporation expanded the interlayer spacing from 0.471 nm to 0.390 nm and increased structural disorder, both of which facilitated enhanced sodium ion storage. More importantly, the F-doped electrode formed a SEI enriched with inorganic NaF nearly twice that of the undoped sample. This optimized SEI also exhibited lower charge-transfer resistance and improved Na⁺ diffusion kinetics, contributing to superior cycling stability (315.7mAhg⁻¹ retained after 100 cycles at 100mAhg⁻¹) and enhanced rate performance. These effects are further supported by Density functional theory (DFT) calculations (Fig. 10), which reveal pronounced charge redistribution upon fluorine incorporation, an increased density of electronic states near the Fermi level, and a reduced Na⁺ migration energy barrier compared to F-free defective carbon. So, based on this study precisely regulated fluorine doping, particularly when combined with complementary strategies such as carbon coating and post-annealing, can harmonize bulk structural modifications with interfacial stabilization, enabling substantial improvements in long-term electrochemical performance. Collectively, these strategies demonstrate how precise dopant engineering supported by precursor chemistry, optimized dopant ratios, controlled atmospheres, and targeted interphase stabilization can address key challenges associated with Heteroatom-doped NVP cathodes and significantly advance their electrochemical performance.

4. Carbon coating thickness and morphology in NVP cathodes

The thickness and morphology of the carbon coating critically determine the electrochemical performance of Na₃V₂(PO₄)₃ cathodes. An optimized carbon layer improved conductivities by providing continuous charge channels and stabilizing the electrode-electrolyte interface [145]. However, the coating must remain sufficiently thin to avoid blocking Na⁺ ion diffusion, as excessively thick layers act as barriers to ion transport, while nonuniform coatings lead to localized polarization and unstable cycling. Therefore, well-controlled carbon coating thickness is essential to balance electronic conduction, ionic diffusion, and interfacial stability [59,146].

A systematic investigation by Das et al. [147] demonstrated this balance by tailoring carbon layer thickness using polyethylene glycol as a carbon source. Among the sample NVP@C₃(~3 nm), NVP@C₆(~4 - 4.5 nm), and NVP@C₉(~8 - 13 nm), the intermediate NVP@C₆ exhibited the best performance, with a discharge capacity of 104mAh g⁻¹ and 77 % retention after 100 cycles. Thinner coatings (~3 nm) provide inadequate conductivity, while thicker ones (~13 nm) restricted Na⁺ transport and caused severe capacity loss, establishing that a moderate coating thickness of around 4-5 nm ensures optimal conductivity without impeding ion diffusion.

In a complementary approach, Shen et al. [148] investigated the correlation between carbon content and coating behavior by preparing NVP/C composites with carbon loadings from 5 % to 15 %. The NVP/C-10 % sample, featuring a uniform amorphous carbon coating, displayed the best performance, delivering 124.1 mAhg⁻¹ at 0.1C, retaining 78.5 mAhg⁻¹ at 200C, and maintaining 83.9 % capacity after 10,000 cycles. Insufficient carbon (5 - 7.5 %) resulted in poor conductivity, while excessive carbon (12.5 - 15 %) hindered Na⁺ diffusion. This study reinforced the importance of precise thickness control to balance electronic conductivity and ionic transport. Similarly, Zhao et al. [149] achieved an ultra-thin and uniform carbon coating (~2 nm) using a dual-complexing sol-gel strategy with citric acid and glycine. The optimized NVP/CG -5.0 electrode showed excellent performance, 108.3 mAhg⁻¹ at 0.5C, 88.2 mAhg⁻¹ at 20C, and 81.3 % retention after 2000 cycles, demonstrating that a highly uniform, thin coating can minimize diffusion barriers while maintaining strong electronic connectivity. This work highlights that precisely engineered ultra-thin

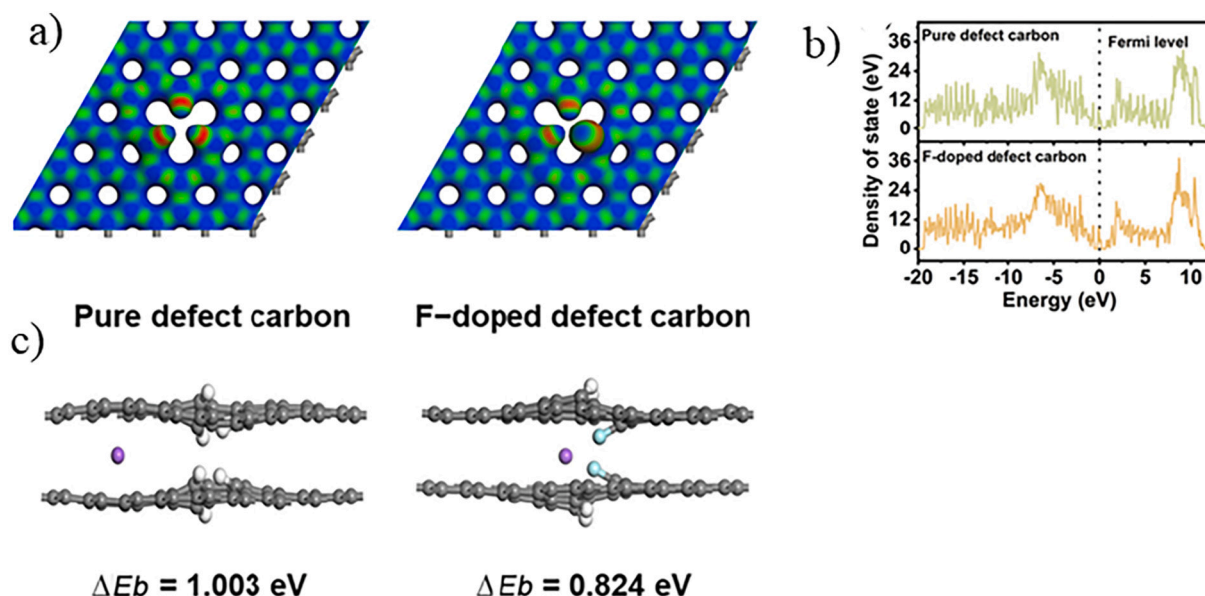


Fig. 10. (a) Differential charge density of F-free and F-doped defective carbon, showing Fluorine-induced charge redistribution. (b) density of states of the corresponding structures, indicating enhanced electronic states near the Fermi level after F-doping. (c) calculated Na⁺ migration energy barriers for insertion/extraction in F-free and F-doped defective carbon.

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coatings can outperform thicker layers by enabling rapid electron and ion transport.

Yao et al. [150] extended this concept by introducing nitrogen doping into an ultra-thin (~ 2 nm) carbon layer using an ionic liquid precursor. The optimized NVP@C-N150 composite combined thinness with chemical functionality, achieving 113 mAhg^{-1} at 1C, 71 mAhg^{-1} at 80C, and 85 mAhg^{-1} after 5000 cycles. The nitrogen-doped layer, rich in pyridinic and pyrrolic nitrogen, introduced defects and active sites that boosted electronic conductivity and interfacial charge transfer, compensating for the minimal thickness. In summary, these studies demonstrate that the ideal carbon coating thickness typically falls between 2 and 5 nm, provided the coating is uniform and chemically optimized, while excessive thickness (> 10 nm) leads to transport limitations.

In addition to coating thickness, particle morphology significantly affects Na^+ diffusion and electron transport. Carbon materials play a pivotal role in directing the formation of well-defined NVP nanostructures ranging from porous and nanoflake to nanofibrous and flower-like architectures, which shorten diffusion pathways, increase electrolyte-accessible surface area, maintain structural integrity during cycling, and ultimately enhance electrochemical performance.

Duan et al. [151] synthesized an NVP@C core-shell nanocomposite

via a hydrothermal-assisted sol-gel process using ascorbic acid and PEG-400 as carbon sources and growth controllers. The resulting ~ 40 nm NVP cores were uniformly coated with a few-nanometre-thick amorphous carbon shell, forming a well-defined nanoscale interface that facilitated rapid Na^+ and electron transport while providing mechanical stability. This electrode delivered 104.3 mAhg^{-1} at 0.5C and retained 96.1 % of its capacity after 700 cycles, illustrating that nanosized cores with uniform carbon shells can simultaneously ensure conductivity and durability.

Surfactant-assisted synthesis offers further control over morphology. Zhao et al. [152] demonstrated that the hierarchical porous carbon-coated $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ nano-flakes exhibit outstanding sodium storage performance owing to their Unique structural features. As shown in Fig. 11a-c, FESEM images reveal that the as-prepared NVP nano-flakes form a well-organised hierarchical nano array network with large open spaces, smooth surfaces, and uniform nanoflake dimensions. Several dozen nanometres thick and several hundred nanometres wide. These features promote efficient electrolyte penetration and fast Na^+ diffusion. Fig. 11d and e further confirm through TEM that the hierarchical architecture consists of numerous ultrathin nanoflakes. HRTEM (Fig. 11f) reveals a thin, partially graphitized carbon layer only for nano meters thick, uniformly coating the NVP surface, enhancing electronic

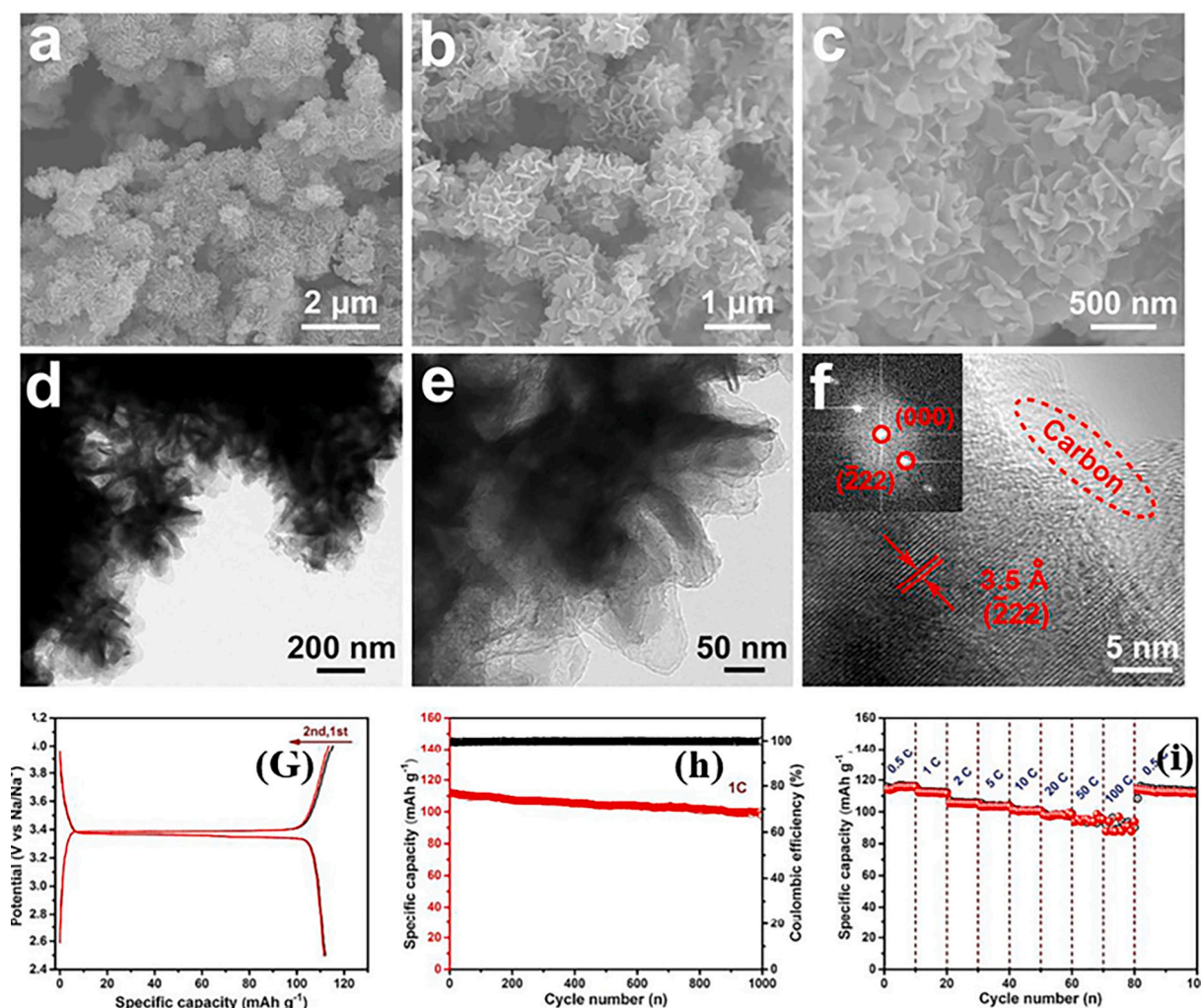


Fig. 11. (a–c) FESEM images of the synthesized $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ nanoflakes at low and high magnifications, showing the hierarchical nanoarray architecture (d, e) TEM images confirming the ultrathin nanoflake structure and (f) HRTEM image with the corresponding Fourier transform (FFT) pattern, revealing the thin carbon coating and high crystallinity of the NVP nanoflakes. (g) First and second charge–discharge curves of the as-synthesized $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ nanoflakes at 1C within 2.5–4.0 V vs. Na/Na^+ (h) cycling performance at 1C and (i) rate capability illustrating the electrode's excellent stability and high-rate performance. (Reproduced with permission from [152] Copyright 2018 Elsevier.)

conductivity and enabling rapid electron transport. The lattice fringes with a d-spacing of 3.5 Å, corresponding to the (222) planes, along with the FFT pattern, confirm the high crystallinity of the NVP nanoflakes. This optimized nanostructure contributes to a high reversible capacity of 114.2 mAhg⁻¹ at 0.5C, an excellent rate capability of 87.7mAhg⁻¹ at 100C, and remarkable cycling stability (10,000 cycles with only 0.0048 % capacity decay per cycle at 20C) as discussed in Fig. 11 (g-i).

Morphology control through carbon-assisted templating has also shown remarkable effectiveness. Jiang et al. [153] confined NVP nanoparticles within a mesoporous CMK-3 matrix to form a core-shell NVP@C@CMK-3 composite. The double-carbon structure created a hierarchical conductive framework with efficient Na⁺ and electron transport, and excellent electrolyte access, minimizing polarization and sustaining long-term cycling with 78 mAhg⁻¹ at 5C after 2000 cycles. Similarly, Sun et al. [154] developed N-doped hard/soft double-carbon-coated NVP hybrid-porous microspheres, combining hierarchical porosity with dual-carbon conductivity enhancement. This structure provided a large electrode-electrolyte contact area and efficient pseudocapacitive behavior, delivering 93 mAhg⁻¹ at 10C, 81 mAhg⁻¹ at 30C, and stable cycling with 72.9 % retention after 1000 cycles. The results clearly demonstrate that integrating hierarchical porosity with conductive carbon networks strongly dictates charge kinetics and electrode stability. Extending this approach, Jiang et al. [155] introduced N, B co-doped carbon to construct a flower-like NVP@C-BN morphology, where ultrathin 2D nanoplates self-assembled into an open framework. The combination of hierarchical porosity and heteroatom doping enhanced electrolyte penetration and stress tolerance, achieving 84 mAhg⁻¹ at 100C and 87 mAhg⁻¹ after 100 cycles in full cells.

Three-dimensional carbon scaffolds provide an additional strategy to optimize morphology and mechanical resilience. Zhong et al. [156] anchored carbon-coated NVP particles onto a freestanding graphite foam (NVP@C-GF), creating a 3D conductive framework that facilitated rapid ion transport and mitigated volume changes. The electrode delivered 92 mAhg⁻¹ at 20C and maintained 54 mAhg⁻¹ at 100C after 20,000 cycles, highlighting the structural robustness of such architectures. Similarly, Gu et al. [157] embedded NVP nanoparticles within expanded graphite, establishing a continuous conductive network superior to those using carbon nanotubes or carbon black. This composite achieved 111.4 mAhg⁻¹ at 1C, 105 mAhg⁻¹ at 50C, and retained 48 mAhg⁻¹ after 20,000 cycles, demonstrating how macroscopic conductive frameworks can effectively integrate nanoscale activity while maintaining mechanical stability.

One-dimensional nanofibrous morphologies further enhance charge transport continuity and structural integrity. Wu et al. [158] produced uniform, spindle-free NVP/C nanofibers via an oxalic-acid-assisted electrospinning method, forming smooth, continuous 1D networks with well-embedded NVP nanoparticles. The resulting electrodes delivered 114 mAhg⁻¹ at 0.05C, 78.1 mAhg⁻¹ at 10C, and retained 97 % of their capacity after 100 cycles. Liu et al. [159] applied an ionic-liquid-assisted electrospinning process to prepare free-standing NVP/C nanofibrous mats with cross-welded fibers. These mats enhanced mechanical flexibility and created abundant ion-transport channels, achieving 117.4 mAhg⁻¹ at 0.1C and retaining 75.2 mAhg⁻¹ at 5C over 1000 cycles. Finally, Zhao et al. [160] combined hierarchical micro/nano morphologies by assembling microscale particles from interconnected nanoflakes coated with N-doped carbon. This design provided rapid carrier transport, efficient electrolyte penetration, and robust structural integrity, resulting in 79.1 mAhg⁻¹ at 200C, 73.4 % capacity retention after 10,000 cycles, and 212 Whkg⁻¹ energy density in a pouch-type full cell. In short, these studies demonstrate that optimizing carbon coating thickness alongside tailored particle morphologies ranging from nanoscale cores and porous matrices to nanofibers and hierarchical 3D frameworks enables rapid electron and ion transport, high structural stability, and superior cycling performance. Precise control of synthesis parameters, including carbon source, preparation method, and reaction conditions, allows the design of architectures that balance conductivity,

ionic diffusion, and interfacial stability. Table 3 summarizes representative NVP composites, highlighting how carbon-assisted morphologies and synthesis strategies directly influence rate capability, capacity, and cycling stability, reinforcing the importance of structural design in achieving high-performance NVP cathodes.

Achieving optimal electrochemical performance of NVP cathodes requires not only understanding how carbon coating thickness and morphology influence Na⁺ transport and electronic conduction but also establishing synthesis strategies capable of precisely controlling these parameters. Carbon coating thickness is primarily governed by the amount and nature of the carbon precursor, the degree of polymerization or chelation in sol-gel networks, and the thermal profile, including temperature, heating rate, and atmospheric composition that regulates carbon evolution and graphitization. At the same time, particle morphology is tuned by precursor solution chemistry, the use of templating or surfactant agents, and the choice of synthesis route, such as hydrothermal, Solvothermal, electrospinning, combustion, or rapid thermal techniques. Collectively, these factors define a practical toolbox that enables researchers to engineer carbon shells, pore structures, and particle architectures in a coordinated manner to optimize electronic connectivity, Na⁺ mobility, and interfacial stability [161–163]. Many studies demonstrate how fine control of these parameters can be achieved in practice. For example, Kate et al. [164] showed that careful thermal management during citric-acid-based sol-gel synthesis, followed by calcination in Ar–H₂ at 800–950 °C, dictates both the porosity and graphitization of the resulting carbon network. Their optimized 900 °C treatment produced a highly graphitized carbon, enhanced mesoporosity, and a slightly expanded lattice, enabling fast Na⁺ diffusion and long-term cycling stability (93 % retention after 1400 cycles at 10C). In the liquid phase domain, Chen et al. [165] demonstrated that reaction temperature and PH during rapid precipitation (70–90 °C) are critical for tuning fluorine incorporation, phase purity, and primary grain formation of Na₃V₂(PO₄)₂O₂F (NVPOF). A subsequent starch-derived carbon coating created a uniform conductive shell in their NVPOF/C-90 (at 90 °C) composite, achieving excellent kinetics and 92 % retention after 200 cycles. Meanwhile, Li et al. [166] employed flash joule heating technology to produce an ultra-thin ~2 nm carbon shell in a single-step synchronous crystallization-carbonization process. The extremely rapid heat delivery enabled uniform graphitic coating formation, enhanced conductivity, and high-rate cycling performance (84 % retention after 3000 cycles at 30C), with reliable operation down to -40 °C, demonstrating that heat-transfer kinetics alone can act as a powerful lever for coating precision.

In parallel, Gu et al. [167] emphasized that hydrothermal parameter tuning (especially PH and temperature) enables precise control over particle morphology, yielding uniform NVP nanorods with shortened Na⁺ pathways when paired with an optimized carbon layer. This architecture delivered a superior rate and cycling performance, underscoring that morphology and coating must be co-designed. Complementary insights come from studies that explicitly target nanoscale control of carbon thickness and surface architecture. Huang et al. [168] developed an ascorbic acid-assisted route in which ascorbic acid simultaneously acts as a reductant, converting (V⁵⁺ to V³⁺), and a carbon source. By fixing the ascorbic acid to vanadium ratio and optimizing calcination (750 °C, 8Hr), they produced mesoporous NVP nanoparticles (100–200 nm, 2–15 nm pores) encapsulated by a continuous, highly graphitized ~7 nm carbon shell with a low sp³/sp² ratio (0.26). This dual control internal mesoporosity and a well-ordered sp²-rich outer shell significantly enhanced ion diffusion and electronic mobility. In combustion synthesis, Vali et al. [169] showed that fuel composition and precursor delivery strongly govern particle size and coating behavior. Their spraying-assisted glycine-nitrate process produced fine, homogeneous NVP particles upon calcination at 900 °C, and incorporation of glucose (25 wt%) yielded an in-situ carbon coating essential for achieving 60mAhg⁻¹ at 20C. This case illustrated how droplet evaporation dynamics and combustion energetics jointly determine

Table 3Effect of carbon sources and synthesis routes on the morphology and electrochemical properties of carbon-modified $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes.

Composition	Preparation Method	Carbon Source	Morphology	Electrochemical Performance (Rate, Capacity [mAhg^{-1}], Cycles, Retention [%])	Ref
NVP/C	Hydrothermal	PEG	Porous	5C, 94.3, 400, 93.3 %	[171]
N-HSDC/NVP-HMs	Solvothermal	Ethylenediamine (EN) + Ethylene Glycol (EG)	Microspheres	10C, 93, 1000, 72.9 %	[154]
NVP/C	Solvothermal	polyethylene glycol (PEG) + Cetyltrimethylammonium bromide (CTAB)	Nanoflowers	1C, 115.2200, 87.7 %	[172]
NVP/C	Hydrothermal	Hydrogel	Nanoflakes	20C, 109.510000, 79.1 %	[173]
NVP/C	Pyrolysis	Ethylene Glycol	Agglomeration-Resistant-2D Nanoflakes	100C, 84.1, 50000, 78.5 %	[174]
NVP/C	Electrospinning	Polymer Precursor	Uniform-1D Nanofibers	0.05C, 114.0, 100, 97 %	[158]
NVP/RGO-CNTs	Freeze-Drying	RGO + CNTs	3DHybrid Network	1C, 105, 500, 98 %	[175]
NVP@C-RGO	Spray-Drying	RGO + Amorphous Carbon	Microspheres	10C, 92.6100, 95.5 %	[124]
NVP/C	Electrospinning	Polymer Precursor	1D Nanofibers	0.1C, 103, -, -	[176]
NVP/MWCNTs	Sol-Gel	Multi-walled Carbon Nanotubes (MWCNTs)	Porous Microsphere Network	1C, 90, 400, 90 %	[177]
NVP/C	Spray-Drying + Carbothermal	CNTs + Amorphous Carbon	Microspheres	20C, 76.9150, 84.3 %	[178]
NVP@NSC	Facile Solid-State	N/S Dual-Doped Carbon	Core-Shell	50C, 105.0, 5000, 82.1 %	[179]

morphological and coating uniformity. A more sophisticated multi-step strategy was developed by Das et al. [170] who synthesized ~40 nm NVP nanoparticles via microwave-assisted hydrothermal methods and used PEG-400 to form a conformal carbon shell morphology (NVP/C). To further increase electronic percolation without thickening the coating, they embedded the core-shell particles into a reduced graphene oxide network, producing the hierarchical NVP/C@rGO composite. This layered design, combining size-controlled cores, uniform PEG-derived shells, and a 3D rGO matrix, achieved exceptional rate performance and cycling stability.

These various case studies collectively provide evidence that the carbon coating thickness and morphology in NVP cathodes require very precise engineering, and this engineering is influenced by the selection of precursors and their concentrations, the behavior of polymerization or complexation, the thermal profile (temperature, ramp rate, and atmosphere), reaction temperature, and PH. The ability to control these synthesis parameters can lead to ultimate and rational control over graphitization, coating conformality, pore structure, and particle morphology. All these aspects are heeded while tuning the electronic conductivity, Na^+ transport kinetics, structural robustness, and long-

term interfacial stability in carbon-modified NVP systems.

5. Electrolyte compatibility and interfacial behavior with carbon-modified NVP cathodes

5.1. Electrolytes compatibility with carbon-modified NVP cathode

The interplay between electrolyte formulation and carbon modification plays a critical role in optimizing the electrochemical performance of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ -based cathodes for sodium-ion batteries. Due to the intrinsically low electronic conductivity of NVP, carbon modification strategies are widely employed to enhance electronic pathways and surface interactions. However, their effectiveness is highly dependent on the electrolyte environment, which governs the formation and stability of the solid electrolyte interphase, ion transport kinetics, and interfacial resistance [180–182]. This chapter reviews the compatibility of various electrolyte systems, organic, ionic liquid, aqueous, gel polymer, and solid-state, with carbon-modified NVP cathodes and gives a summary of all in a table (Table 4).

Table 4

Electrolyte types and electrochemical performance of carbon modified NVP-based cathodes.

Cathode Composition	Electrolyte Type	Electrolyte Composition	Rate Performance	Cycling Stability	Ref
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Organic Liquid	1 M NaPF ₆ in EC/PC (1:1 w/w)	82 % capacity retention at 5C	89.5 % capacity retention after 1000 cycles	[199]
$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{C}$	Organic Liquid	1 M NaClO ₄ in EC/DMC/EMC (1:1:1)	95 mAhg ⁻¹ at 10C	91.9 % capacity retention after 500 cycles	[200]
$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{rGO}/\text{CNT}$	Organic Liquid	1 M NaPF ₆ in diglyme	121.7 mAhg ⁻¹ at 0.5C	90.4 % capacity retention after 500 cycles at 1C	[201]
$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{C}/\text{CNT}$	Organic Liquid + Additive	1 M NaClO ₄ in EC/PC with 5 wt% FEC	113.0 mAhg ⁻¹ at 1C	98.2 % after 300 cycles at 1C	[202]
$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{CQD}$	Organic Liquid + Additive	1 M NaClO ₄ in PC with 5 wt% FEC	126.6 mAhg ⁻¹ at 0.2C	90.2 % capacity retention after 6000 cycles at 30C	[96]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{CNT}$	Organic Liquid + Additive	1 M NaClO ₄ in EC/DMC (1:1 v/v) with 5 wt% FEC	103.2 mAhg ⁻¹ at 0.2C	92.6 % capacity retention after 150 cycles at 10C	[178]
$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{C}$	Ionic Liquid	1 M Na[FSA] in [C ₆ C-pyrrr][FSA]	121.0 mAhg ⁻¹	91.6 % capacity retention after 500 cycles	[203]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Hybrid Ionic Liquid	0.5 M NaTFSI in PC + 10 wt% [C ₆ Pyr][PF ₆]	100.0 mAhg ⁻¹	67.0 % capacity retention; 99.05 % Coulombic efficiency	[204]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Hybrid Ionic Liquid	1 M NaFSI in EC/PC + [Campyr][TFSI]	115.0 mAhg ⁻¹ at 0.2C	95.0 % capacity retention after 100 cycles	[45]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Aqueous Electrolyte	1 M Na ₂ SO ₄	209.0 F g ⁻¹ at 8.5C (1 A g ⁻¹)	80.0 % capacity retention at 8.5C	[205]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Gel Polymer Electrolyte	MATEPP:MMA:TFMA (2:1:1) + 90 wt% liquid electrolyte	117.8 mAhg ⁻¹ at 0.1C	81.8 % capacity retention after 4500 cycles at 5C	[206]
$\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	Solid-State Electrolyte	Na _{3.16} Zr _{1.84} Y _{0.16} Si ₂ P _{0.12} (NASICON-type)	106.6 mAhg ⁻¹ at C/10, 64.5 mAhg ⁻¹ at 5C	78.3 % capacity retention after 1100 cycles at 2C	[207]

5.1.1. Organic liquid electrolytes

Organic liquid electrolytes, particularly carbonates and ether-based systems, are among the most widely investigated for sodium-ion batteries due to their high ionic conductivity and tunable electrochemical properties. Their compatibility with carbon-modified $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes significantly influences cycling stability, rate performance, and interfacial kinetics. Carbon coatings and carbon nanostructures on NVP particles improve electrolyte wettability, facilitate uniform solid electrolyte interphase formation, and enhance Na^+ diffusion, collectively promoting long-term durability [180,183].

Within carbonate-based systems, common formulations include 1 M NaClO_4 or NaPF_6 in mixtures such as propylene carbonate (PC), ethylene carbonate (EC) /diethyl carbonate (DEC), or EC/ethyl methyl carbonate (EMC), often supplemented with additives like fluoroethylene carbonate (FEC) to improve SEI stability. Building on this principle, Qin et al. [184] demonstrated that embedding $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ nanoparticles in a 3D carbon nanotube network (NVPF@C/CNTs) significantly enhances compatibility with a conventional carbonate electrolyte (1 M NaClO_4 in PC with 5 % FEC). The amorphous carbon coating combined with the conductive CNT network promotes rapid electron transport, buffers volume changes during cycling, and supports a stable SEI. As a result, the cathode delivers a high reversible capacity of 107 mAhg^{-1} over 200 cycles at 0.2C and maintains 68 mAhg^{-1} at 10C (Fig. 12a, b), illustrating the synergistic role of carbon modification and carbonate electrolytes in stabilizing the cathode-electrolyte interface.

Expanding upon electrolyte engineering for enhanced stability and safety, Liu et al. [185] investigated a nonflammable triethyl phosphate (TEP)-based electrolyte (0.9 M NaClO_4 with 5 % FEC) with a carbon-coated NVP cathode. The TEP electrolyte, while inherently safer than traditional carbonates, relies on FEC to form a robust SEI. The system exhibited excellent interfacial compatibility, enabling high-rate capability (73.1 mAhg^{-1} at 30C) and remarkable long-term cyclability with

79.1 % capacity retention after 10,000 cycles. A symmetric NVP/NVP full cell further confirmed stable operation, maintaining 88.9 % capacity over 500 cycles at 2C. These results highlight that careful selection of non-flammable electrolytes and SEI-forming additives can complement carbon modification to achieve both high safety and electrochemical durability.

Complementing these carbonate-based strategies, ether-based electrolytes provide an alternative pathway to enhance interfacial properties with carbon-modified NVP cathodes. Glyme-based solvents, such as diglyme (DGM), combined with sodium salts like NaCF_3SO_3 , offer superior Na^+ solvation and fast interfacial kinetics, though their oxidative stability is limited ($<4.0 \text{ V}$ vs. Na/Na^+) [186]. Shi et al. [187] addressed this limitation by introducing vinylene carbonate (VC) as a cosolvent in a NaCF_3SO_3 -DGM (Sodium trifluoromethanesulfonate dissolved in diglyme) electrolyte, extending the oxidative stability window to 4.15 V and enabling compatibility with high-voltage NVP@C cathodes. The co-oxidation of VC and DGM led to the formation of a uniform, ionically conductive CEI, suppressing electrolyte decomposition and stabilizing long-term cycling. HOMO/LUMO energy-level analysis confirmed the electronic compatibility between the solvents and the additive, with the reduced LUMO of VC ensuring preferential SEI stabilization at the anode and suppressing unwanted side reactions (Fig. 12c). The optimized system achieved 87 % capacity retention over 1000 cycles in half cells, while full cells paired with FeS@C anodes delivered 108.4 Whkg^{-1} with 67 % retention. This work demonstrates that careful solvent engineering and additive selection in ether-based systems can provide a stable interface and complement carbon modifications to achieve durable, high-performance sodium-ion batteries.

Taken together, these studies illustrate a progressive and complementary approach to organic liquid electrolytes: conventional carbonate systems deliver stable cycling and high-rate performance, non-flammable TEP-based electrolytes enhance safety, ionic liquid

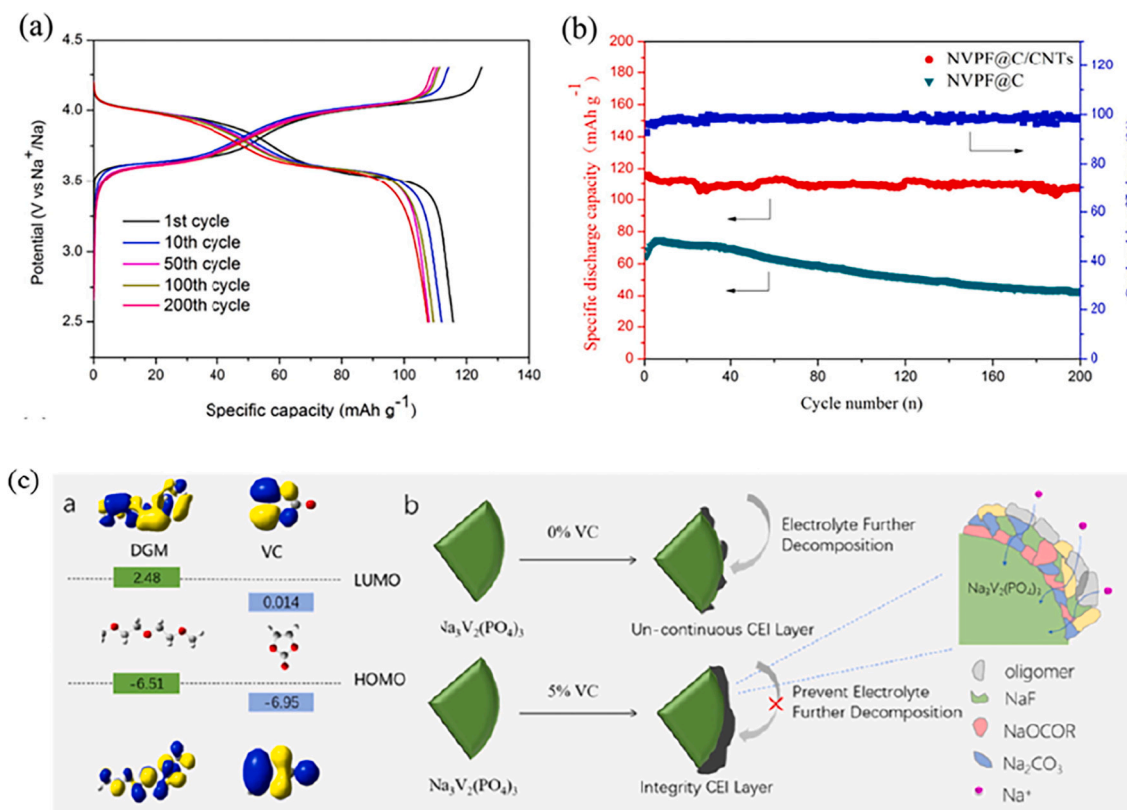


Fig. 12. (a) Galvanostatic charge-discharge curves of NVPF@C/CNTs (2.5–4.3 V) over different cycles; (b) Cycling performance and Coulombic efficiency of NVPF@C/CNTs and NVPF@C at 0.2C. Reproduced with permission from [184] Copyright 2022 Elsevier. (c) HOMO-LUMO levels and molecular structures of DGM and VC, illustrating VC's surface protection role on $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ @C. Reproduced with permission from [187] Copyright 2020 Elsevier.

additives optimize interfacial kinetics, and ether-based co-solvent systems extend oxidative stability while maintaining robust CEI. The integration of carbon modification with tailored electrolyte design is therefore central to achieving long-life, high-efficiency sodium-ion batteries.

5.1.2. Ionic liquid electrolytes

Ionic liquid (IL)-based electrolytes have emerged as a promising

strategy for enhancing the interfacial stability, thermal safety, and electrochemical performance of carbon-modified $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes. ILs are intrinsically nonflammable, thermally robust, and exhibit wide electrochemical windows, making them particularly suitable for high-voltage sodium-ion batteries. When paired with carbon-modified NVP, ILs facilitate the formation of thin, uniform, and ionically conductive cathode-electrolyte interphases, which minimize polarization and improve long-term cycling [188].

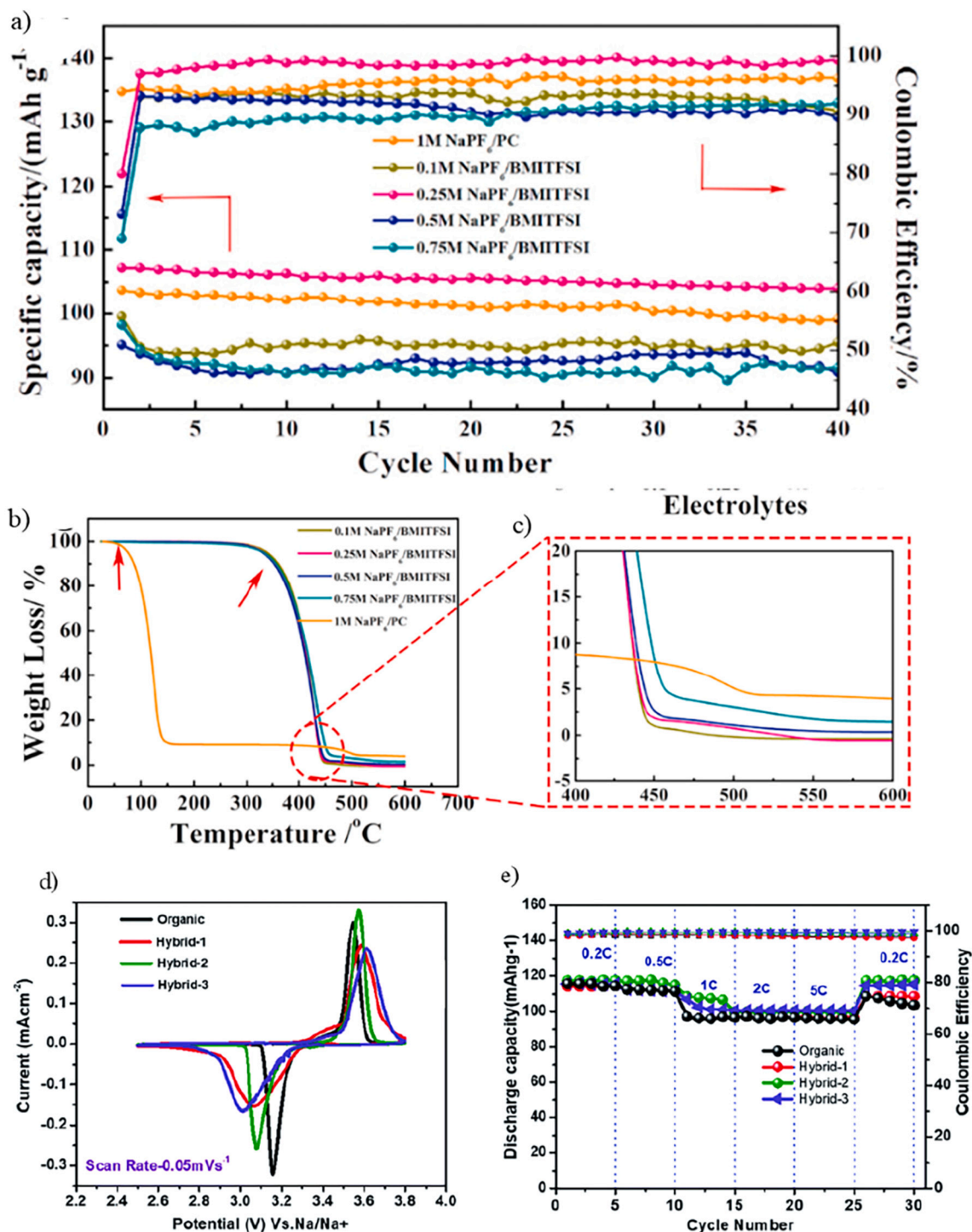


Fig. 13. (a) Cycling performance and coulombic efficiency of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cells using electrolytes with varying NaPF_6 concentrations in BMITFSI/PC at 0.1C. (b, c) Thermogravimetric analysis (TGA) curves of 1 M NaPF_6/PC and IL-based electrolytes with different salt concentrations over the full range. Reproduced with permission from [190] Copyright 2018 Elsevier. (d) Cyclic voltammetry of NVP@C at a scan rate of 0.05 mV s^{-1} . (e) Rate performance of NVP@C at different C-rates. Reproduced with permission from [45] Copyright 2018 Royal Society of Chemistry.

Manohar et al. [189] demonstrated that an IL electrolyte (1 M NaFSI in $C_3\text{mpyrFSI}$, comprising sodium bis(fluorsulfonyl)imide dissolved in *N*-propyl-*N*-methyl pyrrolidinium bis(fluorsulfonyl)imide) paired with NVP@C provides exceptional long-term cycling stability and high energy density. The system maintained 89 % capacity retention after 5000 cycles at an ultra-high rate of 10C. In full-cell configurations with a hard carbon anode, it achieved an energy density of 368 Wh kg^{-1} and 75 % capacity retention over 100 cycles. The excellent performance was attributed to the formation of a stable and uniform passivation layer on both the NVP@C cathode and hard carbon anode, effectively controlling SEI formation and protecting the carbon coating. This study provides definitive evidence that pure IL electrolytes are highly compatible with carbon-modified NVP, enabling ultra-long cycle life and high energy density.

Building upon these findings, Manohar et al. [45] further explored a hybrid IL electrolyte, combining 1 M NaFSI in carbonate solvents with 50 vol% $C_3\text{mpyrTFSI}$ (*N*-propyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide), paired with a carbon-coated NVP cathode. This hybrid system addressed the limitations of conventional organic electrolytes, where SEI layers were thicker and less uniform, leading to reduced long-term stability. The optimized hybrid electrolyte enabled a high discharge capacity of 115 mAh g^{-1} at 0.2C and 95 % capacity retention over 100 cycles (Fig. 13d, e). Advanced characterization revealed that the IL component promoted a thinner, more uniform, and highly Na^+ permeable SEI, effectively stabilizing the carbon coating and suppressing electrolyte decomposition. This demonstrates the synergistic effect of combining carbon modification with IL additives to enhance interfacial kinetics and durability.

To demonstrate the practical advantages of ILs in mitigating the flammability and thermal degradation issues associated with traditional electrolytes, Wu et al. [190] investigated the application of a novel IL electrolyte, $\text{NaPF}_6/\text{BMITFSI}$ (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide), for sodium-ion batteries employing $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes. Their study was specifically aimed at enhancing both the safety and electrochemical behavior of the system. This IL-based electrolyte not only addressed the fire hazard and thermal instability characteristics of conventional organic solvents but also supported stable interfacial chemistry, enabling extended cycling life. As shown in Fig. 13b and c, thermogravimetric analysis confirmed the IL's remarkable thermal stability, maintaining structural integrity up to 350°C , vastly outperforming NaPF_6/PC , which begins to decompose near 60°C . Furthermore, its self-extinguishing nature (25 s/g vs. 210 s/g for NaPF_6/PC) validated its superior flame-retardant characteristics. Electrochemically, the optimized 0.25 M $\text{NaPF}_6/\text{BMITFSI}$ formulation delivered an initial capacity of 107.2 mAh g^{-1} and retained 104 mAh g^{-1} after 40 cycles, as shown in Fig. 13a. This study underscores the dual benefits of IL electrolytes in advancing SIB technologies, offering high thermal safety and electrochemical reliability, and thus laying a foundation for the development of safer, high-performance IL systems.

This narrative demonstrates that IL electrolytes, when thoughtfully combined with carbon modification, are essential for achieving stable interfaces, efficient Na^+ transport, and exceptional cycling performance, paving the way for practical, high-performance sodium-ion batteries.

5.1.3. Aqueous electrolytes

Aqueous electrolytes offer a safe, cost-effective alternative to organic systems due to their non-flammability, low toxicity, high ionic conductivity, and simplified cell design. However, their narrow electrochemical stability window ($\sim 1.23 \text{ V}$) has historically limited compatibility with high-voltage cathodes such as $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, prompting the development of advanced formulations to extend this window and enhance electrolyte interfacial stability [191]. Water-in-salt electrolytes (WiSEs), including highly concentrated NaTFSI and NaOTf solutions, suppress free water molecules, thereby expanding the electrochemical window beyond 2.5 V and enabling more stable operation of high-voltage cathodes, including carbon-modified NVP and its

fluorinated derivatives.

Building upon this foundation, Song et al. [192] demonstrated that a carbon-coated NVP composite ($\sim 5 \text{ wt\%}$ carbon) exhibited enhanced electrolyte compatibility in aqueous sulfate electrolytes (Li_2SO_4 , Na_2SO_4 , K_2SO_4). The carbon layer facilitated electronic conductivity and contributed to surface capacitance, improving charge transfer at the carbon–electrolyte interface. Optimal compatibility was achieved with 1 M Na_2SO_4 , where the hydrated Na^+ radius ($3.58 \text{ \AA}$) matched the NASICON framework, resulting in high capacitance (209 F g^{-1} at 8.5C) and Na^+ diffusion coefficients on the order of $10^{-10} \text{ cm}^2 \text{ s}^{-1}$. Despite these advantages, cycling stability was limited, with capacitance retention dropping to 32 % after 30 cycles and Coulombic efficiency of $\sim 80 \%$, due to oxidative dissolution, structural degradation, and parasitic water-splitting reactions at the carbon–electrolyte interface (Fig. 14a, b). These findings highlight that while carbon modification enhances kinetics and interface charge transport, interfacial instability with the aqueous medium remains a major limitation.

Tediashvili et al. [193] further clarified the influence of electrolyte composition and pH on carbon–electrolyte compatibility. NVP@C suffered significant vanadium dissolution in 1 M Na_2SO_4 at neutral (pH ~ 7) and acidic (pH 4) conditions, with V^{5+} predominating at near-neutral pH and V^{4+} appearing under acidic conditions. This interfacial degradation led to rapid capacity fade, structural breakdown, and loss of electrochemical activity, as confirmed by cyclic voltammetry, XRD, redox titration, and RRDE analyses. In contrast, the fluoride-substituted analogue $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ maintained structural integrity and suppressed vanadium leaching, demonstrating how cathode surface chemistry interacts with the aqueous electrolyte to improve stability. These results indicate that while carbon coatings enhance electronic conductivity and charge transfer, the nature of the electrolyte and pH critically governs interfacial compatibility and long-term stability.

Collectively, these studies emphasize that achieving stable aqueous performance of carbon-modified NVP cathodes requires strategies that optimize both the electrode surface and electrolyte: neutral or buffered electrolytes, pH control, highly concentrated water-in-salt formulations, and cathode modifications such as fluoride substitution (Fig. 14c–f). When combined, these approaches enhance interfacial stability, reduce parasitic reactions, and preserve structural integrity, enabling more reliable performance of NASICON-type cathodes in aqueous sodium-ion batteries.

5.1.4. Gel polymer electrolytes

Gel polymer electrolytes (GPEs) represent a promising class of hybrid electrolytes that bridge the gap between liquid and solid-state systems by combining the high ionic conductivity of liquid electrolytes with the mechanical stability and safety of polymer matrices. This hybrid nature allows GPEs to overcome challenges such as leakage, poor interfacial contact, and safety concerns that limit conventional liquid systems. Their semi-solid framework ensures both structural integrity and intimate electrode–electrolyte contact, making them particularly suitable for use with NASICON-type cathode materials such as carbon-modified $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ [194].

Building on this foundation, Gao et al. [195] developed a cross-linked poly (methyl methacrylate) (PMMA)-based GPE via in situ polymerization in a NaClO_4 -containing carbonate solvent. When paired with a carbon-coated NVP cathode (3.4 wt% carbon), the system achieved a high reversible capacity of 111.5 mAh g^{-1} at 0.2C, excellent rate performance (60.8 mAh g^{-1} at 10C), and nearly 100 % capacity retention after 100 cycles. Electrochemical impedance spectroscopy (EIS) revealed minimal increases in both the solid–electrolyte interphase and charge-transfer resistance during cycling, confirming strong electrochemical compatibility between the carbon-coated NVP surface and the GPE matrix. This stability was maintained even at elevated temperatures (60°C), underscoring the thermal and interfacial robustness of the system. The synergistic interplay between the conductive carbon layer and the stable polymer–electrolyte network enables efficient Na^+ /

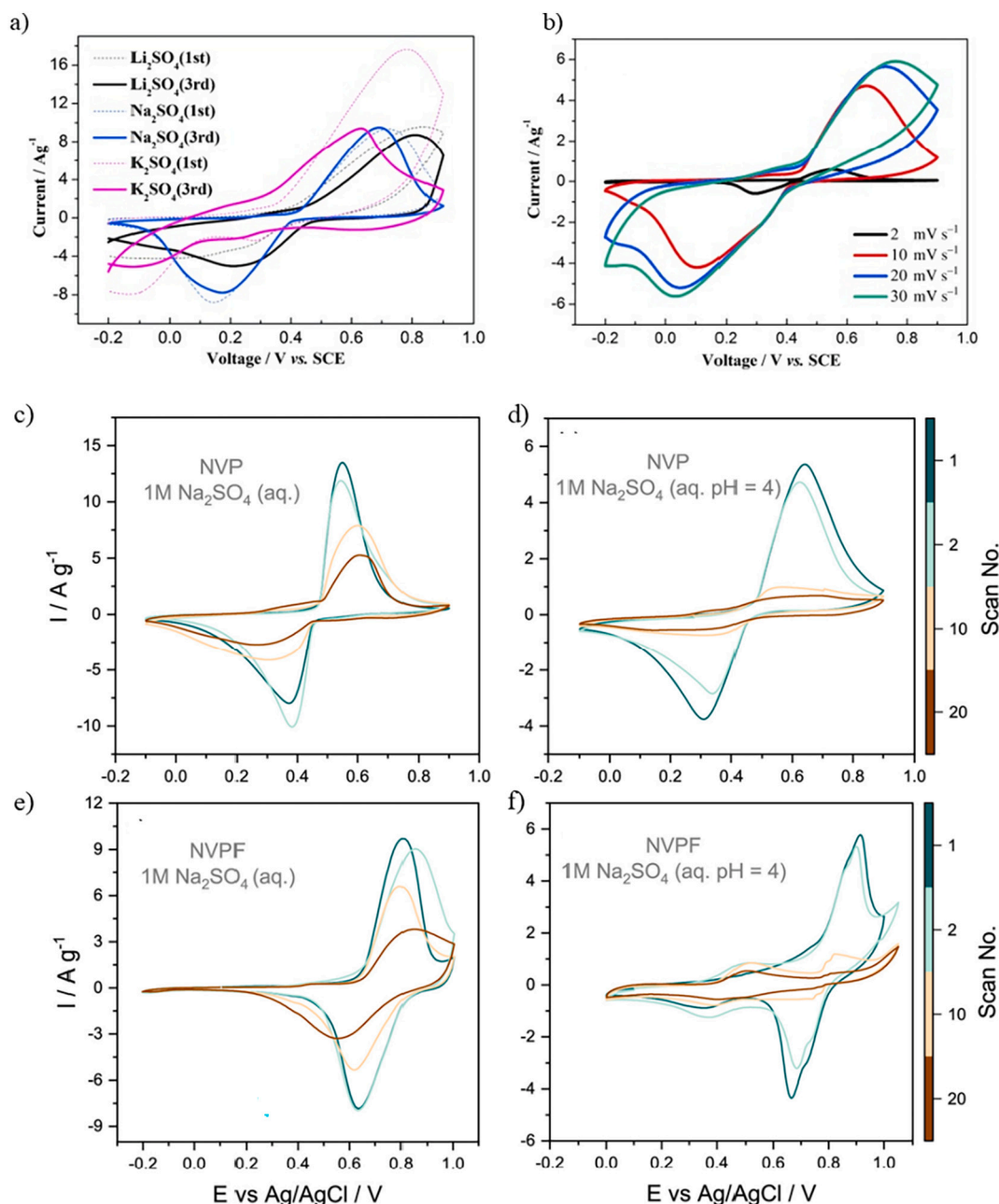


Fig. 14. (a) First and third cyclic voltammetry (CV) curves of Na₃V₂(PO₄)₃ (NVP) in 1 M Li₂SO₄, Na₂SO₄, and K₂SO₄ electrolytes, scanned between 0.2 and 0.9 V vs. SCE at 5 mV s⁻¹. (b) Successive CV curves of NVP in 1 M Na₂SO₄ at varying scan rates (2, 10, 20, and 30 mV s⁻¹). Reproduced with permission from [192] Copyright 2014 Wiley-VCH. (c–f) CV curves of Na₃V₂(PO₄)₃ and Na₃V₂(PO₄)₂F₃ electrodes recorded at 5 mV s⁻¹ over the 1st, 2nd, 10th, and 20th cycles. (c, e) show measurements in unbuffered 1 M Na₂SO₄ electrolyte, while (d, f) present results in citrate-buffered 1 M Na₂SO₄ (pH = 4). (c, d) correspond to Na₃V₂(PO₄)₃, and (e, f) correspond to Na₃V₂(PO₄)₂F₃. Reproduced with permission from [193] Copyright 2023 Electrochemical Society.

electron transport and suppresses degradation reactions at the electrode-electrolyte interface.

Further advancing the design, Zhang et al. [196] introduced a polydopamine-modified polyurethane GPE (PDA@PU-GPE) that exemplifies excellent interfacial compatibility with carbon-modified NVP cathodes. The PDA coating enhances chemical stability and provides strong interfacial adhesion, suppressing electrolyte decomposition and minimizing parasitic side reactions. As evidenced by EIS analysis, the NVP/PDA@PU-GPE cell maintained an almost constant interfacial resistance (~300 Ω) even after 1000 cycles, whereas unmodified PU-based GPEs exhibited significant resistance growth. The system also demonstrated enhanced Na⁺ diffusion kinetics and reduced polarization, resulting in a high-capacity retention of 84 % after 1000 cycles at

2C (Fig. 15). This superior performance reflects the formation of a durable and conductive interphase that effectively stabilizes the carbon–electrolyte interface during prolonged cycling.

In summary, these studies underscore the crucial role of interfacial compatibility between carbon-modified NVP cathodes and GPE systems in achieving stable and efficient sodium-ion battery operation. The carbon coating not only enhances electronic conductivity but also provides a favorable surface for polymer-electrolyte adhesion, mitigating issues such as vanadium dissolution, dendrite formation, and SEI instability. Meanwhile, the tailored polymer matrices, whether PMMA-based or PDA-modified PU, enable high ionic mobility, thermal stability, and interfacial integrity. As a result, the synergistic combination of carbon modification and advanced GPE design offers a powerful

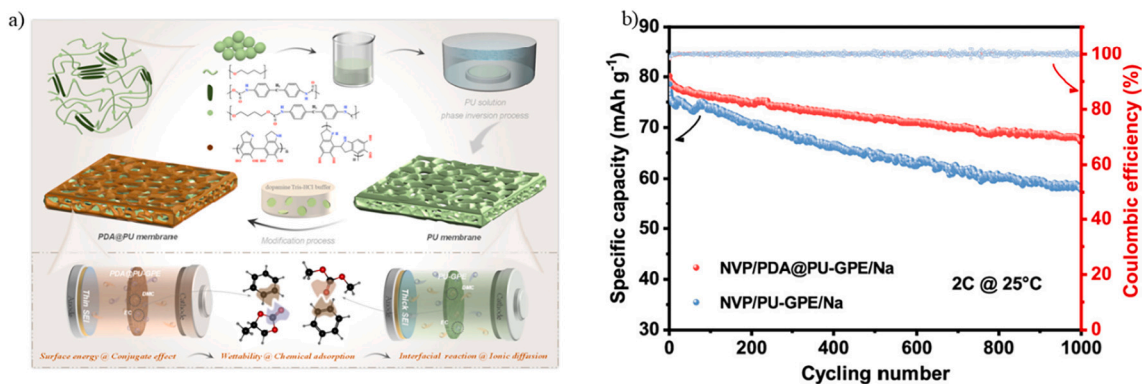


Fig. 15. (a) Preparation schematic of PU and PDA@PU gel polymer membranes. (b) Cycling performance of NVP/PU-GPE/Na and NVP/PDA@PU-GPE/Na cells at 2C, showing improved stability with PDA modification. (Reproduced with permission from [196] Copyright 2024 American Chemical Society.)

pathway toward safe, high-performance, and durable sodium-ion batteries. Future progress in polymer chemistry, interphase engineering, and electrolyte formulation will be essential to further enhance these systems and translate laboratory success into practical, scalable energy storage technologies.

5.1.5. Solid-state electrolytes

Solid-state electrolytes (SSEs) have emerged as a transformative class of materials for safe, high-energy density sodium-ion batteries due to their intrinsic non-flammability, superior mechanical strength, and ability to suppress dendrite formation. Among SSEs, NASICON-type ceramics such as $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ (sodium zirconium silicon phosphate) are particularly promising for integration with carbon-modified $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes, offering high ionic conductivity and chemical stability. However, pure ceramic electrolytes often exhibit poor solid-solid contact with electrode surfaces, resulting in high interfacial

resistance and rapid capacity fade [197].

Cheng et al. [198] demonstrated that these limitations can be effectively addressed by hybridizing NASICON ceramics with a flexible polymer, creating a hybrid solid electrolyte (HSE) composed of PVDF-HFP polymer and $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ceramic. The study revealed that while the pure NASICON ceramic exhibited a high interfacial resistance and rapid capacity degradation, incorporation of the polymer phase generated a more adaptive, continuous interface and reduced resistance. The polymer matrix provides a “soft contact” with the cathode, accommodating volume changes during cycling and maintaining intimate adhesion with NVP/C particles. Concurrently, the carbon coating on NVP forms a porous, conductive framework that enhances electron transport and expands electrolyte contact area, facilitating rapid Na^+ transfer across the interface. As a result, the HSE-based full cell achieved a stable reversible capacity of 98 mAhg^{-1} and retained 85 % capacity after 175 cycles at 0.5C (Fig. 16).

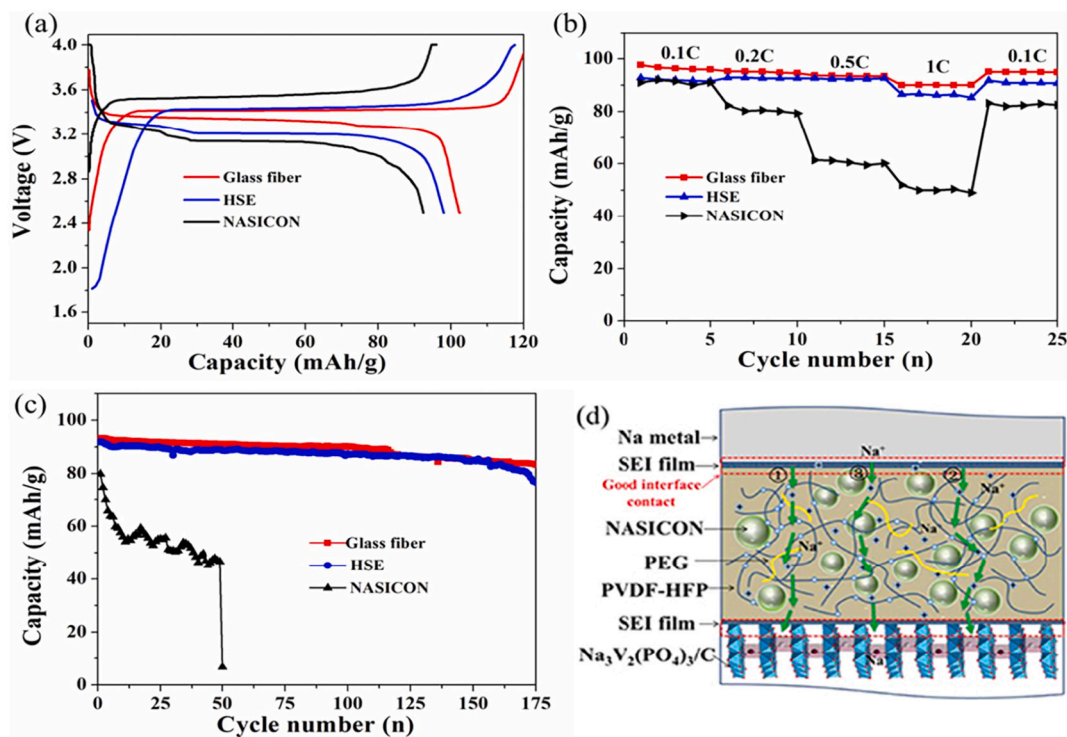


Fig. 16. (a–c) Electrochemical performance of SIBs using different electrolytes: charge-discharge profiles at 0.2C, rate capabilities, and cycling stability at 0.5C. (d) Schematic illustration of Na^+ transport pathways in NASICON ceramic, PVDF-HFP polymer, and hybrid solid electrolytes. Reproduced with permission from [198] Copyright 2020 IOP.

This work demonstrates that hybrid polymer-ceramic electrolytes, when combined with carbon-modified NVP cathodes, can effectively overcome interfacial polarization and mechanical mismatch. Importantly, it highlights that the conductive and protective properties of carbon coatings are integral to achieving long-term cycling stability, offering a viable pathway for high-performance, all-solid-state sodium-ion batteries.

5.2. Interfacial behavior and stability of carbon-modified NVP cathode in contact with electrolyte

The cathode-electrolyte interfacial area of carbon-modified $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes plays a decisive role in determining electrochemical stability, Na^+ transport kinetics, and overall sodium-ion battery performance. Beyond improving bulk conductivity, carbon modification critically influences the physicochemical processes occurring at this interface [208]. The interfacial stability and performance of carbon-electrolyte systems are strongly dependent on the surface chemistry, electronic structure, and morphology of the carbon coating. Functionalized carbon layers, particularly those doped with Heteroatoms such as nitrogen, sulfur, or fluorine, enhance surface energy and electrolyte wettability, enabling homogenous ion transport and stable electrode-electrolyte contact. Conductive carbon frameworks also help to homogenize charge distribution, minimize local overpotentials, and suppress parasitic side reactions. Operando XRD analysis (Fig. 17c) has confirmed the structural robustness of NVP/C@CNT cathodes during cycling, illustrating the crucial role of the conductive carbon network in preserving interfacial integrity and ensuring sustained electrochemical activity [209].

Supporting this, Zhang et al. [210] demonstrated the synergistic impact of integrating carbon nanotubes and fluorine doping in $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ cathodes. CNT incorporation enhanced both electronic conductivity and Na^+ diffusion, leading to the formation of a thinner, denser, and more stable cathode-electrolyte interphase. TOF-SIMS analysis (Fig. 17a) revealed a higher NaF_2^- fragment density and reduced CEI thickness for NVPF@3 %CNT compared to pristine NVPF. In situ XRD (Fig. 17b) further confirmed the framework's ability to buffer volume variation (2.31 %) and sustain reversible lattice shifts, demonstrating mechanical stability during Na^+ insertion and extraction. Although fluorine doping supports high-voltage operation and structural resilience, it can accelerate electrolyte decomposition; however, the CNT conductive network mitigated this by stabilizing the CEI and

maintaining low interfacial impedance, yielding 94 % capacity retention after 200 cycles at -10°C . These findings highlight that combining carbon architecture with fluoride doping can effectively resolve both kinetic and interfacial challenges in high-voltage NVPF systems.

While the formation of the solid electrolyte interface is typically associated with anodes, high-voltage cathodes such as NVP and NVPF also undergo electrolyte decomposition and CEI evolution, especially inorganic or ionic liquid electrolytes. Carbon coating acts as a dual-function barrier, physically limiting direct contact between active material and electrolyte, and also chemically buffering reactive species. Uniform and conformal carbon coatings suppress parasitic oxidation, stabilize interfacial structures, and extend cycling life. Hu et al. [211] designed a hierarchical microsphere NVPF@CN cathode and employed a dual-anion ether-based electrolyte ($\text{NaPF}_6 + \text{NaBF}_4$ in diglyme) to regulate the interfacial chemistry. The tailored electrolyte composition facilitated the formation of an inorganic-rich CEI containing NaF and NaB_xO_x Species, which mitigated electrolyte decomposition at voltages up to 4.6 V. This stable CEI promoted Na^+ transfer, minimized electronic leakage, and yielded exceptional cycling stability (up to 2000 cycles at 10°C) alongside superior low-temperature performance.

The chemical structure and porosity of carbon coatings also play pivotal roles in defining interfacial reactions. Oxygen-containing functional groups (hydroxyl, carbonyl, or carboxyl) can influence ion diffusion and CEI composition through redox or adsorption interactions with electrolyte components, while hierarchical porosity enhances Na^+ transport and electrolyte infiltration during high-rate operation. However, excessive surface area can accelerate electrolyte degradation, emphasizing the necessity of optimizing carbon structure and surface chemistry [212,213].

The electrolyte environment itself has a direct and significant impact on interfacial behavior and side-reaction mechanisms [214]. In aqueous electrolytes, the high polarity and reactivity of water molecules can lead to vanadium dissolution, oxygen evolution, and degradation of the phosphate framework in NVP, particularly under high operating voltage. Hydrolysis induced by water promotes the leaching of vanadium species and destabilizes lattice oxygen. Recent studies have demonstrated that adding Zn^{2+} or phosphate additives to aqueous systems can create protective inorganic-rich CEI layers (e.g., Zn-P-O or $\text{Na}_x\text{PO}_y\text{F}_z$ phases). These layers effectively passivate reactive sites and reduce structural degradation. Acting as a chemical shield, these interfacial layers prevent direct contact between water and carbon-NVP surface while preserving ionic conductivity [215].

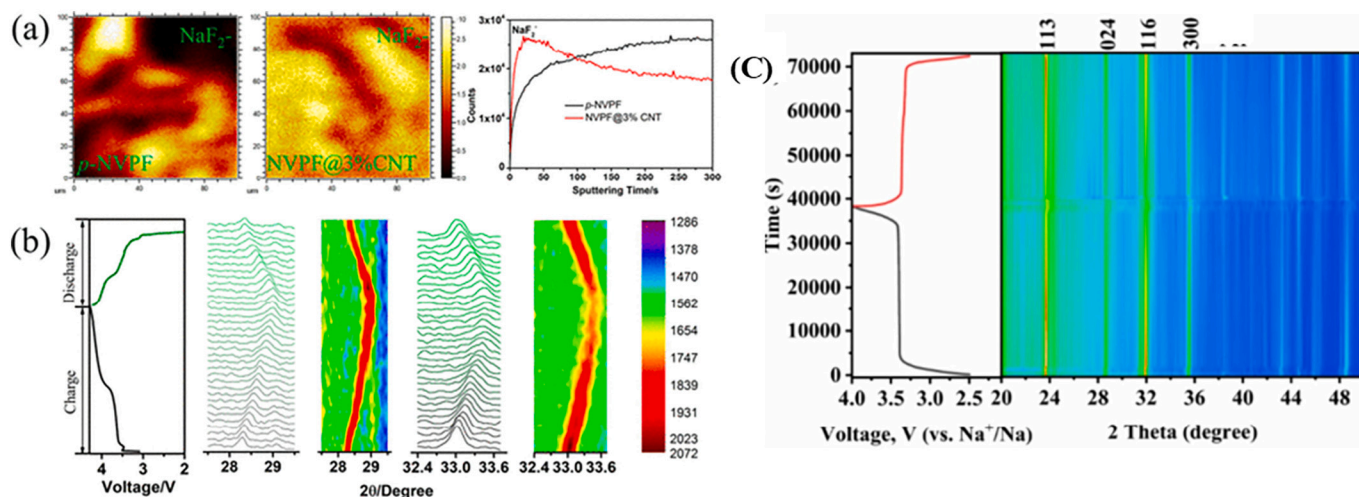


Fig. 17. (a) TOF-SIMS NaF_2^- (sodium fluoride species) mapping and depth profiles of pristine NVPF and NVPF modified with @3 % CNT cathodes. (b) In-situ XRD of NVPF@3 % CNT during first-cycle (de)sodiation at 0.2C with zoomed regions at $27.5-29.5^\circ$ and $32.4-33.7^\circ$, alongside the corresponding voltage curve. Reproduced with permission from [210] copyright 2023 American Chemical Society. (c) operando XRD result for NVP/C@CNT. Reproduced with permission from [209] copyright 2024 Chemical Engineering Journal.

In GPE, semi-solid polymer matrices effectively combine high ionic conductivity with mechanical stability, enhancing electrolyte retention and interfacial adhesion. However, at high voltages, oxidation of the polymer or solvent can occur, leading to interfacial degradation. Research has shown that PVDF-HFP- NaClO_4 -based GPEs can mitigate these reactions by maintaining stable Na^+ transport pathways and reducing polymer phase decomposition. Additionally, the carbon coating on NVP improves interfacial compatibility by protecting active sites from oxidative damage and stabilizing the solid electrolyte interface. Consequently, carbon-modified NVP cathodes, when paired with optimized GPEs, exhibit reduced interfacial impedance growth and enhanced cycling stability, even under thermal or high-rate stress [216].

For solid-state electrolytes, the elimination of liquid components resolves dissolution-related issues but introduces mechanical and chemical incompatibility at the rigid electrode-electrolyte interface. This mechanical mismatch can lead to interfacial strain, microcracks, and localized Na^+ transport barriers, ultimately increasing interfacial resistance and accelerating degradation. Recent advancements in ferroelectric-engineered and composite SSEs have addressed these challenges by introducing flexible interfacial architectures and conductive carbon frameworks. These engineered interlayers can alleviate mechanical stress, improve ionic percolation, and prevent phase separation. Significantly enhancing interfacial kinetics and cycle stability [217].

In summary, diverse electrolyte systems, aqueous, gel-polymer, and solid state, each face distinct interfacial degradation challenges. However, these issues can be effectively addressed through rational carbon engineering techniques such as conformal coating, hetero-atom doping, and conductive networks. Optimizing both carbon surface design and electrolyte formulation is essential for establishing a stable, low-resistance, and self-stabilizing interface between NVP and the electrolyte. This synergistic approach promotes structural integrity, facilitates efficient Na^+ transport, and extends cycle life, ultimately advancing the development of practical, high-energy density and durable sodium-ion batteries.

6. Challenges and future outlook for carbon-modified NVP cathodes and advanced electrolyte integration

Carbon modification has emerged as a highly effective strategy to enhance the electrochemical performance of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes in sodium-ion batteries. Despite its promise, several challenges remain that must be addressed to ensure the commercial viability and long-term stability of this approach.

- i. One major challenge is optimizing the carbon content and structure. While a carefully engineered carbon coating can significantly improve electronic conductivity and facilitate Na^+ ion diffusion, using too much carbon can dilute the active material. This, in turn, lowers specific capacity and energy density. Striking the right balance between carbon content and active material is essential to maintain high electrochemical performance.
- ii. Additionally, the type of carbon used, whether amorphous, graphitic, or nanostructured, like carbon nanotubes or graphene, plays a critical role in determining the electrical and mechanical properties of the cathode. The goal is to develop uniform coatings, highly conductive and lightweight, all while preserving high energy density and cycle stability.
- iii. Scalability and cost-effectiveness of carbon modification techniques present another hurdle. Many advanced methods, such as sol-gel processing, chemical vapor deposition, and hydrothermal treatments, offer excellent performance but are often energy-intensive, time-consuming, and costly. These limitations hinder large-scale manufacturing.

- iv. Besides carbon modification, an electrolyte selection is also essential to achieve optimal performance and stability of carbon-modified $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes. Carbon coatings can modify interfacial properties, affecting electrode interaction with different electrolytes. Though organic electrolytes are common, they can suffer from stability problems, particularly at high voltages. Solid-state and gel polymer electrolytes have safety advantages but are susceptible to inferior interfacial contact and ion conductivity. Ionic liquids, while conductive and stable, are held back by high cost. The electrolyte thus needs to be carefully selected to work in tandem with the carbon coating to enable efficient Na^+ transport, stable interfaces, and prolonged cycle life.

To overcome this, researchers are turning to low-cost, renewable carbon sources such as biomass derivatives (e.g., sucrose, citric acid, cellulose). These sustainable alternatives not only cut costs but also support environmentally friendly manufacturing. Additionally, innovative techniques like microwave-assisted carbonization and rapid pyrolysis show promise for producing high-quality coatings more efficiently and with lower energy demands.

Looking ahead, the next wave of advancements is likely to come from integrated surface engineering approaches. Combining carbon coatings with heteroatom doping (such as nitrogen, fluorine, sulfur, or boron) or metallic dopants (like tin or molybdenum) has demonstrated synergistic effects, including improved Na^+ diffusion, better structural stability, and longer cycle life. Moreover, blending carbon with conductive polymers or oxide additives could further enhance both electrochemical performance and mechanical durability. These multifunctional hybrid materials represent a compelling direction for future NVP cathode development.

From a broader perspective, ensuring long-term safety, sustainability, and cost-efficiency is critical for real-world deployment. This includes improving electrode-electrolyte compatibility, enhancing interfacial stability, and avoiding the use of toxic or scarce materials. Successfully addressing these issues will position carbon-modified NVP cathodes as a scalable, reliable, and eco-friendly solution for sodium-ion battery applications.

7. Conclusion

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes have attracted considerable interest as a promising option for sodium-ion batteries with their stable NASICON framework, high working voltage, and good thermal stability. Their practical application, however, is still limited by intrinsically poor electronic conductivity and interfacial issues, especially when combined with traditional electrolytes. This review thoroughly discussed recent progress in carbon modification approaches and electrolyte engineering to tackle these issues. Carbon-based modifications from in situ coating with organic precursors to incorporation of nanostructured carbons and heteroatom-doped matrices have been shown to bring significant improvement in electrical conductivity, Na^+ ion diffusivity, and cycling stability. Special focus was given to the role of carbon coating thickness and morphology in optimizing electrochemical performance. Meanwhile, the interfacial behavior between carbon-modified NVP cathodes and various electrolyte systems, such as organic, ionic liquid, aqueous, gel polymer, and solid-state electrolytes, was critically compared. The synergistic effect of designed surface modification and electrolyte compatibility was identified as a crucial factor in achieving accelerated ion transport, stable electrode-electrolyte interfaces, and long-term durability.

In spite of significant advances, there are still difficulties in the optimization of carbon content, the minimization of process complexity and cost, and scalability. The combination of carbon modification with heteroatom doping and multifunctional hybrid systems is an exciting frontier. In addition, the innovation of high-performance, low-cost, and

environmentally friendly electrolytes that are compatible with carbon-engineered surfaces will be crucial for the commercialization of NVP-based sodium-ion batteries.

In summary, carbon modification and electrolyte development need to go in parallel to release the full potential of NVP cathodes. Advances in scalable synthesis procedures, further insight into electrode-electrolyte interfacial mechanisms, and the design of integrated cathode-electrolyte architecture are needed for future studies. These will lead the way toward the next generation of safe, sustainable, and high-efficiency sodium-ion energy storage devices.

CRediT authorship contribution statement

Dibora Temesgen Birusew: Writing – original draft, Data curation. **Kabelo Ledwaba:** Writing – review & editing, Supervision, Resources. **Mpfunzeni Raphulu:** Writing – review & editing, Resources. **An Hardy:** Writing – review & editing, Resources. **Nithyadharseni Palaniyandy:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article.

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