Advances in metal phosphides for sodium-ion batteries

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Abstract
Sodium-ion batteries (SIBs) have been extensively studied as the potential alternative to lithium-ion batteries (LIBs) due to the abundant natural reserves and low price of sodium resources. Nevertheless, Na+ ions possess a larger radius than Li+, resulting in slow diffusion dynamics in electrode materials, and thus seeking appropriate anode materials to meet high performance standards has become a trend in the field of SIBs. In this context, owing to the advantages of high theoretical capacity and proper redox potential, metal phosphides (MPs) are considered to be the promising materials to make up for the gap of SIBs anode materials. In this review, the recent development of MPs anode materials for SIBs is reviewed and analyzed comprehensively and deeply, including the synthesis method, advanced modification strategy, electrochemical performance, and Na storage mechanism. In addition, to promote the wide application of the emerging MPs anodes for SIBs, several research emphases in the future are pointed out to overcome challenges toward the commercial application.

KEYWORDS
anode materials, high capacity, metal phosphides, Na storage mechanism, sodium ion batteries

1 | INTRODUCTION

With the continuous consumption of fossil fuels, environmental pollution is becoming more and more serious (e.g., greenhouse effect, ozone layer destruction, acid rain and so on). It is stringent to explore clean and pollution-free renewable energy sources to replace fossil fuels, such as wind, tidal, geothermal, and solar energy. However, these new energy sources heavily rely on the natural conditions, such as sunshine and wind, suffering from regionalism and intermittence, and therefore are hard to be integrated into the electrical grid directly. As such, large-scale energy
storage system (ESS) is highly desirable for load-leveling, that is, storage of energy until needed by the electrical grid. Among all of the ESS technologies, secondary battery technology is the most competitive route for large-scale power storage coming from strengths of adaptability, efficient energy transduction, and easy maintenance. In the past decades, the advantages of high energy density, long service time, and good rate capability make lithium-ion batteries (LIBs) to be the most attractive ESS. Further- more, LIBs have also been commercialized in portable energy solutions, especially in the field of electric vehicles and portable electronic devices, which greatly alleviate our reliance on fossil fuels but increase the demand on lithium resources. However, the low natural reserves and uneven distribution of lithium resources have raised the concerns of short supply of LIBs. Therefore, it is imperative to design a novel battery system possessing the characteristic of low cost, environmentally friendliness, and high natural abundance to replace the LIBs.

Sodium, the sixth most abundant element on the earth (ca. 2.74% in crust), is the second lightest alkali metal element that shares similar physical as well as chemical properties to lithium in many aspects, from which sodium is expected to replace lithium in secondary batteries. Besides, for the application in sodium-ion batteries (SIBs), the electrochemical redox potential of Na is very ideal, that is, -2.71 V versus the standard hydrogen electrode. Also, compared with Li, Na ions show smaller Stroker’s radius owing to their weaker Lewis acidity, which decreases the activation energy of ion diffusion and promotes the ion mobility in the electrolyte. Furthermore, due to the chemical inertness of Na ions toward Al, the Cu current collector used in LIBs can be replaced by Al in SIBs, which greatly reduces the production costs. Based on these outstanding merits, SIBs show strong competitiveness among various secondary batteries, especially as a large-scale ESS. However, Na (1.02 Å) possesses a larger ionic radius than that of Li (0.76 Å), which gives rise to slow migration and thus sluggish reaction kinetics in solid-state electrode for SIBs. Over the past years, the electrochemical performance of SIBs has been greatly improved owing to the extensive efforts devoted into this area. For example, NASICON-type cathode materials with satisfactory performance for SIBs have been developed. But their commercialization is still a long way off as many issues remain, for example, the unsatisfactory performance of the anode materials. Seeking suitable anode materials is critical to the further commercialization of SIBs.

In the past few years, metal phosphides (MPs) have been proved to be ideal anode materials for SIBs (Figure 1). As compared to the other type of anode materials (e.g., carbonaceous materials, alloying materials, transition metal oxides, transition metal chalcogenides, and so on), MPs demonstrate enormous superiorities in terms of their intrinsic properties and electrochemical reaction mechanisms. (i) Theoretically, MPs possess much higher gravimetric and volumetric-specific capacities (e.g., 1132 mA h g⁻¹ and 6650 mA h cm⁻³ for Sn₄P₃, and 1616 mA h g⁻¹ and 6890 mA h cm⁻³ for SnP₃), which is mainly derived from the conversion of large-capacity element P to Na₃P (i.e., MPₓ → 3Na⁺ + 3xe⁻ → xNa₃P + M). Moreover, for those whose metal elements can react with Na, such as Sn₄P₃, SnP, and GeP, Na⁺ will react with both metal and P elements to form NaᵧM and Na₃P phase mixture (i.e., MPₓ → NaᵧM + Na₃P). The extra alloying reaction between the reactive metal and Na⁺ further increases the capacity of electrode. (ii) MPs exhibit higher electrical conductivities (e.g., 30.7 S cm⁻¹ for Sn₄P₃ and 1.0 × 10⁶ S cm⁻¹ for GeP₃). The metal atoms in MPs act as electronic pathways to drastically enhance the electronic conductivity, which leads to higher electrochemical performance of SIBs. Besides, metal particles generated via the reversible or irreversible conversion reaction during the process of sodiation/desodiation can make electrode more conductive and thus promote the Na storage performance. (iii) In SIBs, MPs show appropriate redox potentials (i.e., ~0.4 V, resulted from 3Na⁺ + P + 3e⁻ → Na₃P), which is beneficial to achieve high-energy-density batteries. For example, when using NaₓVₓ(PO₄)₂F₃ (NVPF) as cathode and tin phosphides (SnPₓ) as anode for a full SIB, based on their theoretical capacity and redox potential, it can provide specific energy of ~400 Wh kg⁻¹ theoretically, which is calculated from the total mass of positive and negative electrodes, which is close to that of a commercialized...
LIBs system containing a lithium transition metal oxide cathode and a graphite anode.

All these advantages make MPs prominent anode materials for SIBs. However, MPs also suffer from some problems, such as severe volume expansion and sluggish diffusion kinetics, thus leading to electrode pulverization and rapid capacity decay during cycling. To address these issues, a diversity of impressive modification strategies have been proposed and systematically investigated, including (i) designing ingenious nano-micro structure (e.g., sandwich-like Ni$_2$P nanoarray, 3D hierarchical rose-like Ni$_2$P@rGO, and ultrathin few-layer GeP nanosheets), which possesses plenty of space for volume expansion and increases the contact area between electrolyte and electrode materials to promote the diffusion of Na$^{+}$ and improve the stability of electrodes during the sodiation/desodiation processes; (ii) mixing with conductive carbonaceous materials (e.g., CuP$_2$/C composites, Sn$_4$P$_3$/reduced graphene oxide nanohybrids, and carbon-coated CoP$_3$ nanocomposites) to buffer volume variations and increase electrical conductivity of the electrodes; (iii) doping elements to improve the electrical conductivity of the electrodes (e.g., sulfur-doped CoP). At present, combining multiple strategies to synergistically improve the performance of SIBs, such as nanochain-like structure composed of hollow yolk-shell Sn$_4$P$_3$@C nanospheres, P doped onion-like carbon layers coated FeP, core-shell Ni$_2$P@carbon, flower-like Fe-doped CoP, cross-linking hollow carbon sheet encapsulated CuP$_2$ nanocomposites, and so on, has become the mainstream. Except for structural engineering on electrode materials, constructing self-supporting electrodes without binder and conductive agents is another attractive approach to decrease the resistance and “dead area,” and thus can improve the electrochemical performance of SIBs. For example, Cu$_3$P nanowires grown on the Cu substrate, CoP$_3$ microwires arrays on carbon felt have been directly used as the free-standing anodes for SIBs and enhanced Na storage performance was achieved.

In this review, the latest progress and prospects of MPs anode for SIBs were summarized. Since the electrochemical properties of MPs anode are closely related to their compositions and structures, this review comprehensively presented the structural manipulation strategies of tin phosphides (SnP$_x$), iron phosphides (FeP$_x$), nickel phosphides (NiP$_x$), copper phosphides (CuP$_x$), cobalt phosphides (CoP$_x$), germanium phosphides (GeP$_x$), and other MPs to enhance the electrochemical performance in SIBs. We believe this review will provide valuable guiding information to the readers about the design of MPs anode materials and their application in high-performance SIBs.

2 | MPs

2.1 | Tin phosphides

As a kind of promising SIB anode, tin phosphides have been extensively investigated in recent years owing to relatively high theoretical volumetric and gravimetric-specific capacities and electronic conductivities. In addition, SnP$_x$ also show a low redox potential, which is beneficial to achieve higher working voltage and energy density when applied in full cells.

Among SnP$_x$, the tin-rich Sn$_4$P$_3$ is the most widely studied anode material for SIBs. It shows a layered structure composed of alternately packed Sn and P layers along the c-axis (Figure 2A). Based on the reaction mechanism of Sn$_4$P$_3$ + 24Na$^+$ + 24e$^- \rightarrow Na_{15}Sn_4 + 3Na_3P$, Na$_{15}Sn_4 \leftrightarrow 4Sn + 15Na^+ + 15e^-$ and Na$_3P \leftrightarrow 3Na^+ + P + 3e^-$, Sn$_4$P$_3$ shows an extremely high theoretical volumetric-specific capacity of 6650 mA h cm$^{-3}$ exceeding the 5710 mA h cm$^{-3}$ for bare phosphorus. Moreover, Sn$_4$P$_3$ also shows a higher electronic conductivity than that of red phosphorus (i.e., 30.7 S cm$^{-1}$ for Sn$_4$P$_3$ vs. $\sim$10$^{-12}$ S cm$^{-1}$ for red P). In addition, SnP$_x$ material has also been studied. It is a layered structure consisted of Sn-P-P-Sn sandwiches arranged along the c-axis (Figure 2B). According to the
sodiation/desodiation process of 4SnP + 27Na+ + 27e– → Na36Sn4 + 4Na3P. Na36Sn4 ↔ 4Sn + 15Na+ + 15e– and Na3P ↔ 3Na+ + P + 3e–, the theoretical capacity of SnP can be up to 1209 mAh g–1.19 Besides, the phosphorus-rich SnP3 is also an excellent anode material for SIBs. SnP3 also has a layered structure, consisting of corrugated layers stacked along the c-axis with weak van der Waals force, in which the layers show puckered arsenic-type honeycomb structure composed of puckered P6 rings (Figure 2C).41 Its theoretical capacity reaches 1616 mAh g–1, which comes from the electrochemical reaction of SnP3 + 9Na+ + 9e– ↔ Sn + 3Na3P and 4Sn + 15Na+ + 15e– ↔ Na36Sn4.16 Moreover, SnP3 exhibits the highest volumetric capacity of 6890 mAh h cm–3 among the reported anode materials for SIBs.

To this end, researchers have tailored the structure of SnP3 with various chemical and physical methods. For example, Sn4P3 nanoparticles were prepared via a simple solvothermal method by reacting white phosphorus with SnCl2·2H2O and NaBH4 in N,N-dimethylformamide (DMF) solvent. The Sn4P3 microtubes were prepared by the same method, except that sodium dodecyl sulphate was added.42 Sn4+xP3@amorphous Sn-P nanoparticles were prepared by a simple ball-milling approach under argon protection employing Sn and red P powders as the starting materials.43 The pomegranate-structured Sn4P3@C nanospheres were obtained by phosphorization of SnO2/C nanospheres with NaH2PO2 at a relatively low temperature of 280 °C.44 The multi-shell Sn4P3 nanospheres were obtained by a simple and low-temperature solvothermal method.45 SnP0.94 nanoparticles encapsulated in a carbon matrix were prepared by electrospinning followed by reduction and phosphorization of SnO2 into SnP0.94.46

For SIB study, Kim et al15 firstly evaluated the electrochemical performance of Sn4P3 anode, which exhibited an excellent Na storage property (i.e., 718 mA h g–1 at 100 mA g–1) and showed a negligible capacity fading over 100 cycles. The redox potential of Sn4P3 is ∼0.3 V, which can ensure the high energy density of the full cells. At the same time, Li et al43 adopted a low-speed ball milling route to fabricate the Sn4+xP@amorphous Sn-P composites (Sn4+xP@(Sn-P)) as anode for SIBs. With 5% fluoroethylene carbonate additive added in the electrolyte, which was helpful to form more stable solid electrolyte interphase layer on the surface of the electrode, the Sn4+xP@(Sn-P) showed an initial discharging/charging capacity of 1030/892 mA h g–1 at 100 mA g–1, respectively, and held 465 mA h g–1 after 100 cycles. Moreover, it also showed excellent rate capability. The mechanism of Sn4P3 with the excellent Na storage properties has been extensively investigated.37,47,48 It was found that Sn and P phases are gradually separated during the initial charge process, with the Sn nanoparticles uniformly distributed in the P substrate, electrochemically activating the P phase. On the other side, the P matrix and the produced Na3P can act as the protective substrate for preventing the aggregation of Sn nanoparticles (Figure 3). This synergistic effect makes Sn4P3 an excellent anode material for SIBs.

However, the large volume expansion (490% from P to Na3P and 525% from Sn to Na36Sn4) induced severe structural collapse of Sn4P3 during Na insertion/extraction processes, causing the loss of electrical activity, pulverization of electrode materials along with the rapid performance deterioration.49 Rational structural design and surface modification with conductive carbonaceous materials are effective ways to eliminate these concerns. For example, Li et al17 proposed a solution-based low-temperature phosphorization route employing the Sn/rGO composites and red P as raw materials to fabricate novel Sn4P3/rGO hybrids (Figure 4A), in which the Sn4P3 nanoparticles (∼6 nm) were evenly attached to the rGO nanosheets, forming interconnected 3D mesoporous architectures (Figure 4B). When evaluated in SIBs, the Sn4P3/rGO hybrids exhibited significantly improved electrochemical performance on the part of large Na storage capacity (656 mA h g–1 at 100 mA g–1), excellent rate property (391 mA h g–1 at 2 A g–1), and ultrastable long-term cycling life (more than 1500 cycles). Choi et al40 designed and synthesized a Sn4P3-C composite nanosphere with core-shell structure and controllable size by a simple hydrothermal process combined with carbonization and phosphorization route (Figure 4C). As the anode for SIBs, the Sn4P3-C composite nanospheres exhibited an ultrastable cycling performance (i.e., 430 mA h g–1 at 2 A g–1 after 2000 cycles, as shown in Figure 4D).

On the basis of above works, various nanostructures have been developed.28,45,51–53 For example, Huang et al45 adopted a simple low-temperature solvothermal method to prepare a multi-shell Sn4P3 (Figure 5A) with a large specific surface area and interlayer spacing, which shortened the pathway of Na+ diffusion and provided sufficient space for volume expansion, thus improving the stability of the electrode and extending the cycling life of the SIBs (Figure 5B). The multi-shell Sn4P3 anode materials achieved a great Na storage property (770 mA h g–1 after 50 cycles at 50 mA g–1). Ran et al54 developed a biomimetic heterostructure Sn4P3, resembling a bottle brush, grown on CNT (Sn4P3@CNT/C) via a hydrothermal reaction combined with a thermal treatment (Figure 5C). The CNT studdle served as the electron transport channels and provided stable mechanical support, the Sn4P3 “fructus” provided larger contact area with electrolyte and shorter pathway for ion diffusion, and the amorphous carbon coating on the Sn4P3 surface buffered volume expansion and promoted the electrolyte penetration (Figure 5D). With this hierarchical structure design, Sn4P3@CNT/C anode achieved a large Na storage capacity (742 mA h
g$^{-1}$ at 200 mA g$^{-1}$) and an outstanding rate performance (449 mA h g$^{-1}$ at 2 A g$^{-1}$ after 500 cycles). Moreover, Zhao et al.$^{28}$ proposed and fabricated a nanochain-like architecture using hollow yolk-shell Sn$_4$P$_3$@C nanospheres as precursor (Sn$_4$P$_3$@CNF) through an electrospinning method (Figure 5E). The one-dimensional (1D) carbon nanofibers evenly interconnected with the hollow Sn$_4$P$_3$ nanospheres to obtain a necklace-like structure with excellent electrical conductivity (Figure 5F). With this unique design, the Sn$_4$P$_3$@CNF anode materials showed a great Na storage property of 251 mA h g$^{-1}$ at 2 A g$^{-1}$ over 4700 cycles, and ultrastable cycling life reaching to 14000 cycles with a large remaining capacity of 158 mA h g$^{-1}$ at 5 A g$^{-1}$.
Sn agglomeration is another issue that hampers the electrochemical performance of Sn₄P₃. Wang et al.⁵⁵ tried to inhibit the Sn agglomeration by introducing high-density TiC into Sn₄P₃ and achieved a more stable cycling performance (300 mA h g⁻¹ or 700 Ah L⁻¹ at 100 mA g⁻¹ over 100 cycles). Because of the presence of high-density TiC, gravimetric capacity of Sn₄P₃/TiC anode slightly decreased, but the volumetric capacity improved significantly compared to addition of conductive carbonaceous materials. To make up for the lost capacity, Lan et al.⁵⁶ replaced TiC with SbSn, which possessed both high density and high capacity, and the Sn₄P₃/SbSn nanocomposite delivered a higher capacity of 615 mAh g⁻¹ at 100 mA g⁻¹ and superior capacity retention.

In addition to the most widely studied Sn₄P₃, SnP, and SnP₃ have also been applied as anodes for SIBs, but not been extensively explored.⁶,¹⁹ Liu et al.¹⁹ used a liquid-phase route to fabricate a novel SnP nanosphere with the size of 35 ± 5 nm, achieving a large capacity of 600 mA h g⁻¹ at 100 mA g⁻¹, showing almost no decay over 200 cycles. This excellent Na storage property was originated from the small size of the crystals as well as the composition and phase of SnP, in which the pulverization and major phase separation were effectively prevented during the process of sodiation/desodiation. For SnP₃, Fan et al.¹⁶ proposed that the reversible conversion reaction happened in SnP₃ could partially repair the pulverization of Sn and P. And based on this theory, they synthesized the SnP₃/C composites for the first time by simple ball milling, which delivered a great rate property of ~400 mA h g⁻¹ even at 2560 mA g⁻¹ and displayed a high capacity of 810 mA h g⁻¹ at 150 mA g⁻¹ over 150 cycles without noticeable capacity decay.

### 2.2 Iron phosphides

According to the phase diagram of Fe-P,⁵⁷ iron phosphides show a diversity of compositions and crystal structures depending on the synthesis reaction temperature, pressure, and phosphorus concentration. Benefited from the elemental abundance, low cost, and environmentally friendliness, FePₓ have been applied in various fields, among which FeP and FeP₄ have been successfully used in SIBs.

FeP is the most extensively studied anode material for SIBs, which possesses an orthorhombic phase consisting
of FeP₆ with shared edges and faces (Figure 6A). It possesses a high capacity of ~926 mA h g⁻¹ in theory, derived from the reactions of FeP + 3Na⁺ +3e⁻ → Fe + Na₃P and Na₃P → P + 3Na⁺ + 3e⁻. Metallic iron is formed during the electrochemical reactions, and acts as a conductive matrix to facilitate the electrode to conduct electrons and mitigate volume variation. FeP₄, as another iron phosphides used in SIBs, has a monoclinic phase, containing octahedron trimer made up of FeP₆ octahedra with shared edge (Figure 6B). Among all FePₓ materials, FeP₄ has the largest proportion of P, thus with the highest theoretical-specific capacity expectedly. But there has been very little research on the application of FeP₄ in SIBs, and its Na storage mechanism is still unclear and needs further study. As for FeP₂, although it has been applied in LIBs, and there have been attempts to use it in SIBs, no significant electrochemical reactivity has been observed in SIBs because of the low operating potential (≤0 V vs. Na⁺/Na). In the past few years, FePₓ with various morphologies have been prepared by physical and chemical methods with different precursors, such as ball milling of iron and phosphorus, phosphorization of ferric inorganics, metal organic framework (MOF)-derived phosphorization, electrochemical deposition, arc discharging, and so on. Li et al. firstly explored the Na storage property of FeP nanoparticles (size: 30–50 nm), which exhibited a high initial capacity of 765 mA h g⁻¹ at 50 mA g⁻¹, but showed a poor cycling stability. At the same time, Yang et al. adopted the same synthesis method to obtain FeP/graphite composite, which achieved a capacity of 240 mA h g⁻¹ (according to the weight of FeP) after 70 cycles. From these initial investigations, the electrochemical performance of FeP as the anode for SIBs is unsatisfying, for example, the unstable cycling performance, unsatisfactory rate capability, and relatively low capacity, which is caused by the unsatisfactory electronic conductivity, poor electrical reaction kinetics, and intense volume expansion during the insertion of Na⁺.

To solve the above problems, rational design of the microstructure of FePₓ and introduction of conductive carbonaceous materials has been proved to be effective. For example, Han et al. carried out a nanoconfinement reaction to prepare a mesoporous framework of amorphous FeP coated by a carbon layer that was further attached to carbon nanotubes (CNT@FeP@C, as shown in Figure 7A). The amorphous FeP was intrinsically isotropic in nature without any framework, which could reduce volume expansion and release volume strains to improve the structural stability during the reversible insertion/extraction of Na⁺. When evaluated in SIBs, it showed improved electrochemical performance with an excellent Na storage ability (i.e., 415 mA h g⁻¹ at 100 mA g⁻¹ after 100 cycles, as shown in Figure 7B) and a great rate capability (i.e., 391, 342, 313, 296, and 268 mA h g⁻¹ at 0.2, 0.4, 0.8, 1.0 and 1.5 A g⁻¹, respectively, as shown in Figure 7C). Jiang et al. applied a simple low-temperature chemical deposition method coupled with the phosphorization and reduction processes to prepare FeP nanoparticles (<100 nm) attached onto 3D porous rGO matrix (FeP@rGO). The porous structures promoted the ion diffusion, and the presence of rGO improved the electrical conductivity. Therefore, it exhibited impressive electrochemical properties, achieving a high capacity of 389 mA h g⁻¹ at 100 mA g⁻¹ over 250 loops and a great rate adaptability. Shi et al. prepared FeP quantum dots anchored onto P-doped 3D octahedral carbon framework (FeP@OCF) interconnected by CNTs via an in situ reductive phosphatization/carbonization of MOF (Figure 7D). The nanostructure in the architecture enabled fast reaction kinetics, while the microstructure helped keeping the structural stability (Figure 7E). The composite material showed impressive electrochemical rate capability, delivering a capacity of 262 mA h g⁻¹ even at an extremely high rate of 20 A g⁻¹ (Figure 7F).
In addition to the above mentioned ingenious structural designs, there are many other impressive structures designed. For instance, the hollow FeP@carbon nanocomposites embedded in graphene (H-FeP@C@GR) were prepared by sequential hydrothermal, carbon coating, phosphorization, and carbothermic reaction (Figures 8A and 8B). They were fabricated by the phosphorization method with Prussian blue analogue as the precursor (Figures 8C and 8D). FeP nanorod arrays attached to the carbon cloth (FeP NAs/CC) were achieved by hydrothermal method and subsequent phosphorization process (Figure 8E). FeP@C nanorods encapsulated in rGO (FeP@C/rGO) were synthesized by a hydrothermal, rGO modification, and subsequent phosphorization process (Figure 8F). All of these ingenious
structural designs have led to excellent Na storage performance.

Currently, a little work has also been done in exploring application of FeP₄ in SIBs, but have not widely explored for SIBs. Zhang et al. synthesized FeP₄ materials by ball milling method using the phosphorus and iron powder as raw materials. When evaluated as negative electrode for SIBs, the obtained FeP₄ showed a large discharge capacity of 1137 mA h g⁻¹ accompanied by 84% Coulombic efficiency during the first discharging-charging process at 89 mA g⁻¹. It retained a high capacity of 1023 mA h g⁻¹ after 30 cycles, displaying excellent sodium storage capability.

2.3 Nickel phosphides

Nickel phosphides have been considered as a class of promising anode materials for SIBs owing to their abundant resources, high theoretical-specific capacity, and high electronic conductivity. Specifically, Ni₂P and NiP₃ have received extensive attention and been explored as promising anode electrodes during the past few years, which achieve impressive Na storage performance for SIB application. The theoretical-specific capacity of hexagonal Ni₂P (Figure 9A) is as high as 530 mA h g⁻¹, derived from the conversion reaction of Ni₂P + 3Na⁺ + 3e⁻ → 2Ni + Na₃P. The sodiation of cubic NiP₃ (Figure 9B) can be described by the reaction of NiP₃ + 9Na⁺ + 9e⁻ ↔ 3Na₃P + Ni. However, the inherently excessive volume variation of NiP₃ during the successive sodiation/desodiation processes causes the electrode material to pulverize and aggregate and thus leads to unsatisfactory rate property and unstable cycling life. It is critical to develop effective strategies to solve the above two issues and improve the sodium storage performance of NiPₓ.
To improve the sodium storage performance of Ni$_2$P, constructing nanocomposite structure with highly conductive carbon is an effective method. Wang et al.\textsuperscript{83} reported Ni$_2$P nanoparticles-assembled sub-microspheres coated with a glucose-derived carbon shell (Figures 10A and 10B). The hybrid electrode material exhibited a much better sodium storage performance (Figures 10C and 10D) than that of pure Ni$_2$P sub-microspheres, mainly because the uniform carbon shell effectively improved the conductivity of Ni$_2$P-based anode material and alleviated...
the volume expansion during the cycles. Zhou et al.\textsuperscript{82} immobilized Ni$_2$P nanoparticles into porous carbon networks, which showed an enhanced Na storage property of 932 mA h g$^{-1}$ at 50 mA g$^{-1}$ in the first discharge. Shi et al.\textsuperscript{84} reported monodispersed Ni$_2$P attached to N, P-co-doped carbon nanosheets (Ni$_2$P@NPC), which exhibited a remarkable reversible discharge capacity and outstanding long-term durability for sodium storage (e.g., 181 mA h g$^{-1}$ at 0.5 A g$^{-1}$ after 1200 cycles). Additionally, graphene is often used to construct nanocomposite structures as a result of its flexibility, excellent conductivity, and large surface area. Wu et al.\textsuperscript{85} prepared graphene/Ni$_2$P hybrid through solvent-thermal and phosphating reaction, which achieved a large capacity of 511 mA h g$^{-1}$. Miao et al.\textsuperscript{86} fabricated a Ni$_2$P@carbon/graphene aerogel (Ni$_2$P@C/GA) through a solvothermal reaction and in-situ phosphorization process (Figures 10E and 10F). The as-prepared Ni$_2$P@C/GA retained a specific capacity of 125 mA h g$^{-1}$ at 1 A g$^{-1}$ over 2000 cycles. Dong et al.\textsuperscript{87} constructed a sandwich-like nanostructure composed of Ni$_2$P nanoarray and N-doped graphene (Ni$_2$P/NG/Ni$_2$P). The intense reciprocity between Ni$_2$P and the N-doped graphene could alleviate electrode pulverization and aggregation by limiting the conversion of phosphides. When used as negative electrode materials for SIBs, the Ni$_2$P/NG/Ni$_2$P electrode achieved a large reversible capacity of 188 mA h g$^{-1}$ at 500 mA g$^{-1}$.

Recently, self-supported Ni$_2$P-based anodes without any binder and additives have received much research attention.\textsuperscript{77} For example, Li et al.\textsuperscript{86} fabricated Ni$_2$P nanoflakes anchored uniformly on 3D graphene which was in situ grown on Ni foam (Ni$_2$P/3DG, Figures 11A and 11B). It delivered a large reversible capacity of 403 mA h g$^{-1}$ at 200 mA g$^{-1}$ over 100 cycles, and a remarkable rate adaptability of 273 mA h g$^{-1}$ at 1 A g$^{-1}$. Furthermore, the charging/discharging mechanism was explored by ex-situ XRD, which demonstrated the conversion reaction mechanism within the Ni$_2$P nanoflakes electrode (Figure 11C). Wang et al.\textsuperscript{77} prepared Ni$_2$P nanosheets on carbon cloth and achieved an enhanced Na storage performance (i.e., 399 mA h g$^{-1}$ at 0.2 A g$^{-1}$). The electrode material can be tightly bonded with the current collector so that the diffusion pathway of Na$^+$ during the processes of charging and discharging was reduced. In the work of Zhao et al.\textsuperscript{80} hexagonal Ni$_2$P nanosheets anchored on 3D graphene wrapped nickel foam were fabricated by chemical vapor deposition, followed by a hydrothermal treatment and gas-phase phosphating. Notably, the structures and sizes of Ni$_2$P were controllable by tuning the pH values. When pH = 4, the hierarchical Ni$_2$P/3DG interdigitated

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**FIGURE 11** (A) Schematic diagram of the preparation of Ni$_2$P/3DG nanoflakes array. (B) SEM images of Ni$_2$P/3DG on nickel foam. (C) Ex-situ XRD patterns of the Ni$_2$P/3DG electrode at various voltage states. Reproduced with permission.[86] Copyright 2019, Wiley
networks were obtained, delivering a large specific capacity (314 mA h g$^{-1}$ at 100 mA g$^{-1}$ for 100 cycles) accompanied by prominent rate capability with ultralong cycling life (e.g., 155 mA h g$^{-1}$ at 1 A g$^{-1}$ after 1000 cycles).

Apart from Ni$_2$P, other Ni phosphides such as NiP$_3$, Ni$_{12}$P$_5$, and Ni$_5$P$_4$ have also been investigated. Fullenwarth et al. studied the Na storage mechanism and behavior of NiP$_3$ as a negative electrode. The NiP$_3$ electrode exhibited an impressive reversible capacity of 900 mA h g$^{-1}$ after 15 cycles for SIBs. Ihsan-Ul-Haq et al. synthesized NiP$_3$/CNTs by a high-energy ball milling of red P and Ni to form NiP$_3$ particles, which was subsequently ball-milled with CNTs for 5 h. The as-prepared NiP$_3$/CNTs composite achieved a large capacity of 853 mA h g$^{-1}$ accompanied an acceptable retention ratio of >80% after 120 cycles under 200 mA g$^{-1}$ and a superior rate capability of 364 mA h g$^{-1}$ at 1.6 A g$^{-1}$. Guo et al. adopted refluxing method to synthesize carbon coated Ni$_{12}$P$_5$ attached to rGO nanosheets (Ni$_{12}$P$_5$@C/GNS) forming a special hollow structure. When applied as anode for SIBs, the hollow Ni$_{12}$P$_5$@C/GNS composite showed great Na storage property (i.e., 235 mA h g$^{-1}$ at 100 mA g$^{-1}$). Zheng et al. reported a 3D hierarchical nanostructures with Ni$_5$P$_4$ nanospheres wrapped by rGO (Ni$_5$P$_4$@rGO) through a sequential hydrothermal and phosphidation treatment of highly folded spherical α-Ni(OH)$_2$. The Ni$_5$P$_4$@rGO composite delivered a specific capacity of 304 mA h g$^{-1}$ at 0.2 A g$^{-1}$ after 200 cycles.

Besides of stoichiometric Ni phosphides, nonstoichiometric Ni phosphides are also compelling. For instance, Hao et al constructed a particle-in-nanoplate architecture where self-assembled Ni$_{2.3}$FeP$_{3.4}$ nanoparticles intertwined with the carbon nanotubes (Ni$_{2.3}$FeP$_{3.4}$/CNTs) by a facile hydrothermal process accompanied by high-temperature pyrolysis and phosphidation process. The Ni$_{2.3}$FeP$_{3.4}$/CNTs nanoarchitecture had excellent sodium storage performance (335 mA h g$^{-1}$ at 100 mA g$^{-1}$) and highly stable cycling capability (143 mA h g$^{-1}$ at 1 A g$^{-1}$ over 120 cycles).

2.4 | Copper phosphides

Up to now, in the P-Cu diagram, there only exist three copper phosphides (Cu$_x$P$_y$) compounds (i.e., CuP$_2$, Cu$_3$P and Cu$_2$P$_7$), and all of them have been used as anodes for SIBs. As the most common conductive material, copper possesses excellent electrical conductivity. The metallic copper nanoparticles formed during the sodiation process can act as the highly conductive channels to enhance the electron transfer in the electrode and thus promote the alloying reaction between P and Na$^+$. P-rich CuP$_2$ shows a layered structure, in which the pairs of copper atoms are evenly embedded between two corrugated phosphorus layers stacked along the a-axis (Figure 12A). Moreover, one unit of CuP$_2$ can react with six sodium derived from conversion and alloying reaction of CuP$_2$ + 6Na$^+$ + 6e$^- \leftrightarrow 2$Na$_3$P + Cu, corresponding to 1282 mA h g$^{-1}$ in theory. However, a few researchers put forward the possibility that the conversion reaction is irreversible, thus the Na storage mechanism should be expressed as CuP$_2$ + 6Na$^+$ + 6e$^- \rightarrow 2$Na$_3$P + Cu and Na$_3$P.
↔ 3Na⁺ + 3e⁻ + P. To clarify the Na storage mechanism, more accurate and advanced testing methods are needed. For metal rich Cu₃P, its crystal structure can be described as a complex array in interconnected PCu₆ trigonal prisms with one additional Cu atom outside each of the rectangular and trigonal faces of the prisms (Figure 12B). As the anode for SIBs, it possesses a relatively low theoretical capacity of 363 mA h g⁻¹ based on the reaction of Cu₃P + 3Na⁺ + 3e⁻ ↔ Na₃P + 3Cu. However, its volumetric capacity can reach 3020 mA h cm⁻³, which is about three times that of graphene (830 mA h cm⁻³). Besides, Cu₃P does not encounter the solvent co-intercalation issues as in the graphitic materials.98–100

Cu₂P₇ possesses a layered structure consisting of repeated chains of P atoms, in which alternating patterns of Cu or Cu-P are connected to a zig-zag chain of P atoms, as shown in Figure 12C.101 Moreover, it shows the smallest bandgap which implies the best electronic conductivity among the P-Cu compounds.91,102 All of these strengths of Cu₂P₇ not only enhance the electron and Na-ion transportation but also create much active sites endowed by interfacial coupling. It shows a large theoretical capacity of 1636 mA h g⁻¹ derived from the reversible reaction of Cu₂P₇ + 21Na⁺ + 21e⁻ ↔ 7Na₃P + 2Cu.

Zhao et al.93 prepared the composites of CuP₂ mixed with carbon black (CuP₂/C) via a method of two-step ball milling and evaluated its Na storage property as negative electrode materials for SIBs. The CuP₂/C electrode achieved a charge capacity of 470 mA h g⁻¹ during the first cycle at 150 mA g⁻¹ and reserved 430 mA h g⁻¹ after 30 loops. The relatively unsatisfactory cycling life and limited rate adaptability were attributed to the insufficient conductivity, huge volume expansion, and nano-crystal agglomeration during the Na⁺ insertion/extraction processes.103

To achieve better Na storage performance, the microstructure of CuP₂/C has been carefully tailored. The well-designed nanostructures can enable the electrode to be fully exposed to the electrolyte. And the carbonaceous materials can act as a buffer phase to mitigate the volume changes, a matrix to mitigate aggregation, as well as the conductive agents to enhance the electron conduction of the electrode.104 Chen et al.32 prepared a nanocomposite with CuP₂ encapsulated in the cross-linked hollow carbon sheets (CHCS-CuP₂) via a surfactant-assisted wet-chemical precipitation method (Figure 13A). The cross-linked hollow structure provided sufficient buffer space for volume expansion and the carbon shells possessing good electrical conductivity promoted the charge transfer. Benefited from these strengths, the as-prepared electrode material achieved a great Na storage property of 451 mA h g⁻¹ at 80 mA g⁻¹, and the capacity retention reached 90.9% after 200 cycles (Figure 13B). And it also emerged an enhanced rate property (i.e., 167 and 137 mA h g⁻¹ at 1280 and 2560 mA g⁻¹, respectively, as shown in Figure 13C). Duan et al.95 fabricated carbon nanosheets with uniformly dispersed CuP₂ (CuP₂/C) by thermal reduction and phosphorization of freeze dried CuCl₂/chitosan monolith (Figures 13D and 13E). In this structure, the carbon nanosheets with great electrical conductivity not only effectively promoted charge transfer, but also alleviated volume expansion. Thus, the CuP₂/C electrode possessed a large specific capacity of 477 mA h g⁻¹ at 200 mA g⁻¹, remained 91% capacity after 200 cycles (Figure 13F).

Heterointerface construction is considered to be a new and promising strategy in preparing electrode materials with enhanced performance.105,106 Li et al.102 constructed Cu₂P₇/CuP₂/C hybrid with abundant phase boundaries, providing abundant active sites for Na-ion storage and inducing positively interfacial coupling effect like the built-in electric field to promote electronic and ionic transfer rate. As such, it achieved a great Na storage property of 1254 mA h g⁻¹ (4685 mA h cm⁻³) over 100 charging-discharging process at 200 mA g⁻¹. Li et al.107 synthesized Cu₃P and Co₃P hybrid interlinked by N-doped carbon fibers by forming self-standing three-dimensional (3D) electrode. The presence of Co₃P improved the cycling capability and reversibility of Cu₃P, and the as-prepared electrode achieved a stable capacity around 166 mA h g⁻¹ after 50 cycles.

The self-standing electrodes without binder or conductive additives that will increase the resistance and “dead area” of electrode are very desirable. However, it remains significant challenge to build self-standing electrodes from copper phosphides because they are mostly irregular particles with a wide size-distribution. Fan et al.33 prepared Cu₃P nanowire grown on Cu foil substrate (CPNWs) by in-situ growth and phosphorization method and finally obtained an additive free electrode (Figures 14A and 14B). This novel electrode possessed good electrical conductivity due to the presence of Cu substrate and the existence of undesirable interface introduced by the additive. With these improvements, the as-prepared electrode exhibited an excellent rate performance (Figure 14C). Moreover, it also showed an outstanding reversible capacity of 249 mA h g⁻¹ after 50th cycles at 100 mA g⁻¹ (Figure 14D).

2.5 Cobalt phosphides

Based on the stoichiometries between cobalt and phosphorus, cobalt phosphides (Co₃Pₓ) with diverse crystal structures have been determined, mainly involving CoP,108 Co₂P,109 Co₃P,110 Co₄P,26 and Co₅P₄.34 Owing to the high theoretical capacity (~1000 mA h g⁻¹) and low
operating voltage (<0.3 V vs. Na⁺/Na), all of them have been regarded as promising anodes for SIBs.

Li and co-workers, for the first time, explored orthorhombic CoP nanoparticles as anode materials for SIBs. They found that the charge-discharge plots of CoP were similar to those of iron phosphide (FeP) in SIBs, inferring that they had a similar sodium storage mechanism. Thus, the reaction equation was listed as follows: CoP + 3Na⁺ + 3e⁻ → Co + Na₃P; Na₃P ↔ P + 3Na⁺ + 3e⁻. The CoP nanoparticles achieved 770 mA h g⁻¹ during the process of first discharge (lower than the theoretical capacity of 894 mA h g⁻¹) and decayed to 58 mA h g⁻¹ soon after 25 cycles due to the inferior conductivity and severe volume change. The cycling performance of CoP electrodes is yet to be improved to satisfy the requirement of commercial application. To rationally design CoPₓ-based compounds to optimize the electrochemical performance, researchers primarily focused on (i)
fabricating a porous architecture with high specific surface area to provide abundant active sites and relieve the large volume variation caused by the conversion and alloying reactions\cite{111,112}; (ii) constructing micro-nano sized CoP$_x$-based composites with consecutive conductive matrix (e.g., carbon nanotubes, carbon paper, and graphene) to reduce the diffusion path of Na$^+$ and increase the charge transfer kinetics\cite{113–118}; and (iii) improving the electronic conductivity via elemental doping in the CoP$_x$ (e.g., Fe, Mo, N) or in the conductive supports (e.g., N/S-doped carbon materials)\cite{27,31,109,119–124}.

For example, in Liu’s study, a hierarchical hollow CoP@C composite was prepared by controlling the atmosphere and temperature during the heat treatment.\cite{112} The hollow spherical structure of the CoP@C prepared at 600$^\circ$C (CoP@C-600) was well retained even after hundreds of cycles, showing excellent structural stability. It was therefore found that the CoP@C-600 composite showed better cycling and rate performance when applied to anode of SIBs. Impressively, even tested at a high rate of 1 A g$^{-1}$, 52.4% residual capacity ratio was delivered after 7000 loops. Using fibrous elastin proteins as the carbon source and soft template, Guo et al.\cite{113} prepared a 1D carbon-supported CoP nanofibrous through an oil-phase method. The as-prepared product was composed of CoP nanoparticles around 5–10 nm anchored on the interior of the carbon support, which kept the structural integrity upon repeated cycling. Therefore, the 1D CoP@C nanofibrous delivered an excellent rate capability (315 mA h g$^{-1}$ at 5 C, 1 C = 893 mA g$^{-1}$) and ultrastable cycling performance (300 mA h g$^{-1}$ after 1000 cycles). Wang et al.\cite{115} prepared CoP confined in a multidimensional hierarchical carbon architecture with 1D dual-carbon-layer capsule and 3D graphene network support (CoP@DC@GR) via a hydrothermal method coupled with post phosphorization treatment. The 1D dual carbon layer (internal porous carbon shells and external nanosized carbon walls) could effectively keep 0D CoP nanoparticles away from aggregation, while the 3D graphene network stabilized the host framework. Therefore, the CoP@DC@GR...
 Researchers have also devoted much effort to fabricate self-supported binder-free CoPₓ electrodes. Ge et al. designed a binder-free MOF-derived porous CoP/C with core/shell structure fixed on 3D rGO grown on the nickel foam matrix (CoP@C-RGO-NF) for SIB anode. This unique core/shell-type hierarchical architecture was conducive to a full contact between electrode and electrolyte. The synergistic effect of the carbonaceous substrate and the hierarchical porous structure endowed the CoP@C-RGO-NF anode with outstanding electrochemical performance (i.e., 473 mA h g⁻¹ at 100 mA g⁻¹ over 100 loops). Zhang et al. introduced polypyrrole (PPy) as a conductive carbon coating layer of core CoP nanowires that arrayed on the carbon paper (CoP@PPy NWs/CP), forming a freestanding binder-free electrode (Figure 15A). The PPy coated on the surface of CoP nanowire by forming Co-N bonds, which could effectively avoid structural degradation upon repeated cycling, as well as increased the charge transport kinetics, but also improved cycling durability. It delivered 801 mA h g⁻¹ during the first charging process at 0.1 A g⁻¹ with 81.3% retention after 100 cycles.

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transport kinetics because of its 3D diffusion pathways (Figure 15B). As a result, the CoP@PPy NWs/CP electrode displayed extremely stable cycling performance (almost no capacity fading after 4000 cycles at 1250 mA g\(^{-1}\)) as well as large specific capacities (530 and 237 mA h g\(^{-1}\) at 125 and 2500 mA g\(^{-1}\), respectively). Similarly, Sun et al.\(^{34}\) have designed a novel binder-free CoP\(_4\)-carbon felt composite (CoP\(_4\)/CF) that gathering the strengths of abundant pore structure, superfine nanoparticles and 3D conductive carbon framework. As captured in Figure 15C, this unique design could shorten the Na\(^+\) solid-state diffusion length and accommodate the volume variation upon sodiation/desodiation processes. Remarkably, at a relatively low potential window of 0.01–1.5 V vs. Na\(^+\)/Na, the resultant CoP\(_4\)/CF anode showed a decent cycling property with 90% capacity kept after 1000 charging/discharging loops at 1 A g\(^{-1}\) and a superior rate property with a capacitance of 535 mA h g\(^{-1}\) at 4 A g\(^{-1}\) in half-cell testing (Figure 15D). More importantly, the full cell assembled with CoP\(_4\)/CF anode and Na\(_3\)V\(_2\)(PO\(_4\))\(_2\)F\(_3\) cathode displayed great electrochemical performance in terms of relatively high operating voltage (~3.0 V), large specific capacity (553 mA h g\(^{-1}\)), and superior energy density (280 Wh kg\(^{-1}\)).

Doping CoP\(_x\)/C with other elements is another strategy to address the issues mentioned above regarding CoP-based anodes. In Xu’s work, a hierarchical flower-like Fe-doped CoP array was grown on the carbon membrane (CoP/CM) and used as anode for SIBs.\(^{31}\) The elemental Fe played a role in assisting the formation of hierarchical flower-like morphology during the synthesis process. Also, doping of Fe element increased the internal electron conduction. When evaluated at 100 mA g\(^{-1}\), the Fe-doped CoP/CM anode displayed a stable-specific capacity of 515 mA h g\(^{-1}\), while the CoP/CM electrode only had 345 mA h g\(^{-1}\). In terms of rate capability, the as-optimized Fe-doped CoP/CM anode provided a reversible capacity of 208 mA h g\(^{-1}\) at 2000 mA g\(^{-1}\), much higher than that of 82 mA h g\(^{-1}\) for CoP/CM. CoP nanoparticles evenly distributed in N-doped carbon nanosheets (CoP/CNS) have been prepared by Kang’s group via solvothermal followed by direct calcination treatment using Co-MOF as both C, N and Co source and self-template, red P as the P source.\(^{121}\) The skeleton of Co-MOF effectively prevented the agglomeration of CoP nanoparticles upon the phosphorization process. Benefited from the ultrafine CoP particles (~11.3 nm), the robust P-C bonds, and the N doping, the sodium storage capability of the CoP/CNS was 598 and 174 mA h g\(^{-1}\) at 0.1 and 20 A g\(^{-1}\), respectively. It also performed well in terms of cycling performance at 1 A g\(^{-1}\), maintaining a capacity of 386 mA h g\(^{-1}\) after 900 cycles, achieving a high capacity retention of 98.5%. Zhao et al.\(^{125}\) proposed a hierarchical micro-/nanostructured hybrids with CoP uniformly embedded in N-doped carbon nanowire with reduced graphene oxide coating (CoP@NC/rGO) for SIBs. It was featured with a superior cycling stability (550 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\), after 300 cycles).

### 2.6 Germanium phosphides

As a member of the Group IV-Group V elements, germanium phosphide (GeP\(_x\)) has diverse phases, for example, GeP, GeP\(_3\), and GeP\(_5\), which have been extensively investigated for energy storage.\(^{126}\) Among these compounds, GeP\(_3\) (Figure 16A) and GeP\(_5\) (Figure 16B) show rhombohedral crystalline structure and belong to R-3m space group, in which their cell parameters are \(a = 3.467\ \text{Å}, c = 10.040\ \text{Å}\) and \(a = 7.050\ \text{Å}, c = 9.932\ \text{Å}\), respectively. And they share a very similar rhombohedral black P-like layered structures, in which the zigzag planes of randomly arranged P and Ge atoms in corresponding proportions are stacked along the c axis.\(^{18,127}\) GeP exists in the tetragonal form (Figure 16C) with the cell parameters of \(a = 3.544\ \text{Å}\) and \(c = 5.581\ \text{Å}\) and holds a layered structure consisting of puckered sheets with thickness of 7.8 Å stacked together by van der Waals forces.\(^{24,128}\) All of them possess 2D layered structures which benefit the rapid diffusion of ions. Besides, when serving as anodes for SIBs, the Ge element in the GeP\(_x\) can react with sodium to form NaGe. However, the huge volume change from the conversion reaction between
GeP$_x$ and Na$_3$P will cause the pulverization of active materials, resulting in the poor cycling performance in practical applications. Fortunately, such 2D layered structure showed both high electrical conductivity and good structural flexibility when bonded with carbon (i.e., P-O-C and P-C bonds).$^{18,129}$ As well documented in the literature, conversion-type electrodes have been widely combined with carbon-based materials to alleviate the volume expansion and improve the cyclability, igniting broad research interests in the structural design of carbonaceous germanium phosphides composites.

Up to now, all kinds of GeP$_x$ have been successfully fabricated, the synthetic methods are still limited, and mainly is high energy ball milling method.$^{18,127,130–134}$ In addition, the other methods have also been developed to a lesser extent, such as one-step and template-free approach, oriented growth technique,$^{135}$ lithiation-assisted chemical exfoliation technique, and electrospinning approach coupled with phosphorization process.$^{137}$ Among the GeP$_x$-based systems, the layered GeP$_3$ possesses the highest P content and shows higher metallic conductivity even than that of graphite,$^{132,138}$ Using a method of high-energy milling, Li et al prepared a GeP$_5$/C composite through a two-step high-energy ball milling method.$^{132}$ When evaluated as anode in the half cells at 100 mA g$^{-1}$, it showed a low redox potential of 0.4 V, a great Na storage property of 1250 mA h g$^{-1}$ (93% Coulombic efficiency in the first cycle), and an excellent capacity holding ratio of 98% after 60 cycles. Moreover, the GeP$_5$/C electrode also possessed a considerable rate property. The great Na storage property and high Coulombic efficiency of GeP$_5$/C were derived from its binary sodium-reactive components and high metallic conductivity. Impressively, the full cells consisted of GeP$_5$/C and Na$_3$V$_2$(PO$_4$)$_3$/C displayed an average output voltage of 2.65 V, a high capacity of 800 mA h g$^{-1}$, and a good capacity holding ratio of 80% after 60 cycles. According to the ex-situ XRD and HR-TEM results, the sodium storage behavior of GeP$_3$ was described as follows: GeP$_3$ + 16Na$^+$ + 16e$^- \rightarrow 5$Na$_3$P + NaGe for initial discharge process and 5Na$_3$P + NaGe $\leftrightarrow$ 5P + 16Na$^+$ + Ge + 16e$^-$ for subsequent cycling processes.

Layered GeP$_3$, featured with the same rhombohedral crystalline structure as GeP$_5$, was introduced as a promising anode for SIBs by Kim et al for the first time.$^{127}$ It was demonstrated from the first-principles calculation results that GeP$_3$ showed softer bonding traits than GeP$_5$. As expected, it can effectively accommodate the mechanical stress and deformation during the process of sodiation/desodiation, resulting in higher capacity and more stable cycling performance of GeP$_3$ than that of GeP$_5$. In their work, the discharge/charge capacities of 1274/1269 mA h g$^{-1}$ were maintained after 150 cycles in GeP$_3$, which was better than that of GeP$_5$ (the discharge/charge capacities were 1087/1083 mA h g$^{-1}$). Using a simple solid-state approach, Nam et al$^{134}$ prepared GeP$_3$/C nanocomposite via a simple ball milling process and further investigated its electrochemical behavior and reaction mechanism as anode for SIBs. The GeP$_3$/C anode exhibited an outstanding specific capacity of 984 mA h g$^{-1}$ after 30 cycles at 50 mA g$^{-1}$ with a high initial Coulombic efficiency of 81.3% and a remarkable rate property of 520 mA h g$^{-1}$ at 1.9 A g$^{-1}$. Based on the ex-situ results, such as EXAFS, XRD, and HR-TEM, the reaction mechanism of GeP$_3$ was confirmed and collected in Figure 17A. During the Na$^+$ insertion process, the GeP$_3$ experienced a one-step conversion reaction. On the other hand, the GeP$_3$ underwent a two-step desodiation process, in which Na$_2$P and NaGe were converted firstly to a Na$_3$GeP$_3$ ($x \leq 2.4$) phase and finally regenerated the pristine GeP$_3$. As a result, the sodium storage mechanism of GeP$_3$ can be summarized as follows: GeP$_3$ $\rightarrow$ NaGe + Na$_3$P for one-step sodiation process and NaGe + Na$_3$P $\rightarrow$ Na$_3$xGeP$_3$ ($x \leq 2.4$) $\rightarrow$ GeP$_3$ for two-step desodiation processes.

Based on the first-principles calculations and experimental validation, Kim and co-workers investigated the key parameters that are essential to achieve fast kinetics and high capacity in designing GeP$_3$ anode, such as electron transport, elastic softness, and thermodynamic phase stability, and compared them with those of the black phosphorus (BP).$^{139}$ In terms of electron transport, resulting from the electron donation from Ge to P coming from their different electronegativity, the band gap and electron hopping barrier of GeP$_3$ are both lower than that of BP. Furthermore, owing to the elastic softness, the GeP$_3$ showed lower strain energy and higher Na$^+$ diffusion coefficient than BP during sodiation process. Consequently, the GeP$_3$ electrode in their work exhibited outstanding sodium storage properties with a discharge capacity of 197 mA h g$^{-1}$ even at 20 A g$^{-1}$. Moreover, Wang et al$^{140}$ prepared a dual-carbon modified germanium phosphide composite (GeP$_3$/C@rGO) by high-energy ball milling method followed by solution-based ultrasonic process encapsulating the resultant GeP$_3$/C in graphene. From the results of ex-situ XPS and EIS, the carbon layer effectively stabilized the interior GeP$_3$ nanoparticles, while the graphene network protected the exterior surface from electrolyte attack. Besides, the synergy between the dual-carbon matrix brought higher electric conductivity, provided the largest surface area that ensured Na$^+$ and electron fast diffusion, and effectively suppressed the volume variation and loss of active materials during cycling (Figure 17B). Therefore, the GeP$_3$/C@rGO achieved excellent electrochemical performance in terms of high capacity (1084 mA h g$^{-1}$ at 50 mA g$^{-1}$), superior rate property (435 mA h g$^{-1}$ at 5 A g$^{-1}$), and
ultrastable cycling performance (823 mA h g⁻¹ after 400 loops at 0.2 A g⁻¹).

The tetragonal GeP shows a unique layered structure stacked by Van der Waals interaction, which is in favor of the diffusion and accommodation of sodium ions. Shen et al explored the real-time dynamic reaction process and the sodium storage mechanism of GeP. They noticed that the individual GeP nanoflake showed a width of 0.93 μm before sodiation and then expanded to 1.25 μm at the fully sodiated state, corresponding to a total area expansion as high as 248%. Interestingly, GeP nanoflake maintained the structural integrity without obvious crack or fracture. As observed from the in-situ TEM, the reaction mechanism of GeP was illustrated in Figure 18D. The GeP experienced a multi-step reaction process during the first sodiation, that is, intercalation-type and alloy-type reaction, converting to Na₃GeP (0 < x < 1/3), layered NaGe₃P₃, and amorphous NaGe and Na₃P (0 < y ≤ 3) step by step. Therefore, the reaction mechanism of GeP can be summarized as follows: 3GeP + Na⁺ + e⁻ → Na₃GeP₃, NaGe₃P₃ + (2+3y)Na⁺ + (2+3y)e⁻ → 3NaGe + 3Na₃P and Na₃P + (3-y)Na⁺ + (3-y)e⁻ → Na₃P. After that, when tested within 0.005-2.5 V versus Na⁺/Na, a high discharge/charge capacity of 1124/996 mA h g⁻¹ was obtained in the initial cycle. However, it showed rapid capacity fading accompanied with the cracking on the surface of GeP electrode, which may be ascribed to the huge volume expansion originated from the formation of amorphous alloy NaGe and Na₃P. To balance the storage capacity and the lifespan, the operating voltage range was further narrowed. As a result, the GeP electrode displayed an initial capacity of 520 mA h g⁻¹ and kept at 330 mA h g⁻¹ after 100 cycles in the voltage range of 0.15-1.5 V at 0.1 A g⁻¹.

As mentioned above, hybridizing germanium-based phosphides with carbon materials are favorable to release the stress strain during cycling and thus enhance the electrochemical performance. Yang et al has successfully trimmed the particle size of the bulk GeP down to 2D nanosheets through a lithiation-assisted chemical exfoliation technique. In this work, the N-butyl-lithium was used
as the lithium donor, which could be intercalated into the interlayers of GeP to facilitate exfoliation of the bulk GeP. Then a composite electrode, that is, few-layer GeP/rGO (FL-GP/rGO), was achieved after sequential sonic bath, freeze-drying and calcination treatments. Impressively, the FL-GP/rGO anode showed satisfactory sodium storage capability in both half- and full-cells (cathode: Na3V2(PO4)3). For instance, it achieved a large specific capacity (504 mA h g\(^{-1}\) at 100 mA g\(^{-1}\)) and a great rate adaptability (250 mA h g\(^{-1}\) at 2 A g\(^{-1}\)) in the half-cells.

2.7 Other transition MPs

There are a large number of other transition MPs formed through the alloying of transition metals (i.e., V, Ti, W, Zn, Mo, etc.) with phosphorus to form MPs (MP\(_x\)) with various compositions, structures, properties, and reaction mechanism.\(^{141-150}\)

For example, due to the various oxidation states of vanadium, vanadium-based phosphides can exist in different phases, such as V\(_4\)P\(_7\), VP\(_2\), VP\(_4\), and so on. Their potential as electrodes for energy storage has been revealed.\(^{141-145}\) For instance, Kim et al.\(^{143}\) prepared pure V\(_4\)P\(_7\) nanoparticles by a high-energy ball milling route and applied them as anode materials for SIBs. From the results of ex-situ XRD, TEM, XANES, and EXAFS, the sodium storage of V\(_4\)P\(_7\) was found to be realized through the topotactic insertion/extraction without any structural conversion (i.e., V\(_4\)P\(_7\) + \(x\)Na\(^+\) + xe\(^-\) \(\leftrightarrow\) Na\(_x\)V\(_4\)P\(_7\)), while amorphous Li-V-P ternary phase was formed when it was used as anode for LIBs. With such intercalation mechanism, the V\(_4\)P\(_7\) electrode exhibited superior cycling stability in the common organic electrolyte, showing a discharge reversible capacity of 234 mA h g\(^{-1}\) at 100 mA g\(^{-1}\) and almost no capacity decay. However, its rate capability was unsatisfactory (i.e., 90 mA h g\(^{-1}\) at 800 mA g\(^{-1}\)), demanding further development. In Kaushik’s study, a composite composed of crystalline V\(_4\)P\(_7\) and amorphous P (V\(_4\)P\(_7\)/SP) was prepared through a high-energy milling method.\(^{144}\) When the V\(_4\)P\(_7\)/SP electrode was tested at 298 K, specific capacities of 588 and 155 mA h g\(^{-1}\) were obtained at 100 and 2000 mA g\(^{-1}\), respectively. Besides, when ionic liquid (Na[FSA]-[C\(_3\)C\(_1\)prr][FSA]) was used as the electrolyte, this
composite displayed excellent rate performance at 363 K. Unfortunately, its cycling stability was inferior at both 298 and 363 K, which was attributed to the huge volume expansion resulted from the conversion reaction between amorphous P and Na3P during sodiation/desodiation process. The sodium storage capability of VP2 was evaluated by Hagiwara and coworkers using ionic liquid as electrolyte.145 The sodium (de)intercalation mechanism in VP2 was investigated by ex-situ XRD, XAFS, and MAS NMR techniques. As illustrated in Figure 19A, the VP2 underwent partial conversion during the discharging process (i.e., $\text{VP}_2 + 3x\text{Na}^+ + 3xe^- \leftrightarrow \text{VP}_{2-x} + x\text{Na}_3\text{P}$). The battery systems cycled well at high temperatures owing to thermal stability of ionic liquid. For the rate capability at 363 K, the VP2 anode yielded stable discharge capacities of 241, 212, and 131 mA h g$^{-1}$ at 0.1, 1.0, and 8.0 A g$^{-1}$, respectively. Furthermore, when tested at 500 mA g$^{-1}$, the VP2 electrode retained 102.4% capacity after 500 cycles at 363 K (Figure 19B). Nevertheless, the electrochemical performance of pure vanadium-based phosphides is far below their theoretical capacities.

In the case of TiP$_x$, it possesses the necessary conditions to achieve superior sodium storage property, such as great electrical conductivity, large storage capacity and fast ion diffusion.147,148 Based on these advantages, a few studies have been made on TiP$_x$ in LIBs,151,152 but the research on its sodium storage performance is still lacking. Very recently, Cheng et al148 adopted first-principle calculations to analyze the feasibility of the Ti$_2$P monolayer as the electrode material for SIBs, indicating that Ti$_2$P monolayer can realize energy storage by adsorption of Na$^+$ on the surface and showing a high storage capacity of 846 mA h g$^{-1}$ theoretically. Moreover, Ti$_2$P monolayer showed a lower Li/Na diffusion barrier of 12–16 meV, which was much lower than that of other 2D anode materials. All of these theoretical results made Ti$_2$P a promising candidate electrode material for SIBs. In addition to the theoretical analyses, a composite composed of red phosphorus, crystalline TiP$_2$, and a conductive carbon network (P-TiP$_2$-C) was reported by Kim et al as the anode materials for SIBs.147 The crystalline TiP$_2$ and carbon matrix in this material acted as the buffer to mitigate the huge volume variation and promote the electronic conductivity of the electrode. Consequently, when charged-discharged at 200 mA g$^{-1}$, the P-TiP$_2$-C composites showed a capacity of 755 mA h g$^{-1}$ in the first discharge and achieved 80% capacity retention at 100th cycle. In contrast, the anode without TiP$_2$ displayed an initial capacity of 1531 mA h g$^{-1}$ at the same rate, which dropped rapidly to 97 mA h g$^{-1}$ (6% of its initial capacity) after 30 cycles. Furthermore, the rate performance was also superior to that of P-C electrode.

The Zn-based phosphides are also regarded as promising anodes for SIBs since the Zn in ZnP$_x$ material can contribute to the relaxation of the volume change upon
sodiation/desodiation processes. Nam et al.\textsuperscript{149} prepared a C-modified \( \text{Zn}_2\text{P}_2 \) composite (\( \text{Zn}_2\text{P}_2\)-C) as anode for SIBs, in which the amorphous carbonaceous material helped to improve the reactivity and reversibility of \( \text{Zn}_2\text{P}_2 \) for \( \text{Na}^+ \). As illustrated schematically in Figure 19C, the \textit{ex-situ} TEM observation demonstrated that the crystallite size of \( \text{Zn}_2\text{P}_2 \) in the composite was reduced after cycling, reducing the diffusion distance of \( \text{Na}^+ \) and easing the volume expansion of \( \text{Zn}_2\text{P}_2 \). As a result, the \( \text{Zn}_2\text{P}_2\)-C delivered a capacity of 1070 mA h g\(^{-1}\) during the first discharge process, accompanied by a Coulombic efficiency of 66\% at 50 mA g\(^{-1}\) and retaining 883 mA h g\(^{-1}\) after 130 loops. Meanwhile, an outstanding rate capability (350 mA h g\(^{-1}\) at 2.7 A g\(^{-1}\)) and good cycling performance (\sim 100\% capacity retention at 0.9 A g\(^{-1}\) over 200 cycles) were realized. The electrochemical reaction mechanism of \( \text{Zn}_2\text{P}_2 \) was investigated through a series of \textit{ex-situ} techniques, such as XRD, XANES, and EXAFS, which revealed a one-step reversible conversion/recombination reaction upon \( \text{Na}^+ \) insertion/extraction processes, corresponding to 13\( \text{Zn}_2\text{P}_2 \) + 79\( \text{Na}^+ \) + 79e\(^-\) \leftrightarrow \text{Na}_7\text{Zn}_{13} + 26\text{Na}_3\text{P} \) (Figure 19D).

Theoretical capacity of Mo-based phosphides (MoP) is calculated to be 633 mA h g\(^{-1}\) derived from the conversion between MoP and \( \text{Na}_3\text{P} \), making it possible to be an excellent negative electrode for SIBs. Unfortunately, it is also disturbed by the poor cycling stability and rate performance. Huang et al.\textsuperscript{150} designed an amorphous carbon-coated MoP nanorod (MoP@C) through a method of solid phase reaction under elevated temperature. \textit{In-situ} XRD result showed that hexagonal MoP underwent a reversible conversion/alloying reaction during the \( \text{Na}^+ \) insertion/extraction process, in other words, the MoP was converted into hexagonal \( \text{Na}_3\text{P} \) and cubic molybdenum with \( \text{Na}^+ \) insertion, and it returned to MoP after \( \text{Na}^+ \) extraction (i.e., \( \text{MoP} + 3\text{Na}^+ + 3\text{e}^- \leftrightarrow \text{Na}_3\text{P} + \text{Mo} \)), contributing to the high sodium storage capacity (Figures 19E and 19F). At a low rate of 100 mA g\(^{-1}\), the MoP@C nanorods sustained 396 mA h g\(^{-1}\) even after 800 cycles. It also showed good rate adaptability and ultra-long term service life, achieving an acceptable capacity of 118 mA h g\(^{-1}\) at 1600 mA g\(^{-1}\) and retaining 105 mA h g\(^{-1}\) with 89\% capacity retention after 10000 cycles. Yin et al.\textsuperscript{151} fabricated hollow MoP nanospheres wrapped by 3D rGO via hydrothermal process followed by a phosphorization treatment. With the help of cage-like rGO network and hollow nano-sized structure, the volume variation of MoP could be effectively buffered, and thus guaranteeing the electrode materials against pulverization during \( \text{Na}^+ \) (de)intercalation processes. As such, it exhibited a high specific capacity (354 mA h g\(^{-1}\) at 1 A g\(^{-1}\) after 600 cycles), superior rate performance (133 mA h g\(^{-1}\) at 20 A g\(^{-1}\)), and ultrastable cycling performance (183 mA h g\(^{-1}\) at 10 A g\(^{-1}\) after 3000 cycles). Recently, Fu et al.\textsuperscript{152} prepared MoP@N-doped carbon nanofibers (MoP@NCNFs) through an electrospinning method combined with an \textit{in-situ} carbothermic self-reduction process. The MoP nanoparticles were uniformly spread on the crosslinked 1D nanofibers, which can avoid the aggregation of MoP-based nanoparticles as well as relax their volume stress upon phase conversion. Furthermore, with increased pseudocapacitive contribution at higher current rates, a decent sodium storage property can be guaranteed. Consequently, when used as anode materials for SIBs, the MoP@NCNFs delivered the reversible-specific capacities of 404, 238, 198, 143, and 135 mA h g\(^{-1}\) at 0.1, 2, 5, 10 and 20 A g\(^{-1}\), respectively.

3 | SUMMARY AND OUTLOOK

Sodium is similar to lithium in physical and chemical properties, while sodium shows higher natural abundance, lower cost, suitable operating voltage, and feasibility with light aluminum as substrate; therefore, compared with LIBs, SIBs show strong competitiveness in the field of large-scale energy storage. However, the bigger radius of \( \text{Na}^+ \) makes it more challenging to seek suitable electrode materials for SIBs, hindering their further development. MPs anode has received tremendous concentration focused on their advantages of large theoretical-specific capacity, low redox potential, and high electric conductivity. Despite the great potential of MPs, the feasibility in their commercial application is still under debate, and many critical issues need to be addressed. For example, almost all MPs are troubled by the large volume expansion during the process of Na insertion/extraction, which can lead to the electrode pulverization and thus electrochemical performance degradation. In addition, the feasibility of MPs as anode material is plagued by their sluggish diffusion kinetics, slow reaction kinetics (based on the conversion reaction), and so on. Therefore, researchers are adopting various modification methods to improve the Na storage performance of MPs. For better comparison, we have summarized the electrochemical properties of the typical MPs for SIBs that have been reported (as shown in Figure 20 and Table 1), on basis of which we make bold predictions about the research direction in this field, mainly including the experimental, theoretical and computational capabilities.

In principle, the Na storage capacity lies with the composition and structure of the material. Therefore, the development of MPs with new composition and structures is essential to maintain their competitiveness in SIBs. With the joint efforts from both the research and industry community, so far a diversity of MPs have been successfully synthesized through varied methods (e.g., hydrothermal, solvothermal, ball milling, electrostatic spinning, and so on). However, most of these preparation processes must
| Element                  | Electrode materials          | Rate capability                          | Cycling performance                                     | Ref. |
|--------------------------|------------------------------|------------------------------------------|---------------------------------------------------------|------|
| Sn-P                     | Sn$_4$P$_3$ particles        | —                                        | 718 mA h g$^{-1}$ @ 0.1 A g$^{-1}$, 100 cycles          | 15   |
| Sn$_4$P$_3$ @ (Sn-P)     |                              | 543 mA h g$^{-1}$ @ 0.1 A g$^{-1}$       | 465 mA h g$^{-1}$ @ 0.1 A g$^{-1}$, 100 cycles, 92.6% retention for 2nd cycle | 43   |
| Sn$_4$P$_3$/C             |                              | 650 mA h g$^{-1}$ @ 0.1 A g$^{-1}$       | 86% retention @ 0.1 A g$^{-1}$, 150 cycles             | 37   |
| Sn$_4$P$_3$/rGO           |                              | 670 mA h g$^{-1}$ @ 0.1 A g$^{-1}$       | 362 mA h g$^{-1}$ @ 1.0 A g$^{-1}$, 1500 cycles        | 17   |
| Sn-P compounds           | (98.3 wt% Sn$_4$P$_3$ + 1.7 wt% Sn) |                                        | 510 mA h g$^{-1}$ @ 0.1 A g$^{-1}$, 92.6% retention for 2nd cycle | 162  |
| Sn$_4$P$_3$/CN            |                              | 650 mA h g$^{-1}$ @ 0.1 A g$^{-1}$       | 86% retention @ 0.1 A g$^{-1}$, 150 cycles             | 37   |
| Sn$_4$P$_3$/rGO           |                              | 670 mA h g$^{-1}$ @ 0.1 A g$^{-1}$       | 362 mA h g$^{-1}$ @ 1.0 A g$^{-1}$, 1500 cycles        | 17   |
| Sn-P compounds           | (98.3 wt% Sn$_4$P$_3$ + 1.7 wt% Sn) |                                        | 510 mA h g$^{-1}$ @ 0.1 A g$^{-1}$, 92.6% retention for 2nd cycle | 162  |
| Pomegranates-structured Sn$_4$P$_3$/C | | 800 mA h g$^{-1}$ @ 0.1 A g$^{-1}$, 120 cycles | | 44 |
| Multi-shell Sn$_4$P$_3$ NSs |                              | 727 mA h g$^{-1}$ @ 0.05 A g$^{-1}$     | 303 mA h g$^{-1}$ @ 0.2 A g$^{-1}$, 500 cycles, 63% retention | 45   |
| Sn$_4$P$_3$ nanotops      |                              | 749 mA h g$^{-1}$ @ 0.05 A g$^{-1}$     | 400 mA h g$^{-1}$ @ 0.5 A g$^{-1}$, 50 cycles, 82% retention | 163  |
| Sn$_4$P$_3$/TiC           |                              | 727 mA h g$^{-1}$ @ 0.05 A g$^{-1}$     | 303 mA h g$^{-1}$ @ 0.2 A g$^{-1}$, 500 cycles, 63% retention | 45   |
| core–shell Sn$_4$P$_3$–C  |                              | 650 mA h g$^{-1}$ @ 0.1 A g$^{-1}$       | 420 mA h g$^{-1}$ @ 2 A g$^{-1}$, 2000 cycles          | 50   |
| Sn$_4$P$_3$/SbSn          |                              | ~680 mA h g$^{-1}$ @ 0.05 A g$^{-1}$    | 415 mA h g$^{-1}$ @ 0.5 A g$^{-1}$, 100 cycles, 74% retention | 56   |
| Hollow Sn$_4$P$_3$/C      |                              | 555 mA h g$^{-1}$ @ 0.2 A g$^{-1}$       | 372 mA h g$^{-1}$ @ 0.2 A g$^{-1}$, 200 cycles          | 51   |
| Sn$_4$P$_3$–P@graphene    |                              | 815 mA h g$^{-1}$ @ 0.2 A g$^{-1}$       | 550 mA h g$^{-1}$ @ 0.5 A g$^{-1}$, 1000 cycles         | 156  |
| Hollow Sn$_4$P$_3$/C      |                              | 424 mA h g$^{-1}$ @ 0.2 A g$^{-1}$       | 205 mA h g$^{-1}$ @ 2 A g$^{-1}$, 4000 cycles          | 52   |
| Sn$_4$P$_3$/graphene aerogel |                            | 787 mA h g$^{-1}$ @ 0.1 A g$^{-1}$     | 657 mA h g$^{-1}$ @ 0.1 A g$^{-1}$, 100 cycles, 77% retention | 164  |
| C@Sn$_4$P$_3$@HCF         |                              | 205 mA h g$^{-1}$ @ 0.05 A g$^{-1}$     | 219 mA h g$^{-1}$ @ 0.1 A g$^{-1}$, 200 cycles          | 165  |
| Sn$_4$P$_3$/C             |                              | 650 mA h g$^{-1}$ @ 0.1 A g$^{-1}$       | 420 mA h g$^{-1}$ @ 1 A g$^{-1}$, 400 cycles          | 166  |
| Sn$_4$P$_3$@CNF           |                              | 872 mA h g$^{-1}$ @ 0.1 A g$^{-1}$       | 336 mA h g$^{-1}$ @ 1 A g$^{-1}$, 500 cycles          | 54   |
| Sn$_4$P$_3$@CNT/C         |                              | 980 mA h g$^{-1}$ @ 0.2 A g$^{-1}$       | 449 mA h g$^{-1}$ @ 2 A g$^{-1}$, 500 cycles, 70% retention | 53   |
| Sn$_4$P$_3$@CNF           |                              | 479 mA h g$^{-1}$ @ 0.1 A g$^{-1}$       | 158 mA h g$^{-1}$ @ 5 A g$^{-1}$, 1400 cycles          | 28   |
| Sn$_4$P$_3$/HC            |                              | 460 mA h g$^{-1}$ @ 0.1 A g$^{-1}$       | ~310 mA h g$^{-1}$ @ 1 A g$^{-1}$, 400 cycles, 88% retention | 167  |
| BLCNTs@Sn$_4$P$_3$/C      |                              | ~530 mA h g$^{-1}$ @ 0.1 A g$^{-1}$   | 227 mA h g$^{-1}$ @ 0.2 A g$^{-1}$, 2000 cycles        | 168  |
| Sn$_4$P$_3$/Co$_2$P@C     |                              | 290 mA h g$^{-1}$ @ 0.1 A g$^{-1}$       | 186 mA h g$^{-1}$ @ 1 A g$^{-1}$, 400 cycles, 86.9% retention | 169  |
| SnP$_2$/C                 |                              | 860 mA h g$^{-1}$ @ 0.08 A g$^{-1}$     | 805 mA h g$^{-1}$ @ 0.15 A g$^{-1}$, 150 cycles, ~100% retention | 16   |
| SnP$_2$/HC–γ              |                              | 668 mA h g$^{-1}$ @ 0.1 A g$^{-1}$       | 430 mA h g$^{-1}$ @ 1 A g$^{-1}$, 400 cycles, 86% retention | 158  |
| SnP NCs                   |                              | 645 mA h g$^{-1}$ @ 2.5 A g$^{-1}$       | 600 mA h g$^{-1}$ @ 0.1 A g$^{-1}$, 200 cycles          | 19   |

(Continues)
| Element | Electrode materials | Rate capability | Cycling performance | Ref. |
|---------|---------------------|-----------------|---------------------|------|
| Fe-P    | FeP                 | 765 mA h g⁻¹ @ 0.05 A g⁻¹ | 321 mA h g⁻¹ @ 0.05 A g⁻¹, 60 cycles, 69% retention for 2nd cycle | 60   |
|         | FeP/graphite        | 280 mA h g⁻¹ @ 0.05 A g⁻¹ | 240 mA h g⁻¹ @ 0.05 A g⁻¹, 70 cycles, 58% retention for 2nd cycle | 65   |
|         | CNT@FeP@C           | 391 mA h g⁻¹ @ 0.2 A g⁻¹ | 295 mA h g⁻¹ @ 0.5A g⁻¹, 500 cycles, 90% retention for 2nd cycle | 66   |
|         | rGO@CoP@C-FeP       | 480 mA h g⁻¹ @ 0.1 A g⁻¹ | 456 mA h g⁻¹ @ 0.1 A g⁻¹, 200 cycles | 170  |
|         | FeP/NasGO           | 280 mA h g⁻¹ @ 0.05 A g⁻¹ | 240 mA h g⁻¹ @ 0.05 A g⁻¹, 70 cycles, 58% retention for 2nd cycle | 65   |
|         | FeP@rGO             | 428 mA h g⁻¹ @ 0.05 A g⁻¹ | 299 mA h g⁻¹ @ 0.4 A g⁻¹, 100 cycles, 97.6% retention | 75   |
|         | FeP NAs/CC          | 766 mA h g⁻¹ @ 0.1 A g⁻¹ | 110 mA h g⁻¹ @ 2 A g⁻¹, 500 cycles | 68   |
|         | M-FeP@C             | 532 mA h g⁻¹ @ 0.1 A g⁻¹ | 303 mA h g⁻¹ @ 0.25 A g⁻¹, 100 cycles, 62% retention | 171  |
|         | CNT@FeP-C           | 272 mA h g⁻¹ @ 8 A g⁻¹ | 321 mA h g⁻¹ @ 3 A g⁻¹, 1200 cycles | 172  |
|         | FePNC               | 411 mA h g⁻¹ @ 0.1 A g⁻¹ | 275 mA h g⁻¹ @ 0.2 A g⁻¹, 200 cycles | 71   |
|         | FeP/NPG             | 665 mA h g⁻¹ @ 0.05 A g⁻¹ | 378 mA h g⁻¹ @ 1 A g⁻¹, 700 cycles, 90% retention for 6th cycle | 67   |
|         | IPS/BC              | 613 mA h g⁻¹ @ 0.05 A g⁻¹ | 197 mA h g⁻¹ @ 0.5 A g⁻¹, 500 cycles | 74   |
|         | FeP@C               | 408 mA h g⁻¹ @ 0.1 A g⁻¹ | 185 mA h g⁻¹ @ 1 A g⁻¹, 500 cycles | 72   |
|         | FeP NRs/Ti          | 415 mA h g⁻¹ @ 0.1 A g⁻¹ | 208 mA h g⁻¹ @ 0.5 A g⁻¹, 1000 cycles | 173  |
|         | FeP@OCF             | 705 mA h g⁻¹ @ 0.1 A g⁻¹ | 634 mA h g⁻¹ @ 0.05 A g⁻¹, 50 cycles, 94% retention for 2nd cycle | 22   |
|         | FeP@C/rGO           | 636 mA h g⁻¹ @ 0.02 A g⁻¹ | 451 mA h g⁻¹ @ 0.2 A g⁻¹, 1000 cycles, 88.2% retention for 2nd cycle | 73   |
|         | FeP/C               | 207 mA h g⁻¹ @ 0.05 A g⁻¹ | —                     | 174  |
|         | FeP/rGO             | 421 mA h g⁻¹ @ 0.2 A g⁻¹ | 311 mA h g⁻¹ @ 1 A g⁻¹, 1000 cycles | 69   |
|         | FeP@NC              | 605 mA h g⁻¹ @ 0.1 A g⁻¹ | 400 mA h g⁻¹ @ 0.5 A g⁻¹, 2000 cycles | 70   |
|         | FeP@NPC             | 595 mA h g⁻¹ @ 0.1 A g⁻¹ | 253 mA h g⁻¹ @ 1 A g⁻¹, 300 cycles | 175  |
|         | FeP/C               | 660 mA h g⁻¹ @ 0.1 A g⁻¹ | 531 mA h g⁻¹ @ 0.2 A g⁻¹, 300 cycles | 176  |
|         | YS-Cu-FeP@C         | 406 mA h g⁻¹ @ 0.1 A g⁻¹ | 322 mA h g⁻¹ @ 1 A g⁻¹, 900 cycles | 177  |
|         | Ni₂,FeP₃,₄/CNTs     | 335 mA h g⁻¹ @ 0.1 A g⁻¹ | 143 mA h g⁻¹ @ 1 A g⁻¹, 120 cycles | 90   |
|         | CoP/FeP@PCNFs       | 459 mA h g⁻¹ @ 0.05 A g⁻¹ | 208 mA h g⁻¹ @ 5 A g⁻¹, 1000 cycles, 74% retention | 178  |
|         | FeP/CoP-NA          | 508 mA h g⁻¹ @ 0.2A g⁻¹ | 300 mA h g⁻¹ @ 5 A g⁻¹, 8500 cycles, 92% retention | 179  |
|         | FeP₄                 | —                     | 1023 mA h g⁻¹ @ 0.089 A g⁻¹, 30 cycles, 90% retention | 61   |

(Continues)
| Element | Electrode materials | Rate capability | Cycling performance | Ref. |
|---------|---------------------|-----------------|---------------------|------|
| Ni-P   | NiP/CNT             | 868 mAh g⁻¹ @ 0.1 A g⁻¹ | 364 mAh g⁻¹ @ 1.6 A g⁻¹, 200 cycles, 65% retention | 78   |
|         |                     | 494 mAh g⁻¹ @ 3.2 A g⁻¹ |                      |      |
| Ni₂P@C/GA |                   | 385.8 mAh g⁻¹ @ 0.1 A g⁻¹ | 125 mAh g⁻¹ @ 1 A g⁻¹, 2000 cycles | 30   |
|         |                     | 172.1 mAh g⁻¹ @ 2 A g⁻¹ |                      |      |
| Ni₂PcP/GN |                   | 520 mAh g⁻¹ @ 0.1 A g⁻¹ | 457 mAh g⁻¹ @ 0.3 A g⁻¹, 500 cycles, ~100% retention | 85   |
|         |                     | 291 mAh g⁻¹ @ 5 A g⁻¹ |                      |      |
| Ni₂P/NG/Ni₂P |               | 327 mAh g⁻¹ @ 0.1 A g⁻¹ | 108 mAh g⁻¹ @ 1 A g⁻¹, 400 cycles | 20   |
|         |                     | 152 mAh g⁻¹ @ 2 A g⁻¹ |                      |      |
| Ni₂P@NPC |                    | 293 mAh g⁻¹ @ 0.2 A g⁻¹ | 181 mAh g⁻¹ @ 0.5 A g⁻¹, 1200 cycles | 84   |
|         |                     | 100 mAh g⁻¹ @ 5 A g⁻¹ |                      |      |
| Ni₂P@C-N@CF |                  | 929 mAh g⁻¹ @ 0.05 A g⁻¹ | 167 mAh g⁻¹ @ 2 A g⁻¹, 1000 cycles, 0.06% decay per cycle | 79   |
|         |                     | 197 mAh g⁻¹ @ 2 A g⁻¹ |                      |      |
| Ni₂P/3DG |                    | 733 mAh g⁻¹ @ 0.05 A g⁻¹ | 230 mAh g⁻¹ @ 1 A g⁻¹, 100 cycles | 86   |
|         |                     | 273 mAh g⁻¹ @ 1 A g⁻¹ |                      |      |
| Ni₂P@N, P-C/GN |               | 271 mAh g⁻¹ @ 0.1 A g⁻¹ | 114 mAh g⁻¹ @ 2 A g⁻¹, 3000 cycles | 81   |
|         |                     | 135 mAh g⁻¹ @ 2 A g⁻¹ |                      |      |
| Ni₂P@C |                    | 373 mAh g⁻¹ @ 0.05 A g⁻¹ | 296 mAh g⁻¹ @ 0.05 A g⁻¹, 100 cycles | 83   |
|         |                     | 106 mAh g⁻¹ @ 0.8 A g⁻¹ |                      |      |
| Ni₂P@CNS/CC |                 | 514 mAh g⁻¹ @ 0.1 A g⁻¹ | 399 mAh g⁻¹ @ 0.2 A g⁻¹, 100 cycles, 90% retention | 77   |
|         |                     | 68 mAh g⁻¹ @ 2 A g⁻¹ |                      |      |
| Ni₂P@PSC |                    | 328 mAh g⁻¹ @ 0.05 A g⁻¹ | 295 mAh g⁻¹ @ 0.05 A g⁻¹, 100 cycles | 82   |
|         |                     | 77 mAh g⁻¹ @ 3.5 A g⁻¹ |                      |      |
| Ni₂P/3DG |                    | 606 mAh g⁻¹ @ 0.05 A g⁻¹ | 155 mAh g⁻¹ @ 1 A g⁻¹, 1000 cycles | 80   |
|         |                     | 158 mAh g⁻¹ @ 1 A g⁻¹ |                      |      |
| Ni₂P@C |                    | 311 mAh g⁻¹ @ 0.1 A g⁻¹ | 292 mAh g⁻¹ @ 0.1 A g⁻¹, 300 cycles | 180  |
|         |                     | 203 mAh g⁻¹ @ 1 A g⁻¹ |                      |      |
| Ni₂P@ACNT(CTAB) |              | 105 mAh g⁻¹ @ 4 A g⁻¹ | 150 mAh g⁻¹ @ 0.1 A g⁻¹, 100 cycles | 181  |
|         |                     |                      |                      |      |
| Ni₂P@rGO |                   | 394 mAh g⁻¹ @ 0.1 A g⁻¹ | 124 mAh g⁻¹ @ 1 A g⁻¹, 500 cycles | 95   |
|         |                     | 206 mAh g⁻¹ @ 5 A g⁻¹ |                      |      |
| Ni₁₂P₃@C/GNS |                  | 172 mAh g⁻¹ @ 0.05 A g⁻¹ | 165 mAh g⁻¹ @ 0.1 A g⁻¹, 500 cycles | 88   |
|         |                     | 106 mAh g⁻¹ @ 2 A g⁻¹ |                      |      |
| Cu-P   | CuP₂/C              | 550 mAh g⁻¹ @ 0.05 A g⁻¹ | 430 mAh g⁻¹ @ 0.15 A g⁻¹, 30 cycles | 93   |
|         |                     | 178 mAh g⁻¹ @ 2 A g⁻¹ |                      |      |
| Cu₂P/C |                   | 481 mAh g⁻¹ @ 0.1 A g⁻¹ | 430 mAh g⁻¹ @ 0.2 A g⁻¹, 100 cycles, 95.5% retention | 182  |
|         |                     | 308 mAh g⁻¹ @ 0.8 A g⁻¹ |                      |      |
| Cu₂P/C |                   | 630 mAh g⁻¹ @ 0.1 A g⁻¹ | 477 mAh g⁻¹ @ 0.2 A g⁻¹, 200 cycles, 91% retention | 95   |
|         |                     | 263 mAh g⁻¹ @ 0.8 A g⁻¹ |                      |      |
| Cu₃P@GNs |                   | 804 mAh g⁻¹ @ 0.1 A g⁻¹ | ~700 mAh g⁻¹ @ 0.1 A g⁻¹, 25 cycles | 94   |
|         |                     | 508 mAh g⁻¹ @ 5 A g⁻¹ |                      |      |
| CPNW   |                    | 362 mAh g⁻¹ @ 0.1 A g⁻¹ | 134 mAh g⁻¹ @ 1 A g⁻¹, 260 cycles, 0.12% decay per cycle | 33   |
|         |                     | 138 mAh g⁻¹ @ 5 A g⁻¹ |                      |      |
| Cu₃P@C |                   | 342 mAh g⁻¹ @ 0.1 A g⁻¹ | 118 mAh g⁻¹ @ 5 A g⁻¹, 2000 cycles, 72.8% retention | 161  |
|         |                     | 105 mAh g⁻¹ @ 10 A g⁻¹ |                      |      |
| Double shelled Cu₃P |     | 325 mAh g⁻¹ @ 0.05 A g⁻¹ | ~290 mAh g⁻¹ @ 0.05 A g⁻¹, 100 cycles, 87.7% retention | 183  |
|         |                     | 166 mAh g⁻¹ @ 1 A g⁻¹ |                      |      |
| Cu₃P/rGO |                 | 364 mAh g⁻¹ @ 0.02 A g⁻¹ | 117 mAh g⁻¹ @ 1 A g⁻¹, 2500 cycles | 184  |
|         |                     | 48 mAh g⁻¹ @ 5 A g⁻¹ |                      |      |
| Cu₂P₇-BP-MWCNT |             | 1460 mAh g⁻¹ @ 0.05 A g⁻¹ | 1170 mAh g⁻¹ @ 0.05 A g⁻¹, 200 cycles, 83% retention | 185  |
|         |                     | 580 mAh g⁻¹ @ 5 A g⁻¹ |                      |      |
| Cu₂P₇/CuP₂/C |            | 1300 mAh g⁻¹ @ 0.05 A g⁻¹ | 1254 mAh g⁻¹ @ 0.2 A g⁻¹, 100 cycles | 102  |
|         |                     | 550 mAh g⁻¹ @ 3 A g⁻¹ |                      |      |

(Continues)
| Element | Electrode materials | Rate capability | Cycling performance | Ref. |
|---------|---------------------|-----------------|---------------------|-----|
| Co-P | A-CoP/C,N,B -650 | 355 mAh g⁻¹ @ 0.025 A g⁻¹ 122 mAh g⁻¹ @ 1 A g⁻¹ | 217 mAh g⁻¹ @ 0.2 A g⁻¹, 100 cycles, 86.3% retention | 109 |
| Co₂P-3D PNC | | 322 mAh g⁻¹ @ 0.05 A g⁻¹ 179 mAh g⁻¹ @ 3 A g⁻¹ | 271 mAh g⁻¹ @ 0.5 A g⁻¹, 700 cycles | 122 |
| Co₂P/NC | | 429 mAh g⁻¹ @ 0.05 A g⁻¹ 193 mAh g⁻¹ @ 2 A g⁻¹ | 132 mAh g⁻¹ @ 1 A g⁻¹, 2500 cycles | 160 |
| CoP | | 570 mAh g⁻¹ @ 0.1 A g⁻¹ 80 mAh g⁻¹ @ 2 A g⁻¹ | 315 mAh g⁻¹ @ 0.1 A g⁻¹, 25 cycles, 70% retention | 92 |
| CoP@C-rGO-NF | | 713 mAh g⁻¹ @ 0.1 A g⁻¹ 155 mAh g⁻¹ @ 1.6 A g⁻¹ | 473 mAh g⁻¹ @ 0.1 A g⁻¹, 100 cycles | 111 |
| CoP/CNS | | 614 mAh g⁻¹ @ 0.05 A g⁻¹ 90 mAh g⁻¹ @ 50 A g⁻¹ | 386 mAh g⁻¹ @ 1 A g⁻¹, 900 cycles, 98.5% retention for 2nd cycle | 121 |
| CoP/rGO | | 535 mAh g⁻¹ @ 0.1 A g⁻¹ 381 mAh g⁻¹ @ 2.0 A g⁻¹ | 490 mAh g⁻¹ @ 0.1 A g⁻¹, 100 cycles | 186 |
| CoP@PPy NWs/CP | | 530 mAh g⁻¹ @ 0.125 A g⁻¹ 237 mAh g⁻¹ @ 2.5 A g⁻¹ | 369 mAh g⁻¹ @ 1.25 A g⁻¹, 1000 cycles | 117 |
| CoP/C/GA | | 330 mAh g⁻¹ @ 0.05 A g⁻¹ 143 mAh g⁻¹ @ 2 A g⁻¹ | 173 mAh g⁻¹ @ 2 A g⁻¹, 4000 cycles, 115.2% retention | 116 |
| CoP@DC@GR | | 748 mAh g⁻¹ @ 0.1 A g⁻¹ 271 mAh g⁻¹ @ 2 A g⁻¹ | 398 mAh g⁻¹ @ 0.5 A g⁻¹, 300 cycles, 70% retention | 115 |
| CoP@NC/rGO | | 694 mAh g⁻¹ @ 0.1 A g⁻¹ 353 mAh g⁻¹ @ 3.2 A g⁻¹ | 550 mAh g⁻¹ @ 0.1 A g⁻¹, 300 cycles | 125 |
| S-CoP@NPC | | 244 mAh g⁻¹ @ 0.2 A g⁻¹ 143 mAh g⁻¹ @ 5 A g⁻¹ | 230 mAh g⁻¹ @ 0.2 A g⁻¹, 370 cycles | 27 |
| CoP@C | | 330 mAh g⁻¹ @ 0.1 A g⁻¹ 209 mAh g⁻¹ @ 2 A g⁻¹ | ~120 mAh g⁻¹ @ 1 A g⁻¹, 7000 cycles, 52.4% retention for 2nd cycle | 112 |
| Fe-CoP/CM | | 625 mAh g⁻¹ @ 0.1 A g⁻¹ 208 mAh g⁻¹ @ 2 A g⁻¹ | 324 mAh g⁻¹ @ 0.5 A g⁻¹, 500 cycles | 31 |
| CoP/CC | | 707 mAh g⁻¹ @ 0.1 A g⁻¹ 53 mAh g⁻¹ @ 2 A g⁻¹ | 117 mAh g⁻¹ @ 1 A g⁻¹, 2000 cycles | 187 |
| CoP@C/C | | 449 mAh g⁻¹ @ 0.1 A g⁻¹ 162 mAh g⁻¹ @ 5 A g⁻¹ | 329 mAh g⁻¹ @ 0.2 A g⁻¹, 150 cycles | 120 |
| CoP@GF | | 368 mAh g⁻¹ @ 0.05 A g⁻¹ 164 mAh g⁻¹ @ 0.4 A g⁻¹ | 305 mAh g⁻¹ @ 0.05 A g⁻¹, 200 cycles | 118 |
| CoP₁@C | | 344 mAh g⁻¹ @ 0.025 A g⁻¹ 136 mAh g⁻¹ @ 0.25 A g⁻¹ | 212 mAh g⁻¹ @ 0.1 A g⁻¹, 80 cycles, 77.6% retention | 26 |
| CoP₂/CF | ~1000 mAh g⁻¹ @ 0.3 A g⁻¹ 535 mAh g⁻¹ @ 4 A g⁻¹ | 582 mAh g⁻¹ @ 1 A g⁻¹, 1000 cycles, 90% retention | 34 |
| Ge-P | MGeP₂ | 977 mAh g⁻¹ @ 0.12 A g⁻¹ 117 mAh g⁻¹ @ 12 A g⁻¹ | 278 mAh g⁻¹ @ 1.2 A g⁻¹, 200 cycles | 135 |
| GeP-black P | | 985 mAh g⁻¹ @ 0.05 A g⁻¹ 275 mAh g⁻¹ @ 5 A g⁻¹ | 890 mAh g⁻¹ @ 0.05 A g⁻¹, 100 cycles | 133 |
| GeP nanoflakes | | 400 mAh g⁻¹ @ 0.1 A g⁻¹ 110 mAh g⁻¹ @ 4 A g⁻¹ | 330 mAh g⁻¹ @ 0.1 A g⁻¹, 100 cycles | 136 |
| FL-GP/rGO | | 570 mAh g⁻¹ @ 0.1 A g⁻¹ 230 mAh g⁻¹ @ 2 A g⁻¹ | 230 mAh g⁻¹ @ 1 A g⁻¹, 250 cycles | 24 |
| GeP/CN | | 831 mAh g⁻¹ @ 0.1 A g⁻¹ 382 mAh g⁻¹ @ 3 A g⁻¹ | 553 mAh g⁻¹ @ 0.5 A g⁻¹, 350 cycles | 155 |
| GeP₃/C | ~920 mAh g⁻¹ @ 0.95 A g⁻¹ 520 mAh g⁻¹ @ 1.9 A g⁻¹ | 934 mAh g⁻¹ @ 0.05 A g⁻¹, 30 cycles, 94.9% retention | 134 |

(Continues)
TABLE 1 (Continued)

| Element | Electrode materials | Rate capability | Cycling performance | Ref. |
|---------|---------------------|-----------------|---------------------|------|
| GeP/C  | —                   |                 | 409 mA h g⁻¹ @ 5 A g⁻¹, 30 cycles, 58% retention | 130  |
| GeP₃−MWCNT | 1798 mA h g⁻¹ @ 0.1 A g⁻¹, 1091 mA h g⁻¹ @ 5 A g⁻¹ | 1430 mA h g⁻¹ @ 0.5 A g⁻¹, 200 cycles, 91.43% retention for 2nd cycle | 131  |
| Zn-P  | ZnP₂ bundles | 600 mA h g⁻¹ @ 0.1 A g⁻¹, 280 mA h g⁻¹ @ 5 A g⁻¹ | 600 mA h g⁻¹ @ 0.1 A g⁻¹, 85 cycles | 159  |
| ZnP₂-C | ~850 mA h g⁻¹ @ 0.09 A g⁻¹, 350 mA h g⁻¹ @ 2.7 A g⁻¹ | 883 mA h g⁻¹ @ 0.05 A g⁻¹, 130 cycles | 149  |
| Mo-P  | MoP nanorods | 460 mA h g⁻¹ @ 0.05 A g⁻¹, 116 mA h g⁻¹ @ 1.6 A g⁻¹ | 118 mA h g⁻¹ @ 1.6 A g⁻¹, 10000 cycles, 88.8% retention | 150  |
| MoP/C | 359 mA h g⁻¹ @ 0.05 A g⁻¹, 174 mA h g⁻¹ @ 1 A g⁻¹ | 180 mA h g⁻¹ @ 0.5 A g⁻¹, 250 cycles, 87.4% retention | 188  |
| MoP/CnNWs | 293 mA h g⁻¹ @ 0.1 A g⁻¹, 71 mA h g⁻¹ @ 20 A g⁻¹ | 106 mA h g⁻¹ @ 1 A g⁻¹, 3500 cycles, 0.013% decay per cycle | 189  |
| H-MoP@cGO | 520 mA h g⁻¹ @ 1 A g⁻¹, 133 mA h g⁻¹ @ 20 A g⁻¹ | 183 mA h g⁻¹ @ 10 A g⁻¹, 3000 cycles | 153  |
| MoP@NCNFs | 404 mA h g⁻¹ @ 0.1 A g⁻¹, 135 mA h g⁻¹ @ 20 A g⁻¹ | 117 mA h g⁻¹ @ 2 A g⁻¹, 1000 cycles | 154  |
| MoP/Cu₃P@cC | 598 mA h g⁻¹ @ 0.1 A g⁻¹, 103 mA h g⁻¹ @ 10 A g⁻¹ | 132 mA h g⁻¹ @ 5 A g⁻¹, 6000 cycles | 190  |
| V-P  | VP₂ (90 °C) | 241 mA h g⁻¹ @ 0.1 A g⁻¹, 131 mA h g⁻¹ @ 8 A g⁻¹ | 212 mA h g⁻¹ @ 0.5 A g⁻¹, 500 cycles, 102.4% retention | 145  |
| V₄P₇ | 235 mA h g⁻¹ @ 0.05 A g⁻¹, 90 mA h g⁻¹ @ 0.8 A g⁻¹ | 122 mA h g⁻¹ @ 0.5 A g⁻¹, 500 cycles, 96% retention | 143  |
| W-P  | WP/CC | 502 mA h g⁻¹ @ 0.1 A g⁻¹, 56 mA h g⁻¹ @ 2 A g⁻¹ | 50 mA h g⁻¹ @ 2 A g⁻¹, 1000 cycles | 146  |
| Mn-P  | MnP₄/G20 | 724 mA h g⁻¹ @ 0.05 A g⁻¹, 385 mA h g⁻¹ @ 2 A g⁻¹ | 446 mA h g⁻¹ @ 0.5 A g⁻¹, 250 cycles | 157  |

be combined with the high temperature phosphorization process, which consumes huge energy and produces toxic gases (PH₃). In addition, the preparation of some MPs is still very challenging, such as vanadium phosphides, which can only be prepared by ball milling method. Therefore, MPs with innovative synthesis methods are highly demanded. One direction is to rely on the phase diagram, which can guide the synthetic chemistry of MPs. The other direction is to scale up the existing strategies, to achieve mass production for commercial application.

Understanding the ions storage mechanism and the relationship between performance and composition/structure is very important to realize further application of MPs in energy storage. At present, sodium storage mechanism for some MPs is still unclear or controversial, which seriously hinders their development and application. To our delight, the in-situ characterization techniques and theoretical calculations in the field of batteries are becoming increasingly mature, providing a solid support for the detailed and in-depth study of the electrode evolution at nanoscale or even atomic level. Undoubtedly, the in-depth understanding of how MPs store energy will effectively guide their further application in SIB systems.

Another important factor that needs to be taken into consideration before their commercial application is the compatibility between anode and cathode materials, and electrolyte. Cathode materials with excellent electrochemical properties for SIBs have been reported, while the underdeveloped anode materials have become a stumbling block to the development of full SIBs. In view of this, the MPs anode materials with larger specific capacity and lower redox potential hold great potential to achieve large capacity and high energy density. In our opinion, the synergistic effect between anode and cathode materials, and electrolyte is indispensable to the development of full SIBs. While the relationship between the anode and cathode materials has rarely been reported. In the future, the research on the full cells should focus more on the in-depth understanding of the various reactions occurred internally.
FIGURE 20 Comparison of the electrochemical performance of advanced MPs (e.g., GeP$_3$, FeP$_4$, NiP$_3$, Sn$_4$P$_3$, Cu$_2$P$_2$, MnP$_4$, FeP$_3$, CoP$_3$, SnP$_3$, Zn$_3$P$_2$, Ni$_2$P$_3$, MoP$_4$, WP$_4$, Zn$_2$P$_2$, Co$_2$P$_3$, Ni$_3$P$_4$, Co$_3$P$_2$, Cu$_3$P$_2$, V$_4$P$_7$, and Ni$_{12}$P$_5$).

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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