DEVELOPMENT OF ADVANCED ANODE MATERIALS AND SOLID-STATE ELECTROLYTE FOR SODIUM-ION BATTERY

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ABSTRACT

Na-ion batteries (NIBs) are promising candidates for widely used Li-ion batteries (LIBs) and have attracted increasing attention due to the abundance of sodium sources, the even global distribution of such sources, and NIBs’ similar intercalation chemistry to LIBs. However, the current existing anode materials are still not satisfying for the practical application due to their low specific capacity or limited cycling life. Therefore, Chapter 3 and 4 focuses on development of phosphorus-based anode material for NIBs. In Chapter 3, phosphorus-graphene nanosheet (P/G) hybrid is synthesized by ball-mill method and show extremely high specific discharge capacity of 2077 mAhg\(^{-1}\) for the initial cycle as well as capacity retention of 95% relative to the second cycle after 60 cycles. Taking the facile and general method as well as the low cost starting materials into account, this promising P/G hybrid nanostructured anode has a great potential for practical application in high performance NIB. In Chapter 4, two phosphorus-carbon composites, P@carbon nanotube (P@CNT) and P@porous carbon, are developed. Nano-sized phosphorus particles have been deposited on the surface of two carbon hosts through well-controlled vaporization-deposition-conversion method. By confining P inside micropores of carbon host, P@porous carbon composite exhibits a high initial specific capacity of 1705 mAhg\(^{-1}\), (~ 852 mAhg\(^{-1}\) composite) and superior capacity retention of 92% after 100 cycles and 46% after 1000 cycles, which is much better than that for P@CNT composite.

All the above mentioned work have been done by using organic liquid electrolyte. It is well known that severe safety issues exist in NIBs because of extremely high reactivity of sodium metal in volatile and flammable organic liquid electrolyte. Solid-state NIB with solid-state electrolyte (SSE) is attractive because it can potentially address the safety issues and also achieve long cycle life. Therefore, Chapter 5 and 6 focus on development of sulfide-based solid-state electrolyte for NIBs. In Chapter 5, a new Na-ion SSE, Na\(_3\)P\(_{0.62}\)As\(_{0.38}\)S\(_4\), has been discovered with
an exceptionally high conductivity of 1.46 mS cm\(^{-1}\) at room temperature, enhanced moisture stability, superior electrochemical stability and performance. In Chapter 6, a new Na-ion superior conductor, Na\(_{11}\)Sn\(_{1.94}\)PS\(_{12}\), with a unique structure different from that for any reported solid-state electrolyte has been developed and exhibits a superior grain conductivity of 3.0 mS cm\(^{-1}\) and total ionic conductivity of 1.06 mS cm\(^{-1}\) at 25 °C.
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Chapter 1
Development of Sodium-ion Batteries

1.1 Introduction

Electrical energy storage technologies are critically needed to address the electric grid’s most pressing need for improved stability, resiliency and efficiency, and to enable use of intermittent renewable energy sources such as wind and solar. Electrochemically-based electrical energy storage can efficiently store energy in chemical form and reversibly release it according to demand, making it well-suited to respond to changing grid needs.[1-3] In addition, electrochemical energy storage possesses a number of desirable features, including pollution-free operation, high round-trip efficiency, and flexible power and energy characteristics to meet different grid functions.[4] Although today’s lithium-ion batteries (LIBs) possess high energy density and good cycle life, battery cost and material availability remain major issues and prevent widespread use of LIBs for energy storage in the grid.[4,5] A substantial part of the material cost stems from the lithium precursor, lithium carbonate. The dramatic growth in demand for LIBs from power electronics, electric vehicles, and the electric grid has significantly driven up the price of Li$_2$CO$_3$ to around 4500 USD/ton in 2010.[6] In addition, although supplies are not in immediate danger of exhaustion, lithium abundance is comparatively low, and supplies are likely to dwindle – with increasing costs leading up to that point – in the foreseeable future.[4,6,7]

Na-ion batteries (NIBs) present an alternative to the much more heavily studied LIBs. Sodium carbonate is much cheaper than lithium carbonate, with a cost of only around 200 USD/ton in mid-2014.[8] It is also several orders of magnitude more abundant; sodium is the sixth most abundant element in the earth’s crust.[9] with extractable sodium carbonate reserves
totaling at least 23 billion tons in United States alone and at least 47 billion tons globally, over
300 times larger than globally-identified lithium carbonate reserves. In addition, low-cost
electrode materials have been identified for NIBs.[10-13] These factors, combined with the
promise of capitalizing on the similarity of the Na-ion system to the Li-ion system to speed up
development, have prompted increasing research on NIBs in recent years.[6,14]

1.2 Principle of Na-ion battery

A rechargeable battery is made up of one or more electrochemical cells that are connected in a suitable way to provide the required voltage or capacity. Each cell is composed of cathode and anode (both sources of reversible electrochemical reactions) separated by an electrical insulated membrane and a liquid electrolyte solution containing dissociated salts (as shown in Figure 1-1). During charge process, Na-ions transfer from cathode to anode through inner circuit formed by electrolyte, and meanwhile, electron transfer from anode to cathode through outer circuit. For the discharge process, both Na-ions and electrons transfer back via the previous circuit. The amount of electrical energy, expressed either per unit of weight (Whkg⁻¹) or per unit of volume (WhL⁻¹), that a battery is able to deliver is a function of the voltage (V) and capacity (Ahkg⁻¹ or mAhg⁻¹), calculated by Faraday’s law (Eq. 1-1).

\[
q = \frac{nF}{3.6 M}
\]  
(Eq. 1-1)

where,

\[ q = \text{Specific capacity (mAhg}^{-1}) \]

\[ n = \text{Electrons-transfer number (dimensionless)} \]

\[ F = \text{Faraday constant (sAmol}^{-1}) \]

\[ M = \text{molecular weight of electrode material (gmol}^{-1}) \]
The max capacity of the battery can thus be described by the equation and graphs shown in Figure 1-2. If the capacity of the anode is kept constant at 372 mAhg\(^{-1}\), the overall battery capacity will reach up to 130 mAhg\(^{-1}\) when the capacity of cathode increases from 130 to 200 mAhg\(^{-1}\). If the capacity of the cathode is kept constant at 200 mAhg\(^{-1}\), the overall battery capacity will reach up to 180 mAhg\(^{-1}\) when the capacity of anode increases from 370 to 2000 mAhg\(^{-1}\). It is clear that both cathode and anode determines the overall battery specific capacity.
1.3 Cathode materials for Na-ion battery

Layer-structured oxides Na_xMO_2 (M = Ni, Co, Mn, Fe, etc.) is a very important group of cathode materials in NIBs. The structure of these materials are composed of alternative Na layers and transitional metal (TM) layers in the oxygen framework. Various arrangement of Na layers and TM layers as well as different Na positions in the structure categorize these cathode materials into two main groups: O3 type and P2 type (shown in Figure 1-3). The first letter “O” or “P” refers to the nature of the site occupied by Na-ion (prismatic or octahedral), and “2” or “3” refers to the number of transition metal layers in the repeat unit perpendicular to the layering. Figure 1-3a shows the O3-type structure has the Na-ion layers and TM layers closely packed in the ABCABC pattern. P2-type structure (Figure 1-3b) has the ABBA pattern.
Both O3-\text{Na}_x\text{CoO}_2 (0.83<x<1) and P2- \text{Na}_x\text{CoO}_2 (0.67<x<0.8) were studied as cathode material in NIBs, inspired by the success of LiCoO\textsubscript{2} in LIBs. However, the battery performance of Na\textsubscript{x}CoO\textsubscript{2} is not as good as its lithium counterpart owing to the larger ionic radius of Na\textsuperscript{+} (1.06 Å) than that for Li\textsuperscript{+} (0.76 Å). The delivered specific capacity of 70-100 mAh\textsuperscript{−1} is only 30 – 43% of the theoretical capacity (235 mAh\textsuperscript{−1} based on the composition NaCoO\textsubscript{2}). \cite{15} Na\textsubscript{x}MO\textsubscript{2} is considered to be more promising than Na\textsubscript{x}CoO\textsubscript{2} due to its low cost. O3- Na\textsubscript{x}MO\textsubscript{2} delivered a capacity of 185 mAh\textsuperscript{−1} within the voltage range from 2 to 3.8 V and retained the capcity of 132 mAh\textsuperscript{−1} after 20 cycles. By moving the cut-off voltage to 4 V, the P2- Na\textsubscript{0.7}MO\textsubscript{2} delivered a capacity of 163 mAh\textsuperscript{−1} with capacity retention of ~ 67% after 50 cycles. Another attractive cathode material is NaFeO\textsubscript{2}, while whose lithium counterpart has no electrochemical acitivity against lithium. NaFeO\textsubscript{2} has a potential plateau at 3.3 V (v.s. Na\textsuperscript{+}/Na), corresponding to the
oxidation of Fe\(^{3+}\) to Fe\(^{4+}\), and could deliver a reversible capacity of 80-100 mAh\(^{-1}\) within the voltage range from 2 to 3.4 V. But moving the cut-off voltage to 3.5 V results in the fast capacity decay caused by irreversible structure change and Na-ion conduction path loss.

Mimicking its analogue LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\), NaNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) has also been studied as cathode, which shows a reversible capacity of 120 mAh\(^{-1}\), within voltage range from 2 – 3.75 V (v.s. Na\(^+\)/Na). The report of P2-Na\(_{2/3}\)Fe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) further boosts the development of cathode materials for NIBs. It delivered a reversible capacity of 190 mAh\(^{-1}\) in the potential range of 1.5–4.3 V, ~78.5% of the theoretical capacity (242 mAh\(^{-1}\)). However, the issue of its poor cycling stability needs to be addressed, which is due to complicated phase transmission from P2 (P6\(_3\)/mmc , pristine) to O4 (P6\(_3\), fully charged) to P2 (P6\(_3\)/mmc, 3.4–2.0 V) and to P2 (C\(_{mcm}\), 2.0–1.5 V). Ni substitution in NaNi\(_{0.25}\)Mn\(_{0.25}\)Fe\(_{0.5}\)O\(_2\) shows better capacity retention of 90.4% after 50 cycles. But further investigations on the effect of Ni substitution should be conducted because of lower delivered capacity of 140 mAh\(^{-1}\) and thinner voltage window 2.1 – 3.9 V in comparison with P2-Na\(_{2/3}\)Fe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\).

1.3.2 NASICON type cathode materials

NASICON is an acronym for sodium (NA) Super Ionic CONductors, which is a promising cathode candidate for NIBs. NASICON Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) is a typical cathode with the theoretical capacity of 117 mAh\(^{-1}\), due to the redox reaction V\(^{3+/4+}\). In the structure, tetrahedral PO\(_4\) and octahedral VO\(_6\) are connected through common corner and build the fast Na-ion conduction pathways. Compared to its high ionic conductivity, electrical conductivity of Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) is a critical issue. Therefore, various of Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/carbon composites have been developed as cathode and showed greatly impressive electrochemical performance. By dispersing
Na$_3$V$_2$(PO$_4$)$_3$ nanograins on acetylene carbon nanospheres, the composite reveals reversible capacity of $\sim$117 mAh$^{-1}$ at 0.5 C and 97 mAh$^{-1}$ at 5 C with capacity retention of $\sim$96.4% after 200 cycles. Later, the core-shell structured Na$_3$V$_2$(PO$_4$)$_3$@carbon (thin layer of carbon coating on the surface of Na$_3$V$_2$(PO$_4$)$_3$ paticles) was developed with well-controlled carbon cocontent in the final products. The one with carbon content of 6% exhibits a reversible capacity of 114 mAh$^{-1}$ at 1 C with capacity retention of 50% after 1000 cycles. Other carbon materials, like 1D carbon nanotude and 2D graphites, are also introduced into the system to enchance the overall electrical conductivity of the composite. However, the performance of these obtained cathode materials are not as good as abovementioned ones.

1.3.3 Other Na-ion cathodes

Besides the abovementioned layer-structured oxides and NASICON type cathode, there are many other categories of Na-ion cathodes, like pyrophosphates, fluorophosphates, sulfates and etc.. Pyrophosphates Na$_2$MP$_2$O$_7$ (M = Fe, Co, Mn) is an attractive family of Na-ion cathodes, because of their structural diversity and stability, and high Na-ion mobility. Take Na$_2$FeP$_2$O$_7$ as an example. It possesses a 3D conduction channel for Na-ions, built by Fe$_2$O$_{11}$ dimers and bridged P$_2$O$_7$ groups. The cathode material delivers a reversible capacity of 90 mAh$^{-1}$ within voltage window 2 – 4.5 V. Similarly, Na$_2$CoP$_2$O$_7$ exhibites a reversible capacity of 80 mAh$^{-1}$.

In the case of fluorophosphates, Na$_2$FePO$_4$F and Na$_2$CoPO$_4$F are potential candidates for cathode in NIBs, both of which have 2D conduction pathway for Na-ions. Those two materials show similar reversible capacity of 100 mAh$^{-1}$, but with different potential plateau 3 V (v.s. Na$^+$/Na) for Na$_2$FePO$_4$F and 4.3 V (Na$^+$/Na) for Na$_2$CoPO$_4$F.
Studies on sulfates are limited. Alluaudite-type $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ and krohnkite-type $\text{Na}_2\text{Fe}_2(\text{SO}_4)_2\cdot2\text{H}_2\text{O}$ are two examples. The former one shows a reversible capacity of 100 mAh$^{-1}$ with an average working potential at 3.8 V, while the latter one with 70 mAh$^{-1}$ and 3.25 V.

1.4 Anode materials for Na-ion battery

Besides cathode, anode materials also play an important role in determining the battery’s specific capacity, and thus energy density and specific power (Figure 1-2). The challenges in developing Na-ion anodes have been significant. Graphite, the most popular Li-ion anode cannot be directly used in NIBs due to the larger size of Na$^+$ and hence the higher intercalation barrier.[16-18] Si, one of the most promising next-generation anode materials for LIBs appears to be inert to sodium insertion at temperatures up to at least 60°C.[19,20] The major scientific challenge therefore resides in developing suitable anode materials that could be applied in NIBs.

1.4.1 Hard carbon

Currently hard carbon, also known as non-graphitizable carbon, is a widely-used anode material for NIBs. Its voltage profiles is shown in Figure 1-4 with Na metal as counter electrode and different organic electrolytes. There are two typical voltage regions: a slope (region I) and a plateau (region II, near 0 V), corresponding to the Na-ions intercalation into graphene interlayers and filling of pores in the carbons, respectively.
The development of high-capacity carbon compounds for NIB was triggered by the work from Stevens and Dahn in 2000, who found that glucose-derived hard carbon exhibited a reversible capacity of ~ 300 mAh g\(^{-1}\) in NIB. After this, carbon black was found to be electrochemical active against Na and delivered a reversible capacity of 200 mAh g\(^{-1}\) in a full cell with Na\(_{0.7}\)CoO\(_2\) as cathode. Carbon nanofibers obtained from cellulose achieves a stable capacity of 176 mAh g\(^{-1}\) under the current density of 200 mAg \(^{-1}\) over 600 cycles. Open nanoporosity in hard carbon is found to affect the specific capacity of hard carbon anodes. Bommier et al. discovered that increasing surface area resulted into lower specific capacity.

### 1.4.2 Sb-based anode

Alloy-type anode materials such as Sb, Sn, Ge, and P are considered to be promising candidates for anode in NIB, due to their high theoretical capacity as shown in Figure 1-5.
Micron-sized Sb has been demonstrated as a promising anode in NIBs with a very stable capacity of 500 – 600 mAhg\(^{-1}\). Interestingly, Sb shows a better cycling stability in NIB than that in LIB, which is in great contrast with the common sense that better capacity retention is achieved in LIB rather than NIB due to smaller ionic radius of Li\(^+\). The possible reason for this phenomena could be attributed to the reduced anisotropic mechanical stress due to the repeated formation of only one crystalline phase for Na (Na\(_3\)Sb) instead of three crystalline phases for Li (Sb, Li\(_2\)Sb, Li\(_3\)Sb). The rate performance of Sb anode could be enhanced by decreasing particle size into nanoscale. 20 nm Sb nanocrystals could still deliver the capacity of 500 mAhg\(^{-1}\) even at the current density of 20 C. But the largely increased surface area due to decreasing particle size leads to a lower initial coulombic efficiency, which is ascribed to the decomposition of electrolyte on the Sb surface to form solid-electrolyte interphase (SEI).

For alloy-type material, large volume expansion upon sodiation is a sever issue. The volume change for Sb during sodiation/desodiation could reach up to 293 % (from Sb to Na\(_3\)Sb). Therefore, the issues caused by volume change need to be addressed in order to achieve good cycling stability. Sb-based binary alloy compounds M\(_x\)Sb\(_y\) (M = Mo, Al, and Cu) are thus

Figure 1-5. Theoretical gravimetric and volumetric specific capacities of various anode materials for Na-ion batteries. Ref[22]
developed, where electrochemical inactive M serve as buffering matrix to accommodate the volume change of Sb. Thin film AlSb and Mo$_2$Sb$_7$ show a similar capacity of ~ 400 mAh g$^{-1}$ with no observation of crystalline phase upon sodiation/desodiation. In contrast, Cu$_2$Sb follows the conversion mechanism, where Na converted Cu$_2$Sb to crystalline Na$_3$Sb and Cu. Beside building alloy compound, carbon matrix is also introduced to the system, not only enhancing overall electrical conductivity but also suppress the volume change caused by Sn. Sn/C composite, obtained by mechanical milling of commercial Sb powder and conductive carbon, exhibits a reversible capacity of ~ 640 mAh g$^{-1}$ with negligible capacity decay over 100 cycles. Moreover, Sb/CNT and Sb/carbon fiber are also developed by ball milling and electrospinning, respectively. Both of these two composites achieved high reversible capacity (> 400 mAh g$^{-1}$) and good cycling stability (>100 cycles).

1.4.3 Sn-based anode

Sn-based alloy material is another promising group of anode materials in NIB. The theoretical capacity of Sn is 847 mAh g$^{-1}$, corresponding to the formation of Na$_{15}$Sn$_4$. Similar with Sb, Sn also suffers from large volume change (420%) upon sodiation. In order to achieve stable cycling performance, two strategies “alloy compounds and carbon matrix” are also adopted for Sn-based anode. Take Sn$_{0.9}$Cu$_{0.1}$ as an example. The compound was synthesized using a surfactant-assistant wet chemistry method, and showed a reversible capacity of 420 mAh g$^{-1}$ at 0.2 C with capacity retention of 97% in 100 cycles. The addition of Cu into Sn is found not only to greatly reduce charge transfer resistance, thus enhancing rate performance, but also suppress the aggregation among nanoparticles, ensuring a long-term cycling stability. Other Sn-Cu binary systems, like (Cu$_6$Sn$_3$)$_{1-x}$C$_x$ ($x = 0.15 – 0.52$), are also studied as anode in NIB, and found to achieve improved electrochemical performance. For Sn/carbon composite, carbon matrix was
built to accommodate for large volume change of Sn. Sn nanoparticles coated by carbon was
developed by carbonization of tin oxide nanoparticles dispersed in resorcinol-formaldehyde gels
in an argon atmosphere. The composite shows a promising cycling stability. However, the
thickness of carbon layer on the Sn particles play a great role in determining specific capacity and
rate performance, due to its effects on Na-ion diffusion. Other carbon materials, like CNT-coated
soft cellulose fibers, graphene, graphene oxide, were also introduced to the system serving as
buffer matrix to alleviate volume change of Sn. In addition to those two common strategies,
developing a proper binder is another effective method to address the issues caused by large
volume change. In the case of Sn, three-dimensional cross-linkable binders such as polyacrylic
acid (PAA) and carboxymethyl cellulose (CMC) was developed to enhance the cycle
performance, mainly due to its ability of keeping the integrity of the electrode by inhibiting the
deformation of electrode.

1.4.4 Phosphorus-based anode

As shown in Figure 1-5, phosphorus (P) has the highest gravimetric (2595 mAhg\(^{-1}\)) and
volumetric capacity among alloy anode materials in NIB. It was found to electrochemically
sodiate and form Na\(_3\)P when used as anode in NIB. Phosphorus has three main allotropes: white,
black and red. White phosphorus is poison and chemically not stable, which cannot be used as
anode materials. Black phosphorus is thermodynamically and chemically most stable one and has
higher conductivity than red phosphorus. However, its synthesis is difficult and requires high
temperature and high pressure, which leads to the lowest commercial value among the three
forms. Different from white and black phosphorus, red phosphorus is chemically stable,
abundant, low-cost and eco-friendly, which make it promising for high-energy LIBs. Red P thus
has attracted great attention as the most outstanding anode candidate for next generation NIBs,
exhibiting the following remarkable merits: 1) an extremely high theoretical capacity of 2595 mAhg\(^{-1}\) based on the fully alloy sodiated state (Na\(_3\)P); 2) a relatively safer operational potential (0.45V \(\text{vs Na/Na}^+\)); 3) eco-friendliness and abundance. Despite those advantages of P, its intrinsic drawbacks are the main hurdles for its practical application. Firstly, it has a very low electronic conductivity (1×10\(^{-10}\) S cm\(^{-1}\)), which makes electrochemical redox reactions difficult. Secondly, P suffers an extremely large volume variation (up to 300%) during sodium insertion and extraction. This volume change can cause critical issues including pulverization of the active material, unstable growth of the solid-electrolyte interphase (SEI), and loss of contact between the active material and the conductive matrix, leading to poor capacity, low coulombic efficiency, and fast capacity fading. The situation becomes even worse when making it for practical application that necessitates the operation at high temperature (>50 °C). These low conductivity and extreme volume changes present crucial challenges for overcoming the failure mechanism of P anodes and must be addressed in order to enhance the conductivity, secure the stability of the entire electrode and thereby improve the battery performance.

Similar with other alloy-type materials (Sb, Sn, and etc.), alloy compounds and carbon matrix have been utilized to address its two intrinsic issues. In the alloy compound case, M\(_x\)P\(_y\) (M = Sn, Co, Ni, and etc.) have been studied as anode materials in NIB. Sn\(_4\)P\(_3\) was prepared by mechanical milling method with a reversible capacity of 700 mAhg\(^{-1}\) and negligible capacity decay within 100 cycles. The addition of Sn into P not only enhance its electrical conductivity, but also inhibits the aggregation of Na\(_3\)P/P nanoparticles. NiP\(_3\) is another promising anode candidate and was prepared by solid-state reaction. The material delivered a higher specific capacity of 1000 mAhg\(^{-1}\) than that for Sn\(_4\)P\(_3\), but with a worse capacity retention of 89 % within 15 cycles. The poor cycling stability is possibly due to agglomeration of active material and continues decomposition of electrolyte on the newly exposed surface, which indicates that the
amount of metal (Sn, Ni, and etc.) into P has a great effect on cycling stability of the final alloy compound.

In the case of P/carbon composite, various kinds of materials have been developed. Amorphous red P/carbon composite was firstly reported in 2013 as anode for NIB with a high reversible capacity of 1890 mAhg\(^{-1}\) and great cycling stability over 30 cycles. Considering its low redox potential, the obtained P/C composite enables the NIBs to have energy density similar with that of LIBs. A similar work was also reported by Qian et al., which showed a reversible capacity of 1750 mAhg\(^{-1}\) and capacity retention of 57% in 140 cycles. Fluoroethylene carbonate (FEC) was introduced into electrolyte as additive in both of these two works, which were found to greatly enhance the cycling stability of the anode material, probably due to its role in keeping the stability of SEI. Besides 0 D material, 1 D carbon materials, like carbon nanotube and carbon nanofiber, are also introduced to the system to form P/CNT or P/CNF composite. Red P/single-walled CNT composite was developed by vaporization-conversion-deposition method and delivered a high reversible capacity of 700 mAhg\(^{-1}\) based on the total mass of P/C composite under the current density of 50 mAg\(^{-1}\)\_composite. The composite showed a reversible capacity of ~250 mAg\(^{-1}\)\_composite and high capacity retention of 80% after 2000 cycles under the current density of 2000 mAg\(^{-1}\)\_composite. 2D material graphene is also utilized to accommodate the large volume of P upon sodiation/desodiation. The composite P encapsulated in graphene scrolls was developed and characterized as anode in NIB, which delivered a high reversible capacity of 2355 mAhg\(^{-1}\) and an excellent capacity retention of 92.3% after 150 cycles under the current density of 250 mAg\(^{-1}\). In addition to these abovementioned carbon materials, the P/C composite by encapsulating P into porous carbon have been developed. P/MOF-derived nitrogen-doped microporous carbon with P content of 22.6 wt% delivered a reversible capacity of 600 mAhg\(^{-1}\) after 100 cycles under the current density of 150 mAg\(^{-1}\), and 450 mAhg\(^{-1}\) after 1000 cycles under the current density of 1000 mAg\(^{-1}\).
1.5 Solid-state electrolyte for Na-ion battery

Liquid electrolytes composed of Na-ion salts (e.g., NaClO₄ or NaPF₆) and organic solvents (e.g., ethylene carbonate or dimethyl carbonate) are generally used. These electrolytes cause serious safety concerns, plus some extra troubles as they are quite vulnerable to violent decomposition due to extremely high reactivity of Na metal deposited from overcharging. Replacing the flammable liquid electrolyte with solid-state electrolyte (SSE) would make batteries much safer and achieve long cycle life, and thereby accelerate their deployment in critical energy technologies where safety is a major concern such as in large-scale energy storage.

In order to meet the all-solid-state battery’s requirements, Na-ion SSE need to possess: 1) high ionic conductivity to reduce the resistance polarization effects; 2) good thermodynamic stability in a wide temperature range; 3) great physical and chemical compatibility with anode and cathode materials. The reported Na-ion SSEs could be categorized into several groups that are summarized below.

1.5.1 Beta-alumina

β-alumina is a well-known SSE used in high-temperature Na-sulfur battery and Na-metal chloride batteries. There are two types of β-alumina based on their different crystal structures: β-Al₂O₃ with space group 194 (P6₃/mmc) and β”-Al₂O₃ with space group 160 (R3m). The composition for those two are Na₂O-(8-11)Al₂O₃ and Na₂O-(5-7)Al₂O₃, respectively, where β”-Al₂O₃ has lower content of alumina but with higher ionic conductivity. The crystal structure of β”-Al₂O₃ is shown in Figure 1-6, where the basic unit is composed of spinel blocks and conduction planes. The spinel blocks is a four layer ABCA stack of oxygen and aluminum ions, while the conduction plane contains fewer oxygen ions and more rooms for Na-ions.
Single crystals of $\beta''$-Al$_2$O$_3$ shows a high ionic conductivity of 0.1 S cm$^{-1}$ in the plane direction at room temperature, which could reach up to 1 S cm$^{-1}$ at 300 °C. In contrast, polycrystalline $\beta''$-Al$_2$O$_3$ exhibits a lower ionic conductivity of 0.24 S cm$^{-1}$ at 300 °C and 0.38 S cm$^{-1}$ at 400 °C. Although $\beta''$-Al$_2$O$_3$ shows impressive ionic conductivity, its harsh synthesis condition makes its large-scale application complicated and expensive. For the solid-state synthesis method, it is very difficult to obtain a uniform product, in which other phases, like $\beta$-Al$_2$O$_3$ and NaAlO$_2$, are formed along grain boundaries. Also, the wetting issue of Na metal on the surface of $\beta''$-Al$_2$O$_3$ forces its application at high temperature (like 300 °C), under which Na metal becomes liquid.
1.5.2 NASICON type solid-state electrolytes

Another promising candidate is NASICON-type SSE, which was first developed by Goodenough et al. in 1976, showing a high ionic conductivity. The original NASICONs are Na$_{1+x}$Zr$_2$Si$_{3-x}$P$_{3-x}$O$_{12}$ (0≤x≤3), of which Na$_3$Zr$_2$Si$_2$PO$_{12}$ shows room-temperature conductivity of 5.3 mS cm$^{-1}$. The crystal structure of Na$_3$Zr$_2$Si$_2$PO$_{12}$ is shown below in Figure 1-7, which has 3D network. The SiO$_4$ and PO$_4$ tetrahedral share the common corner with ZrO$_6$ octahedra, and for every two octahedral sites there are three tetrahedral sizes comprising two silicate and one phosphate center. Na-ions are locating in the interstitial sites, and migrate within a zigzag-shape 3D conduction pathway. Besides its high ionic conductivity, its excellent stability against moisture is another advantage in practical application. However, this material has a low stability in contact with molten sodium metal or molten sodium salts, which greatly inhibits its application in Na metal battery (e.g. high-temperature Na-S battery).

![NASICON structure in rhombohedral symmetry, showing ZrO$_6$ and (Si,P)O$_4$ polyhedra. Dark-shaded circles represent Na(1) positions, light-shaded circles represent Na(2) positions, and curved arrow represents the conduction path of Na$^+$ ions.[23]](image)
Na$_4$Zr$_2$Si$_3$O$_{12}$ mixed with TiO$_2$ was also developed as SSE for NIB, and exhibited a room-temperature ionic conductivity of 0.49 mScm$^{-1}$. Compared to this, NASICON material Na$_{1.8}$Ti$_{1.2}$Al$_{0.8}$(PO$_4$)$_3$ showed a lower ionic conductivity of $10^{-5}$ S cm$^{-1}$ at 200 °C.

### 1.5.3 Sulfide-based solid-state electrolytes

Sulfide-based SSE is another promising candidate because of their high ionic conductivity, good contact with electrode, low-temperature process capability, and low grain boundary resistance, which have been proved in all-solid-state LIBs.[24-29] Na$_3$PS$_4$, a classic sulfide SSE for NIB, was firstly discovered by Jansen and Henseler in 1992, exhibiting relatively low ionic conductivity of $1 \times 10^{-3}$ mScm$^{-1}$ at room temperature. The obtained Na$_3$PS$_4$ is determined to be tetragonal phase in the space group $P-42_1c$ (No. 114) with two formula units per unit cell. The temperature dependent ionic conductivity of tetragonal Na$_3$PS$_4$ (t-Na$_3$PS$_4$) is shown in the Figure 1-8a. The huge increase in ionic conductivity in the temperature range between 474 and 550 °C is claimed to be due to phase transition according to the differential thermal analysis (DTA) as shown in Figure 1-8b. However, the claimed “phase transition temperature” is so close to the melting temperature (510 °C), which makes the explanation on the ionic conductivity enhancement questionable.
Inspired by this work, Hayashi et al. developed glass-ceramic Na$_3$PS$_4$, and claimed it a stabilized “high-temperature phase” in ref [34]. The obtained Na$_3$PS$_4$ has a different XRD pattern from the reported t-Na$_3$PS$_4$ (Figure 1-9), and was indexed by a cubic phase. However, this “cubic” phase is equivalent to tetragonal phase to some extent based on the DFT calculations, see details in Appendix A. The obtained Na$_3$PS$_4$ shows a much higher ionic conductivity of 0.2 mS cm$^{-1}$ at room temperature and wide voltage window (from -0.5 to 5 V) against sodium metal.
Even though the ionic conductivity reaches 0.2 mScm\(^{-1}\) for glass-ceramic Na\(_3\)PS\(_4\) sample, it is still one magnitude lower than that for liquid organic electrolyte (1~6 mScm\(^{-1}\)). More efforts have been made to further enhance the ionic conductivity of Na\(_3\)PS\(_4\) to improve the performance of all-solid-state NIB. Those work could be categorized into two groups based on cation or anion doping/substitution. For the cation doping/substitution, Tanibata et al. synthesized glass-ceramic electrolyte 94Na\(_3\)PS\(_4\)
\(\cdot\)6Na\(_4\)SiS\(_4\) (mol\%) with ionic conductivity of 0.74 mScm\(^{-1}\).[32] Similar with Na\(_3\)PS\(_4\), two Na\(^+\) sites (Na1 and Na2) are also found in the 94Na\(_3\)PS\(_4\)
\(\cdot\)6Na\(_4\)SiS\(_4\). The larger site-occupancy of Na2 would be a possible reason for this improvement in Na\(^+\) conductivity. Besides Si atom, antimony (Sb) was also introduced to the system to obtain Na\(_3\)SbS\(_4\). Hui Wang et al. synthesized tetragonal Na\(_3\)SbS\(_4\) by eliminating H\(_2\)O from Na\(_3\)SbS\(_4\)
\(\cdot\)9H\(_2\)O at different temperatures.
(from 50 to 200 °C). The sample after heat treatment at 150 °C shows the highest room-temperature ionic conductivity of 1.05 mScm⁻¹ (Figure 1-10).

![Figure 1-10. a) Arrhenius plots of Na₃SbS₄·9H₂O and Na₃SbS₄. b) Room temperature ionic conductivity (left y-axis) and activation energies (right y-axis) versus the temperature of heat treatment.][33]

Simultaneously and independently, Abhik Banerjee et al. also developed Na₃SbS₄ via solid-state reaction, which exhibits room-temperature ionic conductivity of 1.1 mScm⁻¹.[34] They also developed solution processes to synthesize Na₃SbS₄. Even though solution method leads to lower ionic conductivity (0.23 mScm⁻¹ from methanol solution, 0.26 mScm⁻¹ from water solution), intimate contact between SSE Na₃SbS₄ and cathode NaCrO₂ is obtained by solution processed coating Na₃SbS₄ onto NaCrO₂ particles, which greatly decreases the interfacial resistance between Na₃SbS₄ and NaCrO₂, hugely improves the electrochemical performance of all-solid-state NIB (Figure 1-11).
Figure 1-11. Results of Na$_3$SbS$_4$-coated NaCrO$_2$ (NCO). a) HRTEM image of FIB-sectioned Na$_3$SbS$_4$-coated NCO. b) Annular dark-field (ADF) TEM image of FIB-sectioned Na$_3$SbS$_4$-coated NCO and its corresponding EDXS elemental maps. c) Initial charge–discharge voltage profiles (50 mAc m$^{-2}$, 30 °C). d) Nyquist plots of NCO/Na-Sn all-solid-state cells. Results of the mixed electrode and the Na$_3$SbS$_4$-coated NCO electrode are compared. The cells were fabricated by pressing at 370 MPa. The NCO:Na$_3$SbS$_4$ weight ratio is 87:13. [34]
Besides cation doping/substitution, anion doping/substitution is also demonstrated to improve ionic conductivity of Na$_3$PS$_4$. Iek-Heng Chu et al. synthesized Cl-doped tetragonal Na$_3$PS$_4$ with room-temperature ionic conductivity of 1.14 mScm$^{-1}$.[35] Long Zhang et al. substituted Se for S in Na$_3$PS$_4$ to obtain Na$_3$PS$_4$-$_x$Se$_x$ SSE.[36] With increasing the concentration of Se in Na$_3$PS$_4$-$_x$Se$_x$ tetragonal phase Na$_3$PS$_4$ gradually changes to the cubic phase Na$_3$PSe$_4$ with space group $I-43m$ (No. 217). The room-temperature ionic conductivity of Na$_3$PS$_4$-$_x$Se$_x$ SSE is shown in Figure 1-12, in which the as-prepared Na$_3$PS$_4$-$_x$Se$_x$ shows ionic conductivity increases with the concentration of Se and reaches the highest value of 1.16 mScm$^{-1}$ when $x = 1$.

Figure 1-12. a) Powder XRD profiles of Na$_3$PSe$_4$ and the obtained Rietveld refinement fit. b) Room-temperature ionic conductivity and the cell parameter of Na$_3$PSe$_{4-x}$S$_x$ as a function of the S content x.[36]

1.6 Scope and Dissertation

In the above introduction, we discussed the major issues and briefly reviewed the development of rechargeable Na-ion batteries. Despite tremendous recent research progresses,
there is long way to go before achieving the commercialization of practical high-energy and long-life Na-ion batteries.

To make Na-ion batteries feasible, several issues still need to be overcome. A promising anode material should be developed with high specific capacity and long cycle life. The red phosphorus anode has the highest theoretical capacity (2565 mAhg\(^{-1}\)) among all reported anode materials. However, its poor electrical conductivity (1×10\(^{-10}\) S cm\(^{-1}\)) and large volume change (up to 300\%) upon sodiation/desodiation restricts the practical application of red phosphorus. In addition, liquid organic electrolyte shows great safety concern due to the flammable and volatile nature. Replacing the liquid organic electrolyte by solid-state electrolyte is a promising strategy to improve the safety of NIBs. However, current existing SSE are not satisfying due to either lower room-temperature ionic conductivity, poor electrode-electrolyte contact, or moisture instability.

To address the issues identified above, we developed: 1) chemically bonded phosphorus/graphene hybrid as a high performance anode for sodium-ion batteries, 2) phosphorus-porous carbon composite as a high performance anode for sodium-ion batteries, 3) Na\(_3\)P\(_{0.62}\)As\(_{0.38}\)S\(_4\) with exceptionally high ionic conductivity and improved moisture stability for solid-state sodium-ion batteries, and 4) Na\(_{11}\)Sn\(_2\)PS\(_{12}\) with high ionic conductivity for solid-state sodium-ion batteries.
Chapter 2
Experimental Methods

Tremendous techniques and methods have been developed to evaluate battery systems. In this chapter, introductions will be given on the electrochemical and physiochemical methods that are used in this dissertation for testing and characterization of the batteries, including the electrode materials and solid-state electrolytes.

2.1 Energy storage evaluation

Rechargeable battery is a system that can repeat convert chemical energy to electrical energy and vice versa. Its capability to hold electrical energy could be described by “energy density”, which has the unit “Wh kg⁻¹” and is determined by the working voltage and specific capacity of the battery. Capacity measures the total amount of charge involved in the electrochemical reactions. Specific capacity (Ah kg⁻¹ or mAh g⁻¹) and volumetric capacity (Ah L⁻¹) are usually used to represent capacity per unit mass or capacity per unit volume, respectively. Voltage with the unit “V” is the electrical potential between cathode and anode. Energy density of a cell could be calculated according to Eq. 2-1.

\[ U = V \cdot q \]  
(Eq. 2-1)

Where,

- \( U \) = Energy density (Wh kg⁻¹)
- \( V \) = Working voltage of the cell (V)
- \( q \) = Specific capacity (Ah kg⁻¹ or mAh g⁻¹)
Accordingly, increasing working voltage and improving specific capacity are two main strategies to enhance the energy density of the battery.

Another important feature of the battery is power density (W kg\(^{-1}\)), indicating the rate at which energy is transferred. It is calculated according to the Equation 2-2

\[
P = \frac{V \cdot I}{M} \quad \text{(Eq. 2-2)}
\]

Where,

\[P = \text{power density (W kg}^{-1}\text{)}\]
\[V = \text{working voltage of the battery (V)}\]
\[I = \text{current (A)}\]
\[M = \text{mass of battery (kg)}\]

Current is often expressed as a C-rate, a measure of the rate at which a battery is discharged/charged relative to maximum (or normalized) capacity. For example, 1 C rate means the battery is discharged or charged to its maximum capacity within 1 hour. When C-rate is used to describe the current density, the maximum capacity is also required to be specified.

“Cycle life” is another description regarding the cycling performance of battery. It is the number of complete charge/discharge cycles that the battery is able to support.

2.2 Electrochemical characterization techniques

2.2.1 Coin cell fabrication

Coin cells are used for battery characterization in this dissertation. Figure 2-1 shows the structure of coin cells. It is composed of negative case, stainless steel spacer, Na foil as anode, separator, working electrode, and positive case. Liquid organic electrolyte is used to fill the pores in separator and working electrode. The working electrode is made by mixing active materials,
conductive additive (generally carbon), and binder (e.g., polyvinylidene fluoride (PVDF), sodium carboxymethyl cellulose (NaCMC)) in a solvent (e.g. N-methyl-2-pyrrolidinone (NMP), DI water). The slurry is stirred over night before casting onto current collector (anode materials on Cu foil, cathode on Al foil). The casted electrode is dried at 100 °C under vacuum for at least 5 hours. Drying procedure greatly depends on the binder and will be specified in the later chapters. After drying, the electrode sheets are punched into round pieces (12 mm in diameter, 1.13 cm²) and assembled into CR2016 coin cells with Celgard 2325 separator. The whole process is under Argon atmosphere.

Figure 2-1. Schematic illustration of the coin cell.

All-solid-state battery is also characterized in coin cell, which shares the similar structure. However, separator is not involved in the all-solid-state battery and replaced by solid-state electrolyte layer. The working electrode is not casting onto Al or Cu foil any more. The mixture of active material, conductive additive, and solid-state electrolyte is ball milled before pressing onto electrolyte layer as working electrode. All the process is completed within glovebox filled with Ar gas.
2.2.2 Battery cycling

The repeated galvanostatic charging and discharging is the most straightforward electrochemical evaluation technique for a rechargeable battery cell. Specifically, a constant current is applied during cycling, and the resulting voltage change of the cathode (working electrode) is measured versus the Na anode. The charging/discharging process stops when the voltage reaches a pre-determined value. The capacity of the working electrode can be obtained from the calculation based on current and the charging/discharging time. Coulombic efficiency reflects the faradaic loss between the charge and discharge capacity, and can be calculated according to the Eq. 2-3.

\[
\partial = \frac{Q_{\text{discharge}}}{Q_{\text{charge}}} \tag{Eq. 2-3}
\]

where

\( \partial = \) coulombic efficiency

\( Q_{\text{discharge}} = \) discharge capacity (mAh, mAh\(^{-1}\))

\( Q_{\text{charge}} = \) charge capacity (mAh, mAh\(^{-1}\))

This measures the efficiency with which charge (electrons) are transferred in a system facilitating an electrochemical reaction.

In this dissertation, three types of battery testing systems from different companies have been used for battery cycling tests. They are: Land CT2001A from Landt Instruments Inc. (China), Neware-BTS 5V1mA or 5V10mA from Neware Technology Ltd. (China), and BT2000 from Arbin Instruments (USA).
2.2.3 Cyclic voltammetry

The cyclic voltammetry (CV) test is a common electrochemical characterization technique used for investigating the reversibility of redox chemical reactions. The working electrode is scanned under a constant voltage rate (e.g. 1 mVs\(^{-1}\), 0.1 mVs\(^{-1}\)) within a pre-determined voltage window (e.g. from 0.01 to 2.5 V for phosphorus based anode and form -0.5 to 5 V for solid-state electrolyte). During this process, the current response is plotted as a function of the applied potential. The redox potential of a reaction is judged to be at the voltage of the corresponding peak in the CV plot.

2.2.4 Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) test is a common electrochemical characterization technique used for investigating different electrochemical process at different frequencies. For example, applying a small AC sinusoidal wave to a battery at high frequencies measures only the equivalent series resistance and inductance of the cell. At high to mid-frequency, electrode reactions dominate the spectra. At lower frequencies, the AC input stimulates the long time constant processes such as migration and diffusion. Models based upon passive circuit elements such as capacitors/resistors/inductors can faithfully simulate the internal electrical properties of the cell (Figure 2-2) EIS is also used to detect the grain resistance and/or grain boundary resistant of the solid-state electrolyte in this dissertation.
2.3 Physicochemical characterization techniques

The phase, structure, and morphology changes of the electrode/solid-state electrolyte materials determine the performance and the life of a battery. To better understand these and provide knowledge for improving the batteries, a series of physicochemical analytical techniques are needed.
2.3.1 X-ray diffraction

X-ray diffraction (XRD) relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. A primary use of the technique is the identification and characterization of compounds based on their diffraction pattern.

The dominant effect that occurs when an incident beam of monochromatic X-rays interacts with a target material is scattering of those X-rays from atoms within the target material. In materials with regular structure (i.e. crystalline), the scattered X-rays undergo constructive and destructive interference. This is the process of diffraction. The diffraction of X-rays by crystals is described by Bragg’s Law, \( n\lambda = 2d \sin(\theta) \). The directions of possible diffractions depend on the size and shape of the unit cell of the material. The intensities of the diffracted waves depend on the kind and arrangement of atoms in the crystal structure. However, most materials are not single crystals, but are composed of many tiny crystallites in all possible orientations called a polycrystalline aggregate or powder. When a powder with randomly oriented crystallites is placed in an X-ray beam, the beam will see all possible interatomic planes. If the experimental angle is systematically changed, all possible diffraction peaks from the powder will be detected.

The resolution of the characterization depends on the wavelength of the X-ray. X-rays with two wave length (0.1174 Å and 1.541 Å) are used in this dissertation to identify and characterize as-prepared materials.

2.3.2 Scanning electron microscopy

Scanning electron microscopy (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals include external morphology (texture), chemical composition, crystalline structure, and orientation of materials
making up sample. A wide range of magnifications is possible for SEM, from about 10 times to more than 500,000 times. At the highest magnification, SEM can achieve resolution better than 1 nm.

SEM is commonly coupled with energy dispersive X-ray spectroscopy (EDS or EDX), to determine the chemical composition of materials down to a spot size of a few microns and to create element composition maps over a much broader raster area. It should be noted that EDS analysis is semi-quantitative, and should be coupled with other quantitative analysis techniques (e.g. inductively coupled plasma atomic emission spectroscopy) to determine the chemical composition more accurately.

### 2.3.3 Transmission electron microscopy

Transmission electron microscopy (TEM) is a very powerful and useful tool for material characterization. A high energy beam of electrons is transmitted through a very thin specimen, during which process electrons interacting with the atoms within the specimen to generate signals including morphology, crystal structure, dislocations, and grain boundaries and so on. Chemical analysis could also be performed from both electron energy loss spectroscopy (EELS) and dispersive X-ray spectroscopy (EDS). High resolution TEM (HRTEM) with resolution of ~0.05 nm enables the instrument's user to examine fine details - even as small as a single column of atoms.

The TEM imaging was carried out on a JEOL 2010F TEM/STEM in the Materials Characterization Lab at Penn State.
2.3.4 Inductively coupled plasma atomic emission spectroscopy

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is an analytical technique used for the detection of trace materials. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. It is a flame technique with a flame temperature in a range from 6000 to 10000 K. The intensity of this emission is indicative of the concentration of the element within the sample. In this dissertation, the ICP-AES is used to determine the composition of as-prepared solid-state electrolytes.
Chapter 3

Chemically Bonded Phosphorus/Graphene Hybrid as a High Performance Anode for Sodium-Ion Batteries

3.1 Introduction

Lithium-ion batteries (LIBs) have achieved great success as energy storage devices for portable electronics in the past two decades. However, the increasing demand for emerging applications, such as electric vehicles and grid storage for intermittent power sources like wind and solar, has raised concerns about the feasibility of continuing to increase LIBs production.[37-39] Due to the limited and globally uneven distribution of lithium resources, it is expected that the cost of LIBs will dramatically increase in the near future.[6] Therefore, exploiting novel low-cost energy storage devices using naturally abundant raw materials will soon be required. Ambient temperature Na-ion batteries (NIBs) are promising candidates and have attracted increasing attention due to the abundance of sodium sources, the even global distribution of such sources, and NIBs’ similar intercalation chemistry to LIBs.[7,14,40] Mimicking the interlayered transition metal cathode materials of LIBs has allowed the successful development of various cathode materials for NIBs, including NaCoO₂,[41] NaFePO₄,[42] and Na₀.₄₄MnO₂,[43] by replacing Li ions with Na ions. Unfortunately, the graphite anode commonly used in lithium systems does not intercalate sodium to any appreciable extent, as the Na ions have a much larger radius of 1.02 Å (~55% larger than the Li ion radius of 0.76 Å). This is a serious hurdle for practical application of NIBs and necessitates design of new anode materials to allow reversible and rapid Na-ion insertion and extraction. Much effort has been devoted to novel anode materials for NIBs, involving carbon-based materials (hard carbon and doped carbon),[44] metal oxide
anode materials (TiO$_2$ and NiCo$_2$O$_4$),[45,46] and intermetallic metal anode materials (Sn, Ge, and Pb).[47-49] Despite some encouraging progress, the specific capacity of these materials is still low (less than 1000 mAh$^{-1}$) and the cycling life is poor. Recently, phosphorus was found to be electrochemically active for sodium ions, forming sodium phosphide (Na$_3$P) upon complete reaction of Na with P.[50,51] This three-electron-transfer reaction of phosphorus provides an extremely high theoretical capacity of 2595 mAh$^{-1}$, the highest among known anode materials for NIBs. The pioneering research on P anodes was conducted by Yang’s and Lee’s groups, who developed phosphorus anodes through the high-energy ball-milling of red phosphorus and carbon black.[50,51] The phosphorus anode in Yang’s research delivered an initial capacity of 1800 and 600 mAh$^{-1}$ after 140 cycles at a current density of 263 mAg$^{-1}$; Lee’s study presented a slightly higher capacity of $\sim$2000 mAh$^{-1}$ at a lower current density of 150 mAg$^{-1}$, with 30 cycles of battery performance shown. Very recently, carbon nanotubes (CNTs) were employed as the conducting matrix to improve electrical conductivity of phosphorus and the resulting phosphorus/CNT composite delivered a capacity of 1675 mAg$^{-1}$ at the first discharge and $\sim$500 mAh$^{-1}$ capacity after 20 cycles.[52]

Though very promising, this battery performance is still unsatisfactory, particularly with regards to the cycling stability. There are several likely reasons for this. First, red phosphorus has a very low electrical conductivity ($1 \times 10^{-14}$ Scm$^{-1}$), making the electrochemical redox reaction difficult. Second, similar to silicon in LIBs, the large volume expansions of phosphorus (>300%) may cause many problems for phosphorus anodes. In particular, the large volume change is expected to cause poor electrical contact between phosphorus particles and the conducting matrix, pulverization of phosphorus particles, and continuous growth of the solid electrolyte interphase (SEI).[31] As a result, phosphorus anodes show fast capacity fading, low Coulombic efficiency, and electrode deterioration upon cycling.[53]
One approach to address some of these issues is by using graphene- and graphene stacks (multilayer graphene)-based composites. Such composites with polymers, metals, and metal oxides have also shown good performance in LIBs due to their excellent electrical conductivity and mechanical properties.\[54-56\] The high surface area (theoretically 2630 m²g⁻¹) and flexibility of graphene enable good interfacial contact with particles, allowing it to anchor well-dispersed particles, form a highly conductive matrix between them, and also effectively maintain that contact and prevent particle aggregation during volume expansion/contraction.\[57-59\] Therefore, it is believed that a composite of flexible and electrically conductive graphene with phosphorus could show superior performance in sodium-ion batteries.

Herein, we have developed a novel phosphorus/graphene nanosheets (P/G) hybrid nanostructured anode for sodium-ion batteries through a facile ball-milling process of graphene stacks and red phosphorus. The large surface area and flexibility of graphene nanosheets enable them to partly conform to the phosphorus particles during milling, enhancing the overall conductivity and enhancing the material’s tolerance of the large volume change of phosphorus during cycling by acting as a robust conductive matrix to maintain electrical contact. Moreover, the graphene nanosheets can chemically bond with phosphorus during the milling process, facilitating intimate contact between them and also stabilizing the SEI. Benefiting from this unique hybrid nanostructure and strong chemical bonding between the phosphorus and the graphene nanosheets, the as-synthesized P/G hybrid shows much improved electro-chemical performance compared with a ball-milled phosphorus/carbon black (P/CB) composite when evaluated as a sodium-ion anode, with a high initial capacity of 2077 mAhg⁻¹ and good cycling stability (1700 mAhg⁻¹ after 60 cycles). The low-cost, eco-friendly starting materials of red phosphorus and graphene stacks together with the industry-standard ball-milling approach make this anode material promising for practical application in sodium-ion batteries.
3.2 Experimental Section

Preparation of phosphorus/graphene nanosheet (P/G) hybrid: The P/G hybrid was synthesized through a simple ball-milling approach. The mixture of commercial phosphorus (Afla Aesar, 99%) and graphene stacks (XG Science, XG-300) with the mass ratio of 7:3 was placed in a stainless steel jar and sealed in a glove box under argon protection, followed by ball-milling for 16 hours at a speed of 400 rpm.

Characterization: Power X-Ray diffraction (XRD) was collected on a Rigaku Miniflex II spectrometer with Cu Kα radiation. The morphology of the P/G hybrid was investigated with Scanning Electron Microscopy (Nano630 FE-SEM), Energy-filtered Transmission Electron Microscopy (EF-TEM, JEOL 2010 LaB6) was used for the micro-structure investigation and elemental mapping. Fourier transform infrared spectrometry (FTIR) was performed on a Bruker Vertex V70 spectrometer in diffuse reflection mode with a Spectra Tech Collector II accessory. Samples were diluted with KBr in a weight ratio of ~30:1 KBr:sample.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Kratos XSAM800 Ultra spectrometer. The graphene stacks show a narrow, relatively symmetrical peak. According to the literature (Carbon, 2004, 42, 1713), this peak stems mainly from sp² type carbon (284.6 eV), and was used for charge referencing of the C1s spectrum of this sample. Peak broadening is observed after ball-milling, which stems from formation of sp³ type carbon. The P/G hybrid C1s spectrum was thus charge corrected to 284.8 eV based on this peak. Differential charging was believed to be observed between the carbon and phosphorus in the P/G hybrid, which is unsurprising given the material morphology and the significant difference in conductivity of phosphorus and graphene; phosphorus spectra were thus charge corrected using the P_{2p/2} peak of red phosphorus.
Electrochemical Measurement: Electrochemical tests were performed by using 2016 coin-type half cells assembled with sodium metal as the counter electrode in an Argon-filled glove box. The composites were prepared by coating slurries containing P/G active materials (70wt.%), Super P acetyleneacetylene black (15wt.%), and Sodium Carboxymethylcellulose (NaCMC, 15%) on copper foil. The typical active materials loading of the electrodes was 0.8~1 mg cm$^{-2}$. Electrodes with ball-milled phosphorus/carbon black (P/CB) composite as the active material were fabricated following the same approach and were used as control samples. The electrolyte consists of 1 M NaClO$_4$ in a mixture of ethylene carbonate and diethyl carbonate (1:1 by volume) and fluoroethylene carbonate (FEC, 10 vol.%). Galvanostatic charge/discharge tests were carried out on a Land battery tester between 0 and 2.0 V versus Na$^+$/Na. Cyclic voltammetry (CV) was performed at a scan rate of 0.1mVs$^{-1}$ within the range of 0 - 2.0 V using a CHI 660D electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was carried out by applying a perturbation voltage of 5mV between 10Hz and 100Hz using a Solatron SI 1260 impedance analyzer.

3.3 Results and Discussions

The P/G hybrid was prepared by a facile ball-milling approach as illustrated in Figure 3-1. Commercial red phosphorus and graphene stacks (7:3, weight ratio) were homogeneously mixed in a stainless steel ball-milling jar under argon atmosphere, followed by ball-milling at 400 rpm for 16 h, yielding P/G hybrid materials. It is well-known that a ball-milling approach can effectively grind large bulk materials into microscale or nanoscale particles, and can also mechanically peel apart layered materials through the high energy shear force. Therefore, it is believed that the bulk phosphorus is broken down into smaller particles and the stacked graphene
nanosheets are exfoliated through the homogeneous mixing of these two materials in the ball-milling process.

Figure 3-1. Schematic Illustration of the Synthesis of Phosphorus/Graphene Nanosheets (P/G) Hybrid.

The structures of the P/G hybrid, as well as those of the original graphene stacks and red phosphorus, were examined by powder X-ray diffraction (XRD) and Raman spectroscopy. A strong diffraction peak at 2θ of 26.4° in the XRD pattern of the graphene stacks correspond to (002) planes of hexagonal crystalline graphite (JCPDS No. 41-1487) (Figure 3-2a). Crystalline domain size calculated from the Scherrer equation in the graphene stack is around 16 nm, indicating a few tens of layers of graphene in the stack. In the XRD pattern of P/G, the native graphite peaks disappeared, indicating that the graphene stacks were exfoliated in the ball-milling process. Broad diffraction peaks indicate its amorphous structure in the P/G hybrid. The structure of P/G hybrid is further reflected by the Raman spectra (Figure 3-2b). The spectrum of the
graphene stacks shows a weak D band (1360 cm$^{-1}$) and strong G band (1580 cm$^{-1}$); the D band corresponds to the defects and disorder in the structure of the graphene due to the intervalley scattering, while the G band is related to the E$_{2g}$ vibration of sp$^2$ C atoms in graphene.[60] In contrast to the graphene stacks, the intensity ratio of the D band to the G band ($I_D/I_G$) in P/G hybrid increased from 0.36 to 0.99, suggesting a decrease in the average size of the sp$^2$ domains of graphene in the P/G hybrid from the mechanical shear exfoliation of graphene stacks in the ball-milling process. The decreased layers of graphene in P/G hybrid were also demonstrated by the wave shift of the G band from 1564 to 1594 cm$^{-1}$.[60]

![Figure 3-2](image.png)

Figure 3-2. (a) XRD patterns and (b) Raman spectra of red phosphorus (P), graphene stacks (G), and ball-milled P/G hybrid.

The morphology of the P/G hybrid was further investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The graphene stacks were a few micrometers in size, as shown in the TEM image (Figure 3-3a), and the pristine bulk phosphorus particles were irregularly shaped and up to around 50 μm in size, as shown in the SEM image (Figure 3-3b). The particles in the P/G hybrid after ball-milling were only submicron to a few microns in size, much smaller than those of the bulk phosphorus, as shown in Figure 3-3c. This
decreased particle size and the exfoliation of graphene stacks should lead to a higher surface area if they exist separately. However, the Brunauer–Emmett–Teller (BET) surface area decreases from 87.26 m$^2$g$^{-1}$ in P/G mixtures (without ball-milling) to 24.8 m$^2$g$^{-1}$ in P/G hybrids upon ball-milling (Figure 3-4), while carbon content at the surface increases significantly (Table 3-1). This suggests that the graphene nanosheets are in intimate contact with phosphorus and mainly located on the surface of the phosphorus particles. Moreover, the absence of separate graphene sheets in the P/G hybrid further indicates that the flexible graphene nanosheets intimately contact with red phosphorus particles. To find out if the morphology of the graphene nanosheets was still layered structures in P/G hybrids, the phosphorus was sublimated under vacuum to obtain graphene nanosheets residue for electron microscopy analysis. The TEM image shows that the graphene nanosheets have an exfoliated layered structure and micrometer size (Figure 3-5). To further clarify the structure of P/G hybrid, energy-filtered transmission electron microscopy (EF-TEM) and corresponding element mapping were conducted, as shown in Figure 3-3d–f. The carbon (orange) and phosphorus (purple) can be found all over the samples, indicating the uniform mixing of phosphorus and graphene nanosheets in the hybrid. The size of primary phosphorus domains in the hybrid is in the range of 10–200 nm, while the graphene nanosheets formed a continuous conducting network.
Figure 3-3. (a) TEM image of graphene stacks; (b) SEM images of pristine phosphorus and (c) P/G hybrid; (d) TEM image and corresponding EF-TEM element mapping images of carbon (e) and phosphorus (f) in the P/G hybrid.

Table 3-1. Surface element content of P/G hybrid by XPS and calculated overall element content. *The overall atomic percentages of the P/G hybrid are calculated values based on the weight ratio (7:3 phosphorus:graphene) and atomic mass of phosphorus and carbon.

<table>
<thead>
<tr>
<th></th>
<th>Atomic percentage (%)</th>
<th>C/P ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon</td>
<td>Phosphorus</td>
</tr>
<tr>
<td>Surface</td>
<td>61.69</td>
<td>22.92</td>
</tr>
<tr>
<td>Overall*</td>
<td>47.61</td>
<td>52.38</td>
</tr>
</tbody>
</table>
Figure 3-4. N2 sorption isotherms of (a) P/G mixture (without ball-milling) and (b) P/G hybrid (with ball-milling) and the corresponding BET surface area are 87.26 m$^2$/g and 24.8 m$^2$/g, respectively.

Figure 3-5. TEM image of the graphene nanosheets in the P/G hybrid. The graphene nanosheets were obtained by sublimation of phosphorus away from the P/G hybrid under vacuum.
The interaction between graphene nanosheets and phosphorus particles was further investigated by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). Typically, phosphorus particles are covered with a thin layer of phosphorus-based oxides due to oxidation when exposed to air.[61] This is demonstrated by appearance of P=O (1160 cm$^{-1}$) and P–O (1080 cm$^{-1}$) characteristic peaks in the FT-IR spectra of phosphorus (Figure 3-6a).[62,63] Noticeably, a new peak centered at 1008 cm$^{-1}$ appears in the FTIR spectra of the P/G hybrid while the peak intensity of P=O and P–O decrease. This indicates the formation of P–O–C bonds during ball-milling.[63,64] Three peaks centered at 129.8, 130.7 (shoulder peak), and 134.0 eV were observed in the P$_{2p}$ XPS spectrum of the phosphorus (Figure 3-6b). The peaks at 129.8 and 130.7 eV can be attributed to the P$_{2p3/2}$ and P$_{2p1/2}$, respectively.[65] The relatively broad higher binding energy peak at 134.0 eV arises from phosphates.[66] In contrast, in the P$_{2p}$ spectrum of the P/G hybrid, additional peak intensity is observed at medium binding energy (∼132–133 eV). Although this cannot be said to definitively indicate P–O–C bonding, as peaks related to some types of phosphates can also be found at that binding energy, P–O–C bonds could be expectedly at around this position and so this is consistent with the FT-IR observations. This chemical bonding enables the graphene nanosheets to bind strongly with the phosphorus particles, and thereby helps prevent the loss of electrical contact between phosphorus particles and the conducting network during electrochemical cycling.
Figure 3-6. (a) FT-IR spectra of ball-milled phosphorus (P) and the P/G hybrid; (b) high resolution P2P XPS spectra of P and P/G hybrid.

Figure 3-7a shows the cyclic voltammetry (CV) of the P/G hybrid. Two peaks (I and II) are found in the first cathodic scan. The peak I at 1.0−0.5 V disappears in the subsequent scans, and is most likely due to the electrochemical decomposition of electrolyte during the formation of an SEI film on the P/G electrode surface.[21,53] This also implies that SEI formation occurs mainly during the first cycle. When the potential was further scanned from 0.5 to 0 V, a major cathodic peak II with a noticeable shoulder appears between 0.3 and 0 V, corresponding to sodium ion insertion and formation of Na_xP. Peaks III, IV, and V are visible at 0.53, 0.76, and 1.42 V during the first anodic scan and were also detected in subsequent scans. The peaks possibly correspond to a stepwise sodium ion deinsertion from the fully charged Na_3P phase to form the Na_2P, NaP, and NaP_7 intermediates, respectively.[50,51] In contrast to the CV plot of the P/CB composite control sample, the separation between major cathodic peak II and anodic peak III decreased from 660 mV (for P/CB composite, Figure 3-8) to 630 mV (for P/G hybrid) at the same scanning rate of 0.1 mVs^{-1}. This indicates that the incorporation of highly conductive graphene nanosheets in the hybrid can significantly decrease the polarization of the cells and enhance the kinetics of the electrochemical conversion of Na_xP to P.
Figure 3-7. (a) The cyclic voltammograms of the P/G hybrid anode at a scanning rate of 0.1 mV s\(^{-1}\); (b) typical discharge–charge voltage profiles of the P/G hybrid anode; (c) cycle stability and Coulombic efficiency of the P/G hybrid anode at a current density of 260 mA g\(^{-1}\); (d) rate capability of the P/G hybrid anode. The specific capacity is calculated based on the mass of the phosphorus.

Figure 3-8. The cyclic voltammetry (CV) of the P/CB composite at a scanning rate of 0.1 mV s\(^{-1}\) in the range of 2.0-0 V.
The electrochemical performance of the as-prepared P/G hybrid was further evaluated by galvanostatic charge/discharge. CR 2016 type coin cells were fabricated using sodium as the counter electrode, Celgard 2320 membrane as the separator, and 1M NaClO₄ in EC/DEC (1:1, volume ratio) as electrolyte with 10 vol % fluoroethylene carbonate (FEC) as additive. The typical charge/discharge voltage profiles of P/G hybrid at a current density of 260 mAg⁻¹ in the voltage range of 0−2 V are shown in Figure 3-7b. Two characteristic regions were found in the first discharge curve of the P/G hybrid: (1) one slope in the discharge capacity from 0 to ∼400 mAhg⁻¹ (region I in Figure 3-7b); (2) a small slope and subsequent plateau in the discharge capacity from 400 to ∼2000 mAhg⁻¹ (region II in Figure 3-7b). Three slopes centered at around 0.5, 0.7, and 1.4 V in the charge process were observed. These observations resemble the CV results in Figure 3-7a and are also consistent with the literature values.30 The P/G hybrid anode delivered an initial Coulombic efficiency of 83% and specific capacity of 2077 mAhg⁻¹, corresponding to 80% phosphorus utilization compared with the theoretical specific capacity of phosphorus. A high capacity of 1706 mAhg⁻¹ is still obtained after 60 cycles, which is 95% capacity retention relative to the second-cycle capacity of 1785 mAhg⁻¹. Note that the capacity contributed by graphene nanosheets is negligible considering their much lower capacity (∼65 mAhg⁻¹) as NIBs anode (Figure 3-9). In contrast to the P/G hybrid anode, the P/CB composite shows a lower reversible capacity (1888 mAhg⁻¹) and much faster capacity fading (only 709 mAhg⁻¹ after 60 cycles), as shown in Figure 3-10. Even when compared with the P/CB with high-energy ball-milling approach in the literature,[51,52] our P/G hybrid anodes still show higher active-materials utilization rate and better cycling stability. To the best of our knowledge, this is the first time phosphorus-based anodes show a good capacity retention (>90% within 60 cycles) with a high reversible capacity (>1700 mAhg⁻¹).
Figure 3-9. The specific capacity of graphene stacks cycling at a current density of 260 mAg\(^{-1}\).

Figure 3-10. The cycling stability of the P/CB composite at a current density of 260 mAg\(^{-1}\).
Figure 3-11. (a) Nyquist plot and equivalent circuit model of the P/G hybrid anode before cycling and after cycling in the discharged state. (b) TEM image and corresponding (c) carbon and (d) phosphorus EF-TEM element mapping of the P/G hybrid after 35 cycles.

We also evaluated the rate performance of the P/G hybrid anode with C-rates from 0.05C to 2C (1C = 2600 mAhg$^{-1}$), as shown in Figure 3-7d. As the current density increased, specific capacities of 2164, ~1700, ~1180, and ~750 mAhg$^{-1}$ were obtained at 0.05C, 0.2C, 0.5C, and 1C, respectively. Even at 2C, the composite still delivers a high reversible capacity of ~520 mAhg$^{-1}$. When the rate was restored to 0.5C after 45 cycles of rate testing, the specific capacity in the P/G anode returned to 1262 mAhg$^{-1}$, close to 1285 mAhg$^{-1}$ from the initial 0.5C trial. This indicates that the P/G electrode charge/ discharge was reversible even at high current density. The good rate capability can be ascribed to the decreased size of the phosphorus particles, granting the sodium ions relatively short diffusion paths for sodiation and desodiation, and the much enhanced
electrical conductivity compared to bulk phosphorus due to the incorporation of highly conductive graphene nanosheets.

To better understand the reason for the improved cyclability of the P/G hybrid anode, electrochemical impedance spectroscopy (EIS) and transmission electron microscopy were conducted on the P/G hybrid electrodes, as shown in Figure 3-11. The impedance spectra were analyzed by fitting to an equivalent electrical circuit composed of ohmic resistance (Ri) of electrolyte and cell components; a constant phase element (CPE_{sf+ct}) in parallel with an ohmic resistance (R_{sf+ct}), representing impedance of sodium ion transport through surface films and charge transfer at the electrode/electrolyte interface; and a Warburg impedance (W_0), representing “semi- infinite” charge transfer, as by sodium ion diffusion through the material or electrolyte.[65,67] The combined surface film and charge transfer resistance R_{sf+ct} is 182 Ω after 10 cycles and only increases a little to 191Ω within the following 20 cycles, indicating well-maintained electrical contact and relatively stable SEI layer. In contrast, the R_{sf+ct} of cells with P/CB electrodes exhibits a quick resistance increase (from 195 Ω at the 10th cycle to 300 Ω at the 30th cycle, Supporting Information Figure 3-12), most likely due to an unstable SEI and loss of electrical contact during cycling. This observation also helps explain the stable cycling of the P/G hybrid (Figure 3-7c). Moreover, the phosphorus and graphene nanosheets are connected with each other within the hybrid (Figure 3-11b). The carbon (Figure 3-11c) and phosphorus (Figure 3-11d) were found to be fairly uniformly dispersed in the hybrid material after 35 cycles, indicating that the P/G hybrid still maintains its morphology after cycling. This can prevent capacity fading arising from the electrical contact loss when phosphorus undergoes continuous expansion/contraction during cycling. The maintenance of the good conductive network also enables rapid charge/discharge of phosphorus, as verified by the good rate performance shown in Figure 3-7d.
3.4 Conclusion

In summary, we successfully developed a phosphorus/ graphene nanosheet hybrid nanostructured anode for Na-ion batteries via a simple ball-milling approach with low-cost precursors of red phosphorus and graphene stacks. The graphene around the phosphorus particles via chemical bonding enhanced the electrical conductivity, allowed the graphene to behave as a conductive matrix to maintain electrical contact with phosphorus during the large volume changes, and helped maintain a stable SEI layer. This dramatically improves the electrochemical performance as compared to a phosphorus/ carbon black composite anode, giving an initial specific capacity of 2077 mAhg\(^{-1}\) capacity retention of 95% relative to the second cycle after 60 cycles, with a high Coulombic efficiency of \(~99\%\) after the first cycle. Taking the facile and general method as well as the low cost starting materials into account, this promising P/G hybrid nanostructured anode has a great potential for practical application in high performance Na-ion battery.
Chapter 4

Advanced Anode for Sodium-ion Battery with Promising Long Cycling Stability Achieved by Tuning Phosphorus-Carbon Nanostructure

4.1 Introduction

Electrochemical energy storage technologies are key components of the future renewables-friendly power grid with high energy efficiency, stability, and resilience. Na-ion batteries (NIBs) have the potential to compete with widely-used Li-ion batteries (LIBs) and change the landscape of electrochemical energy storage, owing to the significant cost advantage and abundance of sodium precursor.\cite{21,40,68,69} Because of the similar intercalation chemistry with LIB, various cathode materials, including Na$_x$NiO$_2$, Na$_{2/3}$Fe$_{1/2}$Mn$_{1/2}$O$_2$, Na$_3$V$_2$(PO$_4$)$_3$, and Na$_3$V$_2$(PO$_4$)$_2$F$_3$, have been developed by mimicking their counterparts in LIBs and have shown promising electrochemical performance.\cite{70-73} However, the graphite-based anode materials that is successful in LIBs cannot be used in NIBs due to the larger size of Na ions (2.04 Å) relative to channel size of graphite layers (1.86 Å), a critical issue inhibiting the practical application of NIBs.\cite{74-76} The major scientific challenge for NIBs therefore resides in developing new anode materials with high specific capacity and long-term cycling stability.

Red phosphorus (P) has been found to be a promising anode material for NIB, not only because of its extremely high theoretical capacity of 2595 mAh$^{-1}$ by taking 3 Na ions to form Na$_3$P, but also because of its eco-friendly, low-cost, abundance in nature, and high chemical stability.\cite{77-79} Despite these advantages, two intrinsic issues prevent real application of red phosphorus: 1) low electronic conductivity (1×10$^{-10}$ Scm$^{-1}$) makes electrochemical redox reactions difficult; 2) large volume change (up to 300%) upon sodiation/desodiation causes
pulverization of the active material, unstable growth of solid-electrolyte interphase (SEI), low
coulombic efficiency (CE), and rapid capacity decay.\cite{61,80,81}

To address the aforementioned issues, a well-known strategy is to develop proper
nanostructured P-carbon (P-C) composites, not only enhancing the overall conductivity but also
accommodating large volume changes of P.\cite{22,82-87} Yang et al. reported the ball-milled
amorphous P-carbon black composite with intimate contact between amorphous P cluster and
highly conductive carbon, which exhibited high reversible capacity of $\sim 1500 \text{ mAh} \cdot \text{g}^{-1}$ for the
initial cycle, and $\sim 1000 \text{ mAh} \cdot \text{g}^{-1}$ after 80 cycles.\cite{51} Lee et al. also reported a similar amorphous
P-C composite with a higher reversible capacity of $\sim 1890 \text{ mAh} \cdot \text{g}^{-1}$ for the initial cycle as well as
good capacity retention of $\sim 93\%$ within 30 cycles.\cite{50} Inspired by these pioneering work, other
highly conducive carbon materials, like graphene, carbon nanotube (CNT), and porous carbon,
have been utilized to prepare P-C composite. P-graphene composite with P-O-C chemical
bonding was prepared by ball milling method and delivered a high reversible capacity of $\sim 1700
\text{ mAh} \cdot \text{g}^{-1}$ after 60 cycles.\cite{79} Zhu et al. deposited red P onto tangled single-wall CNT bundles
with content of P $\sim 40\%$, which showed a reversible capacity of $260 \text{ mAh} \cdot \text{g}^{-1}$ after 2000
cycles.\cite{88} Li et al. encapsulated the red P within the mesoporous carbon with content of P $\sim 31.54\%$
achieving reversible capacity of $1020 \text{ mAh} \cdot \text{g}^{-1}$ after 210 cycles.\cite{89} They also confined
the P into nitrogen-doped microporous carbon obtaining P@N-MPC composite with the content
of P $\sim 22.6\%$, which showed reversible capacity of $\sim 450 \text{ mAh} \cdot \text{g}^{-1}$ after 1000 cycles.\cite{90}

All these P-C composites could be categorized into two groups based on the different P-C
nanostructures: 1) without porous structure that confines P inside, like amorphous P-carbon black,
P-graphene, and P-CNT; 2) with porous structure that P could be confined inside, like P-
mesoporous carbon and P@N-MPC. Although better sodium storage performances are achieved
for P-C composites based on these two types of nanostructures than pristine P anode, the effect of
nanostructure (with/without porous structure to confine P) on the cycling stability of P anode is still unclear, especially for P-C composites with high P content (≥ 48 wt%).

Herein, we develop a well-controlled vaporization-deposition-conversion method to synthesize two P-carbon composites: P@YP composite with P particles being confined within nanopores of YP-80F (YP) carbon, and P@CNT with unconfined P deposited on the surface of CNT. Benefiting from the well-controlled method, 1) nano-sized P are achieved to enhance Na-ion diffusion; 2) intimate contact between P and conductive carbon improves the overall electrical conductivity; 3) the generation of white phosphorus is effectively prohibited during synthesis process. The electrochemical performances of these two composites, and the mechanism behind their different cycling stability have been well studied. In the P@YP composite, small size of P particles (≤ 2 nm) due to confinement in the nanopores of YP carbon greatly shortens the Na-ion migration path, leading to good rate performance. In addition, P@YP composite with porous structure confines P inside, accommodating its large volume change upon sodiation/desodiation, resulting in a stable SEI layer, guaranteeing an outstanding long-term cycling stability with superior capacity retention of 92% after 100 cycles and 46% after 1000 cycles with respect to the second cycle. In contrast, the P@CNT composite with unconfined P shows a rapid capacity decay with capacity retention of ~ 40.6% after 100 cycles, most likely due to unstable SEI and electrical contact loss of active materials during cycling, caused by the large volume changes of unconfined P in the P@CNT composite. The remarkable difference in electrochemical performance indicates the advantage of the nanostructure with confinement effects on P.
4.2 Experimental Section

Synthesis of red P@YP-80F, P@CNT: The P@YP and P@CNT composite were prepared through a vaporization-deposition-conversion method. Commercial red P (Afla Aesar, 99%) and YP-80F microporous carbon (Kuraray Chemicals Manufacturer) or CNT (Industrial Multi-Wall Carbon Nanotubes, Timesnano Inc., China) were mixed together and sealed in a quartz tube under vacuum. The quartz tube was then heated at 450 °C for 3 hours before slowly cooling to 280 °C at a rate of 1 °C/min. After cooling to 280 °C, the tube was kept at this temperature for 24 hours before increasing to 340 °C at a rate of 0.3 °C min⁻¹. The tube was kept at this temperature for 2 hours followed by cooling to 190 °C at a rate of 0.2 °C min⁻¹. Then the tube naturally cooled down to room temperature.

Characterization: Powder XRD was collected on a Rigaku Miniflex II spectrometer with Cu Kα radiation. The morphology of the P@YP and P@CNT composite were investigated with field-emission scanning electron microscope (Nano630 FE-SEM). TEM and EFTEM (JEOL 2010 LaB₆) were used for microstructure investigation and elemental mapping. Raman spectroscopy was performed on Horiba LabRam HR Evolution. Nitrogen adsorption/desorption isotherms were measured with an ASAP 2020 Accelerated Surface Area and Porosimetry System (Micromeritics). The thermogravimetric analysis measurement was carried out in Nitrogen flow using Q600 SDT (TA instruments) at a heating rate of 10 °C/min.

Electrochemical Tests: 70 wt. % active material, 15 wt. % Super P carbon black, and 15 wt. % sodium carboxymethylcellulose (NaCMC) binder were ball-milled to make slurry, which was casted on copper foil and dried at 100°C under vacuum overnight to make working electrodes. The mass loading of electrodes was 1-1.5 mgcm⁻². Electrochemical performance was tested using 2016-type coin cells, with Celgard 2400 polypropylene separator and 1M NaClO₄ in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and fluoroethylene carbonate.
(FEC) (1:1:0.2 by volume) electrolyte. Cells were assembled in an argon-filled dry glove box (MBraun, Inc.). Galvanostatic charge/discharge tests were carried out on a LAND battery tester between 0.01 V and 2.0 V versus Na\(^+\)/Na. Cyclic voltammetry was performed at a scan rate of 0.1 mVs\(^{-1}\) within the range of 0.01-2.5 V using a CHI 660D electrochemical workstation. Electrochemical impedance spectrometry analysis was performed on the same instrument in a frequency range of \(10^5\) – 1 Hz with an amplitude of 5 mV.

4.3 Results and Discussion

The synthesis process of the P@YP and P@CNT composites is schematically summarized in Figure 4-1. Commercially available micro-sized red P is vaporized at 450 °C, encapsulated into pores of YP carbon due to capillary force, and deposited on the surface of the carbon during cooling process (see experimental section for details).[91] For P@CNT composite, red P is downsized to nanoparticles and deposited on the surface of CNT. White P is reported to be generated during vaporization-deposition process, which is highly toxic and chemically unstable (self-ignition exposing to air). The advantage of our vaporization-deposition-conversion method lies in that no white P residue is detected in the final P@YP and P@CNT composite (no self-ignition exposing to air), indicating all white P converts to red P. The content of red P in both P@YP and P@CNT composites are determined to be 48% by thermogravimetric analysis (TGA, Figure 4-2). The as-prepared P@YP composite is also denoted as P@YP-48% in the later section.
Figure 4-1. Schematic illustration of preparation process and sodiation of P@YP and P@CNT composite.

Figure 4-2. Thermogravimetric analysis of a) YP carbon and P@YP composite, b) CNT and P@CNT composite in N₂ atmosphere. The content of P in two composites are the same, of 48%.

The structures of the as-prepared P@YP and P@CNT composites, as well as those of commercial red P, YP-80F porous carbon, CNT and their mixtures, were examined by powder X-ray diffraction (XRD, Cu Kα with wavelength λ = 1.541 Å). As shown in Figure 4-3a, three broad
diffraction peaks at 2θ values of 15.0°, 31.6°, and 45.4° are detected in the XRD pattern of red P powder, indicating its medium-range ordered structure.[51] Two broad bumps at 2θ of 23° and 42° are shown in the pattern of YP carbon, suggesting graphitic carbon with low degree of graphitization. In the pattern of the P@YP composite, the diffraction peaks corresponding to red P and YP are still visible, while the intensity of red P is much weaker than that in P-YP mixture. This is mainly because of P particles being downsized to nanoscale and confined within YP carbon. The structure of P@YP composite was further explored by Raman spectra (Figure 4-3b). The peaks of red P located between 300 cm$^{-1}$ and 500 cm$^{-1}$ disappear in the P@YP composite, while the peaks corresponding to D band and G band of YP persist, suggesting that red P is covered by carbon and mainly encapsulated in the pores of YP carbon, in perfect agreement with the XRD observation. Similarly with P@YP composite, the diffraction peaks corresponding to P and CNT are detected in the XRD pattern of the P@CNT composite (Figure 4-3c), but the intensity of red P is not obviously weakened. In Figure 4-3d, the Raman characteristic peaks of red P are still detectable in the P@CNT composite (Figure 4-3d), which is remarkably different from that for the P@YP composite, suggesting great fraction of unconfined P in the P@CNT composite.
The morphology of P@YP and P@CNT composite were investigated by electron microscopy. Scanning electron microscopy (SEM) images of raw red P, YP carbon, P@YP composite, CNT, and P@CNT composite are presented in Figure 4-4a – f, respectively. It is clearly found that the raw P particles are above 50 µm in size, much larger than that for YP (10 – 15 µm, Figure 4-4b) and CNT (10 – 30 µm in length, Figure 4-4d). After vaporization-deposition-conversion process, similar morphology is shared between YP carbon and the P@YP composite (Figure 4-4b and c), and between CNT and P@CNT (Figure 4-4d and e), with no large P particle residue being detected in the as-prepared P@YP and P@CNT composites. Energy-dispersive X-ray spectroscopy (EDS) mapping of C and P (Figure 4-5) confirm the uniform distribution of P and no agglomeration of red P in the P@YP and P@CNT composites. Energy-filtered
transmission electron microscopy (EFTEM) images and the corresponding elemental mapping of the P@YP and P@CNT composite, shown in Figure 4-6, further confirms the uniform distribution of P within composite in the nano-scale. TEM images of YP carbon and P@YP composite are shown in Figure 4-7a and b, respectively. These clearly show that YP carbon has highly porous structure with pore size of ≤ 2 nm, which is also supported by the nitrogen adsorption/desorption characterization (Figure 4-7c, d). Figure 4-7b shows that the P@YP composite has a morphology similar to YP, suggesting that red P is encapsulated in pores. In order to confirm the occupation of red P within pores of YP carbon, Brunauer-Emmett-Teller (BET) surface area and pore size distribution before and after red P encapsulation in YP are compared. Figure 4-7c shows that YP carbon exhibits typical Type I nitrogen adsorption/desorption isotherms with high BET surface area of 1943.4 m²g⁻¹. After loading red P into YP, the BET surface area of the P@YP composite dramatically drops to 733.2 m²g⁻¹, suggesting the occupation of P in the pores of YP carbon. Additionally, variations in pore size distribution (Figure 4-7d) demonstrates that P is mainly encapsulated in micro pores (pore size ≤ 2 nm). Compared to P@YP composite, TEM image of P@CNT composite shows that nano-sized P is mainly deposited on the outer surface of CNT (Figure 4-8a), consistent with XRD and Raman observations. This is also supported by the BET surface area results. Downsizing red P particle to nanoscale should lead to a larger surface area in P@CNT composite if P particles and CNT exist separately. However, BET surface area decreases from 93.2 m²g⁻¹ in P-CNT mixture to 59.8 m²g⁻¹ in P@CNT composite upon vaporization-deposition-conversion (Figure 4-8b), confirming that P mainly locates on the surface of CNT.
Figure 4-4. SEM images of a) red P, b) YP-80F carbon, c) P@YP composite, d) CNT and e) P@CNT composite.

Figure 4-5. a) SEM image and the corresponding elemental mapping of (a-c) P@YP composite and (d-f) P@CNT composite.
Figure 4-6. TEM image and the corresponding elemental mapping of (a-c) P@CNT composite and (d-f) P@YP composite.

Figure 4-7. TEM images of a) YP-80F carbon and b) P@YP composite. c) Nitrogen adsorption/desorption isotherms and d) pore size distribution of YP carbon and P@YP composite. The corresponding BET surface area are 1943.4 and 733.2 m$^2$g$^{-1}$, respectively.
Figure 4-8. a) TEM images of a) P@CNT composite. b) Nitrogen adsorption/desorption isotherms of P-CNT mixture and P@CNT composite with the corresponding BET surface area are 93.2 and 59.8 m²g⁻¹, respectively.

P-C composites with different nanostructures (with/without porous structure to confine P) are believed to have different electrochemical performance. Therefore, CR2016-coin cells were assembled with P@YP and P@CNT composite as working electrode and sodium foil as the counter electrode. Cyclic voltammetry (CV) of the P@YP and P@CNT composite are shown in Figure 4-9a and b, respectively. For P@YP composite, broad peak centering at ~ 0.75 V is only observed during the initial cathodic scanning, resulting from the electrochemical decomposition of electrolyte during formation of SEI,[53,79] which is consistent with voltage profiles shown in Figure 4-10a. After the first cycle, three peaks centering at ~ 1.2 V (I), ~ 0.37 V (II) and ~ 0.01 V (III) are found in the discharging process, which corresponds to the continuous sodiation process to form Na₃P (x = 1-3) intermediates.[79] Four peaks locating at ~ 0.53 V (IV), ~ 0.67 V (V), ~ 0.83 V (VI) and ~ 1.65 V (VII) are detected in the initial and subsequent anodic scans, which are possibly due to a stepwise desodiation process from the discharged Na₃P phase to form the Na₂P, NaP, and NaP₇ intermediates according to the Na/P phase diagram.[50,51,92] Similar CV spectra is detected for the P@CNT composite in Figure 4-9b, indicating it follows the same electrochemical process as the P@YP composite. However, the separation between major
cathodic peak III and anodic peak V decreases from 689 mV for P@CNT composite to 660 mV for P@YP composite, suggesting enhanced kinetics of the electrochemical conversion of Na$_x$P to P obtained in P@YP composite, mainly due to confining nano-sized P into highly conductive carbon. The typical charge/discharge profiles for P@YP and P@CNT composite in Figure 4-10 greatly resemble the CV results and are consistent with previous work.[85,90]

The cycling performance and coulombic efficiency of the P@YP and P@CNT composite are displayed in Figure 4-9c and d, respectively, where the cells were tested at a rate of 0.1 C in the first cycle for activation and at 0.2 C in the subsequent cycles (1 C = 2600 mAg$^{-1}_p$). The initial discharge and charge capacities of the P@YP composite electrode are 1705 and 1158 mAg$^{-1}_p$, respectively, giving an initial coulombic efficiency (ICE) of ~ 68%. Similarly, P@CNT composite delivers the initial discharging capacity of 1761.4 mAg$^{-1}_p$ with an ICE of ~ 67.6%. The irreversible capacity of the first cycle is mainly from formation of an SEI layer on the surface of porous carbon and CNT, which is also observed for the first cycle of control electrodes using YP carbon and CNT as the active material (Figure 4-11, ICE of ~ 27.3% for YP and ~ 27.5% for CNT). After 100 cycles, the P@YP composite delivers the capacity of 1064 mAg$^{-1}_p$ (~ 510 mAhg$^{-1}_\text{composite}$), having retained 92% of the capacity with respect to the second cycle (1155 mAg$^{-1}_p$), corresponding to a very low capacity fading rate of ~ 0.08% per cycle. The stable cycling capacity of the YP carbon is ~ 80 mAg$^{-1}_p$, and thus neglected for calculating specific capacity of phosphorus. The CE of the P@YP composite quickly reached 99.0% after 7 cycles and stayed above 99.0% in the following cycles. Compared to P@YP composite, the P@CNT composite shows a rapid capacity decay from 1187.6 mAg$^{-1}_p$ for the 2nd cycle to 482 mAg$^{-1}_p$ for the 100th cycle, with the capacity retention of ~ 40.6%. The CE of P@CNT composite fluctuates between 97% and 98% in the first 50 cycles, staying above 98% but lower than 99% in the following cycles.
In order to understand the reason for the difference in cycling stability between P@YP and P@CNT composites, electrochemical impedance spectroscopy (EIS) was conducted on the two electrodes. Figure 4-9e shows the Nyquist plots of the P@YP composite electrode at different cycles, which are composed of a single depressed semicircle at high-frequency region and a spike at low-frequency region. According to previous research, the semicircle corresponds to the impedance of sodium-ion transport through surface films (e.g. SEI) and charge transfer at the electrode/electrolyte interface.[65,67] The EIS spectra at the 10th, 30th and 50th cycle are almost overlapped, showing a relatively constant charging resistance, mainly due to the relatively stable SEI layer formed on the surface of YP carbon. Specifically, YP carbon with porous structure confines P inside, accommodating the volume change of P during sodiation/desodiation process, leading to a stable SEI layer, guaranteeing an outstanding cycling stability. SEM images of P@YP composite electrodes before and after cycling are also compared in Figure 4-12. No obvious fractures are detected in the electrodes after 50 cycles, suggesting the excellent durability of the electrode structure obtained by the P@YP composite, which is believed to be originated from the confining P into porous carbon. In contrast, a much increased semicircle diameter was observed for the P@CNT composite (Figure 4-9f), indicating an increased charging resistance, most likely due to an unstable SEI and electrical contact loss of active materials during cycling, caused by large volume changes of the unconfined P in P@CNT composite. The remarkable difference for the two P-carbon composites in cycling stability and EIS results indicate the advantage of confinement of P within conductive carbon, which could accommodate the huge volume change, leading to stable SEI.
Figure 4-9. Cyclic voltammetry of a) P@YP and b) P@CNT composite at a scan rate of 0.1 mVs$^{-1}$. c) Cycling performance and d) coulombic efficiency of P@YP and P@CNT hybrid within 100 cycles. Electrochemical impedance spectra of e) P@YP and f) P@CNT composite after 10, 30 and 50 cycles.
Figure 4-10. Voltage profiles of the a) P@YP and b) P@CNT composite within the voltage range between 0.01 V and 2 V (vs. Na\textsuperscript{+}/Na). The specific capacity is based on the mass of red P.

Figure 4-11. The specific capacity and coulombic efficiency of a cell with a) YP-80F carbon and b) CNT as the active material cycled at a current density of 260 mAg\textsuperscript{-1} at room temperature.
Figure 4-12. SEM images of P@YP composite electrode a) before cycling and b) after 50 cycles.

In order to further confirm the importance of confining P inside pores of carbon host, the P@YP composite with higher content of P (= 65 wt. % in the composite, denoted as P@YP-65% below) was prepared following the same procedure. As shown in Figure 4-13a, diffraction peaks of red P and YP carbon are detected in the XRD pattern of the P@YP-65% composite, similar to that for P@YP-48% sample. Raman peaks arising from P show up in the P@YP-65% composite (Figure 4-13b), indicating that a great fraction of P is not confined within pores of YP carbon. X-ray photoelectron spectroscopy (XPS) characterization shows that the content of unconfined P at the surface is ~ 9.6% for P@YP-65%, much higher than ~ 6.1% for P@YP-48% (Figure 4-14 and Table 4-1), in a good consistent with Raman characterization. The increase in the content of unconfined P in the P@YP-65% composite is believed to be detrimental to cycling life. The cycling performance and coulombic efficiency of the P@YP-48% and P@YP-65% are compared in Figure 4-13c and d, respectively, where the cells were tested at a rate of 0.1 C in the first cycle for activation and 0.2 C in the subsequent cycles (1 C = 2600 mAg⁻¹). The P@YP-65% sample delivers the specific capacity of 493 mAg⁻¹ after 300 cycles, with the capacity retention of ~ 31.7% with respect to the second cycle. In contrast, the P@YP-48% sample with less amount of unconfined P shows much higher capacity retention of ~ 66.8% after 300 cycles. Additionally,
the average CE for P@YP-65% composite is 98.7% within 300 cycles (Figure 4-13d), which is lower than 99.2% for P@YP-48%. The promising cycling stability of P@YP-48% further demonstrates the importance of confining P within pores of carbon host, which could accommodate the huge volume changes, leading to stable SEI.

Figure 4-13. a) XRD pattern and b) Raman spectra of P@YP-65% composite. c) Cycling performance and d) coulombic efficiency of P@YP-48% and P@YP-65%.
Figure 4-14. High resolution C1s, P 2p, and O 1s XPS spectra of P@YP-48% and P@YP-65% composites.

<table>
<thead>
<tr>
<th></th>
<th>Atomic percentage (%) at surface</th>
<th>P/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>P@YP-48%</td>
<td>6.17</td>
<td>0.068</td>
</tr>
<tr>
<td>P@YP-65%</td>
<td>9.61</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Benefiting from the porous nanostructure, the P@YP composite is expected to have an excellent long-term cycling performance. Figure 4-15a shows the P@YP composite cycling under 0.2 C for 1000 cycles, where the first cycle was under 0.1 C for activation. After 1000 cycles, the P@YP composite still delivers the reversible capacity of 532.8 mAg⁻¹ with high average CE of 99.6% and extremely low capacity deterioration rate of ~ 0.054% per cycle. In case of long-term cycling (≥ 500 cycles), only two works have been reported to date.[88,90] Compared to them, P@YP-48% composite shows a higher content of P (22.6% for Li et al.’s work and 40% for Zhu et al.’s). Moreover, different from high current densities used in their work, P@YP-48% composite was cycled at low current density, under which issues caused by volume change are much more severe. Take all these factors into consideration, the P@YP composite shows a promising cycling stability. The rate performance of the P@YP composite was also evaluated under the current density from 0.1 C to 3 C, as shown in Figure 4-15b. It still delivers a high
reversible capacity of \( \sim 601 \text{ mAg}^{-1} \) \( \sim 300 \text{ mAhg}^{-1}_{\text{composite}} \) even at 3 C. When the rate was restored to 0.5 C, the specific capacity returned to 1016 mAg\(^{-1}\) \( \sim 510 \text{ mAhg}^{-1}_{\text{composite}} \), which is close to the 1079 mAg\(^{-1}\) of the 6th cycle. This indicates that the electrode cycling is reversible even at high current densities.

Figure 4-15. a) Long term cycling performance of P@YP composite. b) Rate performance of P@YP composite at C-rate between 0.1 C and 3 C (1C = 2600 mAg\(^{-1}\)).

4.4 Conclusion

In summary, we successfully developed two P-C composites via well-controlled vaporization-deposition-conversion method: P@YP with P confined inside porous carbon and P@CNT with unconfined P on the surface of the CNT. The small size of P particles (\( \leq 2 \text{ nm} \)) due to being confined in the pores of YP carbon greatly shortens the Na-ion migration path, leading to good rate performance. Additionally, robust porous structure successfully accommodates the volume changes of P during sodiation/desodiation process, resulting in stable SEI layer, guaranteeing an outstanding long-term cycling stability. As a result, high gravimetric specific capacity of 1705 mAhg\(^{-1}\), great average coulombic efficiency of 99.0%, and excellent capacity...
retention of 42% within 1000 cycles are achieved. In contrast, P@CNT composite with unconfined P shows a rapid capacity decay and large increase in charging resistance, probably due to unstable SEI and electrical contact loss of active materials during sodiation/desodiation process, caused by large volume changes of unconfined P in the P@CNT composite. It clearly shows that the well-designed P-C nanostructure with P being confined within highly conductive carbon host could greatly enhance its electrochemical performance.
Chapter 5

Exceptionally High Ionic Conductivity in Na$_{3}$P$_{0.62}$As$_{0.38}$S$_4$ with Improved Moisture Stability for Solid-State Sodium-ion Batteries

5.1 Introduction

Na-ion batteries (NIBs) have the potential to compete with widely used Li-ion batteries (LIBs) for stationary energy storage applications and could revolutionize the landscape of electrochemical energy storage, thanks to the abundance of sodium precursor and its cost advantage.[71,93-96] Severe safety issues exist in NIBs because of extremely high reactivity of sodium metal in volatile and flammable organic liquid electrolyte.[68,74,97,98] Solid-state NIB with solid-state electrolyte (SSE) is attractive because it can potentially address the safety issues and also achieve long cycle life.[40,99,100]

The significant challenge exists in the development of Na-ion SSE with high ionic conductivity that is comparable with liquid counterparts (1 ~ 6 mS cm$^{-1}$ at room temperature) to promote fabrication of safe solid-state NIBs.[101] Oxide ceramic and sulfide glass-ceramic Na-ion conductors as potential Na-ion SSE have been explored.[99,102,103] NASCON-type oxides (such as Na$_{1+x}$Zr$_2$Si$_3$P$_{3-x}$O$_{12}$ with 0 ≤ x ≤ 3)[104-106] and β”-alumina[31,107] are well-known Na-ion SSEs exhibiting high room-temperature ionic conductivity over 1 mS cm$^{-1}$. However, their harsh synthesis conditions (e.g., high synthesis temperature ~ 1200 °C), high annealing temperature (> 1000 °C), and poor room-temperature electrolyte-electrode contact make their large-scale applications complicated and expensive.[23,75,108] In contrast to those oxide-based conductors, sulfide-based SSEs are more promising because of their high ionic conductivity, good contact with electrode, low-temperature process capability and low grain boundary resistance,
which have been proved in all-solid-state LIBs.\[24-29\] Inspired by the success of the Li-ion SSEs, considerable efforts have recently been made on the development of Na-ion sulfide-based SSEs. Glass-ceramic electrolyte Na$_3$PS$_4$\[31,109\] was found to be with a room-temperature conductivity of 0.2 mS cm$^{-1}$, which was increased to 0.74 mS cm$^{-1}$ by silicon doping\[32,110\] and 1.14 mS cm$^{-1}$ by halogen doping.\[35,111\] Anion substitution of S by Se (Na$_3$PSe$_4$)\[36\] and cation substitution of P by Sb (Na$_3$SbS$_4$)\[33,34\] further increased the ionic conductivity to 1.16 and 1.05 mS cm$^{-1}$, respectively. Recently, Richards et al.\[112\] reported a new family of Na$_{10}$MP$_2$S$_{12}$ (M = Sn, Ge and Si) and predicted a super high ionic conductivity of 10.28 mS cm$^{-1}$ for Na$_{10}$SiP$_2$S$_{12}$ based on first-principles simulations. Despite considerable efforts, current Na-ion sulfide-based SSEs, including the aforementioned ones, still suffer from either poor ionic conductivity (< 1 mS cm$^{-1}$) or unsatisfied moisture stability at room temperature, motivating the development of Na-ion SSEs which could address these two challenges.

In the present work, we report a new Na-ion SSE of Na$_3$P$_{1-x}$As$_x$S$_4$ (0 ≤ x ≤ 1). A superior high Na-ion conductivity of 1.46 mS cm$^{-1}$ at room temperature is achieved for x = 0.38 (i.e., Na$_3$P$_{0.62}$As$_{0.38}$S$_4$) – the highest conductivity reported so far in sulfide-based Na-ion conductors. It is further found that Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ possesses good moisture stability, dramatically improved in comparison with Na$_3$PS$_4$. The Na-ion conductor of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ was further examined in a solid-state NIB, demonstrating a stable electrochemical performance. The exceptionally high conductivity in Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ with respect to the endmember compounds Na$_3$PS$_4$ (0.2 to 0.46 mS cm$^{-1}$)\[31,110\] and Na$_3$AsS$_4$ (0.027 mS cm$^{-1}$, see details below) is beyond the current understanding of ionic conductivity for solid-state conductors, for instance the body-centered-cubic like anion framework\[113,114\] and the increased conductivity with increasing volume.\[115\] Density functional theory (DFT) calculations uncover that the improvement of conductivity stems from a longer Na-S bond length in the unstable saddle point structure of transition state, regulated by the duel effects of alloying element arsenic (As), i.e., lattice
expansion for high conductivity and weaker As-S bond (stronger Na-S bond) for low conductivity. The revealed mechanism opens a new avenue to design SSEs with high ionic conductivity and promising moisture stability.

5.2 Experimental Section

Synthesis: Na$_3$P$_{1-x}$As$_x$S$_4$ electrolytes were prepared by ball-mill technique followed by heat treatment. The stoichiometric amounts of Na$_2$S (Alfa Aesar, anhydrous, analytical reagent), P$_2$S$_5$ (Sigma-Aldrich, 99%), and As$_2$S$_5$ (Sigma-Aldrich, 99.99%) were hand-ground before transferring to an agate jar. The mixture was ball-milled for 15 hours at a speed of 510 rpm using a planetary ball mill (Across International). The obtained powders were cold pressed at 400 MPa into a pellet, which was 10 mm in diameter and 0.6 ~ 1.2 mm in thickness. All the processes were protected under Ar atmosphere. The pellet was sealed in an evacuated glass tube and heated up to 270 °C (1 °C min$^{-1}$). It was kept at 270 °C for 2 hours before cooling down to room temperature at the same rate.

Characterization of solid electrolytes: Powder X-ray diffraction (XRD) measurements were performed on a Rigaku Miniflex II spectrometer with Cu $K_\alpha$ radiation, using XRD holder with beryllium window (Rigaku Corp.) for air sensitive samples. Synchrotron X-ray diffraction (SXRD) measurements were conducted at the beamline 11-ID-C of Advanced Photon Source (APS), Argonne National Laboratory, using X-rays with wavelength of 0.11725 Å. The specimens were sealed with Kapton tape in a glovebox filled with high purity Argon (Ar), to avoid any side reactions with the air. Whole pattern fitting refinements on the SXRD data were performed using the JADE 2010 software (Materials Data Corp., California), with polynomial background fitting model at the order of 5. The cross-section morphology of the SSE pellets was investigated using
scanning electron microscope (Nano630 FE-SEM). The P/As ratio was determined by inductively coupled plasma emission spectrometry (ICP-AES, Perkin-Elmer Optima 5300). For moisture stability characterization, the Nalgene™ Transparent Polycarbonate Classic Design Desiccator (~16 L in volume, ThermoFisher Scientific Inc.) was employed, in which the humidity was well controlled by tuning the amount of molecular sieve inside and monitored by a hygrometer. Na$_3$PS$_4$ and Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ pellets were put into the desiccator for air exposure after the humidity inside stabilized at 15%. Powders and pellets were used for XRD and impedance measurements, respectively. To compare the amount of H$_2$S gas released from the Na$_3$PS$_4$ and Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ powder samples, 200 mg of each powder was put into the desiccator where the humidity was tuned to 45% in order to accelerate the H$_2$S gas release, the concentration of H$_2$S was detected by a calibrated gas detector (Honeywell Analytics SPM Single Point Monitor). For ionic conductivity measurements, carbon-coated aluminum foils were pressed onto both faces of pellets under the pressure 400 MPa, serving as blocking electrodes. The pellet was assembled into a 2016-type coin cell with two stainless-steel discs as current collector. Electrochemical impedance spectroscopy measurements were carried out on Solartron ModuLab in the frequency range of 1 MHz to 0.1 Hz with an amplitude of 5 mV. Cyclic voltammetry of Na/Na$_3$P$_{1-x}$As$_x$S$_4$/Sn was measured with the Na metal as counter/reference electrode and Sn as working electrode with a scan rate of 1 mVs$^{-1}$ from -0.5 V to 5 V (vs. Na$^+$/Na) at 80 °C.

Characterization of all-solid-state batteries: All-solid-state Na-ion battery was fabricated by pressing Na-Sn alloy foil and TiS$_2$ powder (Sigma-Aldrich, 99.9%) onto two faces of the pressed Na$_3$P$_{1-x}$As$_x$S$_4$ pellet. The obtained three-layer pellet was assembled into a 2032-type coin cell with stainless-steel discs as current collector. All the processes were under an Ar atmosphere. The cell was cycled galvanostatically at a current density of 4.8 mAg$^{-1}$ (0.02 C, based on the theoretical capacity of TiS$_2$), within the voltage range from 1.17 to 2.4 V using a BTS-5V1mA Neware battery test system.
DFT calculations: All DFT based first-principles calculations in the present work were carried out by the Vienna Ab initio Simulation Package (VASP 5.4.1)\[116\] with the ion-electron interaction described by the projector augmented wave method.\[117\] The selected exchange-correlation (X-C) functional is the improved generalized gradient approximation for densely packed solids and their surfaces, i.e., the PBEsol,\[118\] since it describes well structural and phonon properties of sulfides\[119,120\] as well as diffusion properties.\[121\] In addition, a hybrid X-C functional of Heyd-Scuseria-Ernzerhof (HSE06)\[122\] was also used to get accurate bandgap energy. The migration energies of Na-ion were predicted by the climbing image nudged elastic band (CINEB) method\[123\] using five images according to the mono-vacancy (Va) mediated diffusion mechanism,\[121\] and all the Na-Va migration pathways were calculated when possible. The reported migration energies were based on an average energy from all initial state structures. Phonom calculations were performed by the supercell method as implemented in the YPHON code\[124,125\] with VASP as the computational engine. Other DFT details and results are given in the Supporting Information including, for example, the employed supercells, cutoff energies, and \(k\)-points meshes, as well as the predicted structural, thermodynamic, and migration properties, in comparison with experimental data available in the literature.

5.3 Results and Discussion

Figure 5-1a shows a synchrotron X-ray diffraction (SXRD, wavelength \(\lambda = 0.117415 \text{ Å}\)) pattern of as-prepared Na\(_3\)PS\(_4\) powder together with the corresponding whole pattern fitting refinement with reference to a tetragonal structure of Na\(_3\)PS\(_4\) (PDF 97-007-2860, space group \(P\bar{4}2_1c\)). Calculated R factor and structural parameters are summarized in Table 5-1. We conclude that the as-prepared Na\(_3\)PS\(_4\) is a tetragonal phase due mainly to the following facts: (i) a small R value of 1.58 % is obtained for the refinement and an explicit tetragonal peak of (212) exists in
the SXRD pattern of Na₃PS₄ (Figure 5-1b), and (ii) the cubic phase[32] is equivalent to tetragonal phase to some extent based on the DFT calculations, see details in Appendix A.

Table 5-1. Whole pattern fitting refinements for synchrotron X-ray diffraction patterns of Na₃PS₄ and Na₃P₀.₆₂As₀.₃₈S₄ according to tetragonal structure with space group P42₁c.

<table>
<thead>
<tr>
<th>Materials</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>Volume (Å³)</th>
<th>(R%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₃PS₄</td>
<td>6.967</td>
<td>6.967</td>
<td>7.06</td>
<td>342.7</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>6.952</td>
<td>6.952</td>
<td>7.076</td>
<td>342.0</td>
<td></td>
</tr>
<tr>
<td>Na₃P₀.₆₂As₀.₃₈S₄</td>
<td>7.015</td>
<td>7.015</td>
<td>7.057</td>
<td>347.2</td>
<td>1.94</td>
</tr>
</tbody>
</table>

Figure 5-1. Synchrotron X-ray whole pattern fitting refinements of a) Na₃PS₄ and c) Na₃P₀.₆₂As₀.₃₈S₄. Magnified 2θ of 2.5 – 3.2° for b) Na₃PS₄ and d) Na₃P₀.₆₂As₀.₃₈S₄. The red dot and black solid line represent the experimental data and calculated patterns, respectively. The vertical green bars correspond to the expected positions of Bragg reflections of tetragonal Na₃PS₄. The blue lines at the bottom are the difference between calculated and experimental patterns.
Powder XRD (Cu Kα with wavelength $\lambda = 1.541 \text{ Å}$) patterns of as-prepared Na$_3$P$_{1-x}$As$_x$S$_4$ ($0 \leq x \leq 1$) are compared in Figure 5-2a. Beryllium (Be) peaks, from an XRD holder for air-sensitive samples, were used as an internal reference to detect the peak shift due to As-substitution. The magnified region of 2θ between 35 ~ 37° is shown in Figure 5-2b. The peak at around 36.4°, corresponding to plane (220) for Na$_3$PS$_4$, shifts to a larger d-spacing with increasing As concentration. Considering the larger ionic radius of As$^{5+}$ (0.46 Å) versus P$^{5+}$ (0.38 Å),[126] this suggests that alloying element As is successfully substituted for P$^{5+}$. Figure 5-1c and d show the SXRD pattern and the corresponding whole pattern fitting refinement of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$. Structural parameters as well as calculated R factor, summarized in Table 5-1, show that lattice parameters $a$ and $b$ of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ are elongated while lattice parameter $c$ is slightly compressed, in comparison with Na$_3$PS$_4$. These features of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ are favorable for Na-ion conductivity in terms of structure (see DFT results and discussion below). The P/As molar ratio was determined by inductively coupled plasma emission spectrometry (ICP-AES) and found to be 0.62/0.38.

Figure 5-2. a) Powder XRD patterns of Na$_3$P$_{1-x}$As$_x$S$_4$ electrolytes. Beryllium peaks from air-sensitive holder are marked as star. b) Magnified 2θ of 34.5 – 37.5°.
Figure 5-3a shows Na-ion conductivity in Na$_3$P$_{1-x}$As$_x$S$_4$ at room temperature as a function of $x$. The as-prepared Na$_3$PS$_4$ ($x = 0$) possesses a conductivity $\sigma$ of 0.2 mS cm$^{-1}$, agreeing well with the reported value.[31] The ionic conductivity of Na$_3$P$_{1-x}$As$_x$S$_4$ increases with increasing As concentration, reaching a maximum value of 1.46 mS cm$^{-1}$ with $x = 0.38$ in Na$_3$P$_{0.62}$As$_{0.38}$S$_4$, and then decreases to 0.4 mS cm$^{-1}$ for Na$_3$P$_{0.5}$As$_{0.5}$S$_4$ and 0.027 mS cm$^{-1}$ for Na$_3$AsS$_4$. To the best of our knowledge, 1.46 mS cm$^{-1}$ is the highest ionic conductivity reported so far in sulfide-based Na-ion conductors. It is even comparable to the conductivities in organic liquid Na-ion electrolytes (1 ~ 6 mS cm$^{-1}$ at room temperature).[101] Figure 5-3b shows Arrhenius plots and the corresponding impedance plots of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ within a temperature range between -120 °C and 100 °C. The impedance plots indicate that Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ is a pure ionic conductor, since it consists of a semicircle at high-frequency region and a spike at low-frequency region, corresponding to impedance contributions from (1) the bulk/grain and grain boundary, and (2) the electrode, respectively. The ionic conductivity was calculated based on the total resistance (bulk/grain and grain boundary resistance) obtained from an intercept crossed between the semicircle and the spike on the x-axis. The fitted activation energy is 0.256 eV for Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ as shown in Figure 5-3b, which is lower than those of Na$_3$PS$_4$ (0.289 eV), Na$_3$P$_{0.5}$As$_{0.5}$S$_4$ (0.268 eV), and Na$_3$AsS$_4$ (0.341 eV), as shown in Figure 5-4. Cross-section scanning electron microscopy (SEM) images of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ and Na$_3$PS$_4$ pellets (Figure 5-5) show the intimate contacts between compact particles obtained in both of the two pellets, leading to a high density around 1.95 g cm$^{-3}$ for Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ pellet and 1.74 g cm$^{-3}$ for Na$_3$PS$_4$. Compact microstructure with high density is necessary for a fast ionic diffusion.
Figure 5-3. a) Room-temperature ionic conductivity of Na$_3$P$_{1-x}$As$_x$S$_4$ as function of $x$. b) Arrhenius plots and the corresponding impedance plots of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ within a temperature range between -120 ºC and 100 ºC.

Figure 5-4. Ionic conductivities of Na$_3$PS$_4$, Na$_3$P$_{0.62}$As$_{0.38}$S$_4$, Na$_3$P$_{0.5}$As$_{0.5}$S$_4$, and Na$_3$AsS$_4$ with the corresponding activation energies.
Figure 5-5. Cross-sectional SEM images of a) Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ and b) Na$_3$PS$_4$.

Figure 5-6 shows the temperature-dependent ionic conductivities in Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ along with those in Na-ion conductors reported in the literature.[23,30,31,33,34,36,104-106,127,128] Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ shows a similar conductivity with respect to β-alumina (a mixture of β and β” phases)[23] in the temperature range from 25 to 100 °C, and has at least one magnitude higher in conductivity than those in 50Na$_2$S-50P$_2$S$_5$,[127] 60Na$_2$S-40GeS$_2$,[127] 50Na$_2$S-50SiS$_2$,[127] cubic Na$_3$PS$_4$,[31] and Na$_3$Zr$_2$Si$_2$PO$_{12}$ NASICON.[104,106] Even though the conductivity is slightly lower than the NASICON-type crystal (produced by Cerametec),[106] low-temperature process and good electrode-electrolyte contact offered by sulfide-based SSEs grant advantages for Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ to fabricate all-solid-state NIBs (vide infra). Even at low temperatures, it possesses a decent ionic conductivity, such as 0.2 mS cm$^{-1}$ at -20 °C, showing another advantage comparing to organic liquid electrolyte.[101]
Figure 5-6. Temperature-dependent ionic conductivities of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ in comparison with the reported Na-ion conductors. Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ exhibits the highest conductivity among sulfides and is comparable with β-alumina (a mixture of β and β” phases).

Besides the increased ionic conductivity in Na$_3$P$_{0.62}$As$_{0.38}$S$_4$, it is exciting to find that alloying element As could also improve the moisture stability. Figure 5-7a shows the XRD patterns of Na$_3$PS$_4$ and Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ powders exposed to air with 15% humidity at room temperature for 100 hours. It clearly shows that Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ powders maintain the same XRD patterns after the exposure, while the new peaks (corresponding to the new phases/compositions due to its reaction with moisture) appearing in Na$_3$PS$_4$ powders. The corresponding impedance plots of the Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ pellet barely changes upon the air exposure (Figure 5-7b). In contrast, a large increase in total resistance (bulk/grain and grain boundary resistance) is detected in the Na$_3$PS$_4$ pellet after the air exposure, which may be attributed to the composition or phase changes as indicated by the XRD results. In addition, the activation energies for Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ before and after the air exposure are 0.256 and 0.269 eV, respectively. Differently, a huge increase in
activation energy from 0.289 to 0.325 eV is found in Na₃PS₄ after the air exposure due to its composition or phase changes after reacting with H₂O. H₂S is believed to be one of the products after the reaction with H₂O in air. We thus monitor the concentration of H₂S after exposing Na₃PS₄ or Na₃P₀.₆₂A₀.₃₈S₄ powders in air with a higher humidity of 45%. As shown in Figure 5-7c, from the sample Na₃PS₄, the concentration of H₂S gas is detected to be 1.4 ppm after 30 seconds exposure and gradually increases to 1.8 ppm after 6 minutes. In contrast, no H₂S gas is detected from the Na₃P₀.₆₂A₀.₃₈S₄ powder until the time reaching to 4 minutes. After 6 minutes, the concentration of H₂S reaches to 1.3 ppm, but still lower than that of Na₃PS₄. The excellent moisture stability of Na₃P₀.₆₂A₀.₃₈S₄ mainly results from the moisture reactions shifted from the low energy ones (for example Na₃PS₄ + H₂O → Na₃POS₃ + H₂S) to the high energy ones (for example Na₃P₀.₆₂A₀.₃₈S₄ + H₂O → Na₃P₀.₆₂A₀.₃₈O₃S₃ + H₂S and Na₃P₀.₆₂A₀.₃₈S₄ + 8 H₂O → Na₃P₀.₆₂A₀.₃₈S₄·8H₂O) in terms of DFT calculations (not shown here). The enhanced moisture stability further shows promise of Na₃P₀.₆₂A₀.₃₈S₄ for processing and fabrication of solid-state NIBs in practical applications.

Figure 5-7. a) XRD patterns, b) impedance plots at room temperature under the humidity of 15% and c) time-dependent concentration of H₂S released from Na₃PS₄ and Na₃P₀.₆₂A₀.₃₈S₄ after exposing to the air with 45% humidity.
In an effort to probe the origin of high conductivity in Na$_3$P$_{1-x}$As$_x$S$_4$, Na-ion migration energies – which link directly to activation energy, and in turn, ionic conductivity – are analyzed by DFT calculations for three tetragonal structures of Na$_3$PS$_4$, Na$_3$AsS$_4$, and the simplest structure of Na$_3$P$_{0.5}$As$_{0.5}$S$_4$ (Table 5-2). As demonstrated in one example of Figure 5-8a, two kinds of sodium (Na$_1$ and Na$_2$) together with two types of the nearest Na-Na neighbors with bond lengths around 3.5 Å exist in the tetragonal Na$_3$P$_{1-x}$As$_x$S$_4$, in which the Na$_1$-Na$_2$ bond is roughly along the $a$- and $b$-axis directions and the Na$_2$-Na$_2$ bond along the $c$-axis direction. In addition, the Na$_1$-Na$_2$ bond length is about 0.02 ~ 0.03 Å shorter than the Na$_2$-Na$_2$ case, resulting in lattice parameters $c > a$, for example, $a = 6.952$ Å and $c = 7.076$ Å for Na$_3$PS$_4$ at room temperature.[30] Calculated migration energies as shown in Figure 5-9 reveal that Na-ion jumps along the Na$_1$-Na$_2$ sites are more favorable (with 30 ~ 40 meV lower energy) than those along the Na$_2$-Na$_2$ sites, indicating the $a$- and $b$-axis directions are the dominant diffusion channels of Na-ion in Na$_3$P$_{1-x}$As$_x$S$_4$.

However, the general principle regarding the increase of ionic conductivity with increasing volume (or bond length)[113,115] cannot explain Na-ion migration and the corresponding conductivity as a function of As concentration in the present work (Figure 5-3a), since the volume and various bond lengths (e.g., Na-Na and Na-S bonds) keep increasing with increasing As concentration in Na$_3$P$_{1-x}$As$_x$S$_4$ (Figure 5-10a and Table A-3).
Figure 5-8. Stretching force constants (SFCs) of the low energy structure of Na$_3$P$_{0.5}$As$_{0.5}$S$_4$ from DFT calculations. a) The 128-atom supercell marked by the black unit cell lines used for phonon calculations. Two types of Na atoms refer to the ones in the original tetragonal cell (Na$_1$ in 2b site and Na$_2$ in 4d site of space group $P\bar{4}2_1c$). b) Key SFCs between different atomic pairs. The lines are linear fittings of the Na-X (X = S, As, P, and Na) SFCs, showing the Na-S bonding strength is ultrasensitive to bond length change with respect to the other Na-X pairs.

Figure 5-9. Migration energies from CINEB calculations for tetragonal Na$_3$PS$_4$, Na$_3$P$_{0.5}$As$_{0.5}$S$_4$ (high), and Na$_3$AsS$_4$. The structural details are shown in Table 5-2. Migration energy of Na-ion is mainly controlled by the jump distance of Na-Na sites, and the low migration energy is for the short jump distance between the Na$^1$-Na$^2$ sites.
Figure 5-10. Nearest Na-S bond length and the minimum migration energy of Na-ion in three 127-atom supercells. The nearest Na-S bond lengths in a) the initial states (IS) and, b) the transition states (TS) during Na migrations. One Na vacancy is introduced in each structure, and the simplest $Na_{47}P_8As_8S_{64}$ structure based on the high energy structure of $Na_3P_{0.5}As_{0.5}S_4$ with space group $P4$ is used for simplicity. c) The minimum Na migration energies in these three structures.

To examine the determining factor of Na-ion conductivity in $Na_3P_{1-x}As_xS_4$, bonding strengths between all atomic pairs[129] are illustrated in Figure 5-8b: the stretching force constant (SFC) with respect to bond length for a low energy structure of $Na_3P_{0.5}As_{0.5}S_4$ (Figure 5-8a) from phonon calculations. These force constants are transferable in $Na_3P_{1-x}As_xS_4$ by all examined SFCs from the present phonon calculations, agreeing with the finding in metal alloys.[130] Figure 5-8b shows that the strongest bonding is the P-S pair ($\sim 11.8$ eVÅ$^{-2}$) followed by As-S ($\sim 10.9$ eVÅ$^{-2}$), indicating the formation of $PS_{3}^{3-}$ and $AsS_{3}^{3-}$ anions. The present bond lengths and SFCs of P-S and As-S pairs agree reasonably well with the empirical estimations:[131] bond length of 2.12 Å and force constant $\sim 15$ eVÅ$^{-2}$ for P-S ($PS_{4}^{3-}$); and bond length of 2.22 Å and force constant $\sim 14$ eVÅ$^{-2}$ for As-S ($AsS_{4}^{3-}$). By examining all the Na-X ($X = S, As, P,$ and Na) SFCs, it is shown that the Na-S bonding strength is ultrasensitive to the variation of bond length, since the slope of the Na-S linear fitting is about $13 \sim 16$ times steeper than the other Na-X linear fittings (Figure 5-8b). Hence, the Na-S bond length can serve as a
criterion to judge Na-ion diffusivity and conductivity, but it fails to explain the variation of Na-ion conductivity (Figure 5-3a) based on the stable structures of NaP$_{1-x}$As$_x$S$_4$ as shown in Figure 5-8a.

Following the Na migration path in Na$_3$P$_{1-x}$As$_x$S$_4$, it is found that the nearest Na-S bond length in the transition state (TS) structure, an unstable saddle point related to the highest energy along Na-ion migration, correlates well with the Na-ion migration energy. Figure 5-10a shows that the nearest Na-S bond length in the initial state structure (IS, a stable structure with one Na-vacancy) keeps increasing with increasing As concentration. However, Figure 5-10b shows that the nearest Na-S bond length in the TS structures reaches the maximum at $x = 0.5$, showing a trend inversely proportional to the minimum Na-ion migration energy in Figure 5-10c, in line with the measured Na-ion activation energy and conductivity (Figure 5-3a and Figure 5-4). Based on a binominal fitting for the migration energy data in Figure 5-10c (70.5, 65.9 and 84.0 meV) together with an additional migration energy of 68.5 meV from the low energy structure of Na$_3$P$_{0.5}$As$_{0.5}$S$_4$ (results not shown), the lowest migration energy is found to be at $x = 0.38$, in accordance with the maximum Na-ion conductivity with $x = 0.38$ (Figure 5-3a). The variation of the Na-S bond length in the TS structure (here the mentioned Na is the migrating Na atom) can be understood by the dual effects of alloying element As, viz., (i) lattice expansion as well as bond length (especially Na-S) increase by adding As, promoting the increase of ionic conductivity; and (ii) a weaker As-S bonding compared to the P-S bonding (Figure 5-8b), making the attraction of Na-S stronger and resulting in a shorter Na-S bond length in the predominant TS structure of Na-ion migration (Figure 5-10b) when further increasing As concentration, and hence a lower ionic conductivity. It is expected that the present finding about the dual effects of alloying element on Na-ion conductivity exists also in other chalcogenide-based conductors, since a longer bond length together with a weaker bonding (force constants) have been confirmed for various anions, for example: PS$_4^{3-}$, AsS$_4^{3-}$, AsSe$_4^{3-}$, SbS$_4^{3-}$, SiS$_4^{4-}$, GeS$_4^{4-}$, GeSe$_4^{4-}$, SnS$_4^{4-}$, and SnSe$_4^{4-}$.[131]
Electrochemical stability of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ was evaluated from cyclic voltammetry (CV) of Na/Na$_3$P$_{0.62}$As$_{0.38}$S$_4$/Sn cell at 80°C, with Na as the counter/reference electrode and Sn as the working electrode. As shown in Figure 5-11a, both cathodic and anodic currents are observed near 0 V versus Na$^+$/Na, which corresponds to sodiation with and desodiation from Sn, respectively. No significant oxidation current has been detected up to 5 V. The areas under the curves associated with Na deposition and dissolution process are 283.01 and 263.74 µW, respectively. The corresponding coulombic efficiency is 263.74/283.01 = 93.2%, indicating that the deposition/dissolution of Na is highly reversible. The CV result indicates that Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ has a good compatibility with sodium metal and a wide electrochemical window.[24,31]

![Figure 5-11. Electrochemical performance of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ solid-state electrolyte (SSE). a) Cyclic voltammetry of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ SSE. Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ was tested at 80 °C with Na as the counter/reference electrode and Sn as the working electrode. b) Charge-discharge curves of all-solid-state Na-ion battery Na-Sn/Na$_3$P$_{0.62}$As$_{0.38}$S$_4$/TiS$_2$. The cell was cycled at 80 °C with the current density of 4.8 mAg$^{-1}$ (0.02 C, 1 C = 240 mAhg$^{-1}$) from 1.17 to 2.4 V.](image)

All-solid-state Na-ion battery Na-Sn/Na$_3$P$_{0.62}$As$_{0.38}$S$_4$/TiS$_2$ was fabricated by pressing the Na-Sn alloy foil as anodes and the TiS$_2$ power as cathodes onto two faces of the Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ pellet. The obtained three-layer pellet was assembled into a 2032-type coin cell with stainless-
steel discs as current collector. Figure 5-11b shows the charge-discharge curves of the Na-Sn/Na₃P₀.₆₂As₀.₃₈S₄/TiS₂ cell at 80 °C, under a current density of 4.8 mA g⁻¹ (0.02 C) within the voltage range from 1.17 to 2.4 V. The first discharge and charge capacities are 163 and 118 mAh g⁻¹, respectively, corresponding to a high initial coulombic efficiency of 72.4%. After 9 cycles, the charging capacity still maintains at 103 mAh g⁻¹. The average cell voltage from the 1st to the 9th cycle is 1.77 V, which corresponds to the potential difference between the Na-Sn counter electrode (ca. 0.3 V vs. Na⁺/Na) and the TiS₂ working electrode (ca. 2.0 V vs. Na⁺/Na). We believe that the specific capacity and cycling performance of the cells could be further enhanced by engineering fabrication of the Na-Sn/Na₃P₀.₆₂As₀.₃₈S₄/TiS₂ three-layer pellet with improved interfacial contacts.

The poisonous nature of arsenic compound can raise a concern of toxicity regarding the use of Na₃P₁₋ₓAsₓS₄ solid-state electrolyte. The poor solubility of arsenic sulfides in water and acid, which is quite different from the toxic oxide counterparts, could reduce the toxicity in preparation of Na₃P₁₋ₓAsₓS₄.[132] However, since Na₃P₁₋ₓAsₓS₄ can react with water eventually generating toxic arsenic compound, great attention should be paid when dealing with sulfide electrolytes.

5.4 Conclusion

In summary, a new Na-ion SSE, Na₃P₀.₆₂As₀.₃₈S₄, has been discovered with an exceptionally high conductivity of 1.46 mS cm⁻¹ at room temperature, enhanced moisture stability, superior electrochemical stability and performance. Na-ion conductivity in Na₃P₀.₆₂As₀.₃₈S₄ is higher than that in any other sulfide-based Na-ion conductors reported in the literature and comparable with organic liquid electrolytes currently used in NIBs. Combing experimental results and DFT-based first-principles and phonon calculations, the origin of the
exceptional conductivity in Na₃P₀.₆₂As₀.₃₈S₄ is attributed mainly to a longer Na-S bond length in the unstable transition state structure during Na-ion migration, owing to the dual effects of alloying element As, viz., lattice expansion for a high conductivity and a weaker As-S bond (promoting a stronger Na-S bond in the transition state structure) for a low conductivity. In addition, DFT calculations also identify that the improved moisture stability in Na₃P₀.₆₂As₀.₃₈S₄ stems from the shift of low energy moisture reactions to high energy ones. The uncovered mechanism could be applied to other Na-ion conductors, opening a new pathway for searching advanced SSEs with high ionic conductivity and promising moisture stability.
Chapter 6
A Superior Sodium-ion Conductor

6.1 Introduction

The enhancing demand for energy storage technology in modern society has boosted the fast development of rechargeable batteries in last decades.[37,133] Na-ion batteries (NIBs) have received worldwide resonance due to their high energy density, great abundance of sodium precursor, and huge cost advantage.[68,134] All-solid-state low temperature NIB with inorganic solid-state electrolyte (SSE) is believed to address the severe safety issues caused by the volatile and flammable natures of organic liquid electrolytes, and to revolutionize the landscape of electrochemical energy storage due to the facile device fabrication.[24,26]

However, the development of all-solid-state low temperature NIBs is far short of expectation mainly because of poor ionic conductivity of Na-ion SSEs. The major scientific challenge for all-solid-state NIBs therefore resides in developing new Na-ion SSEs with high room-temperature ionic conductivity. Great efforts have been made into developing crystalline oxides, such as NASCON-type SSE ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ with $0 \leq x \leq 3$) and β”-alumina, both of which still have the highest room-temperature ionic conductivity over 1 mS cm$^{-1}$.[31,104,107,126] But the harsh synthesis conditions (e.g. high synthesis/anneal temperature $> 1000^\circ$C) and poor electrode-electrolyte contact make their large-scale application complicated and expensive.[23,75,108] Besides crystalline oxides, crystalline sulfides ($Na_{10}SnP_2S_{12}$,[112] $Na_3PSe_xS_{4-x}$[36]) and glass ceramics ($Na_3PS_4$[31] $Na_3P_{1.5}Si_xS_{4}$[32] $Na_3P_{1.5}As_xS_4$[69]) have been investigated as battery electrolyte. Unfortunately, most of these materials exhibit the ionic conductivity of the order $10^{1}$ mS cm$^{-1}$, and still need to be further improved. Polymer-based Na-
ion SSEs have also been well studied, which are composed of sodium salts dissolved in polymers like poly (ethylene oxide). However, the ionic conductivity for these materials are pretty low at room temperature (~ $10^{-3}$ mS cm$^{-1}$).[135] Very recently, glass-amorphous Na-ion SSE (Na$_{2.99}$Ba$_{0.005}$ClO+xH$_2$O) has been discovered with very high ionic conductivity of $\sim 10^{-2}$ S cm$^{-1}$, however, the mechanism behind which is still under investigation.[136,137] Despite these considerable efforts, current Na-ion SSEs including the aforementioned ones, are unsatisfying for practical application of all-solid-state low temperature NIBs, motivating the development of new Na-ion SSEs.

Here we report a new Na-ion superionic conductor, Na$_{11}$Sn$_{1.94}$PS$_{12}$, with a unique crystal structure different from that for any reported Na-ion SSEs in the literature. This new phase has three-dimensional (3D) conduction pathway for Na-ions, indicating its high ionic conductivity. In addition, the less occupied Na positions in the structure are the neighbors of the more occupied ones, further promoting the Na-ion transport. Thus, the new Na-ion SSE Na$_{11}$Sn$_{1.94}$PS$_{12}$ exhibits an extremely high total ionic conductivity of 1.06 mS cm$^{-1}$ at room temperature. Furthermore, Na-Sn/TiS$_2$ battery with Na$_{11}$Sn$_{1.94}$PS$_{12}$ as electrolyte shows a promising electrochemical performance, indicating the potential of Na$_{11}$Sn$_{1.94}$PS$_{12}$ in practical application. Considering its unique crystal structure, high ionic conductivity, and excellent electrochemical property, the new conductor Na$_{11}$Sn$_{1.94}$PS$_{12}$ is a promising candidate for SSE in NIBs. We hope the discovery of this new phase would open a gate for identifying new SSEs with high ionic conductivity under the general formula of Na$_{11}$M$_{1.94}$PS$_{12}$ (M = Sn, Ge, Si).
6.2 Experimental Section

Synthesis: $\text{Na}_{11}\text{Sn}_{1.94}\text{PS}_{12}$ were prepared by heating the stoichiometric amounts of $\text{Na}_2\text{S}$ (anhydrous, Alfa Aesar), phosphorus lump (Alfa Aesar, 99.999%), $\text{Sn}$ (Alfa Aesar, 99.995%) and $\text{S}$ (Sigma Aldrich, 99.998%) in an evacuated quartz tube to 600 °C (0.5 °C/min). It was kept at 600 °C for 48 hours before cooling down to the room temperature at the rate of 1 °C/min.

Single crystal X-ray measurement: The X-ray data-sets were collected on a Bruker SMART APEX diffractometer equipped with fine focus Molybdenum X-ray tube (1600 kW, detector at 5.8 cm, $\varphi$ and $\omega$ scan) at room temperature. Software programs that were used for data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT and SADABS; solve and refine the structure: OLEX2.

Characterization of solid electrolytes: Powder X-ray diffraction measurements were performed on a Rigaku Miniflex II spectrometer with Cu $K_\alpha$ radiation. An XRD holder with Beryllium window (Rigaku Corp.) was used for protecting air-sensitive materials. Whole pattern fitting refinements on the powder XRD data were performed using the JADE 2010 software (Materials Data Corp., California), with polynomial background fitting model at the order of 5. The P/Sn ratio was determined by inductively coupled plasma emission spectrometry (ICP-AES, Perkin-Elmer Optima 5300). For ionic conductivities measurement, carbon-coated aluminum foils served as blocking electrodes and were pressed onto both faces of pellets. The 2016-type coin cell was assembled in the glovebox by sandwiching the electroded pellet between two stainless-steel discs as current collector. Electrochemical impedance spectroscopy measurements were carried out on CHI 660D in the frequency range of 1 MHz to 0.1 Hz with an amplitude of 5 mV from -120 to 100 °C. Electronic conductivity was investigated by the Hebb-Wagner polarization method. Cyclic voltammetry of Na/ $\text{Na}_{11}\text{Sn}_{1.94}\text{PS}_{12}$/Na$_3$PS$_4$/Sn was measured with the
Na metal as counter/reference electrode and Sn as working electrode with a scan rate of 1 mVs⁻¹ from -0.5 V to 5 V (vs. Na⁺/Na) at 80 °C.

Battery performance Characterization: All-solid-state Na-ion battery was fabricated by pressing Na-Sn alloy foil and TiS₂ power (Sigma-Aldrich, 99.9%) onto two faces of the pressed Na₃PS₄/Na₁₁Sn₁₉₄PS₁₂ pellet. The obtained pellet was assembled into a 2032-type coin cell with stainless-steel discs as current collector. All the processes were under an Ar atmosphere. The cell was cycled galvanostatically at a current density of 4.8 mAg⁻¹ (0.02 C, based on the theoretical capacity of TiS₂), within the voltage range from 1.17 to 2.4 V using a BTS-5V1mA Neware battery test system.

6.3 Results and Discussion

Na₁₁Sn₁₉₄PS₁₂ was synthesized by heating stoichiometric quantities of Na₂S, Sn, P and S at 600 °C in an evacuated quartz tube (see details in Method section). The powder X-ray diffraction (XRD) pattern of the obtained powder product (Figure 6-1) suggests a new phase with the structure that is different from those of previously reported superionic conductors such as Na₃PS₄, Na₃PSe₄, Na₁₀SnP₂S₁₂, Li₁₀GeP₂S₁₂ and so on. The ratio among four elements was determined by inductively coupled plasma (ICP) spectroscopy and found to be Na:Sn:P:S=10.31:1.94:0.98:12, very close to the ratio among starting materials.
The composition and crystal structure of Na$_{11}$Sn$_{1.94}$PS$_{12}$ were further determined by single crystal X-ray diffraction at 298 K with data collection and refinement details summarized in Table 6-1. This new phase has a tetragonal structure with space group $I4_1/acd$ (no. 142) with the measured lattice parameters $a = 13.5876(12)$ Å and $c = 27.155(5)$ Å. Atom Sn occupies Wyckoff position 16e with site occupancy factor (sof) of 0.95; P in Wyckoff position 8a with sof = 1; S in three kinds of Wyckoff positions 32g with sof ~ 1. The distributions of Na atoms are more complicated over six Wyckoff positions, i.e., 32g (Na1 with sof ~ 0.83), 16f (Na2 with sof ~ 0.98), 16c (Na3 with sof ~ 0.93), 16d (Na4 with sof ~ 0.82), 16e (Na5 with sof ~ 0.95), and 8b (Na6 with sof ~ 0.12). Details of atomic occupancy are summarized in supplementary Table 6-2. The chemical formula from single crystal analysis is Na$_{11}$Sn$_{1.94}$PS$_{12}$, which is in great agreement
with ICP results. Therefore, the composition of the as-prepared material is determined to be

\[ \text{Na}_{11}\text{Sn}_{1.94}\text{PS}_{12} \].

Table 6-1. X-ray data collection, structure solution and refinement data of \( \text{Na}_{11}\text{Sn}_{1.94}\text{PS}_{12} \).

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>( \text{Na}<em>{2.89}\text{P}</em>{0.27}\text{Sn}<em>{0.51}\text{S}</em>{3.15} ) (( \text{Na}<em>{11}\text{Sn}</em>{1.94}\text{PS}_{12} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight (gmol(^{-1}))</td>
<td>235.64</td>
</tr>
<tr>
<td>Crystal color, Shape</td>
<td>brown, plate</td>
</tr>
<tr>
<td>Crystal size (mm(^3))</td>
<td>0.12(\times)0.06(\times)0.05</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>( I4_{1}/acd ) (no. 142)</td>
</tr>
<tr>
<td>Temperature</td>
<td>298(2) K</td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>13.5876(12)</td>
</tr>
<tr>
<td>( c ) (Å)</td>
<td>27.155(5)</td>
</tr>
<tr>
<td>( V ) (Å(^3))</td>
<td>5013.5(12)</td>
</tr>
<tr>
<td>( Z )</td>
<td>32</td>
</tr>
<tr>
<td>( \rho_{\text{calc}} ) (gcm(^{-3}))</td>
<td>2.341</td>
</tr>
<tr>
<td>( \mu ) (mm(^{-1}))</td>
<td>3.118</td>
</tr>
<tr>
<td>( \theta ) range (°)</td>
<td>2.597 – 28.295</td>
</tr>
<tr>
<td>No. of measured reflections</td>
<td>19451</td>
</tr>
<tr>
<td>No. of independent reflections, ( R ) (int)</td>
<td>1565, 0.0192</td>
</tr>
<tr>
<td>No. of independent reflections (( I &gt; 2 \sigma(I) ))</td>
<td>1501</td>
</tr>
<tr>
<td>Parameters</td>
<td>79</td>
</tr>
<tr>
<td>Restraints</td>
<td>0</td>
</tr>
<tr>
<td>( R_1 ) (( I &gt; 2 \sigma(I) )), ( R ) all</td>
<td>0.0314, 0.0323</td>
</tr>
<tr>
<td>( wR_1 ) (( I &gt; 2 \sigma(I) )), ( wR_2 ) (all data)</td>
<td>0.0797, 0.0804</td>
</tr>
<tr>
<td>( GOF ) (all data)</td>
<td>1.054</td>
</tr>
<tr>
<td>Max. peak / hole (e Å(^{-3}))</td>
<td>0.8 / -0.9</td>
</tr>
<tr>
<td>Absorption correction type</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Min./max. transmission</td>
<td>0.7572/0.9</td>
</tr>
</tbody>
</table>
Table 6-2. Details of atomic occupancy in Na$_{11}$Sn$_{1.94}$PS$_{12}$ at 25 °C.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>sof</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1</td>
<td>32g</td>
<td>0.83</td>
<td>0.0103</td>
<td>-0.0168</td>
<td>-0.1254</td>
</tr>
<tr>
<td>Na2</td>
<td>16f</td>
<td>0.98</td>
<td>0.2615</td>
<td>0.0115</td>
<td>-0.1250</td>
</tr>
<tr>
<td>Na3</td>
<td>16c</td>
<td>0.93</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Na4</td>
<td>16d</td>
<td>0.82</td>
<td>0</td>
<td>0.2500</td>
<td>0.0075</td>
</tr>
<tr>
<td>Na5</td>
<td>16e</td>
<td>0.95</td>
<td>0.2500</td>
<td>0.2748</td>
<td>0</td>
</tr>
<tr>
<td>Na6</td>
<td>8b</td>
<td>0.12</td>
<td>0</td>
<td>-0.25</td>
<td>-0.1250</td>
</tr>
<tr>
<td>P</td>
<td>8a</td>
<td>1</td>
<td>0</td>
<td>-0.2500</td>
<td>0.1250</td>
</tr>
<tr>
<td>Sn</td>
<td>16e</td>
<td>0.95</td>
<td>0.2500</td>
<td>0.0249</td>
<td>0</td>
</tr>
<tr>
<td>S1</td>
<td>32g</td>
<td>0.95</td>
<td>0.0843</td>
<td>-0.1604</td>
<td>0.0817</td>
</tr>
<tr>
<td>S2</td>
<td>32g</td>
<td>1</td>
<td>0.1477</td>
<td>0.1244</td>
<td>0.0503</td>
</tr>
<tr>
<td>S3</td>
<td>32g</td>
<td>1</td>
<td>0.1512</td>
<td>-0.0765</td>
<td>-0.0513</td>
</tr>
</tbody>
</table>

Figure 6-2 shows that the discovered Na$_{11}$Sn$_{1.94}$PS$_{12}$ phase possesses considerable Na-ion conduction channels formed by the PS$_4$ and SnS$_4$ tetrahedrons and along such as the $a$-, $b$-, and $c$-axis directions. The partial occupied Na positions, especially Na1, Na4, and Na6, create a large number of vacancies, and hence facilitate the fast Na-ion transport. Interestingly, the less occupied Na1, Na4 and Na6 are the neighbors of the more occupied Na2, Na3, and Na5, further promoting the Na-ion transport.
Figure 6-2. Different views of the single-crystal X-ray structure of Na$_{11}$Sn$_{1.94}$PS$_{12}$, and the white color in Na sphere indicates the ratio of vacancies. The schematic illustration was drawn by using the program VESTA.

In order to characterize ionic conductivity of Na$_{11}$Sn$_{1.94}$PS$_{12}$, 2016-type coin cell was assembled by sandwiching Na$_{11}$Sn$_{1.94}$PS$_{12}$ between two stainless steel discs (as current collector), where carbon-coated aluminum foil was pressed onto the two faces of Na$_{11}$Sn$_{1.94}$PS$_{12}$ serving as blocking electrode. Electrochemical impedance spectroscopies (EIS) were conducted at different temperatures. Figure 6-3a and b show the impedance spectra at T = -120 °C and T = -60 °C, respectively, where the grain semicircle and the high frequency part of the grain boundary impedance are detected at -120 °C, and the transition from the grain boundary impedance to the electrode impedance is detected at -60 °C. The impedance spectra are analyzed by fitting to an equivalent circuit as shown in Figure 6-3a, in which the grain impedance (ohmic resistance in parallel with a constant phase element (R$_g$||CPE$_g$)), the grain boundary impedance (R$_{gb}$||CPE$_{gb}$), and the electrode impedance (CPE$_{ep}$) are represented by circuit elements.[138] The grain conductivity $\sigma_g$=C/R$_g$ was calculated based on the data from equivalent circuit fitting, where C=d/A is the ratio of the pellet thickness d to the sample area A. The total ionic conductivity $\sigma_t$
was calculated based on the total resistance (grain and grain boundary resistance) obtained from the EIS fitting. The Arrhenius plots of the grain conductivity and of the total conductivity are shown in Figure 6-3c, where both $\sigma_g$ and $\sigma_t$ are Arrhenius activated but with different activation energy, $E_A^g = 0.319$ eV and $E_A^t = 0.351$ eV, indicating the contribution of grain boundaries to the total resistance of the sample. Extrapolation of Arrhenius fit for $\sigma_g$ to $T = 25 \, ^\circ\text{C}$ results in a grain conductivity of 3.0 mS cm$^{-1}$, whereas the total conductivity at 25 °C is of 1.06 mS cm$^{-1}$. The electronic conductivity was evaluated by the Hebb-Wagner method[139] using the asymmetric cell (-) Na/ Na$_{11}$Sn$_{1.94}$PS$_{12}$/Al (+) at 25 °C, where carbon-coated aluminum (Al) foil served as blocking electrode. The total electronic conductivity (electron + hole) was calculated to be 7.17×10$^{-9}$ S cm$^{-1}$ at the irreversible interface Na$_{11}$Sn$_{1.94}$PS$_{12}$/Al by linear fitting between 2 V to 4 V (Figure 6-4).
Figure 6.3. Nyquist plot of the impedance for Na$_{11}$Sn$_{1.94}$PS$_{12}$ at a) -120 °C and b) -60 °C. The corresponding equivalent circuit fit curves are displayed as solid lines. c) Arrhenius conductivity plots of total and grain conductivity of as-prepared Na$_{11}$Sn$_{1.94}$PS$_{12}$ pellet from -120 to 40 °C. d) Temperature-dependent ionic conductivities of Na$_{11}$Sn$_{1.94}$PS$_{12}$ and other reported sodium ion conductors.
Figure 6-4. Hebb-Wagner polarization curves obtained from the asymmetric cell (-) Na/Na$_{11}$Sn$_{1.94}$PS$_{12}$/Al (+) at 25 °C. The thickness of the electrolyte (L) is 0.45 mm and the geometrical surface area (S) is 1 cm$^2$. The calculated electronic conductivity is 7.17×10$^{-9}$ S cm$^{-1}$ at the irreversible interface Na$_{11}$Sn$_{1.94}$PS$_{12}$/Al by linear fitting from 2 to 4 V. Red dot line is a guide line for the eye.

Figure 6-3d shows the temperature-dependent ionic conductivities of Na$_{11}$Sn$_{1.94}$PS$_{12}$ together with other reported Na-ion conductors. Na$_{11}$Sn$_{1.94}$PS$_{12}$ shares a similar conductivity with tetragonal Na$_3$P$_{0.62}$As$_{0.38}$S$_4$[69] tetragonal Na$_3$SbS$_4$[33,34] and cubic Na$_3$PSe$_4$[36] within the temperature range from 0 to 40 °C, and has at least one magnitude higher in conductivity than those of tetragonal Na$_3$PS$_4$[30] 50Na$_2$S-50SiS$_2$[127] 60Na$_2$S-40GeS$_2$[127] and Na$_3$Zr$_2$Si$_2$PO$_{12}$.[104] Moreover, decent ionic conductivities are also achieved even at low temperatures, (e.g. 0.11 mS cm$^{-1}$ at -20 °C), showing another advantage comparing with organic liquid electrolyte.
Figure 6-5. a) Cyclic voltammetry of Na/Na$_{11}$Sn$_{1.94}$PS$_{12}$/Na$_3$PS$_4$/Sn. The cells were characterized at 80 °C under the rate of 0.1 mV s$^{-1}$ between -0.5 and 5 V. b) Cycling performance and voltage profiles of the battery Na/Na$_3$PS$_4$/Na$_{11}$Sn$_{1.94}$PS$_{12}$/TiS$_2$. The battery was characterized at 80 °C under the current density of 4.8 mAg$^{-1}$, between 1.17 and 2.4 V.

Electrochemical stability of Na$_{11}$Sn$_{1.94}$PS$_{12}$ was examined from the cyclic voltammetry (CV) spectra of Na/Na$_{11}$Sn$_{1.94}$PS$_{12}$/Na$_3$PS$_4$/Sn cell, with Na as the counter/reference electrode and Sn as the working electrode at 80 °C, where Na$_3$PS$_4$ is employed to separate Na$_{11}$Sn$_{1.94}$PS$_{12}$ and Sn metal. As shown in Figure 6-5a, both cathodic and anodic currents in the first cycle are observed near 0 V versus Na$^+$/Na, corresponding to sodiation with and desodiation from Sn, respectively. No obvious oxidation current has been detected up to 5 V, indicating its good oxidation stability. However, an obvious cathodic peak centered at ~0.44 V is detected in the second cycle, which is probably due to reaction between Na$_{11}$Sn$_{1.94}$PS$_{12}$ and Na metal to form SEI.

The electrolyte Na$_{11}$Sn$_{1.94}$PS$_{12}$ was further examined as solid-state electrolyte in practical Na-ion batteries. Figure 6-5b shows the electrochemical performance of Na-Sn/Na$_3$PS$_4$/Na$_{11}$Sn$_{1.94}$PS$_{12}$/TiS$_2$ battery, which is composed of Na-Sn alloy foil as anode, TiS$_2$ power as cathode, and Na$_3$P$_{0.62}$As$_{0.38}$S$_4$/Na$_{11}$Sn$_{1.94}$PS$_{12}$ as electrolyte, at a current density of 4.8 mAg$^{-1}$.
(0.02 C) within the voltage range from 1.17 to 2.4 V. The battery delivers a charging capacity of around 120 mAhg\(^{-1}\) and good capacity retention of 92% after 10 cycles, demonstrating that Na\(_{11}\)Sn\(_{1.94}\)PS\(_{12}\) could be applied in practical all-solid-state battery.

6.4 Conclusion

The new phase Na\(_{11}\)Sn\(_{1.94}\)PS\(_{12}\) has been found to be with extremely high ionic conductivity of 1.06 mS cm\(^{-1}\) and grain conductivity of 3.0 mS cm\(^{-1}\) at 25 ºC, which is higher than that for most of sulfide materials and comparable with organic liquid electrolyte currently used in NIBs. In addition, the promising performance of all-solid-state battery with Na\(_{11}\)Sn\(_{1.94}\)PS\(_{12}\) as electrolyte demonstrates its great potential in practical application. The discovery of this new phase is believed to open a gate for identifying new SSEs with high ionic conductivity under the general formula of Na\(_{11}\)M\(_{1.94}\)PS\(_{12}\) (M = Sn, Ge, Si).
Chapter 7

Conclusions and Future Work

7.1 Conclusion

This dissertation is focused on development of advanced anode materials and solid-state electrolyte for Na-ion battery (NIB). Due to its high theoretical capacity (2595 mAh g\(^{-1}\)), good chemical stability, and great cost advantage, red phosphorus (P) is considered as a promising anode candidate for Na-ion battery. In order to address its low electrical conductivity and issues caused by large volume change of P upon sodiation/desodiation, highly electronically conductive carbon additive has been involved to form P-carbon (P-C) composites: P/graphene nanosheet hybrid, P@carbon nanotube composite, and P@YP porous carbon composite. All of these developed P-C composites show better electrochemical performance than pristine P.

In order to improve safety of NIB and avoid potential issues caused by volatile and flammable organic liquid electrolytes, sulfide-based solid-state electrolyte has been developed and discussed in this dissertation. Both of Na\(_3\)P\(_{0.62}\)As\(_{0.38}\)S\(_4\) and Na\(_{11}\)Sn\(_{1.94}\)PS\(_{12}\) show high room-temperature ionic conductivity over 1 mS cm\(^{-1}\) and good electrochemical properties in all-solid-state Na-ion battery.

7.2 Suggested future work

For P-based anode, both building chemical bond between P and carbon and confining P into nano pores of carbon host are demonstrated to be effective methods to greatly enhance the
electrochemical performance of P. Combining these two together is believed to further improve
the electrochemical performance. Specifically, develop phosphorus/functionalized porous carbon
nanocomposite as anode for NIBs. Phosphorus is confined within the pores of the carbon and
chemical interaction would be built between phosphorus and carbon through function groups or
doping elements to ensure the intimate contact between them during sodiation/desodiation
process. The properties of the nanocomposites can be tuned by exploring the function
group/doping element on the carbon and its interaction with phosphorus, and thus to produce
synergistic effects towards high capacity anode performance with volume change tolerance and
stable solid-electrolyte interphase.

For sulfide-based solid-state electrolyte, Na_{11}Sn_{1.94}PS_{12} has been demonstrated to have
high room-temperature ionic conductivity over 1 mS cm^{-1}, mainly due to its unique structure with
3D Na-ion conduction pathway and great amount of Na-ion vacancies. Its analogues
Na_{11}M_{1.94}PS_{12} (M=Si, Ge) are also believed to show high ionic conductivity. Also, anion and
cation doping/substitution is considered to further boost the ionic conductivity.
Appendix A

DFT calculations for Na₃PₓAsₓS₄ solid-state electrolyte

Note 1: Cubic versus tetragonal phase of Na₃PS₄

As detailed in Table S2, three phases have been reported and employed for Na₃PS₄ including the perfect cubic (P-cubic), the defect cubic (D-cubic), and the tetragonal phases.[30,32,119] Cubic phase can be described by a sublattice of (Na₁, Va₁)₆(Na₂, Va₂)₁₂P₂S₈ with vacancy (Va) in both the Na¹ and Na¹Ⅲ sites, see Table S2. For composition of Na₆P₂S₈ in the D-cubic phase, the model (5/₆ Na₁, 5/₆Va₁)(1/₁₂ Na₂, 11/₁₂Va₂)₁₂P₂S₈ can be used due to site occupancies of 0.8 for Na¹ site and 0.1 for Na¹Ⅲ site,[32] corresponding to three independent configurations by selecting one Va₁ and one Na₂ atom. The present DFT calculations indicate that the configuration with one Na₂ atom adjacent to Va₁ has the lowest energy (Figure A-1). After structural relaxation, the Na₂ atom in the low energy D-cubic structure moves closer to the adjacent Va₁ site as shown in Figure A-1, and this D-cubic structure is equivalent to the tetragonal structure with space group P₄2₁c (Table A-1) by using a large tolerance for symmetry check. Furthermore, Figure A-2 shows that there are no obvious differences between the calculated XRD patterns from the low energy D-cubic Na₃PS₄ and the tetragonal Na₃PS₄, both with a relatively strong peak around 2θ = 38.85° (Cu Kα), which is absent in the P-cubic structure (Figure A-2). Both the present results as shown in Figure 5-1 and the “cubic” Na₃PS₄[31] show a clear peak around 2θ = 38~39°, indicating the “cubic” phase is, in fact, a tetragonal phase or a mixture of various tetragonal or D-cubic structures. The tetragonal phase is hence adopted in the present work for simulations and discussion. Note that the Na¹ and Na¹Ⅲ sites in tetragonal phase (Figure 5-8a) don’t have the one-
to-one correspondences to the Na\(^{I}\) and Na\(^{II}\) sites in the defect cubic phase (Figure A-1), respectively.

Table A-1. Structural information for the most used Na\(_3\)P\(_{1-x}\)As\(_x\)S\(_4\) structures/configurations in the present work, including the number of atoms in the primitive cell (No. atoms), space group, atoms and their Wyckoff sites, and notes.

<table>
<thead>
<tr>
<th>List</th>
<th>Name</th>
<th>No. atoms</th>
<th>Space group</th>
<th>Wyckoff sites</th>
<th>Notes and references</th>
</tr>
</thead>
</table>
| 1    | P-cubic Na\(_3\)PS\(_4\) (or Na\(_3\)AsS\(_4\)) | 8 | \(\text{I}4\overline{3}m\) (no. 217) | Na: 6b  
P: 2a  
S: 8c | Perfect cubic phase of Na\(_3\)PS\(_4\) (or Na\(_3\)AsS\(_4\)).[32] |
| 2    | D-cubic Na\(_3\)PS\(_4\) (or Na\(_3\)AsS\(_4\)) | 8 | \(\text{I}4\overline{3}m\) (no. 217) | Na\(^{I}\): 6b (0.8)  
Na\(^{II}\): 12d (0.1)  
P: 2a  
S: 8c | Defect cubic phase of Na\(_3\)PS\(_4\) (or Na\(_3\)AsS\(_4\)). Site occupancies are 0.8 for Na\(^{I}\) in Na\(^{I}\) site and 0.1 for Na\(^{II}\) in Na\(^{II}\) sites.[32] |
| 3    | Tetragonal Na\(_3\)PS\(_4\) (or Na\(_3\)AsS\(_4\)) | 16 | \(\text{P}4_{2}1c\) (no. 114) | Na\(^{I}\): 2b  
Na\(^{II}\): 4d  
P: 2b  
S: 8e | Tetragonal phase of Na\(_3\)PS\(_4\) (or Na\(_3\)AsS\(_4\)).[30] These Na\(^{I}\) and Na\(^{II}\) sites are different from the ones in the D-cubic phase. |
| 4    | Na\(_3\)P\(_{0.5}\)As\(_{0.5}\)S\(_4\) (high energy, the simplest structure) | 16 | \(\text{P}4\) (no. 81) | Na\(^{I}\): 1a & 1d  
Na\(^{II}\): 2g & 2g  
As: 1b  
P: 1c  
S: 4h & 4h | The simplest structure of Na\(_3\)P\(_{0.5}\)As\(_{0.5}\)S\(_4\) but with a relatively high energy. Each As atom has eight nearest P atoms with bond length around 6 Å, and this is also true for each P atom. |
| 5    | Na\(_3\)P\(_{0.5}\)As\(_{0.5}\)S\(_4\) (low energy) | 32 | \(\text{P}2_1\) (no. 4) | All atoms: 2a | Each As atom has eight nearest 4 As and 4 P atoms with bond length around 6 Å, and this is also true for each P atom. |
Table A-2. Details of DFT calculations including the employed supercell, total atoms in each supercell (Atoms), \( k \)-points mesh, cutoff energy (\( E_{\text{cut}} \) in eV), the smearing method, and the Note.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Atom s</th>
<th>( k )-mesh</th>
<th>( E_{\text{cut}} )</th>
<th>Smear</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(_{48})((\text{P}<em>1, \text{As}<em>x)</em>{16})S(</em>{64}) (( \delta = 0 ) or ( 1; x = 0 \sim 1 ))</td>
<td>128 or 127</td>
<td>3x3x3 (1x1x1)</td>
<td>28 36</td>
<td>0 -5</td>
<td>Supercells were built based on the tetragonal Na(_3)PS(_4) for enthalpy of mixing (( \delta = 0 )) and CINEB (( \delta = 1 )) calculations. Test calculations were also performed based on the supercells built from the D-cubic Na(_3)PS(_4), showing the similar results.</td>
</tr>
<tr>
<td>Na(_{48})((\text{P}<em>1, \text{As}<em>x)</em>{16})S(</em>{64}) (( x = 0, 0.5, \text{and} 1 ))</td>
<td>128</td>
<td>3x3x3</td>
<td>36</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Na(_6)P(_2)S(_8) (( x = 0, 0.5, \text{and} 1 ))</td>
<td>16</td>
<td>9x9x9</td>
<td>28</td>
<td>0</td>
<td>Test calculations to find the low-energy cubic configuration due to two types of Na atoms in Wyckoff sites 6b and 12d of space group ( I\bar{4}3m ), respectivly[32] (see Table 5-1).</td>
</tr>
<tr>
<td>Na(_6)((\text{P}_1, \text{As}<em>x)</em>{2})S(_8) (( x = 0, 0.5, \text{and} 1 ))</td>
<td>16</td>
<td>4x4x4</td>
<td>28</td>
<td>0 -5</td>
<td>Used for the time-consuming HSE06 calculations. For the case of ( x = 0.5 ), it is a high energy configuration (see Table 5-1).</td>
</tr>
<tr>
<td>Na(_{12})((\text{P}<em>1, \text{As}<em>x)</em>{4})S(</em>{16}) (( x = 0.5 ))</td>
<td>32</td>
<td>4x3x3</td>
<td>28</td>
<td>0 -5</td>
<td>Used for the time-consuming HSE06 calculations of the low energy configuration with ( x = 0.5 ) (see Table 5-1).</td>
</tr>
</tbody>
</table>

\( a \) The same settings as in the VASP code, the number “0” represents the Gaussian smearing method and “-5” the tetrahedron method with Blöchl corrections.[140] The first method (number) is for structural relaxations and the second one is for the final calculations to get accurate energy when applicable.

\( b \) For a full test of enthalpy of mixing for all configurations, the (1x1x1) \( k \)-point mesh, 280 eV energy cutoff, and the Gaussian smearing method were used.
Table A-3. Thermodynamic and structural properties of tetragonal Na$_3$P$_{1-x}$As$_x$S$_4$ with $x = 0, 0.5,$ and $1$, see Table 5-1 for structural details.

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>$\Delta H_{\text{mic}}$ (meV/atom)</th>
<th>$V_0$ (Å$^3$/atom)</th>
<th>$B_0$ (GPa)</th>
<th>$B'$</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal Na$_3$PS$_4$</td>
<td>PBEsol</td>
<td>0</td>
<td>20.936</td>
<td>25.69</td>
<td>5.03</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>PBEsol+HSE06</td>
<td>0</td>
<td>20.903</td>
<td>28.29</td>
<td>5.21</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>21.373$^a$</td>
<td>5.3$^b$</td>
<td>25.3</td>
<td>2.28</td>
<td></td>
</tr>
<tr>
<td>Na$<em>3$P$</em>{0.5}$As$_{0.5}$S$_4$ (low)</td>
<td>PBEsol</td>
<td>0.257</td>
<td>21.263</td>
<td>24.91</td>
<td>4.94</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>PBEsol+HSE06</td>
<td>0.402</td>
<td>21.223</td>
<td>27.89</td>
<td>4.71</td>
<td>2.82</td>
</tr>
<tr>
<td>Na$<em>3$P$</em>{0.5}$As$_{0.5}$S$_4$ (high)</td>
<td>PBEsol</td>
<td>0.680</td>
<td>21.261</td>
<td>24.97</td>
<td>5.08</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>PBEsol+HSE06</td>
<td>0.883</td>
<td>21.260</td>
<td>25.76</td>
<td>5.21</td>
<td>2.85</td>
</tr>
<tr>
<td>Tetragonal Na$_3$AsS$_4$</td>
<td>PBEsol</td>
<td>0</td>
<td>21.568</td>
<td>24.36</td>
<td>5.03</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>PBEsol+HSE06</td>
<td>0</td>
<td>21.521</td>
<td>25.35</td>
<td>5.21</td>
<td>2.67</td>
</tr>
</tbody>
</table>

$^a$ Measured lattice parameters $a = 6.952$ and $c = 7.076$ Å at room temperature.[30]
$^b$ DFT value for tetragonal Na$_3$PS$_4$ by PBEsol in terms of the predicted elastic constants.[119]
$^c$ Predicted value by GGA-PBE functional reported by Materials Project.[141]

Figure A-1. The low-energy defect cubic structure of Na$_3$PS$_4$ with space group $\text{I}43m$. a) Without structural relaxation. b) With structural relaxation. The site occupancy of Na$^\text{I}$ site by Na$_1$ atoms (Wyckoff 6b) is 0.80, and the site occupancy of Na$^\text{II}$ site by Na$_2$ atoms (Wyckoff 12d) is 0.10. The vacancy (Va$_1$) locates in Na$^\text{I}$ site, and the Na$_2$ atom (in Na$^\text{II}$ site) is the closest Na atom to Va$_1$. Note that these Na$^\text{I}$ and Na$^\text{II}$ sites in defect cubic lattice don’t correspond to the Na$^\text{I}$ and Na$^\text{II}$ sites, respectively, in tetragonal Na$_3$PS$_4$ lattice (Figure 5-8a). After relaxation of the defect cubic lattice, it transfer to the tetragonal lattice with space group $P4_2_1_2_c$. 
Figure A-2. Theoretical X-ray diffraction (XRD) patterns of three Na$_3$PS$_4$ in terms of DFT calculations. These XRD patterns were plotted using the wavelength of 1.541 Å (Cu K$_\alpha$), and the defect cubic Na$_3$PS$_4$ is in fact equivalent to the tetragonal phase. The relatively strong peak around $2\theta = 38.85^\circ$ for tetragonal phase, i.e. the tetragonal (212) diffraction, is absent in the perfect cubic phase.

**Note 2:** More details of DFT and phonon calculations

During VASP calculations, 5 electrons ($4s^24p^3$) were treated as valence electrons for As, 7 ($3s^23p^6$) for Na, 5 for P ($3s^23p^3$), and 6 ($3s^23p^4$) for S. Other details, for example, the employed supercells, plane wave cutoff energies, $k$-points meshes, and the smearing methods are shown in Table A-2. For each structure of interest, its equilibrium properties were determined by fitting the DFT energy versus volume ($E$-$V$) data points according to a four-parameter Birch-Murnaghan equation of state (EOS)[142]

$$E(V) = a_1 + a_2V^{-2/3} + a_3V^{-4/3} + a_4V^{-2}$$  \hspace{1cm} (A-1)

where $a_1$, $a_2$, $a_3$, and $a_4$ are fitting parameters. Equilibrium properties determined from this EOS include energy ($E_0$), volume ($V_0$), bulk modulus ($B_0$), and the first derivative of bulk modulus with respect to pressure ($B'$). Five to eight data points within the volume range of -10% $< (V-V_0)/V_0 < 10\%$ were typically used for the present EOS fittings.
Force constants, i.e., the Hessian matrix, were calculated directly using the VASP code (version 5.4.1) in terms of the finite difference method. Correspondingly, phonon properties were calculated by a parameter-free, mixed-space approach as implemented in the YPHON code[124,125] with more details given in a review article[124] and the references within.

**Supplementary Note 3: Partial DFT results**

DFT calculations indicate that the tetragonal Na\(_{48}\)(P\(_{1-x}\)As\(_x\))\(_{16}\)S\(_{64}\) shows a positive enthalpy of mixing (\(\Delta H_{\text{mix}}\)), indicating the existence of miscibility gap and instability of Na\(_{48}\)(P\(_{1-x}\)As\(_x\))\(_{16}\)S\(_{64}\). As an example, Table A-1 shows both the high and low energy structures of Na\(_3\)P\(_{0.5}\)As\(_{0.5}\)S\(_4\).

However, the positive values of \(\Delta H_{\text{mix}}\) are quite small, for example 0.26 ~ 0.68 meV/atom (2.08 ~ 5.44 meV per formula unit) for \(x_{\text{As}} = 0.5\) in terms of the X-C of PBEsol. According to a simple mean field theory,[143] the consolute temperature (\(T_c\)) of miscibility gap can be estimated by,

\[
\Delta H_{\text{mix}} = \Omega x(1 - x) \quad \text{and} \quad T_c = \frac{\Omega}{2k_B}
\]  

where \(\Omega\) is a fitting parameter, \(x\) the mole fraction, and \(k_B\) the Boltzmann's constant. The estimated \(T_c\) values are 48 ~ 126 K (i.e., 87 ± 39 K), indicating Na\(_3\)P\(_{1-x}\)As\(_x\)S\(_4\) is stable at high temperatures such as 100 K and above.

In addition, the equilibrium volume \(V_0\) in Na\(_3\)P\(_{1-x}\)As\(_x\)S\(_4\) increases with increasing As content, and correspondingly bulk modulus \(B_0\) decreases due to the addition of As, see Table A-3 the predicted \(V_0\), \(B_0\), and \(B'\) as well as \(\Delta H_{\text{mix}}\) and bandgap. The present \(V_0\) at 0 K (20.936 Å\(^3\)/atom from PBEsol without zero-point vibrational contribution) for tetragonal Na\(_3\)PS\(_4\) agrees with the measured 21.373 Å\(^3\)/atom at room temperature[30] (see also Table 5-1). In addition, the present \(B_0\) (25.69 GPa) and bandgap (2.08 eV) from PBEsol for tetragonal Na\(_3\)PS\(_4\) agree well with other predictions (25.3 GPa from PBEsol[119] and 2.28 eV from PBE).[141] Furthermore, the results
from the hybrid X-C functional (PBEsol + HSE06) don’t change much the $\Delta H_{\text{mix}}$ values, indicating again that Na$_{3}$P$_{1-x}$As$_{x}$S$_{4}$ is stable at high temperature.
References

[8] Sodium carbonate price per ton, (Alibaba.com)
VITA

Zhaoxin Yu

Zhaoxin Yu was born in Inner Mongolia Province, north eastern China in 1987. He started his Bachelor studies in the Department of Materials Science and Engineering, University of Science and Technology Beijing (USTB) since September 2005. After two years, he joined in Dr. Weihua Qiu’s group in 2007 as an undergraduate student, starting his first research project on organic liquid electrolytes used for Lithium-ion battery (LIB). During the following two years, he accumulated fundamental knowledges on LiBs, found issues of existing organic liquid electrolyte, designed and developed new electrolytes with improved electrochemical performance, and published his first research journal article. It is such a great memory. After receiving his Bachelor degree, Zhaoxin Yu started the Master’s studies in the Department of Materials Science and Engineering, USTB, from 2009 to 2012, under the supervision of Dr. Boping Zhang (USTB) and Dr. Jingfeng Li (Tsinghua University). The research topic changed from LIB to thermoelectrical materials, which filled him with knowledges on ceramics including process, characterization and so on.

After the five years training in scientific research field, Zhaoxin Yu decided to pursue his Ph.D degree and joined the Department of Mechanical and Nuclear Engineering at the Pennsylvania State University in August 2012. Under the supervision of Dr. Donghai Wang, Zhaoxin Yu started his research on the development of electrode materials and solid-state electrolytes for both Lithium-ion and Sodium-ion batteries. Five-year Ph.D study is fast but brings him great fund memories.