Sulfur-Based Electrodes that Function via Multielectron Reactions for Room-Temperature Sodium-Ion Storage

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Abstract

Emerging rechargeable sodium-ion storage systems—sodium-ion and room-temperature sodium–sulfur (RT-NaS) batteries—are gaining extensive research interest as low-cost options for large-scale energy-storage applications. Owing to their abundance, easy accessibility, and unique physical and chemical properties, sulfur-based materials, in particular metal sulfides (MSx) and elemental sulfur (S), are currently regarded as promising electrode candidates for Na-storage technologies with high capacity and excellent redox reversibility based on multielectron conversion reactions. Here, we present current understanding of Na-storage mechanisms of the S-based electrode materials. Recent progress and strategies for improving electronic conductivity and tolerating volume variations of the MSx anodes in Na-ion batteries are reviewed. In addition, current advances on S cathodes in RT-NaS batteries are presented. We outline a novel emerging concept of integrating MSx electrocatalysts into conventional carbonaceous matrices as effective polarized S hosts in RT-NaS batteries as well. This comprehensive progress report could provide guidance for research toward the development of S-based materials for the future Na-storage techniques.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details


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This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/3914
Sulfur-based electrodes via multi-electron reactions for room-temperature sodium-ion storage

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Emerging rechargeable Na-ion storage systems, sodium-ion batteries (SIBs) and room temperature sodium-sulfur (RT-Na/S) batteries, hold great promise as low-cost options for large-scale energy storage. Combined with high capacity and excellent redox reversibility based on multi-electron conversion reactions, the cost efficiency, easy accessibility, unique physical and chemical properties of S-based materials, including metal sulfides (MSₓ) and elemental sulfur (S), endow them promising electrode candidates for Na-storage technologies. Here, we leverage understanding on Na-storage mechanisms of the S-based electrode materials. Recent progresses and strategies for improving electronic conductivity and tolerating volume variations of the MSₓ anodes in SIBs are reviewed. On the other hand, the current advances on optimizing S cathodes in the RT-Na/S batteries are presented. We outline a novel concept of applying MSₓ into RT-Na/S batteries as effective S hosts as well. Additionally, critical issues, current challenges, and future perspectives for S-based electrodes for SIBs and RT-Na/S batteries are discussed. This comprehensive review could provide guidance for potential research directions toward development of S-based materials for the future Na-storage techniques.
Developing efficient, high-safety, low-cost, and environmental friendly battery systems is essential and imperative for globally sustainable energy economy, especially for electric grids and storing intermittent energy from renewable resources such as solar and wind.\(^1\) With decent specific energy (100-265 Wh kg\(^{-1}\)), rechargeable lithium-ion batteries (LIBs) are successfully powering various portable electronic devices and holding great promise for electrical vehicles. However, the resource limitation and cost concerns of LIBs constrain their potentials in large-scale stationary electricity storage. Consequently, cost-efficiency Na-ion storage systems are extensively investigated due to the similar electrochemistry to their Li counterparts.\(^5\)

Rechargeable sodium-ion batteries (SIBs) are expected to be suitable in stationary electricity storage due to the advantages of low cost and decent energy density (BOX 1).\(^6\) However, current SIBs could only deliver low specific energy of \(\sim 150\) Wh kg\(^{-1}\).\(^7,8\) The scientific community, therefore, is striving for surpassing the horizon of the low specific energy. One strategy is to develop conventional SIBs by utilizing high-capacity anodes that undergo multi-electron reactions,\(^9\) such as metals (Sn, Sb),\(^10\)-\(^13\) phosphides-based materials (P and MP\(_x\) with M=Sn, Fe, Ni, Cu, Ge),\(^14\)-\(^23\) and metal sulfides (MS\(_x\) with M=Sn, Sb, Mo, Fe, Co, Ni, Mn),\(^24\)-\(^32\) which could achieve reversible capacity of 400-950 mAh g\(^{-1}\). The reaction mechanisms of these anodes in SIBs are attributed to three types, including intercalation/extraction, conversion and alloying/dealloying. Amongst, materials based on conversion reactions are more feasible due to high accessible capacity and medium volume variations.\(^33\) Another tactic is to directly use Na metal as an anode. Na anode shows low redox potential (-2.714 V) and high theoretical gravimetric capacity (1165 mAh g\(^{-1}\)). When paired with various cathodes, sodium metal batteries could deliver high capacity and energy density.\(^34\)-\(^38\) Especially, light-weight elemental sulfur stands out due to its high theoretical capacity (1675 mA h g\(^{-1}\)) via two-electron conversion reactions from S to Na\(_2\)S.\(^39\)-\(^42\) Thus, room-temperature Na-S (RT-Na/S) batteries emerge by paring a high-capacity Na anode with S cathode (BOX 1). Additionally, sulfur is earth-abundant, low-cost, environmental friendly, and easy to scale up, making it an attractive battery technology for stationary energy storage.\(^43\)
**Metal sulfides anodes for SIBs**

For the anodes based on conversion reactions, metal sulfides (MS$_x$) are more attractive for practical applications ([FIG. 1a](#)), which show much better performance than oxide materials and easier accessibility than phosphides.$^{44,45}$ Additionally, MS$_x$ endow with their unique physical and chemical properties including relatively high electrical conductivity, decent mechanical and thermal stability in contrast to their oxides counterparts.$^{46}$ Several excellent reviews have been devoted to summarize on the synthetic strategies and recent developments of MS$_x$ in SIBs.$^{9,46-50}$ Nevertheless, the understanding on reaction mechanisms of MS$_x$ is limited to general conversion reactions. When we further inquire these reactions, it is insightful that some Na-storage reactions are not only based on conversion reactions but also aided by intercalation or alloying reactions. Three groups of reaction mechanisms, therefore, are concluded for MS$_x$ in terms of conversion, intercalation-assisted conversion, and alloying-assisted conversion ([FIG. 1b](#)), which exhibit increasing theoretical capacity but subsequently deteriorative volume expansion. Unfortunately, all MS$_x$ possess the low electron/ion diffusion nature, thus causing sluggish reaction kinetics and inferior rate capability. The severe volume expansions during sodiation/desodiation are responsible for rapid capacity decay and short cycling lifespan.

Representative MS$_x$ anodes based on these three mechanisms will be discussed, respectively.

**MS$_x$ based on conversion reaction.** Metals in the MS$_x$ are supposed to be inactive for the pure conversion reaction, in which MS$_x$ could be CoS, Co$_9$S$_8$, FeS, CuS, and ZnS. The overall reaction is as fellows.

\[
\text{MS}_x + 2x\text{Na} \leftrightarrow M + x\text{Na}_2S \quad \text{(Conversion)}
\]  

CoS and Co$_9$S$_8$ have been extensively investigated and confirmed the Na-storage mechanism via conversion reaction.$^{51-53}$ As illustrated in [FIG. 2a and b](#), CoS possesses analogous hexagonal structure, with a space group of $P6_3/mmc$ (a=b=3.37 Å and c = 5.14 Å).$^{54}$ In contrast, Co$_9$S$_8$ has a cubic close-packed atoms arrangement with the $Fm\overline{3}m$ group (a = b = c = 9.927 Å).$^{46}$ Yu’s group synthesized a two-dimensional heterostructure of CoS and Co$_9$S$_8$ quantum dots embedded N/S-doped carbon naosheets (CoS$_x$@NSC, [FIG. 2c](#)). The extremely small particle size and heterostructure with highly conductive graphene matrix could simultaneously address the
challenges of low conductivity and volume change. Moreover, a reversible SEI layer was favorably formed on the electrode surface, leading to enhanced reversible capacity.\textsuperscript{51} Troilite iron sulfide (FeS) possesses analogous hexagonal structure as CoS based on NiAs structure, which is more suitable for large-scale application due to its low cost and nontoxicity with relatively high theoretical capacity (610 mA h g\textsuperscript{-1}). Research focuses on fabricating nanostructured FeS materials, which could shorten Na\textsuperscript{+} diffusion distance and favors the infiltration. Moreover, nanostructured FeS is expected to tolerate volume change and alleviate structural degradation. Impressively, Wang \textit{et al.} constructed elaborate yolk-shell FeS/C nanospheres by developing a spatially confined sulfuration strategy (\textbf{FIG. 2d-e}).\textsuperscript{55} Taking the advantages of nanoscale particle and extra free space, this composite achieved superior sodium-storage performance in terms of accessible capacity, cycling stability, and rate capability. Likewise, many other metal sulfides, including nickel sulfides (NiS and Ni\textsubscript{3}S\textsubscript{2}),\textsuperscript{56,57} ZnS,\textsuperscript{58} CuS,\textsuperscript{48} CuS\textsubscript{2},\textsuperscript{59} and MnS,\textsuperscript{32} realize Na-ion storage via the conversion reaction.

**MS\textsubscript{x} based on intercalation-assisted conversion reaction.** Unlike inactive graphite, layered metal dichalcogenides (MX\textsubscript{2}, M = Mo, W, V, Ti; X = S, Se) could achieve better Na-storage performance due to the much enlarged layer distance. As shown in \textbf{FIG. 3a}, the crystal structures, interlayer spacing and the theoretical capacities of MX\textsubscript{2} are illustrated.\textsuperscript{50} The enlarged interlayer can well accommodate relatively large Na ions and alleviate volumetric variation upon sodium storage, leading to coexistence of intercalation and conversion reactions. Molybdenum disulfide, MoS\textsubscript{2}, is the most representative layered transition metal chalcogenide, which has attracted extensive attention due to its high theoretical capacity (670 mAh g\textsuperscript{-1}) and structural peculiarities. The sodium-storage mechanism during discharge process is proven to be as fellows: \textsuperscript{27,60-62}

\begin{align*}
\text{MoS}_2 + 0.5\text{Na} & \rightarrow \text{Na}_0.5\text{MoS}_2 (0.85 \text{ V}) \quad \text{(Intercalation)} \quad (2) \\
2\text{Na}_0.5\text{MoS}_2 + (x-0.5) \text{Na} & \rightarrow \text{NaxMoS}_2 (x < 1.5, 0.75 \text{ V}) \quad \text{(Intercalation)} \quad (3) \\
\text{NaxMoS}_2 + (4-x) \text{Na} & \leftrightarrow \text{Mo} + 2\text{Na}_2\text{S} \quad \text{(below 0.2 V) \quad \text{(Conversion)}} \quad (4)
\end{align*}

More specifically, Li \textit{et al.} further investigated the sodiation process by combining in-situ electronic diffraction and DFT calculations. As shown in \textbf{FIG. 3b}, at the initial stage, Na-ions can
randomly intercalate into the unoccupied interlayer sites of 2H-MoS$_2$, gradually forming 1T-Na$_{0.375}$MoS$_2$, 1T-Na$_{0.625}$MoS$_2$, 1T-Na$_{0.75}$MoS$_2$, and 1T-Na$_{1.0}$MoS$_2$. When the sodiated Na ions are over 1.75, the MoS$_2$-layered structure will disappear with the phase separation and structural collapse, leading to the final formation of Mo and Na$_2$S nanocrystals. This result confirmed the occurrence of intercalation-assisted conversion reaction.$^{63}$

Tremendous research focused on enlarging the interlayer distance of nanosized MoS$_2$, which is expected to enhance sodiation/desodiation kinetics, leading to lower charge transfer resistance and more active sites for Na-ion storage. To deal with the serious restacking and poor electronic and ionic conductivity between adjacent S-Mo-S sheets of the expanded MoS$_2$, various conductive guest materials, including amorphous carbon,$^{64}$ graphene,$^{65}$ polyvinyl pyrrolidone (PVP),$^{66}$ ethylene diaminetrimalydate (EDA),$^{67}$ and poly(ethyleneoxide) (PEO),$^{68}$ are introduced to stabilize the expanded nanostructure. Zhang et al. synthesized ultrathin MoS$_2$ nanosheets (< 10 nm) on the surface of carbon nanotubes, which possessed an expanded spacing of ~ 1 nm. The anode exhibited a specific capacity of ~500 mAh g$^{-1}$ over 80 cycles. The enhanced capacity and long-term stability is ascribed to the nanoscale size, expanded interlayer spacing, and high conductivity (FIG. 3c).$^{69}$ On the other hand, Pyrite MS$_x$ including FeS$_2$ and CoS$_2$ share the similar Na-storage mechanism, in which S$_2^{2-}$ is first reduced to S$^{2-}$ along with Na-ion intercalation, and finally Fe$^{2+}$/Co$^{2+}$ is transformed to Fe/Co along with the generation of sodium sulfides via conversion reaction.$^{37,70-78}$ It should be pointed out that all the intercalation reaction is irreversible and only occurs at the initial discharge process, because the layered structures could be fully destroyed but cannot recover by forming amorphous structure after subsequent conversion reaction.

**MS$_x$ based on alloying-assisted conversion reaction.** Following the conversion reaction, some metals in MS$_x$ are electroactive with Na ions, thus subsequently undergoing alloying/dealloying reactions, in which M could be Sn, Sb, and Bi. Therefore, this type of MS$_x$ tends to possess ultrahigh theoretical capacity (SnS$_2$: 1137 mA h g$^{-1}$, SnS: 1022 mA h g$^{-1}$, Sb$_2$S$_3$: 946 mA h g$^{-1}$) but much serious volume variations. The research relatively focused on addressing the severe volume changes via elaborate nanostructural design.
SnS\textsubscript{2} belongs to space group \textit{P-3m1} with a CdI\textsubscript{2}-type layered structure (\(a = 0.3648\) nm, \(c = 0.5899\) nm). It possesses a layered structure consisting of a layer of Sn atoms sandwiched between two layers of hexagonally packed S atoms, leading to a large interlayer spacing of 0.5899 nm along the \(c\) axis. Assisted by the initial intercalation reaction, SnS\textsubscript{2} can achieve ultrahigh theoretical capacity due to the combination of the high-capacity conversion reaction and alloying reaction.\textsuperscript{79-82}

\[
\text{SnS}_2 + \text{Na} \rightarrow \text{NaSnS}_2 \quad \text{(Intercalation)} \quad (5)
\]

\[
\text{NaSnS}_2 + 3\text{Na} \leftrightarrow 2\text{Na}_2\text{S} + \text{Sn} \quad \text{(Conversion)} \quad (6)
\]

\[
\text{Sn} + 3.75\text{Na} \leftrightarrow \text{Na}_{3.75}\text{Sn} \quad \text{(Alloying)} \quad (7)
\]

Various SnS\textsubscript{2} nanostructures were constructed. FIG. 4a showed ultrathin two-dimensional SnS\textsubscript{2} nanosheets with ultrathin nanostructure (3-4 nm in thickness), which exhibited high Na\textsuperscript{+} diffusion coefficient and fast Na-storage kinetics, leading to remarkably enhanced electrochemical performance.\textsuperscript{80} Meanwhile, the matrixes are expected to accommodate the anabatic volume variation.\textsuperscript{25,79} As displayed in FIG. 4b, Zhang \textit{et al.} reported an elaborate SnS\textsubscript{2}/RGO nanocomposite with few-layered SnS\textsubscript{2} anchored on few-layered RGO, which achieved superior performance in SIBs. The 2D conductive channels constructed by RGO matrix, small lateral size and ultrathin layered SnS\textsubscript{2} are favorable for the rapid Na-ion transport and electrolyte penetration, responsible for the enhanced Na-storage performance.\textsuperscript{83} Moreover, Xiong’s group further optimized SnS\textsubscript{2}/RGO nanocomposite with an ultrafine SnS\textsubscript{2} nanocrystals on RGO \textit{via} the strong chemical bonding (FIG. 4c). The novelty of this work is to fabricate amino-functionalized graphene by one-step synthesis, which served as a strong framework to tight contact of SnS\textsubscript{2} at the interface. Based on the first principles theoretical calculations, the binding energy (BE) of SnS\textsubscript{2}/pristine RGO is only 0.018 eV, which could reach as high as 0.851 eV after EDA functionalization.\textsuperscript{84} SnS has distorted NaCl-type structure, Cao’s group has successfully synthesized SnS@RGO and SnS@C composites, respectively.\textsuperscript{85,86} Zhou \textit{et al.} has achieved the best performance of SnS, in which SnS@G hybrid nansheets exhibited an ultrahigh reversible capacity of 940 mAh g\textsuperscript{-1} and excellent rate capability of 308 mAh g\textsuperscript{-1} at high current (7290 mA g\textsuperscript{-1}).\textsuperscript{87} They concluded a reaction process with orthorhombic-SnS to cubic-Sn then to
orthorhombic-$\text{Na}_3.75\text{Sn}$, which indicated that the well-developed 2D nanostructures with precisely control of their sublayers can undergo conversion process via less structural changes of SnS, leading to high structural stability and cycling stability.

Besides, Sb$_2$S$_3$ reacts with sodium by virtue of joint occurrence of conversion and alloying reactions.

Similarly, optimization of Sb$_2$S$_3$ has focused on the combination of nanostructured Sb$_2$S$_3$ with carbon-based materials. FIG. 4d anchored Sb$_2$S$_3$ on sulfur-doped graphene (Sb$_2$S$_3$/SGS) by strong chemical binding, leading to a robust composite architecture for stable cycling performance. The DFT calculation shows that the adsorption energy between Sb$_2$S$_3$ and SGS is -0.97 eV, suggesting that SGS could adhere to Sb$_2$S$_3$ energetically. Moreover, the final discharge product, Sb, can also be more efficiently immobilized on SGS with much higher adsorption energy (-2.15 eV). More recently, Pan et al. exploited ionic liquid (IL) to assist the preparation of Sb$_2$S$_3$/rGO nanocomposite (IL-Sb$_2$S$_3$/rGO). The 1-butyl-3-methylimidazolium dihydric phosphate was proven to stabilize the graphene oxide and enable uniform coating of Sb$_2$S$_3$ on rGO. The obtained could show better performance than the control sample, retaining a capacity of 495.1 mAh g$^{-1}$ after 80 cycles (FIG. 4e).

**Sulfur cathodes in room-temperature Na-S batteries**

In 2003, high-temperature sodium-sulfur (HT-Na/S) batteries have been primarily manufactured by NGK insulators Ltd., which could operate at 300-350 °C with beta-alumina as Na$^+$-conducting electrolyte between molten Na and S electrodes. However, this technology suffers from safety issue and low specific energy. Thus, room-temperature Na-S (RT-Na/S) batteries were firstly brought out at 2006. Theoretically, It achieves an ultrahigh theoretical capacity of 1675 mAh g$^{-1}$ based on the reversible reactions between S and Na$_2$S. However, RT-Na/S batteries face many challenges in terms of sluggish kinetics and serious polysulfides migration, which induce battery failure with very limited reversible capacity.

**Carbonaceous hosts for S cathodes.** One straightforward countermeasure is exploit physical confinement (physisporition), embedding S into various conductive carbonaceous matrixes that have high surface area and well-designed structures. The intimate contact between S and C host could increase conductivity and electroactivity of sulfur cathode, leading to increased
reversible capacity. Moreover, when the carbon matrixes possess special nanostructures, such as hollow nanospheres and microporous polyhedral host (carbon derived from zeolitic imidazolate framework: cZIF-8), they could effectively suppress the polysulfide diffusion and shuttle via physical confinement for both S and the resultant polysulfides.\textsuperscript{28,95-98} Wang et al. synthesized interconnected mesoporous carbon nanospheres (iMCHS) as an effective S host (FIG. 5a). The carbon nanoshell could accommodate S and confine diffusive polysulfides; Moreover, the mesopores of carbon shells can tightly embed S and polysulfides as well, physically restricting the conversion reactions inside of iMCHS host and suppressing shuttle effect. The obtained S@iMCHS exhibited high reversible capacity of \(\sim 300\) mAh g\(^{-1}\) after 200 cycles (FIG. 5b). Significantly, they proposed a reversible mechanism between \(S_8\) and \(Na_2S_4\), corresponding to a theoretical capacity of 418 mAh g\(^{-1}\).\textsuperscript{99} Archer’s group used cZIF-8 microporous carbon as a effective S host and electrolyte with ionic liquid tethered silica nanoparticle (SiO\(_2\)–IL–ClO\(_4\)) additives to stabilize Na electrodeposition. They proposed a different solid-state transport mechanism without any soluble polysulfide species.\textsuperscript{97} In addition, Guo’s group has achieved very encouraging results by confining small sulfur (allotropes \(S_{2-4}\)) in the microporous carbon sheath. A high reversible capacity (\(\sim 1000\) mAh g\(^{-1}\)) was retained after 20 cycles. The high accessible capacity and stable cyclability were ascribed to the avoidance of shuttle phenomenon in \(S_{2-4}\) without formation of high-ordered polysulfide.\textsuperscript{100} More research effort should be devoted to deeply understand the Na-storage processes of S cathodes, especially in various electrolytes.\textsuperscript{101,102} Combined with the substantial physisorption, modified C host materials that could further chemically interact (chemisorption) with S or/and polysulfide as well, on the other hand, are preliminary studied.\textsuperscript{103,104} Choi’s group fabricated a polyacrylonitrile-derived carbon-sulfur (c-PAN@S) composite with a 1D structure via an electrospinning method. The final C–S composite shows that sulfur could form covalent bonds with the carbon atoms in the PAN-derived carbon matrix or sulfur nanodomains consisting of sulfur atom chains with various lengths. The atomic arrangements of S in the C matrix are responsible for the stable cycling of the obtained c-PAN@S composite (FIG. 5c).\textsuperscript{103} Meanwhile, Manthiram’s group has devoted much effort on the long-chain sodium polysulfide (Na\(_2S_6\)) as active cathodes to deal with the dilemma in RT-Na/S batteries (FIG. 5d). When Na\(_2S_6\) was
fabricated as cathode active materials instead of S, the batteries exhibit much fast kinetics. The charge/discharge curves for the subsequent cycles resemble the regular Na-S batteries, which indicate that the Na-storage mechanism is the same to that for S cathode.\textsuperscript{105} They also studied metal-free Na\textsubscript{2}S anode via the same strategy.\textsuperscript{106}

**Nanostructured metal sulfides host for S cathodes.** Nanostructured metal sulfides in lithium-sulfur batteries, including MnS\textsuperscript{107} CuS\textsuperscript{108} ZnS\textsuperscript{109} NiS\textsubscript{2}\textsuperscript{110} TiS\textsubscript{2}\textsuperscript{111} Co\textsubscript{9}S\textsubscript{8}\textsuperscript{112} FeS\textsubscript{2}\textsuperscript{113} CoS\textsubscript{2}\textsuperscript{114} and SnS\textsubscript{2}\textsuperscript{115} have been investigated as effective conductive polar host materials. These sulfiphilic host materials are a promising new group of candidates, which not only impede the polysulfide dissolution and but also accelerate the conversion process of polysulfides to (di)sulfides or the inverse process. A comprehensive comparison for various sulfides for Li/S batteries have been studied by Cui’s group, in which they concluded that the VS\textsubscript{2}, TiS\textsubscript{2}, and CoS\textsubscript{2} hosts were proven to be more suitable polar hosts than FeS, Ni\textsubscript{3}S\textsubscript{2}, and SnS\textsubscript{2}.\textsuperscript{116}

A few pioneering researches have explored the electrocatalytic phenomenon in RT-Na/S batteries system. Zheng et al. reported nano-copper (1-6 nm) loaded in high-surface-area mesoporous carbon (HSMC-Cu) as a superior S host (**FIG. 5e**). The obtained HSMC-Cu-S cathode showed a high capacity of 610 mAh g\textsuperscript{-1} after 110 cycles. The Cu nanograins in the carbon shell can enhance the overall electrical conductivity of the electrode, leading to high ion accessibility and high electroactivity of S. More importantly, these metal nanograins are expected to be polarized by partial surface sulfurization, which could effectively confine the long-chain sodium polysulfides and curb the serious shuttle phenomenon in this system via the polar-polar interactions between polarized metal nanograins and produced polysulfides.\textsuperscript{117} As illustrated in **FIG. 5f**, Zhang et al. also confirmed the polar-polar interactions between Cu foam and S. The Cu foam would be polarized with the formation of CuS and Cu\textsubscript{2}S during the S electrode preparation. The polarized Cu foam showed high sulfur affinity and were expected to immobilize the produced polysulfide, leading to alleviated shuttle phenomenon.\textsuperscript{118} In addition, a concept of “sulfur-equivalent cathode materials” is brought out recently. Ghosh’s group developed a sulfur copolymer as cathode to address the native downsides of RT-Na/S batteries in terms of polysulfide shuttle effect and low electrical conductivity of elemental S. As shown in **FIG. 5g**, a sulfur-rich copolymer (CS90 with S ratio of ~ 90 wt %) could be formed by incorporating
cardanol-based benzoxazine (Ca) and elemental sulfur. \textsuperscript{119} FIG. 5h shows that 1D chain-like S-rich amorphous MoS\textsubscript{3} also could work as the sulfur-equivalent cathode in RT-Na/S batteries. \textsuperscript{120}

**Conclusions and Perspectives**

In summary, based on multi-electron conversion reactions, the S-based materials, including metal sulfides (MS\textsubscript{x}), elemental S, polysulfides, and S copolymers, could achieve high theoretical capacity, which renders them promising and attractive candidates for various Na-ion technologies.

Taking the advantages of their low cost, high theoretical capacity, and easy accessibility, the MS\textsubscript{x} materials are typically utilized as anodes for conventional SIBs. The multi-electron reaction mechanisms are further generalized into three catalogues, including (I) conversion, (II) intercalation-assisted conversion, and (III) alloying-assisted conversion. It is concluded that all MS\textsubscript{x} are facing the drawbacks in terms of inferior reversibility, voltage hysteresis, cycling stability due to the intrinsic low conductivity and serious volume expansions during sodiation/desodiation. Engineering various nanostructures with high-conductivity C matrixes are the most essential tactics, in which C matrixes provide robust backbones for MS\textsubscript{x} and enhanced overall electrical conductivity. The design and fabrication of nanoarchitectures are very diverse. Ultrasmall nanocrystal can maximum the reaction sites with Na ions, shorten the diffusion path lengths for both electrons and ions, achieving near theoretical capacities. The few-layered nanosheets could provide favorable conductive channels, synergistic interface, plenty of free space, and large surface area. Three dimensional nanoporous structures could further provide extra void space to accommodate the volume changes. Out of the viewpoint of practical application, low-cost MS\textsubscript{x}, such FeS, FeS\textsubscript{2} and Ni\textsubscript{3}S\textsubscript{2}, are worthwhile to put more research effort. MoS\textsubscript{2} has been extensively reported, which can provides rich experience for other MS\textsubscript{x}, especially those with intercalation-assisted conversion reactions. For the ultrahigh-capacity SnS\textsubscript{2}, SnS, and Sb\textsubscript{2}S\textsubscript{3}, various strategies should be utilized, such as elaborate nanostructural control and electrolyte optimization, to deal with the aggravated volume expansions from both conversion and alloying reactions. Furthermore, it is meaningful and instructive to combine the experimental research with theoretical calculation, which is expected to guide the
structural design and large-scale production of MSx with superior electrochemical performance. Seeking suitable cathode materials is imperative for assembly of full cells with MSx anode. More effort should be devoted to develop advanced cathodes and electrolyte with high voltages, therefore, the full cells could achieve decent cycling performance with competitive energy density and power density. On the other hand, it is reasonable to work on Na metal anode, such as deposition/stripping efficiency, safety, electrolyte match issues with MSx cathode in order to explore emerging Na/MSx batteries.

Since the common carbon materials are futile, it is a promising direction to utilize MSx as effective polar S hosts in RT-Na/S batteries (FIG. 6a). We can speculate that the chemical interaction between sulfides and polysulfides could be enhanced by downsizing sulfides nanoparticles in carbon matrixes, more active sites and surface could be exposed and expected to evenly chemical binding with resultant polysulfide. The mechanistic insights into the nature of MSx onto S and polysulfides should be further investigated, including the neglected effects of electroactive sulfides themselves. Several feasible MSx hosts are proposed in FIG. 6b, the redox potential and reaction reversibility of the MSx host with Na ions is considered. CoS, Co3S8, and Co3S4 are suitable as S hosts; because their sodiation potentials are close to or much lower than that of the formation of Na2S. Even though the sodiation potentials overlap with the S cathode, both FeS2 and CoS2 undergo highly reversible intercalation reactions during the voltage window, making them appropriate electrocatalysts as well. Besides, following properties of MSx should be considered to determine an ideal S host, including electrical conductivity, absorption interaction to polysulfide, sodium ion diffusion rate, and energy barrier of Na2S oxidation. DFT simulation can be conducted to guide the rational design for high-performance RT-Na/S batteries. Moreover, the investigation on electrolyte is a key step, which not only can adjust the polysulfide dissolution out of the cathode but also tailor the SEI formation on the Na anode. The typical carbonates with fluoroethylene carbonate (FEC) additives are proven to be good SEI former, which could passivize the anode and prevent the electron transport from anode to electrolyte. In the future, great attention must be paid to conversion mechanisms of soluble polysulfide and insoluble (di)sulfides with different electrolyte systems. This review can shed
light on future design and fabrication of S-based electrodes for extensive Na-ion storage, such as Na-ion batteries, Na/MSx batteries, and RT-Na/S batteries.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
This research was financially funded by the National Key Basic Research Program of China (No. 2016YFB0901500), National Natural Science Foundation of China (Nos.21333007, 21805212) and China Postdoctoral Science Foundation (2017M620332).

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Sodium-ion batteries realize reversible sodiation/desodiation of an anode and a cathode during repeated cycles, which hold great potentials for larger-scale energy storage due to the advantages of low cost and decent specific energy (see the figure, part a). Schematic illustrations of various Li-storage mechanisms are displayed (Black circles: voids in the crystal structure, blue circles: metal, yellow circles: lithium.) Similarly, the anodes in SIBs share the similar Na-storage mechanisms. The intercalation/extraction mechanism features low-electron (< 1) reactions, showing flat plateaus but relatively low capacity. Alloying/dealloying anodes, such as Sn and Sn, have high theoretical capacity but severe volume variations, delivering fast capacity decay and inferior cycling stability. In contrast, conversion-based anodes represent compromise performance, which could achieve decent reversible capacity with prolonged service lifespan (see the figure, part b). On the other hand, a schematic representation of room-temperature Na/S battery on discharge shows the cell chemistry and configuration (see the figure, part c). Theoretical versus practical discharge capacities of RT-Na/S cells are displayed (see the figure, part d). Specifically, the discharge process of a RT-Na/S battery typically
proceeds via a four stage process. In the high oxidation regime (I), a solid-liquid transition occurs from S to dissolved long-chain sodium polysulfide (Na$_2$S$_8$). The second stage (II) is ascribed to a liquid-liquid transition from the dissolved Na$_2$S$_8$ to Na$_2$S$_4$. Subsequently, the dissolved Na$_2$S$_4$ could transit into insoluble Na$_2$S$_3$ or Na$_2$S$_2$ in region (III). The last stage is corresponding to the most difficult interconversion to Na$_2$S (IV).$^{94,121}$
Figure 1. **Representative metal sulfides as anodes in sodium-ion batteries.** (a) Schematic illustrations of metal sulfides anodes for stationary energy storage, such as FeS$_2$, SnS$_2$, MoS$_2$, SbS$_2$, CoS, FeS, and NiS. (b) Metal sulfides with corresponding theoretical capacity in SIBs in terms of conversion reaction (Co$_9$S$_8$, CoS, and FeS), intercalation-assisted conversion reaction (MoS$_2$, Co$_3$S$_4$, CoS$_2$, and FeS$_2$), and alloying-assisted conversion reaction (Sn$_2$S$_3$, SnS, and SbS$_2$).
Figure 2. Nanostructuring metal sulfides with conversion reactions. Different crystal structures of (a) CoS and (b) Co$_9$S$_8$ with permission from REF$^{46}$ Royal Society of Chemistry. (c) Schematic illustrations of nanostructure with CoS$_x$ quantum dots dispersed in NSC nanosheets and the reversible SEI formation on the CoS$_x$@NSC electrode. Adapted with permission from REF$^{51}$ American Chemical Society. (d) SEM image and (e) phase mapping of yolk-shell FeS@C nanospheres. Adapted with permission from REF$^{55}$ Nature Publishing Group.
Figure 3. Nanostructuring metal sulfides with intercalation-assisted conversion reactions. (a) Crystal structures of the typical layered MS$_2$ with the interlayer spacings and theoretical capacities. Adapted with permission from REF.$^{50}$ Royal Society of Chemistry. (b) Electrochemical sodiation process of MoS$_2$ with experimental voltage profile and simulated voltage profile of MoS$_2$ through the intermediated phases. Adapted with permission from REF.$^{63}$ Elsevier. (c) SEM and HRTEM images (inset, corresponding structure model with expanded interlayer spacing), and electrochemical performance of MoS$_2$:C superstructure nanotubes. Adapted with permission from REF.$^{122}$ Elsevier.
Figure 4. Nanostructing metal sulfides with alloying-assisted conversion reactions. (a) TEM image of 2D pure SnS$_2$ nanosheets. Adapted with permission from REF. $^{80}$, American Chemical Society. (b) SEM image with structural illustration (inset) of SnS$_2$/RGO composite. Adapted with permission from REF. $^{83}$, Wiley-VCH. (c) HAADF image and Na-storage performance of SnS$_2$ NC/EDA-RGO nanocomposite. Adapted with permission from REF. $^{84}$, Royal Society of Chemistry. (d) Structural illustration of orthorhombic Sb$_2$S$_3$ and SGS in the composite highlighting the fast Na$^+$ and electron transportation, with optimized structure in the DFT calculation of Sb$_2$S$_3$ and Sb on the SGS (upper panels are top views, and the bottom panels are side views; the gray, yellow, celadon, and white spheres are denoted to be C, S, Sb, and H atoms, respectively). Adapted with permission from REF. $^{90}$, American Chemical Society. (e) SEM image of IL-Sb$_2$S$_3$/Rgo with the corresponding Na-storage cycling performance. Adapted with permission from REF. $^{91}$, Wiley-VCH.
Figure 5. Nanostructuring S-based cathode materials. (a) TEM image of the S@iMCHS with merged elemental mappings of S and C; (b) Cycling performance of the S@iMCHS cathode in RT-Na/S batteries (inset, schematic illustration of the sulfur confinement in the S@iMCHS nanocomposite). Adapted with permission from REF.99, American Chemical Society. (c) An SEM image of the c-PANS NFs via an electrospinning process (inset, left panel), and cycling performance
at 1C of the c-PANS NFs showing the sodiation process with the final C-S covalent bonds. Adapted with permission from REF.103, American Chemical Society. (d) Schematic illustrations of the formation of a Na$_2$S$_6$/multiwaulled carbon nanotube (MWCNT) and Na$_2$S/MWCNT cathodes with the injection of Na$_2$S$_6$ and Na$_2$S catholyte, respectively. Adapted with permission from REF.105,106 American Chemical Society, Wiley-VCH, respectively. (e) Cycling performance and a TEM image (inset) of HSMC-Cu-S cathode in RT-Na/S batteries. Adapted with permission from REF.117, Wiley-VCH. (f) Schematic illustrations of polysulfide absorption of polarized Cu interface based on polar-polar interaction. Adapted with permission from REF.118, American Chemical Society. (g) Proposed chemical structure of CS900 by reaction of Ca monomer with elemental S. Adapted with permission from REF.119, American Chemical Society. (h) A TEM image of 1D chain-like MoS$_3$ cathode. Adapted with permission from REF.120, National Academy of Sciences.
Figure 6. The potential applications of mental sulfides as effective sulfur hosts. (a) Schematic illustrations of S-based cathodes in RT-Na/S batteries. (b) The possible MSₓ as effective electrocatalysts in S cathodes considering the typical redox potential vs Na/Na⁺ from REF.⁹⁹. Adapted with permission from REF.⁹⁹, American Chemical Society.