TOPICAL REVIEW

Recent progresses and challenges of metal sulfides as advanced anode materials in rechargeable sodium-ion batteries

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Abstract
Currently, rechargeable sodium-ion batteries (SIBs) with high voltage and high energy density have attracted considerable attention. However, compared with lithium-ion batteries (LIBs), there are many urgent challenges that need to be solved to achieve the practical application of SIBs. Due to the similar physicochemical properties of sodium and lithium, the study of SIBs is based on LIBs. However, the radius of Na⁺ is larger than that of Li⁺, a limited number of LIBs electrode materials can be used in SIBs, especially anode materials. Graphite can store sodium ions if an ether-based electrolyte is being used. The storage capacity of graphite for sodium is low (∼35 mAh g⁻¹) when traditional carbonate-based electrolyte is used. Therefore, it is vital that anode materials with splendid rate capability, outstanding cycling performance and low cost are developed rapidly. Among all types of anode materials, metal sulfides (MSₓ) with higher theoretical specific capacity and lower cost are an ideal practical anode material. Here, a summary of the recent research advances on MSₓ of SIBs is provided. The crystal structures, sodium storage mechanism and optimization strategies for high performance batteries are summarized. This paper hopes to provide inspiration for the development of MSₓ to assist the development of the next generation of rechargeable battery applications.

1. Introduction

Previously, lithium-ion batteries (LIBs) have been widely used in mobile phones, notebook computers, electric vehicles, and other fields [1]. However, with the large use of LIBs, lithium resources are decreasing year by year leading to an increase in the prices of lithium resources, which in turn, will cause a higher cost of LIBs. Therefore, it is necessary to develop a new generation of secondary batteries with a low cost to replace LIBs. Among range of new energy storage systems, sodium-ion batteries (SIBs) are regarded as a promising generation secondary batteries instead of LIBs [2–4]. Compared to lithium, the abundant availability of sodium resources may reduce the cost of SIBs. Sodium, having similar physicochemical properties to lithium, is larger than lithium (1.07 Å vs. 0.76 Å). Compared to lithium, the potential of sodium is −2.71 V (vs. SHE), which is a little higher than that of lithium (−3.04 V vs. SHE) [5]. Therefore, due to the larger ionic radius, reaction kinetics of Na⁺ ions is slower than that of Li⁺ ions, so most of the electrode materials used in LIBs cannot be directly applicable in SIBs, especially anode materials. For instance, graphite with theoretical specific capacity of 372 mAh g⁻¹ and low cost is difficultly used as an anode for SIBs [6]. According to first-principles study, LiC₆ which is produced during charge/discharge in LIBs is stable while NaC₆, NaC₈, NaC₁₂, and NaC₁₆ are all unstable, so Na-ions are difficult to insert into graphite [7]. In order to achieve the commercialization of sodium ion batteries, a low cost, high electrochemical performance anode for SIBs is sought urgently.
According to sodium storage mechanism, anode materials for SIBs can be divided into three types, intercalation-type materials, conversion-type materials and alloying-type materials. Intercalation-type materials include hard carbon, soft carbon and sodium titanate. In carbonate electrolyte, hard carbon can reveal a reversible capacity of about 300 mA h g\(^{-1}\), but the rate performance is poor and the initial coulombic efficiency (ICE) is lower [8–10]. In ether electrolyte, the ICE of hard carbon is higher than that in carbonate electrolyte (above 90%) [11]. However, the voltage window of ether electrolyte is not wide enough, causing that it is difficult to assemble full cells to achieve practical application. In addition, the voltage plateau of carbon materials is usually lower than 0.1 V which may cause safety problems due to sodium dendrites [12]. In other words, intercalation-type materials have lower specific capacity and voltage plateau, which may not be benefit for large-scale energy storages. Alloying-type materials such as red phosphorus [13], tin [14], and antimony [15] have higher theoretical capacity, but they usually suffer from huge volume change during cycling, causing pulverization and losing electrochemical activity. For example, Sn anodes with a theoretical capacity of 847 mA h g\(^{-1}\) [16] experience massive volume change (256%) during sodiation/desodiation process. Conversion-type materials also have a higher theoretical capacity, but their volume change is less than alloying-type materials due to Na\(_2\)S generation. Compared to alloying-type materials and intercalation-type materials, conversion-type materials may be ideal commercialization anode materials. Metal oxides, one of conversion-type materials, are widely studied in LIBs since 1970s and deliver excellent long cycle life via simple carbon modification and proper morphological design. In contrast, FeO\(_x\) [17], CoO [18] and NiO [19] have little electrochemical activity in SIBs. The oxygen is replaced by sulfur with lower electronegativity, increasing the performance compared to metal oxides. Metal sulfides (MS\(_x\)) are demonstrated to show better electrical conductivity, mechanical and thermal stability, and higher electrochemical activity than the others, attracting enormous attention from researchers. For instance, zinc sulfide [20] and tin sulfide [21] (ZnS\(_x\), SnS\(_x\)) have much higher specific capacity than their oxide counterparts (ZnO\(_x\) [22], SnO\(_x\) [23]).

MS\(_x\) with high electrical conductivity and thermal stability can undergo multi-electron transfer during cycling in SIBs. However, there is not only an urgent needs but a significant challenge to solve the volume expansion during sodiation/desodiation process. In this review, the crystal structures, sodium storage mechanisms, optimization strategies for high performance batteries are summarized to achieve the practical application, prospectively.

2. A brief overview of the MS\(_x\)

SIBs acted as one of the most promising candidates of LIBs, have already achieved attentions from researchers. Electrode materials play an important part in improving electrochemical performance of SIBs, especially anode materials. Among various types of anode materials, MS\(_x\) with high theoretical capacity and low cost are ideal anode materials. The sodium storage mechanism of MS\(_x\) is complicated. In general, there are three types reaction of sodium storage mechanism, conversion reactions, intercalation-assisted conversion reactions and alloying-assisted conversion reactions.

2.1. Sodium storage mechanism

For some MS\(_x\), such as, NiS [24], Ni\(_2\)S\(_2\) [25] and FeS [26], the sodium storage mechanism is conversion reaction. The reaction formula is shown in equation (1) [27].

\[
MS_x + 2xNa \rightleftharpoons M + xNa_2S \quad (Conversion)
\]

(1)

These NiS and Ni\(_2\)S\(_2\) anode materials have been deeply researched and their sodium storage mechanisms have been affirmed by conversion reaction. As shown in Figure 1(a), NiS with a space group of P63/mmc (a = b = 3.43 Å, c = 5.34 Å) belongs to hexagonal system [28] while Ni\(_2\)S\(_2\) has a cubic structure with F-43 m (a = b = c = 5.216 Å) [29]. Dou and co-workers [24] reported a hierarchical hollow NiS spheres nanocomposite through tuning the reaction parameters, which reveals high reversible capacity of 683.8 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\), and stable cycling performance and shows that the sodium storage mechanism is only conversion reaction.

MS\(_x\) (M = Mo, V, Ti) like MoS\(_2\) [30–33] has intercalation-assisted conversion reactions in regard to sodium storage mechanism. As shown in Figure 1(b), MoS\(_2\) with a hexagonal structure of a space group of P63/mmc (a = b = 3.161 Å, c = 12.295 Å) has a large layer distance (6.15 Å) [34, 35]. The large layer distance is beneficial for Na ions to insert and reduce the volume expansion during cycling process. The reactions of sodium storage mechanism are shown in equations (2–4) [36, 37].

\[
MoS_2 + 0.5Na \rightarrow Na_0.5MoS_2 \quad (Intercalation)
\]

(2)
Figure 1. The Crystal structure (a) NiS and Ni₆S₁; (b) MoS₂; (c) SnS₂.

\[ 2Na_{0.5}MoS₂ + (x - 0.5)Na \rightarrow Na_xMoS₂ \text{ (Intercalation)} \]  (3)

\[ Na_xMoS₂ + (4 - x)Na \rightleftharpoons Mo + 2Na₂S \text{ (conversion)} \]  (4)

MSᵸ (M = Sn, Sb) in p-zone have alloying-assisted conversion reactions in SIBs. These kinds of anode materials usually have higher theoretical capacities, for instance, SnS₂ has a theoretical capacity of 1137 mAh g⁻¹. However, they experience large volume variations and attract much attention from researchers. Figure 1(c) shows the crystal structure of SnS₂ [38–40]. SnS₂ belongs to a space group of P-3 m1 (a = b = 3.639 Å, c = 5.785 Å) and has a hexagonal structure. In addition, SnS₂ has a layer structure and Na ions will insert/extract into the layers during charge/discharge process. And its sodium storage mechanism is shown in equations (5–7) [41–43].

\[ SnS₂ + Na \rightarrow NaSnS₂ \text{ (Intercalation)} \]  (5)

\[ NaSnS₂ + 3Na \rightleftharpoons 2Na₂S + Sn \text{ (Conversion)} \]  (6)

\[ Sn + 3.75Na \rightleftharpoons Na_{3.75}Sn \text{ (Alloying)} \]  (7)

These three sodium storage mechanisms are complex but all have advantages. The theoretical specific capacity of conversion reaction is usually lower than that of the other two. The unfavorable volume expansion of intercalation-assisted and alloying-assisted conversion reaction is much heavier. However, all MSᵸ materials show low electron/ion diffusion, resulting in sluggish reaction kinetics and inferior rate capability. To solve these problems, many strategies such as nanocomposites and carbon modification are used to enhance the electrochemical performance of MSᵸ.

2.2. Challenges and solutions

MSᵸ materials have many advantages but there are still challenges that need to be solved urgently. First of all, although the volume variations of MSᵸ materials are less than that of alloying-type materials, the volume variations will cause the pulverization of electrode materials to lose electrochemical activity and poor cycling performance during charge/discharge process. Second, the formation of solid electrolyte interphase (SEI) results in large irreversible capacity in the first cycle. Third, the ion-diffusion in MSᵸ materials is sluggish, leading to poor rate performance. After studying, researchers have found several strategies to solve these problems including structure design, carbon modification and electrode design and electrolyte optimization.
2.2.1. Structural design

There are many methods to synthesize MS\textsubscript{X} anode materials including solvothermal method, chemical vapor deposition (CVD), electrospinning, sulfurization, ball milling and so on. In addition, many MS\textsubscript{X} anode materials need high temperature to prepare. To reduce volume expansion, it is effective to form nanosized particles. Nanosized particles not only provide high surface area but also reduce volume expansion when cycling to improve the electrochemical performance. Xiao et al \cite{44} prepared layer CuS microspheres with pore volumes, delivering excellent cycle life and high rate performance. Due to the unique structure, the diffusion path of Na ions shortened and the material showed a higher reversible capacity of 387.9 mA h g\textsuperscript{−1}. Yu and co-workers \cite{45} reported a novel pine-needle-like CuS self-assembled from hollow nanotubes with fast charge transfer and more Na\textsuperscript{+} active sites which had a charge capacity of 317 mA h g\textsuperscript{−1} at 20 A g\textsuperscript{−1}. Zhang et al \cite{46} designed transition MS\textsubscript{X} hollow nanoparticles@carbon fibers via using seaweed-derived alginate as the template and precursor, exhibiting excellent rate and cycling performance.

2.2.2. Carbon modification

Most MS\textsubscript{X} materials have poor electronic conductivity, leading to poor rate performance. In order to solve this problem, scientists use carbon materials to modify MS\textsubscript{X}, to improve rate performance of materials. Many carbon materials such as GO, rGO and CNTs have been used to improve the electronic conductivity of MS\textsubscript{X}. For example, Li and co-workers \cite{47} reported CNT nanosheets anchored into RGO composites. After RGO modification, the rate performance of CuS is improved and there is still 392.9 mA h g\textsuperscript{−1} at 1 A g\textsuperscript{−1}. Fang et al \cite{48} used a template-based approach to prepare nitrogen-doped carbon-coated CuS\textsubscript{X} bullet-like hollow particles, exhibiting higher reversible capacity of 237 mA h g\textsuperscript{−1} at 5 A g\textsuperscript{−1} and capacity retention of 79\% over 4000 cycles. Yang's group \cite{49} synthesized N,S-codoped CNTs in-suit encapsulating string of NiS\textsubscript{X} nanocrystals which delivered 463 mA h g\textsuperscript{−1} at 0.3 A g\textsuperscript{−1}. A one-dimensional (1D) coaxial Sb\textsubscript{2}S\textsubscript{3}@Ppy anode materials demonstrated 632 mA h g\textsuperscript{−1} after 150 cycles. Hou's group \cite{20} reported a ZnS/N,S co-doped carbon comosite through calcination, revealing outstanding cycling stability (96.9\% capacity retention after 100 cycles at 0.1 A g\textsuperscript{−1}). In other words, carbon modification improves electronic conductivity, resulting in higher rate performance.

2.2.3. Electrode design

In addition to the strategies of the structural design and carbon modification, it is extremely important to design the electrode structure. In general, the current collector in SIBs anodes is copper. However, MS\textsubscript{X} with huge volume expansion will pulverize and deviate from the current collector during charge/discharge. Therefore, designing reasonable electrode structure can help MS\textsubscript{X} materials to keep electrochemical activity and increase contact area with electrolyte. Lamuel et al \cite{51} reported layerwd free-standing papers composed of MoS\textsubscript{2} and rGO which showed a high charge capacity of 230 mA h g\textsuperscript{−1} with Coulombic efficiency reaching approximately 99\%. Li and co-workers \cite{52} fabricated a 3D porous carbon matrix decorated with NiS\textsubscript{X} nanoparticles via a one-step hydrothermal process. And the anode material delivered outstanding rate capability (167 mA h g\textsuperscript{−1} at as high as 20 A g\textsuperscript{−1}), and excellent cycle performance (300 mA h g\textsuperscript{−1} at 1 A g\textsuperscript{−1} after 800 cycles) due to excellent electron/ion transports within 3D active material-carbon network.

2.2.4. Electrolyte optimization

The electrolytes used in SIBs generally include carbonate electrolytes, ether electrolytes, ionic liquid electrolytes, and solid electrolytes. Carbonate, propylene carbonate, diethyl carbonate, and fluoroethylene carbonate are examples of carbonate electrolyte. Carbonate electrolytes will react with polysulfides, causing serious effect on cycling performance, while solid electrolytes have low ionic conductivity and usually are not used at room temperature but high temperature. The cost of ionic liquid electrolytes is higher, so it is difficult to achieve practical application. Ether electrolytes may be a good electrolyte for MS\textsubscript{X} due to the limited polysulfide dissolution and the preservation of the active material during reaction with sodium. Xu and co-workers \cite{54} reported CoS hollow spheres with NaCF\textsubscript{3}SO\textsubscript{3} diethylene glycol dimethyl as electrolyte which exhibited a charge capacity of 470 mA h g\textsuperscript{−1} with 88\% capacity retention at 0.1 A g\textsuperscript{−1} after 100 cycles. In addition, Zhang et al \cite{55} found that for MS\textsubscript{X} anode materials, DME electrolytes could help to optimize SEI composition, facilitate charge transport, reduce the energy barrier for Na ions migration and reinforcing geometry architecture, endowing excellent electrochemical performance.
3. Conversion reactions of metal sulfides

Compared to traditional intercalation anode materials, transition MSx (TMSx) as SIBs anode materials have a series of advantages such as high specific capacities and multiple electron-transfer. TMS such as FeS$_2$ [56], FeS [57], NiS [58], and CoS [59] can exhibit high theoretical capacities ($\geq 589$ mA h g$^{-1}$) at reasonable anodic voltage while traditional hard carbon only deliver capacities about 200 mA h g$^{-1}$. And their sodium storage mechanisms are conversion reactions.

3.1. MnS

There are three types of crystal structure for MnS, $\alpha$-MnS, $\beta$-MnS, and $\gamma$-MnS, respectively. $\alpha$-MnS and $\gamma$-MnS have been deeply studied in LIBs and show excellent electrochemical properties. According to the similar physical and chemical properties of sodium and lithium, $\alpha$-MnS and $\gamma$-MnS are also used as anode materials in SIBs. And the reaction of sodium, storage mechanism is one step reaction, as shown in equation (8) [60]. The theoretical capacity is 616 mA h g$^{-1}$.

$$\text{MnS} + 2\text{Na}^+ + 2\text{e}^- \rightarrow \text{Mn} + \text{Na}_2\text{S}. \quad (8)$$

However, MnS cannot deliver high capacity in laboratories due to volume expansion and poor electronic conductivity. Scientists have done lots of researches to solve the problems. MnS hollow microspheres on reduced graphene oxide sheets was synthesized though a facile hydrothermal method by Liu et al [61]. The materials demonstrated a capacity of 118 mA h g$^{-1}$ at 0.8 A g$^{-1}$ and 308 mA h g$^{-1}$ at 0.1 A g$^{-1}$ after 125 cycles. Chen et al [62] reported a rod-like carbon-coated MnS composite that demonstrated outstanding rate capability with a capacity of 173.9 mA h g$^{-1}$ at 1 A g$^{-1}$ and a satisfied charge capacity of 297 mA h g$^{-1}$ at 100th at 0.05 A g$^{-1}$. Our work groups also do some advanced studies on MnS. As shown in Figure 2(a), $\alpha$-MnS was in situ encapsulated into N$_2$-codoped nanotube-like carbon to form 1D nanostructures [63] with a length of 0.5–1 $\mu$m and diameter of $\approx$ 100 nm. And it shows a reversible capacity of 291 mA h g$^{-1}$ at 0.25 A g$^{-1}$ after 200 cycles. The nanostructures provide large surface area and more active sodium ions storage sites, which can reduce volume expansion and shorten the sodium ion diffusion path to improve the rate performance. In Figure 2(c), the materials show 536 mA h g$^{-1}$ at 0.05 A g$^{-1}$ and even the current density is 1 A g$^{-1}$, it still exists 188 mA h g$^{-1}$.

As mentioned previously, there are advanced strategies to design electrodes. Ma et al [64] designed core–shell carbon-coated MnS structure which was a highly flexible material, showing better cycling performance. Gao and co-works [65] prepared a freestanding flexible electrode via electrospinning. As shown in Figure 2(d), MnSO$_4$ was dissolved in polyacrylonitrile and then formed fibers collected as freestanding flexible electrodes. The SEM image shown in figure 2(e) demonstrated that the materials had a 3D network to improve the electronic conductivity of MnS and increase the wettability of the electrolyte. The electrochemical properties are in Figures 2(f)–(h), the MnS@CNF delivers 220 mA h g$^{-1}$ at a current density of 20 mA g$^{-1}$ and a stable cycling performance which can remain 220 mA h g$^{-1}$ after 200 cycles at 20 mA g$^{-1}$. Compared to copper current collectors, the freestanding flexible electrodes can provide more active sites and sustain huge volume changes. In addition, the electrolyte and the active material can be in sufficient contact which is beneficial to accelerate sodium ions diffusion.

In addition to practical applications, many researchers have studied the full sodium-ion cells. Xu and co-workers [66] assembled sodium-ion full cells with MnS@C and Na$_3$V$_2$(PO$_4$)$_3$. As displayed in Figure 2(i), it shows CV curves of MnS@C/Na$_3$V$_2$(PO$_4$)$_3$ in a voltage window of 1.5–4.0 V. There is a pair of obvious redox peaks consistent with the plateau of the galvanostatic charge and discharge curves. The full cells show a stable cycling performance of 83 mA h g$^{-1}$ at 0.1 A g$^{-1}$ after 180 cycles and brilliant rate performance which deliver 55 mA h g$^{-1}$ at a current density of 1 A g$^{-1}$. Jo et al [67] prepared a NaCrO$_2$/C-$\alpha$-MnS full cell, showing a capacity of 85.03 mA h g$^{-1}$ at 5 C and retain 91% of the initial capacity after 100 cycles at 1 C. In conclusion, the electrochemical performance of MnS is highly improved after modification. The practical application of MnS is also deeply studied, demonstrating the MS$_x$ may be used in the future.

3.2. FeS

Compared to MnS, FeS has low cost and it is friendly to environment. The theoretical capacity of FeS is 606 mA h g$^{-1}$ and FeS belongs to the hexagonal cell system with a space group P6$_3$/mmc ($a = b = 3.43$ Å, $c = 5.79$ Å) [68]. The reaction in sodium-ion half cells is displayed on equations $(9)$–$(10)$ [69–71]. First, FeS will be converted into Na$_x$FeS$_2$ and Fe. Then it will turn into Na$_2$S and Fe which are the final charge product. This means that the electrochemical reaction for FeS may be incomplete during the charge/discharge processes.

$$2\text{FeS} + x\text{Na}^+ + xe^- \rightarrow \text{Fe} + \text{Na}_x\text{FeS}_2 \quad (x \leq 2) \quad (9)$$
Figure 2. (a) SEM image of $\alpha$-MnS@N,S-NTC; the electrochemical performance of $\alpha$-MnS@N,S-NTC (b) cycling performance; (c) rate performance; (d) the Schematic illustration of the synthesis of MnS@CNF; (e) SEM image of MnS@CNF; the electrochemical performance of MnS@CNF; (f) rate performance; (g) cycling performance; (h) galvanostatic charge–discharge profile at 20 mA g$^{-1}$. (i) CV curves, (j) charge–discharge profiles at a current density of 0.1 A g$^{-1}$, and (k) rate and cycling performance of MnS@C//NVP full cells (inset: EIS spectra and optical image displaying one full cell can drive a green LED light).

Panels (a)-(c) Reproduced with permission [63]. Copyright 2018, John Wiley and Sons. Panels (d)-(h) Reproduced with permission [65]. Copyright 2018, John Wiley and Sons. Panels (i)-(k) Reproduced with permission [66]. Copyright 2018, American Chemical Society.

\[
\text{Na}_x\text{FeS}_2 + (4-x)\text{Na}^+ + (4-x)e^- \rightarrow 2\text{Na}_2\text{S} + \text{Fe}
\]  

Flower-like FeS/C composite is synthesized via dopamine coating, hydrothermal sulfurization and thermal reduction methods by Tong et al [72]. The carbon coating improves the electrical conductivity and restrains the volume expansion to enhance the rate and cycling performance. For instance, it has high reversible capacity of 632.2 mA h g$^{-1}$ and 249.8 mA h g$^{-1}$ at 0.1 and 5 C, respectively. The materials retain a stable cycle life of 525.0 mA h g$^{-1}$ at 0.4 C after 100 cycles. Wang et al [73] used CVD to prepare a 3D interconnected FeS@Fe$_3$C@graphitic carbon. The synthesis process is shown in Figure 3(a). The SEM image in Figure 3(b) shows the porous 3D interconnected structure of the sample, which can provide fast electron/Na ion transport pathways to achieve excellent rate capability and stable long-term cycling performance. After 200 cycles, the sample remains 482.2 and 219.8 mA h g$^{-1}$ at 0.2 and 1 A g$^{-1}$, respectively. To raise the ICE, Yang and co-workers [74] reported FeS@C composite through freeze-drying and calcination. The synthesis method is shown in the Figure 3(c), the FeSO$_4$@4H$_2$O/C$_6$H$_7$O$_8$ precursor is obtained by freeze-drying and then the precursor is calcined to obtain the final product. The FeS particles are uniform distribution over the carbon layer which is decomposed by C$_6$H$_7$O$_8$ layer. Chen et al improved the ICE by controlling the range of the voltage window. The Figures 3(d)–(e) show the rate and cycling performance at the voltage window of 0.5–2.5 V (vs. Na/Na$^+$). The ICE of FeS@C is 86.7% due to the little specific surface area, low carbon content and highly reversible reaction. FeS@C demonstrates a stable long-term cycling performance which remains 280.1 mA h g$^{-1}$ at 10 A g$^{-1}$ after 3000 cycles. Xu et al [75] design a 3D grapheme encapsulated core–shell FeS@carbon nanocomposite as a flexible, additive-free and freestanding anode for SIBs. The materials show a high capacity of 358 mA h g$^{-1}$ after 300 cycles at 1 A g$^{-1}$ with a capacity retention of 97.9%. A core–shell FeS@C on 3D N-doped carbon foam was synthesized by Xiong and co-workers. Benefiting from the unique structure, the sample can be used as flexible electrodes and exhibit excellent electrochemical performance.

In order to achieve a practical application, there is a large amount of reports about the sodium-ion full cells. Our work team prepared a pie-like FeS@C nanohybrid via a solid method [26]. Then the full cells are
assembled with Na3V2(PO4)2O2F (NVPOF) as cathode materials. The full cells deliver stable cycling performance which can obtain a specific capacity of 441.2 mA h g⁻¹ at a current density of 0.5 A g⁻¹ after 80 cycles. In other words, carbon modification can enhance the electronic conduction and cut down the particle size improving the electrochemical performance. Controlling the range of voltage window can enhance the ICE and the reversible electrochemical reactions.

3.3. CoₓSₓ

Researchers have paid much attention to cobalt sulfides because of their potential applications in SIBs. Despite of the potential application of cobalt sulfides, there are several challenges including low electronic conductive and volume expansion needed to be urgently solved. There are two main cobalt sulfides, CoS and Co₉S₈. CoS with a space group of P63/mmc (a = b = 3.37 Å, and c = 5.14 Å) belongs to hexagonal system [76–78] while Co₉S₈ has a cubic structure with a space group of Fm-3 m (a = b = c = 9.923 Å) [79]. The reaction of sodium storage mechanism is shown in equations (11–12) [80–82]. The theoretical specific capacities of CoS and Co₉S₈ are 589.6 and 545.5 mA h g⁻¹, respectively.

\[
\text{CoS} + 2\text{Na}^+ + 2\text{e}^- \rightleftharpoons \text{Co} + \text{Na}_2\text{S} \quad (11)
\]

\[
\text{Co}_9\text{S}_8 + 16\text{Na}^+ + 16\text{e}^- \rightleftharpoons 9\text{Co} + 8\text{Na}_2\text{S} \quad (12)
\]

The capacity of bulk carbon-coated cobalt sulfide (CoS) decreases rapidly in the first several cycles due to the huge volume expansion and the unstable SEI. Liu's group [77] prepared a sandwich-like CoS-reduced graphene oxide (CoS/rGO) composite by a hydrothermal method. The CoS/rGO demonstrated a discharge capacity of 230 mA h g⁻¹ after 200 cycles and a brilliant rate capability even up to 2 A g⁻¹. The existence of rGO can enhance the electronic conductivity, offer more activity sites and relieve volume expansion. Wu and co-workers [83] used the hydrothermal method to synthesize peapod-like carbon encapsulated CoS nanowires (CoS⊂carbon). The schematic diagram of peapod-like nanowires is shown in Figure 4(a). The SEM and TEM images of CoS⊂carbon are displayed in Figures 4(b)–(c), delivering the peapod-like structure which can relieve the volume expansion. In addition to rGO, other carbon materials can also be applied to the modification of CoS. CoS hollow nanoparticles on carbon nanotube are prepared by Gao’s team [84].
though a template-free method. The composite show a stable cycling performance that can keep 92% capacity retention at 0.1 $A \, g^{-1}$. In addition, Han et al. [85] report a dual-carbon coating CoS nanocomposite and the SEM and HRTEM images are shown in Figures 4(d)–(e). The materials exhibit cycling stability and higher charge capacity in Figure 4(f). To achieve the practical application of CoS, many scientists have deeply investigated the electrochemical properties of the full cells. Zhou et al. [80] prepared a CoS nanoparticles embedded in porous carbon nanorods and matched sodium-ion full cells with Na$_3$V$_2$(PO$_4$)$_3$ as cathode materials. The full cells deliver 95.6% capacity retention after 100 cycles.

Co$_9$S$_8$ is one of the most studied cobalt sulfides and is an obvious conversion-type material. And the bare Co$_9$S$_8$ has poor rate capability and unstable cycling performance. Hu and co-works [82] designed Co$_9$S$_8$ quantum dots in an inverse opal structured nanohybrid of carbon composite. The unique structure can shorten the sodium ion diffusion path to improve the kinetics of electrochemical reactions. A reversible capacity of 425 and 289 mA h $g^{-1}$ at 0.2 and 5 $A \, g^{-1}$ can be obtained. Zhang et al. [86] prepared Co$_9$S$_8$@C nanospheres by a hydrothermal method, exhibiting a reversible capacity of 601 mA h $g^{-1}$ at 0.01 A $g^{-1}$ and keeping a charge capacity of 305 mA h $g^{-1}$ at 5 $A \, g^{-1}$ after 1000 cycles. A fiber-in-tube Co$_9$S$_8$-carbon/Co$_9$S$_8$ is designed by Li et al. [87]. The materials offer the conductive pathway for electrons and increase the active sites, demonstrating excellent rate capability. A higher reversible capacity of 422 mA h $g^{-1}$ at 10 A $g^{-1}$ can be obtained and the cyclic performance is stable. Wang and co-workers [88] synthesized a Co$_9$S$_8$ embedded in honeycomb-like sulfur doped carbon foam composite material, showing stable cycling performance of 373 mA h $g^{-1}$ at 0.25 C after 1000 cycles.

3.4. NiS
Nickel-based sulfides are the ideal anode materials for SIBs due to their natural abundance and safety. A large number of researchers have reported high performance nickel-based sulfides anode materials for SIBs since the origin of the SIBs. NiS and Ni$_3$S$_2$ as SIBs anodes are both widely investigated. NiS with a space group of P63/mmc (a = b = 3.43 Å, c = 5.34 Å) belonging to hexagonal system [24, 89] has been widely investigated. The reactions of NiS and Ni$_3$S$_2$ are displayed on equations (13–14) [46, 58, 90]. And their theoretical specific capacities are 1774.8 and 447 mA h $g^{-1}$, respectively.

$$3\text{NiS} + 2\text{Na}^+ + 2e^- \rightarrow \text{Ni}_3\text{S}_2 + \text{Na}_2\text{S} \quad (13)$$

$$\text{Ni}_3\text{S}_2 + 4\text{Na}^+ + 4e^- \leftrightarrow 3\text{Ni} + 2\text{Na}_2\text{S} \quad (14)$$

There are many reports on them to improve their performance. Fan and co-workers [28] prepared square NiS nanoplates based on the sulfurization of two-dimensional (2D) Ni-MOF via a bottom-up method. The
material as SIBs anode demonstrate a wonderful 2D structure and 276 mA h g\(^{-1}\) at 0.2 A g\(^{-1}\) at a voltage range of 0.005–3.0 V. Jiang\' group [24] designed a hierarchical hollow spheres structure of NiS\(_2\) through tuning the reaction parameters. As shown in Figure 5(a), the hollow spheres structure was formed by Ostwald ripening mechanism. To adjust the temperatures by stirring, they synthesized four samples and the NS240 showed the best electrochemical performance, displaying a reversible charge capacity of 426.3 mA h g\(^{-1}\) at a higher rate and 499.9 mA h g\(^{-1}\) at 0.5 A g\(^{-1}\) after 50 cycles (Figures 5(b)–(c)). In addition, Lu et al [91] prepared free-standing nickel sulfide nanosheets on CNT films by using silicon oxide as the intermediate via a CVD method. The SEM images in Figures 5(d)–(e) displayed that distribution of NiS nanoparticles on CNTs is uniformed and the electrode material had a highly flexible. It can be noted that the electrode material delivered 227.4 mA h g\(^{-1}\) at a high rate of 3 A g\(^{-1}\). Due to mixed MSx delivering richer redox reaction, Jiang\' group [92] reported a NiS\(_x\) in S-doping rGO composite as SIBs anode. The as-prepared NiS\(_x\)–rGOS composite had a capacity of 516 mA h g\(^{-1}\) at 0.2 A g\(^{-1}\) after 100 cycles and a charge capacity of 414 mA h g\(^{-1}\) at a high rate of 4 A g\(^{-1}\) (Figures 5(f)–(g)). Above all, it can be noted that many researchers pay attention to full batteries matching. Chen and co-workers [58] reported acicular NiS on Ni foam by a low-temperature sulfuration method and used Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) as cathode material to assemble the full cells, revealing its practical application.

3.5. Other metal sulfides

CuS, CuS\(_2\), and ZnS are also examples of conversion MS\(_x\). CuS can reach a theoretical specific capacity of 561.2 mA h g\(^{-1}\) via two electrons transfer. Xiao et al [44] reported layered CuS microspheres via a low cost and effective interaction method. The anode material displayed a charge capacity of 312.5 mA h g\(^{-1}\) and high capacity retention of 90.6% at 10 A g\(^{-1}\) after 1000 cycles, which was due to the unique structure and high pseudocapacitive contribution. Li and co-workers [93] reported ZnS@carbon microfiber networks through a general metal-aspergillus niger bioleaching strategy, demonstrating 455 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\) after 50 cycles. The 1D carbonaceous fiber of ZnS can reduce the volume expansion and enhance electrical conductivity to improve the electrochemical performance.

4. Intercalation-assisted conversion reactions of transition metal sulfides

Among various MS\(_x\), intercalation-assisted conversion reaction-type MS\(_x\) have attracted considerable attention including MoS\(_2\) [94], V\(_2\)S\(_3\) [95], and TiS\(_2\) [96] and so on. They can obtain better sodium-ion storage due to their large layer distance. The great layer distance can not only store sodium-ions but also relieve the volume expansion during charge/discharge process. However, it still remains many challenges that need to solve.

4.1. MoS\(_2\)

MoS\(_2\), a typical 2D layer material, is deeply investigated due to its large interlayer distance with 6.15 Å. MoS\(_2\) is a semiconductor, so the electron conductivity is poor, leading to bad rate capability. It is consisted of a molybdenum atom layer between two sulfur atom layers, and one molybdenum atom is coordinated by six sulfur atoms. In addition, the layers are maintained by weak van der Waals forces, which can host metal cations like graphite. According to the reactions in equations (2)–(4), it is obvious that the metal cations will first insert into interlayer, and then conversion reaction takes place. If MoS\(_2\) fully converts to Mo and Na\(_2\)S, the theoretical specific capacity is 670 mA h g\(^{-1}\).

More specifically, M Mortazavi et al [97] used ab initio characterization to calculate the sodium storage of layer MoS\(_2\) from different crystal systems. According to the calculation results, it is can be found that Na\(^+\) ions insertion in MoS\(_2\) is thermodynamically stable when the entire concentration range is between 0 and 1 against the phase separation of Na. And the electrode potential for layer MoS\(_2\) is 0.75–1.25 V and the largest capacity is 146 mA h g\(^{-1}\) when only Na\(^+\) ions insert into the layers. Furthermore, the energy barrier of 2 H–and 1 T-MoS\(_2\) is 0.68 and 0.28 eV, suggesting that 1 T-MoS\(_2\) has better electrochemical properties. Chen\’s group [97] prepared MoS\(_2\) nanoflowers and controlled the cut-off voltage to the range of 0.4–3 V to obtain high electrochemical properties. When the cut-off voltage was above 0.4 V, only insertion reaction rather than conversion reaction occurs. It exhibits a reversible capacity of 175 mA h g\(^{-1}\) even at 10 A g\(^{-1}\).

Choi et al [98] designed 3D MoS\(_2\)/graphene microspheres with multiple nanospheres, suggesting a discharge capacity of 322 mA h g\(^{-1}\) at 1 A g\(^{-1}\) after 600 cycles and outstanding rate property with a charge capacity of 573 mA h g\(^{-1}\) at 0.2 A g\(^{-1}\). A ultrathin MoS\(_2\) nanosheets material was successfully synthesized though scalable ultrasonic exfoliation technique by Su and co-workers [99], showing high reversible specific capacity of 530 mA h g\(^{-1}\) at 0.04 A g\(^{-1}\). Shi et al [100] designed a sandwich structure with 2D monolayer MoS\(_2\) and carbon interoverlapped nanosheets material, demonstrating a high rate-capability and maintain discharge capacities of 295 and 187 mA h g\(^{-1}\) at high current densities of 10 and 20 A g\(^{-1}\), respectively. Ding\’s group
synthesized few-layer MoS₂ nanosheets on N-doped carbon ribbons by hydrothermal method. The SEM and TEM images of the sample are displayed in Figures 6(a)–(b), exhibiting the few-layer MoS₂ nanosheets are distributed uniform on the carbon ribbons and this will offer a large surface area for electrolyte infiltration and shorten the Na⁺ ions diffusion path. The sample displays 386 mA h g⁻¹ at second cycle and decreases to 345 mA h g⁻¹ at 0.5 A g⁻¹ after 100 cycles with capacity retention of 89%. Ren et al [102] fabricated MoS₂ nanosheets@N-doped carbon nanowall derived by MOF. Figures 6(d)–(e) show that 2D layer structure is well and uniformly coated on carbon fibers, leading to better electrochemical performance. The material exhibits a stable cycling performance at 613.7 mA h g⁻¹ with a capacity retention of 93.9% of the second cycle capacity. The unique structure has a lower Rₑ value of 140 Ω shown in Figure 6(g). Yu’s group [103] prepared a series of MoS₂ nanosheets@nitrogen-doped graphene composites via a solvothermal method. The synthesis method and raw materials are shown in Figure 6(h), revealing that different raw materials can prepare distinct layers of MoS₂ materials. Furthermore, the US-MoS₂@NG demonstrates the best rate performance that has a capacity of 141 mA h g⁻¹ at even 12.8 A g⁻¹. In addition, US-MoS₂@NG shows higher voltage plateau due to the larger distance in MoS₂, leading to the lower barrier energy of Na⁺ ions insertion. Zhao and co-workers [104] designed a sandwich-type nanarchiteature consisted of graphene and few-layered MoS₂ which can shorten the Na⁺-ions diffusion path, delivering stable long-term cycling performance and excellent rate capability that has 253 mA h g⁻¹ at a higher rate of 3 A g⁻¹.
4.2. VS\textsubscript{2}

Compared to MoS\textsubscript{2}, VS\textsubscript{2} has higher electron transport efficiency. VS\textsubscript{2} with intrinsic metallic behavior is one of the most typical 2D layer structure compounds and the interlayer distance is 5.76 Å\cite{105,106}. The VS\textsubscript{2} structure shown in Figure 7(a) is consisted of metal vanadium sandwiched between the two sulfide atoms as S-V-S. Its distance is larger than that of graphite, so it can offer big space to host Na\textsuperscript{+} and faster Na\textsuperscript{+} ions transport. In addition, VS\textsubscript{2} with high abundance and low cost has great advantages in energy storage application. The reactions of it is shown in equations (15–16)\cite{95,107,108} and the theoretical specific capacity is about 932.9 mA h g\textsuperscript{−1}. In spite of high capacity, there are huge challenges including large volume expansion and unstable SEI films.

\begin{equation}
\text{VS}_2 + x\text{Na}^+ + xe^{-} \rightleftharpoons \text{Na}_x\text{VS}_2 \tag{15}
\end{equation}

\begin{equation}
\text{Na}_x\text{VS}_2 + + (4 - x)\text{Na} \rightleftharpoons \text{V} + 2\text{Na}_2\text{S} \tag{16}
\end{equation}

It is noted that many scientists pay attention to VS\textsubscript{2} with high performance. According to DFT calculation, monolayer VS\textsubscript{2} displays a low voltage of 0.48 V for SIBs and has better electrochemical performance in SIBs than in LIBs\cite{109}. Li et al\cite{105} designed a crystalline VOOH-coated VS\textsubscript{2} microflowers structure via a facile one-step hydrothermal method. The unique structure can relieve volume change during cycling. Therefore, the material delivers a high charge capacity of 330 mA h g\textsuperscript{−1} at 0.2 A g\textsuperscript{−1} after 150 cycles. A novel layer-by-layer stacked VS\textsubscript{2} nanosheets was successfully synthesized via a one-step polyvinylpyrrolidone assisted assembly method by Sun and co-workers\cite{106}. As shown in Figures 7(b)–(c), the sample exhibited obvious nanosheets and the layer distance is 5.76 Å which is consistent with VS\textsubscript{2}. The sample has better rate capability that can remain 150 mA h g\textsuperscript{−1} at 20 A g\textsuperscript{−1}. And it has a higher ICE of 85%. Li’s group\cite{95} reported VS\textsubscript{2} nanosheet assemblies through a solvothermal method. The material shows a 2D structure (Figure 7(d)),
and in the CV curves, there are distinct redox peaks. Its curves exhibited distinct cathodic peaks at 1.9, 1.4, and 0.5 V, and a series of anodic peaks at 1.0 and 2.2 V, revealing the sodiation/desodiation process of VS$_2$.

The material as SIBs anode shows outstanding rate and cycling performance in Figures 7(e)–(f). After 200 cycles at 1 A g$^{-1}$, it can achieve $\approx 500$ mA h g$^{-1}$ demonstrating stable cycling performance. Li and co-workers designed a 3D hierarchical VS$_2$ microrods structure to obtain high sodium storage. This unique structure achieved a reversible capacity of 230 mA h g$^{-1}$ at 2 A g$^{-1}$ and had 350 mA h g$^{-1}$ at a current density of 0.2 A g$^{-1}$ after 200 cycles shown in Figure 7(g).

4.3. TiS$_2$

TiS$_2$, a typical 2D layered compound, has high electronica conductivity and can be easily exfoliated into single layers by experiment. In addition, the weight of TiS$_2$ is almost the lowest among TMS. TiS$_2$ with a group space of P-2m1 (a = b = 3.405 Å, c = 5.691 Å) belongs to hexagonal system and the interlayer distance is 5.483 Å [96, 110, 111]. The structure of TiS$_2$ is shown in Figure 8(a). It consists of a Ti atoms layer between two S atoms layers. The electrochemical reactions of TiS$_2$ are displayed in equations (17–18) [112, 113]. It can nearly facilitate a four electron transfer so its theoretical capacity is higher about 957 mA h g$^{-1}$. At first, Na$^+$ ions will insert into the layers and form NaTiS$_2$. Then, NaTiS$_2$ and Na$^+$ undergo a conversion reaction.

$$\text{TiS}_2 + \text{Na}^+ + e^- \rightleftharpoons \text{NaTiS}_2$$ (17)

$$\text{NaTiS}_2 + 3\text{Na}^+ + 3e^- \rightleftharpoons 2\text{Na}_2\text{S} + \text{Ti}$$ (18)

Many groups focus on the two-dimension layer compound TiS$_2$. For instance, Li’s group [110] used DFT to calculate the diffusion kinetics of Na$^+$ ions in both bulk TiS$_2$ and nanostructured TiS$_2$ electrode materials.
According to the results of calculation, it is found that the diffusivity of Na$^{+}$ ions in nanostructures is faster than that in bulk materials, and they found that the Na$^{+}$ ions diffusivity turned out to be much higher than Li$^{+}$ ions diffusivity in nanostructures. Therefore, TiS$_2$ may be an ideal anode material for SIBs. Kloc’s group [111] synthesized TiS$_2$ by chemical vapour transport, demonstrating a reversible capacity of $\sim$ 146 mA h g$^{-1}$ at 0.1 C with the voltage window of 1.05–2.6 V. Tao et al [112] reported TiS$_2$ as an advanced anode for SIBs delivering high electrochemical performance. It has outstanding rate performance which remains 621 mA h g$^{-1}$ even at 40 A g$^{-1}$. Liu et al [96] designed TiS$_2$ nanoplates composites with outstanding rate and stable cycling performance. As shown in Figure 8(b), the plateau of the materials is about 1.7 V and the initial discharge/charge capacities are 234 and 190 mA h g$^{-1}$, respectively, indicating a higher ICE. Hu and co-workers [114] prepared 2D TiS$_2$ nanosheets and tested the electrochemical performance of full cells. The TEM image is displayed in Figure 8(c), revealing the better 2D layer structure. The material exhibited excellent cycling performance which still remained 386 mA h g$^{-1}$ at 200th in ether-based electrolyte (1 M NaClO$_4$ in tetraethylene glycol dimethyl ether) while it had none capacity in carbonate electrolyte. The full cells were assembled with Prussian blue analogues (PBA) as cathode materials. The electrochemical performance is displayed in Figure 8(e). It can be seen that the initial discharge capacities of NS-TiS$_2$ and MP-TiS$_2$ are 82 and 81 mA h g$^{-1}$, and remain 75 and 69 mA h g$^{-1}$ after cycles with corresponding capacity retention is 91.4% and 85.1%, respectively.

4.4. Other metal sulfides

In addition to the above materials, FeS$_2$, CoS$_2$ and NiS$_2$ also belong to intercalation-assisted conversion reactions of TMSx. First, S$_2^{2-}$ is reduced to S$^{2-}$ along with Na$^{+}$ intercalation. Then Fe$^{2+}$/Co$^{2+}$ are transformed to Fe/Co along with the generation of sodium sulfides via a conversion reaction. Anna Douglas et al [56] reported FeS$_2$ nanocomposites with ultrafine nanoparticles revealing a reversible capacity of 500 mAh g$^{-1}$. Lu et al [115] prepared 1D FeS$_2$ nanorods which exhibit ultra-long lifespan (9000 cycles) and high reversible capacity (506.9 mA h g$^{-1}$ at 0.5 A g$^{-1}$). FeS$_2$/CNT neural network nanostructure composite was successfully synthesized by Chen and co-workers [116]. The anode exhibited superior rate performance, 254 mA h g$^{-1}$ at 22 A g$^{-1}$ and stable cycling due to pseudocapacitance. Zhang and co-workers [117] reported 3D spongy CoS$_2$ nanoparticles/carbon composite via a facile freeze-drying method and a hydrothermal process. The anode showed enhanced sodium storage performance due to the electrical conductivity of the carbon matrix and the porous structure. It exhibited 330 mA h g$^{-1}$ at 0.5 A g$^{-1}$ after 60 cycles. Ma et al [118] reported a porous CoS$_2$/C micro-polyhedron composite, revealing a capacity retention of 80% at 0.1 A g$^{-1}$ after 200 cycles for SIBs. Pan’s group [119] designed pomegranate-like clusters with NiS$_2$ nanoparticles on N-doped porous carbon, exhibiting a high charge capacity of 505.7 mA h g$^{-1}$ after 100 cycles at 0.1 A g$^{-1}$. The unique structure inherited from nickel MOFs improved the conductive to enhance the electrochemical performance.
5. Pozen metal sulfides

In addition to TMS, there are many kinds of pozen-MSx. In these kinds of compounds, metal atoms also have electrochemical activity and can react with Na\(^+\) ions which called alloying reactions, such as Sn and Sb. Although these kinds of materials have higher theoretical capacity, they always suffer huge volume variation during charge/discharge process. In order to achieve high rate capability and long-term cycle life, it is necessary to design or synthesize special structure pozen MSx. Recently researchers focus on pozen MSx such as SnS, SnS\(_2\), and SbS\(_2\) and use various strategies to solve these problems.

5.1. SnS and SnS\(_2\)

Tin-based sulfides are one of the most important members of p-zone sulfides, including SnS and SnS\(_2\). SnS with a space group of Cmcm(63) (a = 4.148 Å, c = 4.177 Å) is part of orthorhombic system \([120, 121]\) while SnS\(_2\) has a space group of P-3m1(164) belonging to hexagonal system \([122, 123]\). Their electrochemical reactions of sodium storage are shown in equations \((19–20)\ [124, 125]\) and \((5–7)\). If SnS and SnS\(_2\) have completely reacted, their theoretical specific capacities are 1022 and 1137 mA h g\(^{-1}\), respectively.

\[
\text{SnS} + 2\text{Na}^+ + 2e^- \rightarrow \text{Sn} + \text{Na}_2\text{S} \tag{19}
\]

\[
4\text{Sn} + 15\text{Na}^+ + 15e^- \rightarrow \text{Na}_{15}\text{Sn}_4 \tag{20}
\]

Zhou et al \([120]\) first reported a SnS@graphene architecture nanocomposite through controllable assembly properties, which demonstrated outstanding rate performance of 308 mA h g\(^{-1}\) at 250th at a current density of 7.29 A g\(^{-1}\). A carbon-coated 3D porous interconnected SnS composite was designed by Yu's group via the electrostatic spray deposition technique \([126]\). The nanocomposites have well-organized 3D conductive carbon network to enhance electrochemical properties, suggesting outstanding reversible capacity of 535 mA h g\(^{-1}\) after 300 cycles with capacity retention of \(\approx 80\%\) at 1 A g\(^{-1}\). In addition, the sample exhibits a lower voltage plateau at above 0.4 V which is benefit for matching full-cells with high voltage and high energy density. Zheng and co-workers \([127]\) successfully synthesized ultrafine SnS/SnO\(_2\)/graphene heterostructures to obtain high rate capability and stable cycling performance. The SEM images of C@SnS/SnO\(_2@Gr\) are shown in Figure 9(a), revealing that nanoparticles are homogeneously anchored on graphene nanosheets to enhance conductivity. The rate performance is shown in Figure 9(b), which can obtain a capacity of 430 mA h g\(^{-1}\) at a higher rate of 2.43 A g\(^{-1}\). Figure 9(c) displays the discharge/charge profiles of the sample, indicating a higher ICE of 74.6% and a lower plateau at about 0.5 V. Lou' group \([128]\) designed a hierarchical microboxes material with N-doping carbon coated SnS nanosheets via template method displayed in Figure 9(d). The SEM and TEM images are shown in Figures 9(e)–(g), revealing the material has a hierarchical microbox and nanostructure which can relieve the volume change during cycling. And the sample exhibits 456 mA h g\(^{-1}\) at a rate of 1 A g\(^{-1}\). In addition, Zhang and co-workers \([125]\) designed the hollow nanospheres of SnS/TiO\(_2@Gr\), delivering a capacity of 295 mA h g\(^{-1}\) after 750 cycles at 5.0 A g\(^{-1}\). Full-cells with Na\(_2\)V\(_2\)(PO\(_4\))\(_3@C\) as the cathode and SnS/3DNNG as the anode were assembled by Xiong et al \([129]\). Figure 9(h) shows the schematic illustration of full SIBs and the electrochemical properties of full cells display in Figures 9(i)–(j), demonstrating a corresponding capacity fading from 414.6 mA h g\(^{-1}\) to 354.5 mA h g\(^{-1}\) with a capacity retention of 85.5%.

SnS\(_2\) with a layer distance of 5.899 Å can relieve volume expansion and speed up sodium ion transport to some extent. According to the electrochemical reactions, Na\(^+\) ions will first insert into layers and then alloying reactions occur during sodiation/desodiation. Wang et al \([38]\) prepared a layered SnS\(_2\)-reduced graphene nanocomposite via hydrothermal method, exhibiting 500 mA h g\(^{-1}\) at 400th with a capacity retention rate of 84% at 1 A g\(^{-1}\). Shin's group \([130]\) used first principles study to investigate how a SnS\(_2@Gr\) heterostructure improve the electrochemical properties. It is noted that pristine monolayer SnS\(_2\) will experience huge volume expansion and has high band gap which is harmful for the free flow of electrons. The energy of adsorption at the interface and surfaces of heterostructure in SnS/S graphene is stable which benefit for Na\(^+\) ions diffusion. Wang and co-workers \([131]\) designed SnS\(_2\) nanosheets structure using L-cysteine and SnCl\(_2\) as raw materials via solvothermal and solid methods (Figure 10(a)). NMP is used as solvent and has a suitable surface energy which can effectively stabilize their nanostructures and suppress their further aggregation to form 2D nanosheets. The SEM and TEM images are shown in Figures 10(b)–(c), suggesting unique 2D nanosheets. A flexible SnS\(_2\) nanosheet array material was successfully prepared by Cao's group \([132]\) via a faille hydrothermal method. The SEM images are shown in Figures 10(d)–(e), revealing a wonderful nanoarray was synthesized. The as-prepared sample can be directly used as anode material without binders and conductive additive. Figure 10(f)–g display the electrochemical performance, demonstrating a charge capacity of 1009.7 mA h g\(^{-1}\) at 0.2 A g\(^{-1}\) after 130 cycles and 647.9 mA h g\(^{-1}\) even at...
2 A g\(^{-1}\). Xu et al \cite{133} synthesized a series of different layers SnS\(_2\) nanosheet on N, P-codoped porous carbon materials including dozens layered, few layered and small few layered SnS\(_2\) (Figure 10(h)). From the TEM images in Figures 10(i)–(k), we can find that the D-SnS\(_2\), F-SnS\(_2\) and SF-SnS\(_2\) have above 20 layers, about 10 layers and below 10 layers, respectively. The Figures 10(l)–(m) shows the electrochemical properties of the three materials, revealing SF-SnS\(_2\) has the best performance. According to DFT method, it is found that the exposed facets possess more stable sites for Na storage, and led to lower energy barriers during the Na\(^{+}\)-ions diffusion.

### 5.2. Sb\(_2\)S\(_3\)

Sb\(_2\)S\(_3\) with a space group of Pnma (62) (a = 11.302 Å, b = 3.834 Å, c = 11.222 Å) is part of orthorhombic system \cite{134–136}. Compared to Sb, Sb\(_2\)S\(_3\) offers higher theoretical capacity of 946 mA h g\(^{-1}\) due to providing 12 electrons transfer. In addition, the formation Na\(_2\)S can alleviate volumetric variation when cycling. However, Sb\(_2\)S\(_3\) has large band gap energy (1.72 eV), leading to poor electronic conductivity and low rate capability \cite{137–139}. There are many strategies to solve these problems including, nanostructure, carbon coating, and so on. The reactions are displayed in equations (21–22) \cite{140, 141}.

\[
\text{Sb}_2\text{S}_3 + 6\text{Na}^+ + 6e^- \rightarrow 3\text{Na}_2\text{S} + 2\text{Sb} \quad \text{(21)}
\]

\[
\text{Sb} + 3\text{Na}^+ + 3e^- \rightleftharpoons \text{Na}_3\text{Sb} \quad \text{(22)}
\]

Zhu et al \cite{134} first designed a flower-like Sb\(_2\)S\(_3\) as SIBs anode via polyol reflux process, demonstrating outstanding rate capability with a capacity of 553.1 mA h g\(^{-1}\) even at 2 A g\(^{-1}\) and 641.7 mA h g\(^{-1}\) at 100th when the current density is 0.2 A g\(^{-1}\). Lee’s group \cite{135} reported a Sb\(_2\)S\(_3\) embedded in amorphous P/C composite, exhibiting stable cycling performance with a reversible capacity of 654 mA h g\(^{-1}\) at 0.05 A g\(^{-1}\) after 100 cycles, and outstanding rate capability of 390 mA h g\(^{-1}\) at 2 A g\(^{-1}\). Jeong-Hee Choi et al \cite{136} synthesized Sb\(_2\)S\(_3\)/C nanocomposite material relieving the volume expansion to obtain splenetic electrochemical performance. Yao and co-workers \cite{137} using \textit{in situ} TEM to study the volume expansion of
SSNR/C in sodiation process. Carbon-coated van der Waals stacked Sb$_2$S$_3$ nanorods (SSNR/C) are synthesized by facile hydrothermal growth. Figure 11(a) shows the sequential images taken during sodiation process, exhibiting that the reaction front propagated along the Sb$_2$S$_3$ nanorod axial direction, leaving lighter contrast as a result of Na$^+$ intercalation. Figure 11(b) shows the length of electrode materials during sodiation and it exhibits a linear $L \propto t$ relationship. And the sodiation speeds of the SSNR and SSNR/C are 48.3 and 145.9 (average value) nm s$^{-1}$, revealing that the Na$^+$ diffusion is faster due to the high electron conductivity after carbon coating. The volume changes of SSNR/C are shown in Figure 11(c), after sodiation, the width of SSNR/C is turned from 85 nm to 105 nm with expansion ratio of 123%. The 1D nanorods deliver excellent rate capability of 337 mA h g$^{-1}$ even at 2 A g$^{-1}$ in Figure 11(d). Pan et al [141] reported an ionic liquid-assisted preparation of Sb$_2$S$_3$/reduced graphene oxide nanocomposite via hydrothermal method. The material obtained by this synthesis method has a smaller size and can shorten the sodium ion transport path, thereby obtaining better electrochemical properties. Xie et al [142] applied ZIF-8 as template to prepare multi-shell hollow structured Sb$_2$S$_3$ nanomaterials. Figure 11(e) shows the TEM images, revealing this sample has well hierarchy shell structure to alleviate volumetric variation during sodiation/desodiation process. The multi-shell hollow structure exhibits better cycling performance in Figure 11(f).

6. Outlook and summary

In conclusion, we have summarized recent advances on the novel design to improve the electrochemical performance of MS$_x$ as SIBs anode materials. MS$_x$ have received much attention from scientists due to their high theoretical specific capacities and multielectron reaction mechanism. However, there are many challenges that need to be urgently solved for their practical application. First of all, Na$^+$-insertion and conversion reactions have lead to a huge volume variation for MS$_x$ when cycling. This results in forming unstable SEI film to poor cycling performance. Second, the electron conductivity of MS$_x$ is usually lower, leading to poor rate capability which cannot achieve faster charge and discharge. Third, conversion reactions can introduce soluble intermediates such as polysulfide, especially in carbonate electrolyte, which results in side reactions. These problems can cause severe capacity fade and safety issues. Structure design, carbon modification, electrode design and electrolyte optimization have already been applied to enhance the performance of MS$_x$. For conversion-type and alloying-assisted conversion-type MS$_x$, carbon modification is
the most common strategy to relieve volume expansion and improve electron conductivity. Carbon materials can be obtained by organic carbonization or other synthesis method including Hummer’s method. There are many structures for organic compounds and carbon materials having higher electron conductivity which can improve the electron conductivity of MS\textsubscript{x} to achieve outstanding rate capability. Structure design for MS\textsubscript{x} can provide large surface area to offer more electrochemical active sites. Nanocrystallization is one of most useful ways to enhance electrochemical properties. In addition, porous structure can also offer large surface area and alleviate volume variation. Hierarchical hollow structure can effectively alleviate volume expansion due to the free space and shorten Na\textsuperscript{+}-ions diffusion pathways. Electrolyte optimization may avoid side reactions and reduce the capacity fading because of forming SEI film before electrode materials in the first cycle. What’s more, cut-off voltage control may avoid conversion or alloying reactions to increase ICE and reduce huge capacity fading in the initial cycle.

Intercalation-assisted conversion-type MS\textsubscript{x} including MoS\textsubscript{2} have attracted much attention due to their large layer distance. There is a weak van der Waals force between layers which can host Na\textsuperscript{+} ions and enhance Na\textsuperscript{+} ion transmission speed. Therefore, designing unique structures such as nanoflower can offer more activity sites and shorten the pathway of Na\textsuperscript{+}-ions diffusion. These kinds of materials may experience lower volume expansion due to the intercalation mechanism. In addition, cut-off voltage control can avoid conversion reactions to reduce irreversible capacity and increase the ICE which is benefit for practical application.

Although recent progress on MS\textsubscript{x} has highly improved the electrochemical performance, there are still challenges that need to be solved such as low ICE. For the first several cycles, it remains phase change,
future, MS MnS and NiS with low voltage and large abundance are also worth investigating. It can be seen that in the due to their high theoretical specific capacity and low average work voltage. In addition, other MS caused by their high theoretical capacity and low average work voltage. The table 1 shows the voltage plateaux of most MS causes the voltage plateaux, which has a negative effect on cycling performance and practical application. The voltage plateaux of MSs are summarized in table 1. Compared to alloying-type materials, the voltage plateaux of most MSs are higher. Therefore, SnS2 and Sb2S3 may be more likely used as SIBs anode materials due to their high theoretical specific capacity and low average work voltage. In addition, other MSs including MnS and NiS with low voltage and large abundance are also worth investigating. It can be seen that in the future, MSs will show its importance in next-generation energy storage and conversion devices.

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| Sulfides | Electrochemical reaction | Theoretical capacity (mA h g\(^{-1}\)) | Discharge potential (V vs. Na\(^+\)/Na) | Volume expansion (%) |
|----------|------------------------|----------------------------------------|----------------------------------------|----------------------|
| MnS      | MnS + 2Na\(^+\) + 2e\(^-\) ⇌ Mn + Na\(_2\)S | 616 | 0.4 | 225 |
| FeS      | 2FeS + xNa\(^+\) + xe\(^-\) ⇌ Fe\(_x\)Na\(_{2x}\)FeS\(_2\) + (4 – x)Na\(^+\) + (4 – x)e\(^-\) ⇌ 2Na\(_2\)S + Fe | 606 | 1.09 | 270 |
| CoS      | CoS + 2Na\(^+\) + 2e\(^-\) ⇌ Co + Na\(_2\)S | 589.6 | 1.5 | 291 |
| CuS     | CuS + 2Na\(^+\) + 2e\(^-\) ⇌ Cu + Na\(_2\)S | 545.5 | 0.75 | 315 |
| NiS      | 3NiS + 2Na\(^+\) + 2e\(^-\) ⇌ Ni\(_3\)S\(_2\) + Na\(_2\)SNa\(_2\)S + 4Na\(^+\) + 4e\(^-\) ⇌ 3Ni + 2Na\(_2\)S | 1774.8 | 0.7 | 283 |
| NiS\(_2\) | Ni\(_3\)S\(_2\) + 4Na\(^+\) + 4e\(^-\) ⇌ 3Ni + 2Na\(_2\)S | 447 | 0.94 | 108 |
| CuS     | CuS + 2Na\(^+\) + 2e\(^-\) ⇌ Cu + Na\(_2\)S | 561.2 | 1.56 | 136 |
| ZnS     | ZnS + 2Na\(^+\) + 2e\(^-\) ⇌ Zn + Na\(_2\)S | 551 | 0.6 | 214 |
| MoS\(_2\) | MoS\(_2\) + 0.5Na → Na\(_0\).5MoS\(_2\)2Na\(_0\).5MoS\(_2\) + (x – 0.5)Na → Na\(_x\)Mo\(_2\)Na\(_x\)MoS\(_2\) + (4 – x)Na ⇌ Mo + 2Na\(_2\)S | 670 | 0.5 | 195 |
| VS\(_2\) | VS\(_2\) + xNa\(^+\) + xe\(^-\) ⇌ Na\(_x\)VS\(_2\)Na\(_x\)VS\(_2\) + (4 – x)Na ⇌ V + 2Na\(_2\)S | 932.9 | 1.65 | 210 |
| TiS\(_2\) | TiS\(_2\) + Na\(^+\) + e\(^-\) ⇌ NaTiS\(_2\)aTiS\(_2\) + 3Na\(^+\) + 3e\(^-\) ⇌ 2Na\(_2\)S + Ti | 957 | 1.45, 2.23 | 220 |
| FeS\(_2\) | FeS\(_2\) + 4Na\(^+\) + 4e\(^-\) ⇌ Fe + 2Na\(_2\)S | 894 | 1.4 | 256 |
| NiS\(_2\) | Ni\(_3\)S\(_2\) + xNa\(^+\) + xe\(^-\) ⇌ Na\(_x\)Ni\(_3\)S\(_2\)Na\(_x\)Ni\(_3\)S\(_2\) + (4 – x)Na ⇌ Ni + 2Na\(_2\)S | 874 | 0.9, 1.3 | 230 |
| CoS\(_2\) | CoS\(_2\) + xNa\(^+\) + xe\(^-\) ⇌ Na\(_x\)Co\(_2\)S\(_2\)Na\(_x\)Co\(_2\)S\(_2\) + (4 – x)Na ⇌ Co + 2Na\(_2\)S | 872 | 0.8 | 339 |
| SnS\(_2\) | SnS + 2Na\(^+\) + 2e\(^-\) ⇌ Sn + Na\(_2\)S\(_4\)Sn + 15Na\(^+\) + 15e\(^-\) ⇌ Na\(_2\)Sn\(_4\) | 1022 | 0.66, 1.04 | 343 |
| SnS\(_2\) | SnS + Na → NaSnSnSNaSnS + 3Na ⇌ 2Na\(_2\)S + SnS + 3.75Na ⇌ Na\(_2\)S\(_7\)Sn | 1137 | 0.5 | 315 |
| Sb\(_2\)S\(_3\) | Sb\(_2\)S\(_3\) + 6Na\(^+\) + 6e\(^-\) ⇌ 3Na\(_2\)S + 2Sb\(_2\)S + 3Na\(^+\) + 3e\(^-\) ⇌ Na\(_3\)Sb | 946 | 0.5 | 275 |
