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Phosphorus-Based Materials as the Anode for Sodium-Ion Batteries

Fuhua Yang, Hong Gao, Jun Chen,* and Zaiping Guo*

As a promising alternative to lithium-ion batteries, sodium-ion batteries (SIBs) have recently attracted considerable attention. Enormous effort has been devoted to investigations on the development of suitable active materials in order to improve the energy density of SIBs and give them significant cycling stability. Among the reported anode materials, phosphorus-based materials have been recognized as a major group of promising anode materials, due to the high theoretical capacity of P (2596 mA h g⁻¹) and the abundance of P rock resources. Here, the current progress on P-based anode materials is summarized, including elemental P (red/black phosphorus) and metal phosphides (Co-P, Cu-P, Fe-P, Ni-P, Se-P, Sn-P, Ge-P), and challenges and perspectives are highlighted in order to provide guidance for future research in related areas. Typical articles are also selected as specific examples, elaborating the advances in materials preparation techniques/approaches and in the structural design of P-based materials.

1. Introduction

Despite the huge success of lithium-ion batteries (LIBs), the limited nature of lithium resources has led to a focus on alternative rechargeable battery technologies, such as sodium-ion batteries (SIBs),^[1] potassium-ion batteries,^[2] and aluminum-ion batteries.^[3] SIBs in particular have gained a substantial amount of attention,^[4,5] due to the abundant sodium resources in the Earth's crust and the comparable electrochemical performance to LIBs. Nevertheless, the relatively large size of the Na⁺ ion (the radius of the Na⁺ ion is

55% larger than that of Li⁺) means that conventional LIB electrode materials are not suitable for SIBs. Therefore, developing suitable electrode materials with high theoretical capacity has become one of the key challenges to effectively improving SIB performance, in terms of both energy density and power density.^[6,7] This is because the fundamental electrochemistry of rechargeable battery devices is mainly determined by the selected active electrode materials.

A vast number of studies have been conducted on cathode materials, but the research investigation of promising anode materials is still in a relatively early stage.^[5,8] In the early period, many traditional anode materials with the intercalation mechanism were reported, such as carbonaceous materials and metal oxides,^[7,9] which showed excellent

cycling stability. Their limited theoretical capacities, however, are restricting their further application in SIBs. In order to achieve higher energy density, high-capacity anode materials need to be explored. Among the previously reported high-capacity anode materials (e.g., metals, phosphorus, phosphides, and sulfides), phosphorus-based materials, including elemental P and metal phosphides, are regarded as one of the most promising anode material groups for enhancing the energy density of SIBs.^[7,10] Phosphorus, in particular, has the highest theoretical capacity of 2596 mA h g⁻¹, based on its sodiation mechanism ($P + 3Na^+ + 3e^- \rightarrow Na_3P$), in which three electrons are required to form Na₃P. Combining P with metals to form metal phosphides, such as NiP₃, FeP, CoP, and Sn-P, can also improve the electrical conductivity and prevent the pulverization issue to some extent. In recent years, efforts have been made mainly on three aspects (surface modification, dimension reduction, and structure optimization) to improve the sodium-storage performance of P-based materials. Previous studies have demonstrated that surface modification can improve the electrochemical properties of P-based materials,^[11,12] while dimension reduction and structural optimization facilitate electron/Na⁺ transportation and alleviate the volume expansion (Figure 1).^[13–16]

Here, we focus on the recent progress regarding P-based anode materials for SIBs, especially the structural design and the fabrication process. In addition, we also summarize the various strategies and processing protocols used to enhance the electrochemical performance of the active materials.

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2. Phosphorus

Phosphorus, which is located in the 5A group of the periodic table, has three main allotropes: white, red, and black. Among them, white P (WP) is a chemically reactive and toxic material.^[22] While red P (RP) and black P (BP) are relatively stable, and both of them can effectively accommodate sodium ions,^[23,24] the large volume expansion during the sodiation process results in fast capacity fading of both RP and BP. Furthermore, RP is electrically insulating, while BP is hard to synthesize. Recently, considerable efforts have been made to solve and overcome these problems.

2.1. Red Phosphorus

As a material for SIB anodes, the advantages of RP are obvious:^[7,25–27] i) a high theoretical capacity of 2596 mA h g^{-1} (in view of the reaction of P with three Na^+ to form Na_3P); ii) relatively low redox potential (0.4 V vs Na/Na^+), which could result in high energy density, whereas the redox potential of RP in LIBs is $\approx 0.8 \text{ V}$ versus Li/Li^+ ; and iii) the abundance of P rock resources makes RP favorable for industrialization. Despite the above merits, the poor conductivity ($\approx 1 \times 10^{-14} \text{ S cm}^{-1}$) and the large volume changes ($\approx 400\%$) of the pure RP lead to fast capacity fading and low Coulombic efficiency, thus impeding the application of RP in SIBs.^[23,28–30] To overcome these scientific and technical issues, researchers have designed RP-based composites with various frameworks to improve its conductivity and cycling stability, and the design considerations mainly arise from the following aspects: i) the need to introduce various conductive matrices in order to improve the electronic conductivity and suppress the volume expansion of RP during electrochemical processes; and ii) the need to minimize the RP particle size and even form RP–carbon bonds to control the P volume changes and shorten the ion and electron diffusion lengths during cycling.^[31,32]

2.1.1. Ball/Hand-Milling Processes to Obtain RP/C Composites

Ball milling is one of the main approaches to preparing RP/C composites, due to its advantageous processing properties, such as being facile, simple, and easily scaled up.^[12,33,34] Amorphous RP/C composites produced via the ball-milling method as an anode for SIBs were reported by Oh and co-workers^[12] and Yang and co-workers,^[34] simultaneously and separately in 2013. As shown in the scanning and transmission electron microscopy (SEM and TEM) images (Figure 2a,b) from Oh's work,^[12] the particle size of the final product is uneven, ranging from hundreds of nanometers to several micrometers. This composite delivered a reversible capacity of 1890 mA h g^{-1} at 143 mA g^{-1} , and the capacity fading was less than 7% over 30 cycles (Figure 2c,d). Even though the performance was much better than that of the pure RP electrode, the low current density and limited number of cycles still leave room for improvement.

Similarly, an RP/graphene nanosheet composite was synthesized by the ball-milling method^[35] (Figure 2e). In this

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experiment, it was found that the existence of P–O–C bonds was a critical factor in maintaining contact between the RP and the graphene nanosheets. As a result, an outstanding cycling stability of 1700 mA h g^{-1} for over 60 cycles was obtained (Figure 2f). Despite some advances, the ball-milling strategy still presents some issues: i) ball milling is a high-energy-consuming and structure-destroying process; and ii) the relatively large particle size of RP and the incomplete coverage by

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Figure 1. Schematic illustration of P-based materials as anode for sodium-ion batteries. a) Reproduced with permission.^[17] Copyright 2017, Elsevier. b) Reproduced with permission.^[14] Copyright 2015, Royal Society of Chemistry. c) Reproduced with permission.^[18] Copyright 2017, Elsevier. d) Reproduced with permission.^[19] Copyright 2015, American Chemical Society. e) Reproduced with permission.^[16] Copyright 2017, Wiley-VCH. f) Reproduced with permission.^[11] Copyright 2014, American Chemical Society. g) Reproduced with permission.^[20] Copyright 2016, Wiley-VCH. h) Reproduced with permission.^[13] Copyright 2017, American Chemical Society. i) Reproduced with permission.^[21] Copyright 2015, Nature Publishing Group.

the conductive matrix would hinder future improvement of RP/carbon composites for SIBs.

A simple hand-milling method has also been employed to fabricate an RP/multiwalled carbon nanotube (MWCNT) composite.^[28] Compared with ball-milled composites, the simple hand mixing of RP/MWCNTs with microsized RP and uneven coverage of the MWCNTs resulted in an even faster capacity fading (capacity retention of 76.6% after just ten cycles).

2.1.2. Vaporization/Adsorption Technique to Synthesize RP/C Composites

The vaporization/adsorption strategy is an alternative approach to preparing RP/carbon composites.^[36] Compared to the ball-milling method, the vaporization/adsorption strategy is a nondestructive process, ensuring that the RP is uniformly dispersed in the integrated carbon matrix. Normally, the mechanism for this technique is:^[29,36,19,37] i) the RP is heated to form P_4 vapor at a temperature higher than the RP sublimation temperature; ii) the sublimation is driven by pressure differences, and the P_4 vapor diffuses into the empty spaces of the carbon

framework/matrix, where it is then adsorbed and deposited on the internal surfaces; and iii) after condensation, the P_4 turns back into RP to yield the nanostructured RP/carbon composite.

Wang and co-workers^[19] reported a modified vaporization–condensation method to prepare RP/single-walled carbon nanotube (SWCNT) composites for SIBs. The synthesis was conducted at a higher temperature (600 °C) and under vacuum conditions, which could create a strong driving force to cause easy adsorption of the P_4 vapor into the SWCNTs and is favorable for a uniform dispersion of RP in the SWCNTs. The RP/SWCNT composite exhibited a capacity of $\approx 700 \text{ mA h g}^{-1}$ under 50 mA g^{-1} (based on the composite weight) and a high capacity retention of 80% after 2000 cycles (Figure 3a,b).

Subsequently, an amorphous RP@N-doped graphene (GN)^[38] was synthesized by a phase-transformation route, through which amorphous RP was embedded in the N-doped graphene paper to form a “bread-and-butter”-like structure. The RP@GN composite could demonstrate stable cycling performance and outstanding rate capacity of 809 mA h g^{-1} under 1500 mA g^{-1} (Figure 3c,d). Although greatly enhanced performance was achieved, the uncontrollability of the RP distribution in the traditional vaporization/adsorption technique would affect the loading level and the carbon coverage of the RP.^[13,16]

In order to optimize the loading level and solve the carbon coverage problems for the RP/C composite, our group reported an advanced vapor-redistribution strategy

using an in situ localized redistribution approach to fabricate a C@RP/graphene aerogel (GA) composite.^[20] Graphene aerogel has abundant active sites and an interconnected 3D porous framework, which would provide excellent accommodation for RP particles and a superior 3D conductive network. In the fabrication process, the RP is first incorporated into the GA, and then polypyrrole is utilized to further encapsulate the RP throughout the whole framework, which is followed by vapor redistribution of the localized RP (Figure 4a). Unlike the traditional vaporization/adsorption strategy, where RP vapor is adsorbed from the outside, this technique vapor-redistributes the localized RP throughout the whole structure. This technique can control the distribution paths of the RP vapor and improve the loading level of RP. The C@RP/GA features nano-sized RP homogeneously distributed in and mostly covered by the designed 3D porous structure (Figure 4b,c). The C@RP/GA electrode exhibited a specific capacity of 1867 mA h g^{-1} at 260 mA h g^{-1} after 100 cycles and excellent rate performance (Figure 4d,e).

Compared to the ball-milling method, the vaporization/adsorption technique is a mild process that does not destroy the structure, although the phase-transformation process will

Figure 2. a) TEM and b) SEM images of amorphous RP/C composite. c) Charge-discharge curves and d) cycling performance of RP/C composite. (a-d) Reproduced with permission.^[12] Copyright 2013, Wiley-VCH. e) Schematic illustration of the synthesis of RP/G composite. f) Cycling performance of RP/G composite under 260 mA g^{-1} . (e,f) Reproduced with permission.^[35] Copyright 2014, American Chemical Society.

Figure 3. a) TEM image of RP/SWCNT composite. b) Cycling performance and Coulombic efficiency of the RP/SWCNT composite under 2 A g^{-1} . (a,b) Reproduced with permission.^[19] Copyright 2015, American Chemical Society. c) SEM image of amorphous RP@GN frameworks. d) Cycling performance and Coulombic efficiency of the RP@GN composite. c,d) Reproduced with permission.^[38] Copyright 2016, American Chemical Society.

inevitably generate white phosphorus, which is a toxic and very reactive material.

2.1.3. Other Strategies to Fabricate RP-Based Electrodes

Currently, ball-milling and vaporization/adsorption are the mainstream approaches used to fabricate RP-based composites

for SIB anodes. Although the ball-milling technique is easy and productive, the resultant RP particle size is uneven and not small enough. While the vaporization/adsorption method can reduce the RP particle size to several nanometers, the RP loading level of the composite is normally less than 50%. In light of this, recently, new strategies have been proposed to fabricate RP-based electrode. One representative example is the synthesis of hollow RP nanospheres (HPNs) via a

Figure 4. a) Schematic illustration of the synthesis process for C@RP/GA composite in three steps. b,c) TEM (b) and high-resolution TEM (HRTEM) (c) images of C@RP/GA composite. d,e) Cycling performance (at 0.1C) (d) and rate performance (e) of pre-redistributed RP/GA, RP/GA, C@RP/GA, RP, and C@GA composites. Reproduced with permission.^[20] Copyright 2016, Wiley-VCH.

solvothermal method.^[39] Zhu and co-workers^[39] demonstrated that, as the reaction between NaN_3 and PCl_5 ($10\text{NaN}_3 + 2\text{PCl}_5 \rightarrow 2\text{P} + 10\text{NaCl} + 15\text{N}_2$) proceeds, RP nuclei are assembled around the N_2 bubbles, and thus, when the N_2 bubbles detach from the NaN_3 surface, HPNs are formed. In the report, HPNs were used as anode materials without combining them with carbon. The HPNs, which were 300 nm in size, exhibited a reversible capacity of 1500 mA h g^{-1} at 1300 mA g^{-1} after 80 cycles. Feng and co-workers^[40] reported the sodium behavior of core@shell nanostructured RP@Ni-P. The core@shell RP@Ni-P was synthesized by electroless deposition of Ni on the surfaces of RP particles, and then chemical dealloying was performed in HCl aqueous solution to control the Ni-P shell thickness. As shown in this work, the Ni-P shell plays an important role in the sodium-storage performance of the RP@Ni-P. The Ni-P shell not only facilitates intimate contact between the RP particles and enhances the conductivity of the composite, but also tolerates the large volume expansion during sodiation and maintains a strong electrode structural integrity.

Cui and co-workers^[41] proposed a new method to fabricate an RP/3D-carbon framework (P/C composite), in which P_4O_{10} and poly(ethylene glycol) (PEG) served as the RP and carbon precursors, respectively. P_4O_{10} and PEG were first mixed in an oven at 80°C and then transferred into an alundum boat and heated at 900°C . At the high temperature of 900°C , PEG was carbonized to form a carbon framework, and meanwhile P_4O_{10} was reduced to RP. Thanks to the volumetric shrinkage from P_4O_{10} to RP and the carbon consumption, void space was created, which was large enough for the volume expansion during the RP sodiation. This P/C composite delivered a reversible capacity of 920 mA h g^{-1} at 200 mA g^{-1} after 160 cycles. Chen and co-workers^[31] successfully encapsulated nanosized RP particles in graphene scrolls (P-G) using liquid N_2 to assemble RP and graphene oxide (GO). In the preparation procedure, nanosized RP particles were selected and mixed with GO solution evenly by ultrasonication. When the mixture was subjected to liquid N_2 , the GO rapidly rolled up due to the quick-freezing process, and the RP was encapsulated inside. After a reduction process on the P-GO with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, P-G was obtained. The as-prepared P-G with an RP content of 52.2% showed a reversible capacity of 2355 mA h g^{-1} (based on the RP) with retention of 92.3% after 150 cycles.

Recent progress on the materials synthesis and electrochemical performance of RP-based anodes for SIBs is summarized in Table 1. Overall, the ball/hand-milling synthesized RP composite exhibits relatively inferior sodium-storage performance compared to the other methods, which can be ascribed to the uneven and large particle size, ranging from tens of nanometers to several micrometers.^[16,42] Compared to the ball-milling method, the vaporization/adsorption technique can reduce RP particles to the nanoscale. Decreased particle size is believed to be an effective way to enhance the electrochemical utilization of the RP, not only because of the short Na^+ /electron diffusion paths, but also because the small size can alleviate the strain resulting from the RP volume expansion.^[41,16,34,42] As shown in Table 1, excellent electrochemical performance can be achieved using the vaporization/adsorption

method. Nevertheless, the RP content of most RP-based composites resulting from this technique is typically low (normally below 50%). The use of a large amount of carbon in the RP composite can certainly reduce the energy density of the electrode.^[39]

2.2. Black Phosphorus

BP has a layered structure similar to that of graphite, featuring large interlayer channels, which are large enough to store sodium ions.^[45] Although the theoretical capacities of RP and BP are the same, BP possesses higher bulk electrical conductivity ($\approx 10^2 \text{ S m}^{-1}$ vs $\approx 10^{-14} \text{ S m}^{-1}$ for RP) and higher density (2.69 g cm^{-3} vs 2.36 g cm^{-3} for RP),^[11,21] which are favorable for electron transport and realizing high energy densities, indicating that BP could be a better anode material than RP. Researchers have revealed that pure BP can be directly used as an electrode material. The major issue that is obstructing BP application, however, is the complicated synthesis process.

Typically, BP is derived from WP or RP through various methods, such as high-pressure synthesis,^[46,47] high-temperature annealing,^[46,48] and recrystallization in mercury^[49] or liquid bismuth.^[50] These methods are either time-consuming or use complex apparatus, and also, in some cases, toxic chemicals are involved. A scalable synthesis of BP by a high-energy mechanical-milling method was reported by Park and Sohn.^[24] BP can be prepared at ambient temperature and pressure using this method, but a protective gas needs to be provided during the synthesis process. Lang et al.^[51] proposed a mineralizer-assisted transformation method under simple and safe conditions, although the output of this method was relatively low. To prepare a BP-based anode for SIBs, Komaba and co-workers^[47] put RP into a capsule, which was then pressurized to 4.5 GPa. After heating at 800°C for 1 h, BP was obtained. The as-obtained BP was ball milled with acetylene black to fabricate the BP/C composite.

Cui and co-workers^[21] investigated the sodiation mechanism for BP. Ex situ X-ray diffraction (XRD) results (Figure 5d) revealed that the sodiation process consists of two steps, which include sodium-ion intercalation (between 0.54 and 1.5 V) and a further alloying process (below 0.54 V). In situ TEM (Figure 5a–c) showed that the large volume change of BP ($\approx 500\%$) mainly occurred along the y and z -axial directions. A sandwich-like phosphorene-graphene composite was fabricated, in which the phosphorene was derived from bulk BP particles (Figure 5e,f). The phosphorene-graphene electrode exhibited high reversible capacity and excellent capacity retention at different current densities. Its excellent performance can be attributed to its unique structural design: i) the graphene enhances the electrical conductivity of the whole composite; ii) the 2D nanosheet structure provides short transport distances for sodium ions and electrons; and iii) graphene can serve as an elastic buffer to accommodate the volume changes. Similarly, Shahbazian-Yassar and co-workers^[52] found that Na^+ ions prefer to diffuse along the [100] direction in phosphorene, according to the in situ TEM results.

Table 1. Recent progress on materials synthesis and electrochemical performance of RP-based anodes for SIBs.

Materials description	Synthesis method	RP size	RP content [%]	Electrolyte	Cycling data ^{a)}	Rate capacity ^{b)}	Ref.
RP/Super P	Ball milling	–	70	1 M NaPF ₆ in EC/DEC (1:1)	1200/60th/0.25C	640/4C	[34]
RP/Super P	Ball milling	100 nm–4 μm	70	0.8 M NaClO ₄ in EC/DEC (1:1)	1750/30th/0.143C	1540/2.86C	[12]
RP/Graphene	Ball milling	10–200 nm	70	1 M NaClO ₄ in EC/DEC (1:1) with 10% FEC	1706/0.26C	520/5.2C	[35]
RP-CNT	Ball milling	Sub-micrometer to a few micrometers	≈70	1 M NaClO ₄ in EC/DEC (1:1) with 10% FEC	1586/100th/0.52C	≈850/5.2C	[33]
RP/CNT	Hand milling	Average 3 μm	30	1 M NaClO ₄ in EC/DEC (1:1) with 5% FEC	1283.3/10th/0.14C	–	[28]
RP/C@rGO	Ball milling and spray drying	≈100 nm	23.2	1 M NaPF ₆ in EC/DEC (1:1) with 5% FEC	1935/100th/0.1C	≈1200/2C	[43]
RP@rGO	Vaporization/adsorption	10–600 nm	61.64	1 M NaClO ₄ in DMC with 10% FEC	1482/300th/1.6C	219.5/4.8C	[13]
RP@N-doped microporous carbon	Vaporization/adsorption	<1 nm	22.6	1 M NaClO ₄ in EC/DMC (1:1)	2566/100th/0.15C 1991/1000th/1C	1287/9C	[44]
RP@N-doped graphene	Vaporization/adsorption	–	≈66	1 M NaPF ₆ in EC/DEC (1:1)	≈2287/120th/0.2C ≈1515/350th/0.8C	1226/1.5C	[38]
RP@CMK-3	Vaporization/adsorption	–	31.54	1 M NaClO ₄ in EC/DMC (1:1)	2188/60th/0.52C 1020/210th/13C	650/25.5C	[29]
RP-single-walled carbon nanotube	Vaporization/adsorption	5 μm	≈40	1 M NaClO ₄ in FEC/DMC (1:1)	1275/200th/0.5C 550/2000th/2C	750/2C	[19]
C@RP/graphene aerogel	Vaporization/adsorption	10–20 nm	47.2	1 M NaClO ₄ in EC/DEC (1:1) with 10% FEC	1867/100th/0.26C 1095.5/200th/2.6C	1861/5.2C	[20]
RP/N-doped carbon nanofiber	Vaporization/adsorption	–	27.5	1 M NaClO ₄ in EC/DEC (1:1) with 10% FEC	2658/55th/0.1C	–	[32]
Hollow RP nanospheres	Wet-chemical synthesis	≈300 nm	100	1 M NaClO ₄ in EC/DMC (1:1) with 5% FEC	1675/80th/1.3C 969.8/600th/2.6C	278.4/10.4C	[39]
Core@shell structured RP@Ni-P	Electroless deposition with chemical dealloying	<200 nm	93.83	1 M NaClO ₄ in PC with 5% FEC	1339/200th/0.26C 436/2000th/5C	522/5.2C	[40]
RP/3D carbon framework	Carbothermic reduction	≈10 nm	36	1 M NaPF ₆ in EC/DEC (1:1) with 10% FEC	2555/160th/0.2C	944/10C	[41]
RP in graphene scrolls	Quick-freezing process	100–150 nm	52.2	1 M NaClO ₄ in EC/DEC (1:1) with 5% FEC	2173.7/0.25C	1084/4C	[31]

^{a)}The cycling data are summarized as capacity/corresponding cycle number/corresponding current density. The specific capacity was calculated based on the weight of phosphorus. The unit of capacity is mA h g^{−1}. For all the data, 1C equals 1000 mA g^{−1}; ^{b)}The rate capability is summarized as capacity/corresponding current density. The specific capacity was calculated based on the weight of phosphorus. The unit of capacity is mA h g^{−1}. For all the data, 1C equals 1000 mA g^{−1}.

Dahbi et al.^[47] studied the influence of electrolyte additives on the electrochemical performance of BP. A BP electrode with a fluoroethylene carbonate/vinylene carbonate (FEC/VC) additive always exhibits better results than its counterpart without. Further surface characterization techniques revealed that the FEC/VC additive facilitates the formation of a more stable and thinner solid electrolyte interphase (SEI) layer. This SEI layer creates lower resistance on the BP surface and can protect the electrolyte from decomposition. Therefore, a higher specific capacity and Coulombic efficiency were obtained.

The advantages of the orthorhombic BP are threefold: thermodynamic stability, good electrical conductivity, and the layered crystal structure with a larger interlayer channel size than that of graphite. Compared to the commercially available

RP, however, BP with its complicated synthesis process is still unsuitable for further application.

3. Metal Phosphides

Phosphorus has poor conductivity, while metals such as Cu, Fe, and Co are conductive. Combining P with these metals to form metal phosphides is expected to improve the conductivity of the composite.^[53–57] Conductive metal is formed during the charge–discharge processes and can serve as an electron-transport channel to enhance the conductivity of the electrode materials.^[55] What is more, it is believed that the presence of the secondary ingredient dilutes the concentration of P species and can buffer its volume changes during repeated

Figure 5. a–c) Time-lapse TEM images of sodiation in black. d) Ex situ XRD patterns of black phosphorus taken before charging and after charging down to different voltages. e) TEM image of the phosphorene–graphene hybrid. Scale bar, 2 μm . f) HRTEM image of a cross-section of the phosphorene–graphene hybrid. Reproduced with permission.^[21] Copyright 2015, Nature Publishing Group.

sodiation and desodiation.^[54,55,58,59] For some metal phosphides, metal and phosphorus elements can be converted back to the starting metal phosphide during the desodiation process, thus healing the cracks induced by the sodiation and alleviating the pulverization.^[54,58–60]

3.1. Phosphidation Method

Metal phosphides are usually derived from elemental metals or metal oxides. To prepare metal phosphides, two main phosphidation methods are proposed: ball milling and NaH_2PO_2 phosphidation.

Because of its facility and high productivity, ball milling is widely used to fabricate metal phosphide anode materials. For example, Chou and co-workers^[59] prepared a $\text{Sn}_{4+x}\text{P}_3$ @(Sn–P) compound through ball milling, using red phosphorus and tin powder (in the molar ratio of 3:5) as the starting materials. The obtained product had a particle size of 30–80 nm. It should be noted that the stoichiometric ratio of the starting materials is a crucial parameter in the ball-milling process. In Chou's experiment,^[59] when a Sn:P ratio of 4:3 was used, pure Sn_4P_3 was harvested. Similarly, ternary metal phosphides can also be synthesized using this method.

Ouyang and co-workers^[61] reported a ZnGeP_2/C composite synthesized using the ball-milling method. Zn, Ge, and red P were first subjected to high-energy ball milling to form ZnGeP_2 . Then, high-energy planetary milling of the as-prepared ZnGeP_2 and Super P was conducted to prepare the final ZnGeP_2/C .

NaH_2PO_2 can chemically transform the precursors into metal phosphides at a temperature around 300 $^\circ\text{C}$ without destroying the precursor nanostructure.^[62] This means that NaH_2PO_2 phosphidation can be a good way to prepare nanostructured metal phosphides.^[62–64] Wang and co-workers^[62] reported pomegranate-structured Sn_4P_3 @ spheres synthesized by the NaH_2PO_2 phosphidation method. In this experiment, SnO_2 @C “pomegranates” prepared by the aerosol-spray-pyrolysis method were hand milled with NaH_2PO_2 , and the mixture was then annealed at a temperature of 280 $^\circ\text{C}$ for 10 min. After cooling down and washing the product, pomegranate-structured Sn_4P_3 @ spheres were obtained. Other nanostructured metal phosphides, such as Cu_3P nanowires (CPNWs)^[65] and core-shell CoP @C polyhedra,^[18] were also fabricated using this method.

Apart from the above phosphidation methods, other methods, such as high-temperature annealing,^[66] solvothermal phosphidation,^[67] and the solution chemistry method,^[68] were also reported.

3.2. Reaction Mechanism

To date, reported P-based alloy compounds for SIBs include Co–P (CoP),^[56] Cu–P (CuP₂, Cu₃P),^[65,69] Fe–P (FeP, FeP₄),^[57,70] Ni–P (NiP₃),^[71] Se–P (Se₄P₄),^[54] Sn–P (Sn₄P₃, SnP₃),^[58,72] and Ge–P (GeP₅).^[73] These metal phosphides can be broadly divided into two types: metal inactive and metal active, depending on whether the metal in the metal phosphide is electrochemically active or not. The metal-inactive metal phosphides include Co–P (CoP), Cu–P (CuP₂, Cu₃P), Fe–P (FeP, FeP₄), and Ni–P (NiP₃). The presence of the highly conductive metal in this kind of metal phosphide can improve the electrical conductivity of these compounds.^[55] The capacity of these compounds is only contributed by the P, however, since the metal is totally inactive. Their charge–discharge mechanism can be summarized by the following conversion reaction (Equation (1)):

Unlike the previous type, the metal in the metal-active type is electrochemically active (e.g., Se–P, Sn–P, and Ge–P). Apart from the conversion reaction, an alloying reaction also takes place in these metal-active metal phosphides to form Na_yM:

Because both the metal and the P react with sodium ions, the metal-active metal phosphides usually possess higher theoretical capacities than the metal-inactive ones. The theoretical capacity depends on the species and content of the metal in the metal phosphides.

Ex situ XRD and TEM are usually used to reveal the sodium-storage mechanism of metal phosphides. Electrodes at different discharge–charge states are disassembled and examined to investigate the phase and structure changes during the sodiation/desodiation process. For example, Cu₃P electrodes were tested by XRD.^[65] As shown in the results, during the sodiation process, the peak corresponding to Cu₃P gradually diminished and totally disappeared during the discharge. Meanwhile, a new peak corresponding to the (103) planes of Na₃P emerged, and the intensity of two peaks arising from the Cu content was enhanced, indicating that the Cu₃P was transformed to Na₃P and Cu. For the desodiation process, the reverse composition changes were observed. Therefore, a conversion mechanism for Cu₃P was proposed: Cu₃P + 3Na⁺ ↔ Na₃P + 3Cu. Similarly, Oh and co-workers^[53] also investigated the sodiation mechanism for Sn₄P₃ using ex situ XRD and ex situ TEM. Upon sodiation, the intensity of the XRD peak for Sn₄P₃ decreased, and crystalline NaSn and Na₁₅Sn₄ were observed in the TEM images, indicating that an amorphous Na_xP phase was formed. On desodiation, the intensity of the XRD peak for Sn₄P₃ increased. This suggests that the conversion reaction of Sn₄P₃ to Na_xP and Na₁₅Sn₄ is reversible. Recently, Chen and co-workers^[54]

proposed an Na-storage reaction mechanism for Se₄P₄, using ex situ XRD, ex situ TEM, and in situ Raman techniques.

3.3. Metal-Active Phosphides

Because of their higher theoretical capacity than metal-inactive phosphides, metal-active phosphides have attracted considerable attention, especially tin phosphides. Yang and co-workers^[72] reported an early investigation of Sn₄P₃. Sn₄P₃/C composite was synthesized using the ball-milling method. Ex situ XRD patterns of Sn₄P₃/C at different charge and discharge states indicated the presence of Na₃P and Na₁₅Sn₄, proving that Sn is electrochemically active in the Sn₄P₃/C (Figure 6a,b). This Sn₄P₃/C demonstrated a high reversible capacity of 850 mA h g^{−1} and stable cycling performance, while the Sn/C and P/C composites showed poor capacity retention (≈60% capacity loss in the first 25 cycles) (Figure 6c). Moreover, most of the reversible capacity was delivered at the low potential of ≈0.3 V, meaning that Sn₄P₃ should be a promising anode material for high-energy SIBs. After this, more efforts were made to develop the potential of Sn₄P₃. For example, Liu et al. reported yolk–shell Sn₄P₃@C nanospheres, in which the Sn₄P₃ nanoparticles were surrounded by a carbon shell.^[14] The void space between the Sn₄P₃ particles and the carbon shell was rationally designed to accommodate the volume expansion of Sn₄P₃. Therefore, the presence of an internal void space prevents the nanostructure of this anode material from being destroyed and the SEI layer on the outside surface from being disrupted. Thanks to this unique structure, high reversible capacity, excellent rate performance, and outstanding cycling stability were obtained.

Similar to tin phosphides, selenium phosphide was also proposed as a new metal-active phosphide, by Chen and co-workers in 2017.^[54] A series of characterization results revealed that the sodiation process of Se₄P₄ consists of three steps: i) Se₄P₄ is first transformed to amorphous Na_xSe₄P₄; ii) then Na₂Se and elemental P are formed from Na_xSe₄P₄; and iii) finally, elemental P further reacts with Na⁺ to form Na₃P (Figure 6d–f). During the sodiation process, 20 Na⁺ ions are involved, giving a high theoretical capacity of 1217 mA h g^{−1}. This ball-milling-synthesized Se₄P₄ has a reversible capacity of 1048 mA h g^{−1} (≈86% of the theoretical capacity), and 804 mA h g^{−1} is retained after 60 cycles. It is believed that the excellent cycling stability is attributable to the synergistic effects: during the sodiation process, the elemental P can prevent the aggregation of Na₂Se, while the semiconductive Na₂Se provides conducting pathways to facilitate the reactions of the insulating P.

3.4. Metal-Inactive Phosphides

There is no doubt that the use of an electrochemically inactive metal, such as Cu, Fe, or Ni, can decrease the theoretical

Figure 6. a) Schematic illustration of the Na-storage mechanism in Sn₄P₃ electrode. b) Ex situ XRD patterns of the Sn₄P₃/C electrode at different charge and discharge states. c) Comparison of the reversible capacities of Sn₄P₃/C, Sn/C, and P/C electrodes at a current density of 100 mA g^{−1}. a–c) Reproduced with permission.^[60] Copyright 2014, American Chemical Society. d) Schematic illustration of the sodiation/desodiation of Se₄P₄. e) Ex situ XRD patterns of Se₄P₄ during the electrochemical reaction with Na. f) Ex situ HRTEM images of the electrode at different states in the discharge/charge process. d–f) Reproduced with permission.^[54] Copyright 2016, Wiley-VCH.

Figure 7. a,b) SEM (a) and TEM (b) images of CPNWs. a,b) Reproduced with permission.^[65] Copyright 2016, Wiley-VCH. c,d) SEM (c) and TEM (d) images of the core-shell CoP@C polyhedra anchored on reduced graphene oxide. c,d) Reproduced with permission.^[18] Copyright 2017, Elsevier.

capacity of metal phosphides, since the metal makes no contribution to the capacity of these metal phosphides. Even so, the advantages of the metal-inactive type phosphides are also obvious: i) the metals are highly conductive, which is helpful for fully utilizing the P capacity; ii) these metal-inactive phosphides experience relatively less volume expansion than the metal-active type because no volume expansion occurs in the inactive metals.

Cu₃P nanowires (CPNWs)^[65] grown on a copper current collector were reported by Yan and co-workers. This nanostructured Cu₃P exhibited outstanding cycling stability. This excellent cycling ability was ascribed to the unique 1D features of CPNW and its small size, which are favorable for electrolyte penetration, electron transportation, and strain accommodation (Figure 7a,b). To further verify this, CPNWs with different sizes were synthesized, and it was found that the CPNWs with large size suffered from fast capacity decay. Yin and co-workers^[18] fabricated core-shell CoP@C polyhedra anchored on reduced graphene oxide (rGO) from core-shell Co@C structures derived from zeolitic imidazolium framework-67. The core-shell-structured CoP@C nanoparticles were homogeneously dispersed on the surface of rGO (Figure 7c,d). When used as an anode material for SIBs, this composite exhibited excellent rate performance and long cycling life, which can be explained by the good

conductivity of rGO and the void space in the core-shell structure to buffer the volume expansion.

To fully achieve the potential of both types of metal phosphides, most efforts have been devoted to modifying the electrochemical properties of the electrode. Recent progress has led to great improvements in metal phosphide. As summarized in Table 2, one effective method is tuning the microstructure. Nanosized particles not only provide short diffusion paths for sodium ions and electrons to enhance the rate capability, but also have a large surface area to guarantee adequate contact between the electrode and the electrolyte.^[14,65,17] Another method is synthesizing carbon composite.^[55,58] Much research work has shown that combining metal phosphides with carbon can effectively enhance the conductivity of the metal phosphides.^[55,67] As a supporting material, the carbon matrix can also prevent the aggregation of the homogeneously dispersed metal phosphide nanoparticles and interconnect the separate particles. The initial Coulombic efficiency of many metal phosphide anodes is still less than 70%, which is mainly due to the formation of the SEI layer. Electrolyte research has revealed that the electrolyte additive FEC can help to form a more stable SEI layer, but it also reduces the initial Coulombic efficiency.^[62]

4. Summary and Perspectives

P has the largest theoretical capacity among the potential anode materials for SIBs, but the poor electrical conductivity of RP has impeded its application. Therefore, the use of carbon is important in RP-based electrodes in order to enhance its conductivity. The large amount of carbon that is needed, however, can also decrease the energy density of the RP electrode. To develop a high-energy RP-based electrode, further research should focus on improving the RP loading level. For example, the advanced vapor-redistribution strategy reported by our group can achieve a high RP loading level of $\approx 50\%$,^[20] whereas the RP contents of most RP/C composites prepared by the traditional vaporization/adsorption technique are $\approx 30\%$. Unlike RP, BP has a high electrical conductivity of $\approx 10^2 \text{ S m}^{-1}$, meaning that a conductive matrix such as carbon is not necessary in the BP electrode. The main obstacle for BP is its complicated synthesis process, for which extremely high temperature and pressure are required. Thus, more efforts need to be made to develop a new, simple method to synthesize BP in the future.

For metal phosphides, although the progress made in the past several years is significant, further research is still highly desirable: i) new metal-active phosphides should be developed. Metal-active phosphides represent a promising type of high-energy-density anode material. To date, however, only

Table 2. Recent progress on the material synthesis and electrochemical performance of metal phosphide anodes for SIBs.

Materials description	Synthesis method	Initial Coulombic efficiency	Electrolyte	Cycling data ^{a)}	Rate capability ^{b)}	Ref.
Tin phosphide						
SnP ₃ /C	Ball milling	71.2%	1 M NaClO ₄ in FEC/DMC (1:1)	≈800/150th/0.15C	400/2.5C	[58]
Sn _{4+x} P ₃ @(Sn-P)	Ball milling	≈72%	1 M NaClO ₄ in EC:DEC (1:1) with 5% FEC	465/100th/0.1C	58.2/10C	[59]
Sn ₄ P ₃	Ball milling	≈73%	1 M NaClO ₄ in EC:DEC (1:1) with 5% FEC	650/100th/0.1C	–	[53]
Sn ₄ P ₃ /C	Ball milling	77.3%	1 M NaPF ₆ in EC/DEC with 5% FEC	≈364/150th/0.1C	244/1C	[60]
Sn ₄ P ₃ /rGO	Solvothermal phosphidation	46.6%	1 M NaClO ₄ in PC with 5% FEC	656/100th/0.1C	391/2C	[67]
Sn ₄ P ₃ nanoparticles	Solvothermal phosphidation	≈53%	1 M NaClO ₄ in EC/DEC with 5% FEC	305/10th/0.05C	–	[74]
Yolk-shell Sn ₄ P ₃ @C nanospheres	Solvothermal phosphidation	43.8%	1 M NaClO ₄ in PC with 5% FEC	515/50th/0.1C	421/3C	[14]
Sn ₄ P ₃ @C spheres	NaH ₂ PO ₂ phosphidation	90.7%	1 M NaPF ₆ in dimethoxyethane (DME)	700/120th/0.1C	–	[62]
		72.7%	1 M NaPF ₆ in EC/DMC	380/110th/0.1C		
		59.8%	1 M NaPF ₆ in EC/DMC with 10% FEC	580/120th/0.1C		
Sn ₄ P ₃ nanotops	Solution chemistry method	72.7%	1 M NaClO ₄ in PC with 5% FEC	≈490/80th/0.2C 400/80th/0.5C	339/1C	[68]
Cobalt phosphide						
CoP particle	Ball milling	65.2%	1 M NaClO ₄ in EC:DEC (1:1) with 5% FEC	315/25th/0.1C	80/2C	[56]
CoP@C-rGO-NF (nickel foam)	NaH ₂ PO ₂ phosphidation	47.3%	1 M NaClO ₄ in PC with 5% FEC	437.1/100th/0.1C	46.2/1.6C	[18]
Co ₂ P/Ni ₂ B-Co-doped carbon	High temperature annealing	56.5%	1 M NaPF ₆ in EC/PC	315/70th/0.05C 216.8/100th/0.2C	110/1C	[75]
Copper phosphide						
CuP ₂ /acetylene black	Ball milling	65%	1 M NaClO ₄ in EC:DEC (1:1) with 5% FEC	≈450/100th/0.2C	308/0.8C	[69]
CuP ₂ /Super P	Ball milling	≈67%	1 M NaClO ₄ in EC:DEC (1:1) with 8% FEC	≈430/30th/0.15C	178/2C	[55]
Cu ₃ P nanowire	NaH ₂ PO ₂ phosphidation	80.6%	1 M NaClO ₄ in EC:DEC (1:1) with 5% FEC	249.2/50th/0.1C 215.2/100th/0.2C 178.8/100th/0.5C 133.8/260th/1C	≈120/5C	[65]
Iron phosphide						
FeP ₄	Ball milling	84.1%	1 M NaPF ₆ in EC/DEC with 2% FEC	1023/30th/0.089C	≈930/3.6C	[70]
FeP	Ball milling	60.2%	1 M NaClO ₄ in EC:DEC (1:1)	321/60th/0.05C	–	[57]
FeP/graphite	Ball milling	30.8%	1 M NaClO ₄ in EC:DEC (1:1)	175/70th/0.05C	134/0.5C	[76]
CNT@FeP@C	NaH ₂ PO ₂ phosphidation	–	1 M NaClO ₄ in EC:DEC (1:1)	415/100th/0.1C 295/500 th /0.5C	268/1.5C	[66]
Germanium phosphide						
GeP ₅ /graphite	–	92%	1 M NaClO ₄ in EC:DEC (1:1)	1220/60th/0.1C	900/1.5C	[73]
Nickel phosphide						
NiP ₃	High temperature annealing (HT)	89% (HT)	1 M NaClO ₄ in PC with 5% FEC	≈1075/20th/0.16C (HT)	–	[71]
	Ball milling (BMR)	85.5% (BMR)		≈990/20th/0.16C (BMR)		
	Ball milling (BMS)	97% (BMS)		≈900/20th/0.16C (BMS)		
Selenium phosphide						
Se ₄ P ₄	Ball milling	70.6%	1 M NaClO ₄ in EC/PC (1:1) with 5% FEC	804/60th/0.05C	332/3C	[54]

^{a)}The cycling data are summarized as capacity/corresponding cycle number/corresponding current density. The specific capacity was calculated based on the weight of composite. The unit of capacity is mA h g⁻¹. For all the data, 1C equals 1000 mA g⁻¹. ^{b)}The rate capability is summarized as capacity/corresponding current density. The specific capacity was calculated based on the weight of composite. The unit of capacity is mA h g⁻¹. For all the data, 1C equals 1000 mA g⁻¹.

Sn–P, Ge–P, and Se–P have been reported. Other active metals should be explored to synthesize metal-active phosphides, considering that these metals can effectively accommodate Na⁺. ii) Apart from the electrode materials, research on other

components, such as electrolyte additives and binders, should be conducted. These components also play an important role in electrode performance, but little research has been reported on them.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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