Review

The latest advances in the critical factors (positive electrode, electrolytes, separators) for sodium-sulfur battery

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ABSTRACT

The sodium-sulfur (Na/S) batteries have caused widespread concern owing to the advantages of low cost and high energy density, these advantages make them promising in the large-scale energy storage system. But the research progress in this field is still at the beginning stage and confronts with tough challenges, for example, the low sulfur conductivity and polysulfide shuttle effect. Considering Na/S battery is a complicated system whose reaction mechanism between sulfur and sodium is different from the operating temperatures, positive electrode hosts and electrolytes, thus a comprehensive understanding about the electrochemistry of the Na/S batteries that operating in high-temperature, intermediate-temperature and room-temperature is necessary. In addition, the critical factors (positive electrodes, electrolytes, separators) associated with the development of high energy density and high performance Na/S battery, it also need to be analysed for the successful application in the near future. In this review, the working methods of high-temperature Na/S (HT-Na/S) battery, intermediate-temperature Na/S (IT-Na/S) battery and room-temperature Na/S (RT-Na/S) battery will be compared, and also focus on the latest progress of positive electrodes, electrolytes and separators in Na/S batteries. Finally, we provide an outlook on the state of the art for the production of more efficient and reliable Na/S batteries with rational technique.

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Contents

1. Introduction

Nowadays, the renewable energy research around the world great target for the large—scale energy storage system which have the advantage of high energy density, because the loading level of electricity grid is urgently demanded no matter in the big cities or countryside that with fast economic and social development. Meanwhile, with the development of the large—scale energy storage system, clean energy resources like solar, tide and wind powder which have the intermittent feature can also be effectively utilized to power our society. However, among the existing energy storage systems, although lithium-ion battery has achieved booming development in the past twenty years, its high cost and the limitation of practical energy density ($100-200$ Wh kg^{-1}) make it only favourable for the small/mid-size energy storage like in the electric vehicles (EVs) and portable devices. To develop large-sale energy storage system, it is required to pursuit rechargeable battery system which show the advantages of low cost, long cycle life and high energy density [1,2].

Na/S battery have been extensively researched for the sake of large-scale energy storage system owing to its obviously advantages in low cost and energy density. Comparing with lithium-sulfur (Li/S) battery which only targets for EVs, 760 Wh kg^{-1} is the specific energy density of Na/S battery which is assumed by the scientists [3]. It is higher than practical energy density ($500-600$ Wh kg^{-1}) of Li/S battery [4]. The cost of Na/S battery is $80/KW/year, the cycle life of the HT-Na/S battery is 2500 cycles, it is longer than Li/S batteries of 1500 cycles [5,6]. The commercial production of HT-Na/S batteries are start earlier than other secondary batteries. The suitable power/energy density, long cycle life and high efficiency make the RT-Na/S exceeds the cost and scale requirement for large-scale application. However, the extra expenditure and risks caused by the high operation temperature limit its widely application in EVs. To achieve a wide application, RT-Na/S batteries has attracted great interest in recent years as it avoids the security risks caused by HT-Na/S battery, which can be applied in stationary grid and even EVs. But it needs to mention that RT-Na/S battery still meets the key challenge of fast capacity attenuation in the process of cycling and low reversible capacity. These problems are caused by low electronic conductivity of sulfur and sulfur-containing species forming during the charging/discharging process. Meanwhile, the inevitably dissolution of soluble polysulfide seriously shuttle to the negative electrode and involve in the redox reaction to form insoluble sulphides at the negative electrode surface, which resulting in the low columbic efficiency and loss of active materials. All these problems hinder the further development of RT-Na/S battery.

In the result of solving the problems of RT-Na/S battery, the scientists devoting many enormous efforts from the perspective of new functional materials and novel cell designs. In the past ten years, the researchers develop new positive electrode materials to achieve large reversible specific capacity [3,7—9], The more attention of positive electrode is in sulfur and carbon matrix materials. For example, mesoporous carbon hollow nanospheres, carbon nanofibers and graphene. In the nearby several years, the metal composite with carbon, owing to the better strong polysulfide absorption ability, there is the big improvement in specific capacity. Second, the new electrolytes to reduce the speed of active materials slowly dissolved into the electrolyte. The widely used electrolytes are solid-state electrolytes and ether-based electrolytes, however, the rapid reduce of discharge capacity often happened in solid-state electrolytes and ether-based electrolytes. The carbonate-based electrolyte and ionic-liquid-based electrolyte which show the advantages of better cycle performance and stable electrochemical performance occupy more research space. In addition, many workers from the perspective of surface modification, making the functionalized separators like sodiated Nafion-coated polypropylene membrane or Al$_2$O$_3$-Nafion to further improve cycling stability of Na/S battery.

In this review, the basic working principles of HT-Na/S battery, IT-Na/s battery and RT-Na/S battery were detailed explained, the latest advances and achievements about positive electrode materials, electrolytes and separators for Na/S battery were reviewed and the underlying reaction mechanisms were comprehensively discussed, the applications about Na/S batteries are also mentioned, an outlook on the state of the art for the production of more efficient and reliable Na/S batteries with rational technique was provided.

2. The working principles of Na/S battery

2.1. HT-Na/S battery

The development of the HT-Na/S battery ($300\,°C-350\,°C$) was started from the 1960s, due to the discovery of sodium β-alumina that can work as a solid state ionic conductor for sodium ion but not electron in the high temperature [10]. As demonstrated, in $300\,°C$, the conductivity of ionic for β-alumina approaches that of the aqueous electrolyte, H$_2$SO$_4$ [11]. So the working temperatures of batteries are $300-350\,°C$, not only ensure that the active electrode materials are molten but also take advantage in increase conductivity of the β-alumina. As shown in Fig. 1a, in the HT-Na/S battery
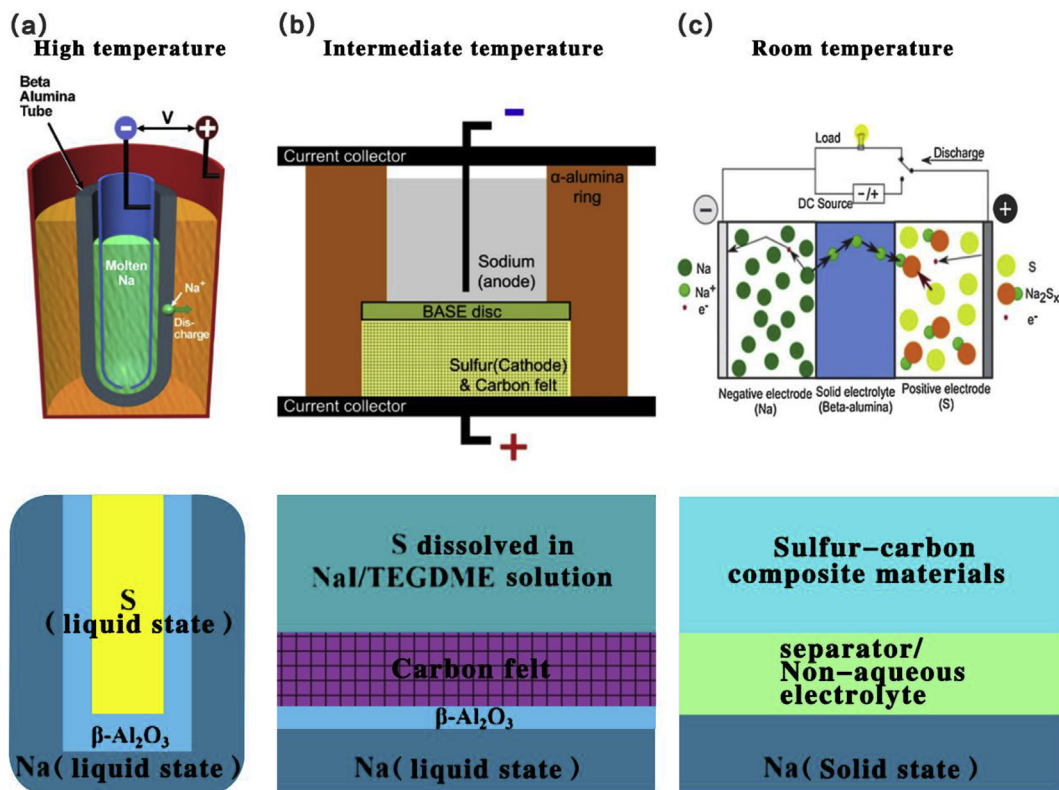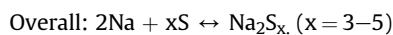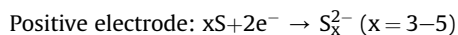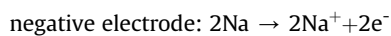
Fig. 1. (a) The design and electrode reactions of a HT-Na/S battery [12]. (b) Schematic diagram of a planar IT-Na/S cell. From Kim et al., J. Power Sources, 2016, 04, 041. Copyright 2016 Elsevier. (c) Reaction principles of RT-Na/S battery. From Oshima, Kajita, and Okuno, applied ceramic technology, 2004, 1, 3. Copyright 2005 Wiley.

system, the molten sodium ($T_m = 98\,°C$) serves as the negative electrode, molten sulfur ($T_m = 115\,°C$) in the container is the positive electrode, sodium β-alumina ceramic serves as both electrolyte and electrodes [12]. Sulfur positive electrode which incorporated by porous graphite felts are usually being selected to improve the electrical conductivity. The reactions of the charge and discharge in the HT-Na/S batteries [13] are:

negative electrode: $2Na \rightarrow 2Na^+ + 2e^-$

Positive electrode: $xS + 2e^- \rightarrow S_x^{2-}$ ($x = 3-5$)

Overall: $2Na + xS \leftrightarrow Na_2S_x$ ($x = 3-5$)

   $E = 2.08 - 1.78\,V$ at $350\,°C$.
   During the processes of discharging, all the active materials are in the state of molten, as the result, only Na_2S_x ($x \geq 3$) which have the melting points below $300\,°C$ are permitted to be produced. In the initial state, both sulfur and sodium polysulfide (Na_2S_5) are coexisted at the voltage of $2.08\,V$ due to their immiscible nature. Afterwards, both of them react with Na and become into a single phase region (Na_2S_4). Na_2S_3 can then form at $1.74\,V$. Therefore, due to Na2S2 and Na2S could not format when upon sodiation considering the high melting point of Na_2S_2 ($T_m = 470\,°C$) and Na_2S ($T_m = 1168\,°C$), only one third theoretical capacity of sulfur in this system can be implement. Despite of that, the depth of discharge (DOD) of Na/S batteries are achieve to 20% after 40,000 + cycles, 90% after 4500 cycles, and 100% after 2500 cycles [5]. Coupling with the advantage of low self-discharging, the HT-Na/S batteries have been commercially available and widely applied in electrical grids.
   However, there are still some challenges existed in HT-Na/S battery. Firstly, the molten polysulfides are highly corrosive to the

current collectors and battery casing at such high working temperature, which directly limits the use of metals and alloys like molybdenum, chromium and stainless steels. In addition, the degradation and breaking of the β-alumina solid electrolyte (BASE) during the operation would result in the direct contact and violent reaction between the molten sulfides and the molten sodium, which have potentially dangerous of a fire or even an explosion. Thus, for the reason of safety, Na/S batteries are not fit for transportation and stationary energy storage system is the major application for them. Besides, although the high temperature increases the conductivity of the sodium β-alumina solid electrolyte, it also inevitably sacrifices a fraction of energy to keep its working temperature, leading to the low overall efficiency (87%) [14]. Meanwhile, we provide an outlook on the state of the art for the production of more efficient and reliable Na/S batteries with rational technique.

2.2. IT-Na/S battery

   The Na/S battery working in the $300-350\,°C$ has great concern of cost and safety issues. There are many reports about the organic solvents or polymers serve as electrolytes which have been used in low- or RT-Na/S batteries. But most of these batteries have the problems of high self-discharging rate and rapid capacity attenuation owing to positive electrode materials dissolved in the electrolytes of liquid or polymer.
   In 2013, researchers in pacific northwest national laboratory (PNNL) reported an IT-Na/S battery (~150 °C) which included solid electrolyte separator of β-alumina with thickness of 600 μm and a catholyte solvent of tetraglyme [15]. Since the ionic conductivity of polymer or liquid electrolytes are much lower than that of β-alumina (thickness: 600 μm) at 150 °C (i.e. $8.5 \times 10^{-3}\,S\,cm^{-1}$), and

the positive electrode materials Na_2S_4 and S have high solubility in the tetraglyme, a great improvement in cycle life is showed by this battery over the high- or room-temperature Na/S batteries. When the operating temperature is 150 °C, there will be no dendrite growth in the negative electrode because sodium is existing in the state of molten. Meanwhile, to improve the power characteristic, the authors also changed the structure of the battery system to base disc instead of the traditional tube construction derived from the high temperature system (Fig. 1b). Although this is a great attempt for improving the power performance, the corrosive and dissolution problems of sodium polysulfides still exist in this temperature, and the practical of base disc IT-Na/S battery system still full of challenges, considering the extremely high requirement for the ceramic electrolyte from the perspective of safety.

2.3. RT-Na/S battery

Owing to the overwhelming advantages of low cost and excellent energy density in the large-scale stationary energy storage, RT-Na/S batteries have caused widespread concern in the nearby years. In this battery system, the positive electrode is sulfur or sulfur composites and negative electrode is sodium metal, instead of using β-alumina, RT-Na/S battery applies organic solvents (ethylene carbonate/propylene carbonate (EC/PC); ethylene carbonate/dimethyl carbonate (EC/DMC)) with sodium salts ($NaClO_4$, $NaNO_3$) as the electrolyte. The principle of discharging in the RT-Na/S batteries are [16]:

negative electrode: $Na \leftrightarrow Na^+ + e^-$

Positive electrode: $nS + 2Na^+ + 2e^- \leftrightarrow Na_2S_n$ ($4 \leq n \leq 8$)

Overall: $S_8 + 2Na^+ + 2e^- \leftrightarrow Na_2S_8$ (2.2 V, $4 \leq n \leq 8$)

$Na_2S_8 + 2Na^+ + 2e^- \leftrightarrow 2Na_2S_4$ (2.2–1.65 V, $4 \leq n \leq 8$)

$Na_2S_4 + 2/3Na + 2/3e^+ \leftrightarrow 4/3Na_2S_3$ (1.65 V)

$Na_2S_4 + 2Na + 2e^+ \leftrightarrow 2Na_2S_2$ (1.65 V)

$Na_2S_2 + 2Na^+ + 2e^- \leftrightarrow 2Na_2S$ (1.65–1.2V)
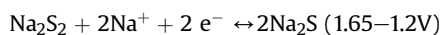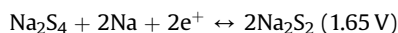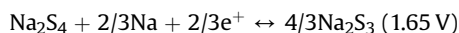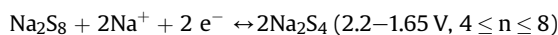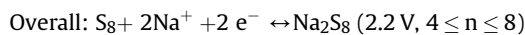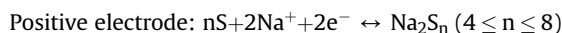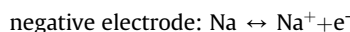
During discharging, sodium metal produces the sodium ions and electrons. The sodium ions go through the electrolyte and move to the sulfur positive electrode to produce sodium polysulfide species (Fig. 1c) [17]. These discharge processes are similar with that of Li/S battery, the capacity generated relies on the redox reaction of polysulfide species, and the theoretical discharge capacity is 1672 mAh g_{ele}^{-1}, which is very appealing for the large-scale energy storage system.

However, in addition to the common issue like poor electronic conductivity of sulfur and solid state discharge product, the RT-Na/S battery also suffers from more tougher problem compared with Li/S battery. For instance, the Na_2S_x ($4 \leq x \leq 8$) is more soluble in organic electrolyte than the corresponding Li_2S_x ($4 \leq x \leq 8$), this inevitable dissolution of Na_2S_x ($4 \leq x \leq 8$) resulting in the more serious shuttle effect between the positive electrode and sodium negative electrode, which lead to the poor cycling stability and high self-discharging rate. Besides, the reducing ability of Na^+ ion is less than that of Li^+ ion, so the kinetics of electrochemical reaction is more sluggish in the RT-Na/S system. Meanwhile, the volume expansion induced by the formation of solid-state discharge product Na_2S is two times larger than that of Li_2S (260% for Na/S versus 80% for Li/S) [18], which can cause the rapid degradation of positive electrode host. Besides, since the big difference in size

between Na atom and Na^+ ion, sodium is more likely than lithium to take shape unsteady electrodeposits and dendrites [19], this can restrict cycling durability and cause serious safety concern. Based on this condition, more improvements are supposed to make for the sake of successful RT-Na/S battery system.

3. The application comparison between Na/S battery and other secondary battery systems

In 1992, the first Na/S battery energy storage system started running in Japan [20]. The power of this battery system is 0.05 MW. In 2002, the company of HGK started commercial production and supply of Na/S batteries [21]. The application of the Na/S batteries focus on the industrial production. The different applications including businesses (29%), electricity (26%), industrial (23%) and water system (22%). As shown in the Table 1 [22]. The advantages of Na/S batteries are high capacity and energy density. Owing to the cheap price of raw materials and nearly 0% daily self-discharge, the HT-Na/S batteries used more widely. The island in Abu Dhabi was reported to use the Na/S battery to provide life electricity, the power could reach 40 MW [20].

The commercial production of the Li/S battery is later than Na/S battery, it starts from 2010, the American company Sion Power used the Li/S battery in large drone [23]. It is the start of small commercial production of Li/S battery. The research about Li/S battery is still in the step of laboratory research, there is a certain distance to widely commercial use. Owing to lithium-ion battery and Li/S battery have the similar closed system, the transfer from lithium-ion battery to Li/S battery is easy to complete [6], so the widely commercial production of Li/S battery is great possibility in the future.

The commercial production of lithium-ion battery is a little earlier than the Na/S battery. In 1991, the Sony started the commercial production of lithium-ion battery [24]. First, it has a big improvement in the area of mobile phone and laptop. Second, in the nearby several years, the lithium-ion battery widely used in products of electronic car, especially the rich-nickel lithium-ion battery [25]. However, in terms of safety, life cycle and high-power discharge, it has the clear disadvantages compared with that of Na/S batteries.

Therefore, compared with other secondary battery systems (Table 2), Na/S batteries have the better cycle performance and low self-discharge for commercial production. In the future, the research may focus on improving the energy density and working voltage of Na/S battery (see Tables 3 and 4).

Overall, the Na/S battery is suitable for commercial production. The mostly used Na/S batteries for commercial productions is HT-Na/S battery. However, owing to the safety issues, this new technology cannot apply widely. The researchers try to find out the more stable RT-Na/S batteries to applied in the real market. Although the initial discharge capacity in the RT-Na/S batteries are high, the problem of poor cycling stability is the gap of commercial used of RT-Na/S batteries. In the recent research, if the RT-Na/S batteries which have the advantages of high initial capacity and excellent cycling stability could success, the commercial used RT-Na/S battery will be coming soon. The researches about the

Table 1
The different percentage in application of sodium-sulfur battery.

Application area	Percentage (%)	Reference
Business	29	[22]
Electricity	26	[22]
Industrial	23	[22]
Water system	22	[22]

Table 2
Comparison the different performance of sodium-sulfur battery, lithium-sulfur battery and rich-nickel lithium-ion battery.

	Sodium-sulfur battery	Lithium-sulfur battery	Rich-nickel lithium-ion battery
Energy density	150–300 Wh/L	350 Wh/Kg	170 Wh/Kg
Cost	$80/KW/year	–	–
Working Voltage	2.075 V	2.4 V	2.4–4.2 V
Rated capacity	244.8 MWh	–	–
Cycle performance	2500 cycles, 90% deep discharge	1500 cycles	2000 cycles
Energy efficiency	>85%	–	–
self-discharge	Nearly 0%	30%	
advantages	1.High capacity 2.High energy capacity 3.Cheap	1.High energy density 2.easy to recycle	1.High energy density 2.High tap density
disadvantages	Poor security	1.Poor cycle performance 2.expensive	1.Short life cycle 2.Poor security 3.serve as high-power equipment, Poor discharge performance

Table 3
Na/S batteries made up by different positive electrode composition, electrolyte composition and lead to the different electrochemical performance.

Positive electrode Material	Sulfur Content in the positive electrode Material (wt %)	Electrolyte	1st cycle Discharge Capacity (mAh g_{sul}^{-1})	Discharge Capacity after n cycles	Reference
CS90 copolymer super C-65 carbon black polyethylene	88.67	1 M NaClO$_4$ and 0.2 M NaNO$_3$ in TEGDME	542	335 (50 cycles)	[26]
S@IMCHs carbon black CMC	N/A	1 M NaClO$_4$ in PC/EC + 5 wt % FEC	1215	340 (100 cycles)	[27]
S$_{1-x}$ Se$_x$ @PCNF thin film	54	1 M NaClO$_4$ in EC/PC	1889 (0.1 A g_{sul}^{-1})	762 (0.1 A g^{-1},100 cycles)	[28]
Carbon fiber cloth	24.4	1.5 M NaClO$_4$+0.3 M NaNO$_3$ in TEGDME	390 (0.1 C)	120 (0.1 C,300 cycles)	[29]
sulfur-microporous carbon carbon black CMC	35	1 M NaPF$_6$+0.25 M NaNO$_3$ in TEGDME	700 (0.1 C)	300 (1 C, more than 1500 cycles)	[30]
Bi$_2$S$_3$@C carbon black carbon nanotubes CMC	N/A	1 M NaClO$_4$ in EC/DEC	550 (0.1 C)	282 (0.1 C,100 cycles)	[31]
CSCM active materials acetylene black carboxyl methylated cellulose	29	1 M NaClO $_4$ in EC/DMC	1100	678 (50 cycles)	[32]
C-PAN super P PVDF	31.42	0.8 M NaClO$_4$ in EC/DMC	796	153 (1 C,500 cycles)	[33]
Sulfurized polyacrylonitrile nanofiber web	41	1 M NaPF$_6$ in EC/DEC	604 (0.01 C)	266 (0.1 C,200 cycles)	[34]
Na$_2$S powder short MWCNTs	55	1.5 M NaClO$_4$ and 0.3 M NaNO$_3$ in TEGDME	660 (C/10)	560 (C/10,50 cycles)	[35]
Na$_3$PS$_4$ nanosized Na$_2$S acetylene black	N/A	120 mg Na$_3$PS$_4$ solid electrolyte	869.2 (50 mA g_{sul}^{-1})	438.4 (50 mA g_{sul}^{-1},50 cycles)	[36]
Na$_2$S Na$_3$PS$_4$ CMK-3	N/A	120 mg Na$_3$PS$_4$ solid electrolyte	N/A	810 (50 mA g_{sul}^{-1}, 50 cycles)	[37]
MoS$_3$ powder carbon black carboxymethyl cellulose	45	1 M NaClO$_4$ in EC/DMC with 8 vol% FEC	460 (23 mA g_{sul}^{-1})	180 (0.45A g_{sul}^{-1},1000 cycles)	[38]
poly(S-PETEA)@C carbon black sodium carboxymethyl cellulose	97.1	1 wt% PETEA, 1 wt% THEICTA and 0.1 wt% HMPP dissolved in 1 M NaTFSI in PC: FEC	877 (0.1 C)	736 (0.1 C, 100 cycles)	[39]

positive electrodes, electrolytes and separators are very important for RT-Na/S batteries to be applied in the real market.

4. Positive electrode

The shuttle effect of polysulfide and the insulating nature of sulfur are the major problems restricting the development of the Na/S batteries, these problems always lead to low electrochemical utilization of sulfur and rapid capacity attenuation. Many methods have been reported to meeting these problems from the positive electrode aspect including packaging sulfur particles into different carbon materials or polymers which can be conducting. The researchers have found out that the Na/S batteries which using the composite positive electrode of active materials and carbon show the improved electrochemical performance. In this part, we will review the latest positive electrode materials for Na/S battery like sulfur-carbonaceous composite, covalent sulfur based carbonaceous materials, sulfurized polyacrylonitrile and sodium sulphide (Na$_2$S) positive electrodes.

4.1. Sulfur-carbonaceous composite positive electrodes

4.1.1. Sulfur-graphene composite materials
In 2017, Mitra et al. used sulfur copolymer (CS90-rGO) as

Table 4
Na/S batteries made up by different electrolyte, positive electrode materials and lead to the different electrochemical performance.

Electrolyte	Sodium ion conductivity (S cm^{-1})	Positive electrode materials	Sulfur content (wt.%)	1st cycle Discharge Capacity (mAh g^{-1})	Discharge Capacity after n cycles (mAh g^{-1})	Reference
1 M NaTf in EC/PC(RT)	4.1×10^{-3}	sulfur powder acetylene black gel electrolyte composition	N/A	165	21 (8 cycles)	[43]
120 mg Na$_3$PS$_4$ solid electrolyte (RT)	N/A	Na$_3$PS$_4$ nanosized Na$_2$S acetylene black	N/A	869.2 (50 mA g^{-1})	438.4 (50 mA g^{-1},50)	[36]
1 M NaCF$_3$SO$_3$ in TEGDME(RT)	N/A	S/C composite material PVDF Super-P	55	855 (1/64 C)	521 (1/64 C, 104 cycles)	[44]
NaTf/EC:PC:EMITf/PVdF-HFP gel polymer electrolyte film (30 °C)	8.4×10^{-3}	elemental sulfur powder acetylene black	N/A	267	N/A	[45]
Na$_{10}$GeP$_2$S$_{12}$(RT)	4.7×10^{-3}	N/A	N/A	N/A	N/A	[46]
1 M NaCF$_3$SO$_3$ in TEGDME(25 °C)	3.9×10^{-3}	elemental sulfur powder carbon PEO in acetonitrile	N/A	538	240 (10 cycles)	[47]
1 M NaClO$_4$ in EC/DMC(RT)	N/A	HSMC-Cu−S composite material acetylene black sodium carboxymethyl cellulose binder	50	1000	610 (0.03 C, 110 cycles)	[48]
1 M NaClO$_4$ EC/DMC(RT)	N/A	PAN-based material acetylene black polytetrafluoroethylene	42	655	500 (18 cycles)	[49]
1 M NaClO$_4$ in EC/PC(RT)	0.9×10^{-3}	MCPS$_1$ or MCPS$_2$ carbon black polymer binder	32	866 (0.1 C)	600 (0.5 C, 100 Cycles)	[50]
1 wt% PETEA, 1 wt% THEICTA and 0.1 wt% HMPP dissolved in 1 M NaTFSI in PC: FEC (25 °C)	3.90×10^{-3}	poly(S-PETEA)@C carbon black sodium carboxymethyl cellulose	97.1	877 (0.1 C)	736 (0.1 C, 100 cycles)	[39]

positive electrode structure for RT-Na/S battery [26]. This composite was synthesized by a facile approach that thermal ring-opening polymerization of benzoxazine in the presence of elemental sulfur (CS90) and in the next step, it composites with reduced graphene oxide (rGO). This method covalently confines sulfur in the CS90 with high content loadings (~87 wt %), effectively solving the limitation caused by the physical sulfur encapsulation method like low loading and nonuniform distribution of sulfur, which is great significance for the greener and large-scale battery applications. On the other hand, although the sodium polysulfide still generated during cycling, this CS90-rGO based positive electrode was proved can effectively reduce the dissolution of high-order polysulfide and alleviated the irreversible deposition of insulating end-discharged product by the ex-situ XRD, XPS results. As a result, while the sulfur content is 60 wt % (based on the positive electrode), CS90-rGO-S copolymer positive electrode delivered an initial reversible capacity of 542 mAh g$_{sul}^{-1}$, and maintained a capacity of 335 mAh g$_{sul}^{-1}$ after cycling for 50 times and the average rate of capacity fading is 0.76% per cycle. Owing to the polymer backbone is formed in suit, the distribution of sulfur is uniform and can achieve the maximum use of sulfur. The rGo can easily dispersed in sulfur copolymer and form a percolation network, because the high surface area and excellent dispersion of rGo. This work proposed brilliant idea that applied raw materials which is low-cost with simple preparation of positive electrode for RT Na/S, which is meaningful for facilitating sodium-based batteries at industrial scale. Evenly distributed sulfur and high sulfur loading rate in graphene are the research targets for researchers to achieve in the future, the aims of inhibit the shuttle effect is also valued by researchers.

4.1.2. Sulfur-mesoporous carbon hollow nanospheres composite materials

In 2016, Dou et al. reported an effective sulfur host for RT-Na/S

battery which is the interconnected mesoporous hollow carbon nanospheres [27]. Since the continuous and interlaced of C backbone and after loaded with sulfur, high structural intimacy, high tap density can be ensured by this structure. In addition, the inner hollow nanospaces not only accommodate high amount sulfur, but also brook the changes of volume of the interior sulfur. Meanwhile, the outer shell can either serves as a highly conductive network for sulfur and transport of electron or acts as open active diffusion channels. Based on the structure advantage, the in-situ synchrotron X-ray diffraction further disclosed the Na-storage mechanism of sulfur as shown in Fig. 2a, the three main peaks are at 7.08° , 10.44° and 11.68° and these three peaks can be indexed in (113), (222) and (026) planes in the S$_8$, when the positive electrode discharged from 2.3 V to 1.6 V, the three main peaks will disappear, and two new peaks will form at 12.06° and 12.54° . When it further discharges to 1 V, there are also two new peaks generated at 13.27° and 14.15° , they could correspond to the planes of (213) and (312) in the Na$_2$S$_4$. Moreover, when it discharges from 1 V to 0.8 V, the new peak appears at 17.14° . When discharge from 2.3 V to 0.8 V, the sulfur are in different forms combined with sodium, including S$_8$, Na$_2$S$_x$ and Na$_2$S$_4$. The sulfur was encapsulated in the hollow space and embedded in the mesopores of iMCHS matrix. When the battery is discharge to 1.6 V, higher polysulfide species (Na$_2$S$_x$, $5 \leq x \leq 8$) gradually formed; then discharge to 1.0 V, Na$_2$S$_4$ phase was formed; finally discharge to 0.8 V, solid state phase Na$_2$S was formed. But when recharged to 2.8 V, the diffraction peak of Na$_2$S was accumulated and it will not reduce into long-chain polysulfides, demonstrating the irreversibility of Na$_2$S. Thus, in the cycling performance (Fig. 2b), we can see that the higher initial discharge capacity is 1215 mAh g$_{ele}^{-1}$(based on the mass of the electrode), which demonstrates the high activity and utilization of sulfur in the positive electrode due to the structure advantage of this carbon hollow nanospheres. But the low-voltage plateau is irreversible in the following cycles. It shown a low reversible
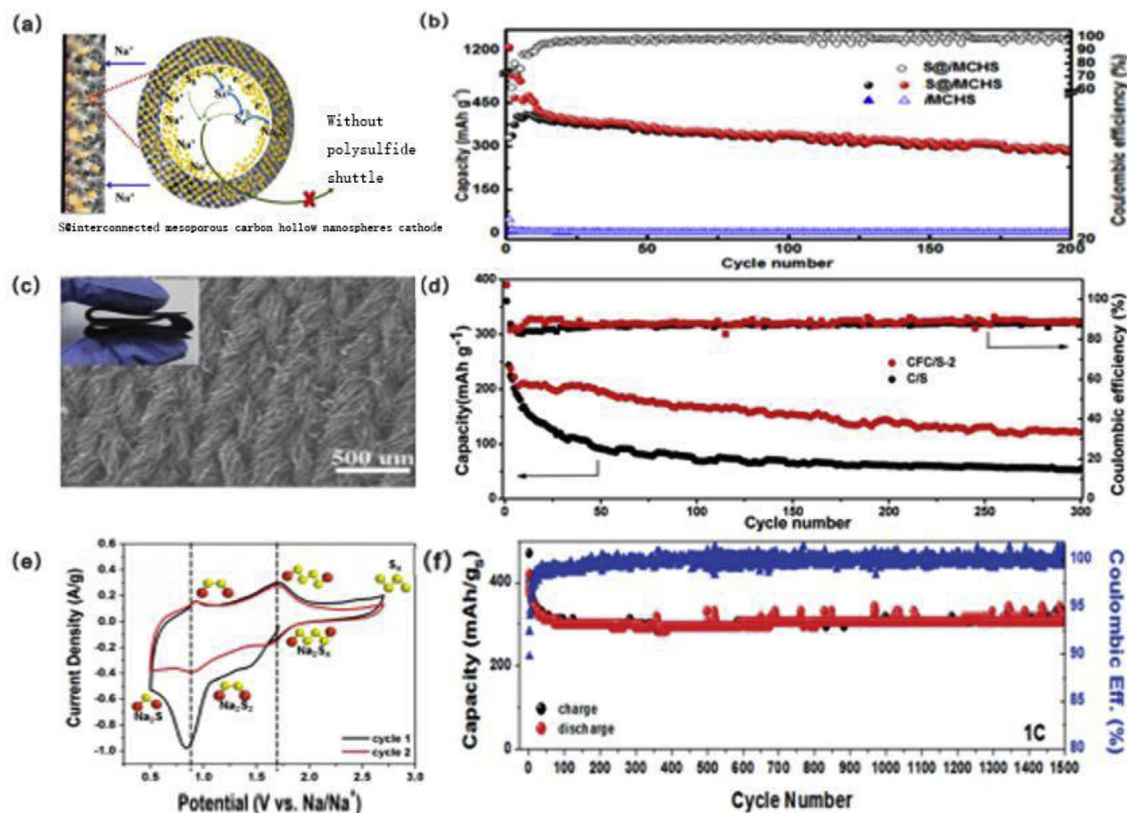
Fig. 2. (a) Summary the confinement of the S@iMCHS nanocomposite. (b) Profiles of galvanostatic charge/discharge for RT-Na/S@iMCHS cells in selected cycles [27]. (c) SEM image of CFC and CFC/S composite which have the excellent flexibility. (d) The performance of cycling of Na/S batteries which use the composite of CFC/S-2 and composite of conventional C/S when cycling at 0.1 C for 300 times [28]. (e) Analyse of sulfur positive electrode at 50 μV s^{-1} in Na/S using cyclic voltammetry. (f) Cycling at 1 C for 1500 times, the capacity of discharge and charge and coulombic efficiency plotted in figure [30].

capacity of 328 mAh g$_{sul}^{-1}$, demonstrating that solid Na$_2$S which prepared by this method are not able to be reversibly oxidized, however, it was placed on the positive electrode nonuniformly. When the times of cycling over 200, the reduction of transfer rate of charge and block ion accessibility caused by accumulated nonconductive Na$_2$S deposition, and resulting in kinetics slowly and polarization seriously, and future leading to the slowly capacity decay and increased charge/discharge potential difference. Qiao et al. reported a new electrode of hollow carbon nanospheres which wreathed by transition-metal (Fe, Cu and Ni) nanoclusters [73]. Although the capacity was rapidly decreased in the first 50 cycles, it exhibited better reversible capacity of 394 mAh g$_{sul}^{-1}$ after 1000 cycles at the rate of 100 mA g^{-1}. It even showed a rate capability of 220 mAh g^{-1} at a high current density of 5 A g^{-1}. As a comparison, the electrode which not forming chemical bonds of Fe–S displayed rapid capacity degradation from an initial reversible capacity of 811 mAh g^{-1} to 57 mAh g^{-1} after only 25 cycles. These metal nanoclusters acted as a very important role to rapidly reduce Na$_2$S$_4$ into short-chain sulfides, thus slowing down the shuttle effect. The main reason for this result is transition-metal (Fe, Cu and Ni) nanoclusters wreathed on the hollow carbon nanospheres improve the reactivity of sulfur via chemical bonds like Fe–S, Cu–S and Ni–S. Moreover, the results also revealed the Fe–S bonds have better performance than that of Cu–S and Ni–S bonds. In the future, the research will focus on not only improve the high sulfur loading rate in cavity, but also improve in carbon mesoporous.

4.1.3. Sulfur-carbon nanofibers composite materials

Interconnected conductive networks and good structural stability are advantages of the carbon nanofibers. In 2016, Yu et al. reported a flexible S$_{1-x}$Se$_x$@porous carbon nanofibers (x ≤ 0.1) thin film as positive electrode for RT-Na/S battery and it exhibited excellent electrochemical performance [28]. As shown in Fig. 2c, this positive electrode was prepared by dipping S$_{1-x}$Se$_x$ into porous carbon nanofibers. Gaining experience from Li/S battery, loading Se into S not only enhanced electronic conductivity of the sulfur, but also inhibition of polysulfide shuttle effect by forming a Se–S bonding. In addition, the porous carbon nanofibers based current collector can easily connect with ions and improve the conductivity and flexibility of the sulfur electrode. Therefore, after cycling for 100 times at the rate of 0.1 A g^{-1} (Fig. 2d), the reversible capacity was maintained at 762 mAh g$_{sul}^{-1}$ and the coulombic efficiency still approached 100%. In spite of the novelty of this work, the reaction mechanism for this positive electrode based RT-Na/S battery is not sufficiently proved and further work still need to do. Later on, Niu et al. also reported a freestanding binder-free positive electrode for RT-Na/S battery [29]. This positive electrode is made by carbon fiber cloth which loaded by sulfur. As for advantages, they have a 3D conductive interconnected network and a high electrolyte absorption rate of 1156%. Even when the areal sulfur loading is 2 mg cm^{-2}, the test results show an initial discharge capacity of 390 mAh g$_{sul}^{-1}$ at the rate of 0.1 C (1 C = 1672 mAh g$_{sul}^{-1}$) and retained capacity of 120 mAh g$_{sul}^{-1}$ after cycling for 300 times. More importantly, the RT-Na/S batteries which is soft-packaged can still keep their capacity stably when the batteries are bent, this is very appealing for the bendable and wearable electronic products to develop in the future.

4.1.4. Sulfur-microporous carbon composite materials

Due to the confinement of microporous carbon, sulfur molecules kept in the system are limited to the sizes of S_{2-4}, which can only process the change from the S_4 molecules to Na_2S_2/Na_2S, eliminates the formation of soluble product Na_2S_x ($4 \leq X \leq 8$), thus effectively avoiding the shuttle effect in the traditional RT-Na/S battery. In 2017, Pint et al. synthesized microporous carbon which derived from sucrose as sulfur host [30]. As confirmed by the Raman spectroscopy, no S_8 peaks which is characteristic was detected and the spectra is shift in the D peak by 17 cm^{-1}, demonstrating that sulfur served as smaller molecules, it will not have crystalline order and fully contained in the carbon material. In addition, the change from the S_4 molecules to Na_2S_2/Na_2S was also clearly illustrated in the cyclic voltammetry (Fig. 2e). Therefore, owing to the sulfur confinement in this microporous carbon (35 wt% sulfur loading) and the sodium mental negative electrode is stable in glyme-based electrolyte, the results showed excellent performance in cycling and capacity. After cycling at 1 C more than 1500 times, the reserve capacity is maintained at 300 mAh g_{sul}^{-1} and the coulomb efficiency is still over 98% (Fig. 2f). This work is appealing for battery design in the future, both for a cheap alternative to LIBs, the competitive positive electrode gravimetric capacity of sulfur positive electrodes derived by sugar are superior to other positive electrodes which are contained by cobalt in LIBs. Owing to the excellent ability of loading sulfur, the microporous carbon play an important role in composite materials for Na/S batteries in the recent years. It results in the inhibition of shuttle effect and better electrochemical performance. To solve the problem of poor conductivity during cycling, Li et al. reported a 3D railway-like network constructed by 1D carbon nanotubes (CNTs) tightly concatenated by nitrogen-doped porous carbon polyhedrons [74]. First, by connecting the isolated parts in series by CNTs, the agglomeration of metal−organic frameworks (MOF) can be weakened. The electrons can well transport between MOF-derived NPCs, which can significantly improve the reaction kinetics. Second, many micropores and mesopores in MOF-derived carbon can provide space to store sulfur as well as the accommodation of volume expansion of sulfur during cycling. Moreover, the 3D structure composed of low-dimensional units also contributes to the structural stability during cycling. When served as cathode materials for Na/S battery, it showed better electrochemical performance, the initial discharge capacity was 601 mAh g_{sul}^{-1} at 0.5C and retention capacity could reach 410 mAh g_{sul}^{-1} after 500 cycles with a capacity decay rate of 0.064% per cycle. The coulombic efficiency was higher than 99% for the whole cycles. The CNT/NPC exhibited high surface area of 2480 m^2 g^{-1} and a pore volume of 1.011 cm^3 g^{-1}. After the infiltration of sulfur, the BET surface area and pore volume of S@CNT/NPC were obviously reduced to 20 m^2 g^{-1} and 0.101 cm^3 g^{-1}, respectively. The uniform dispersion of sulfur in the porous carbon matrix improved the charge transfer dynamics and ensured the high utilization of sulfur. Owing to the high conductivity of CNTs and fast reaction kinetics of the railway-like structure, this electrode delivered capacity of 915 mAh g_{sul}^{-1} at 0.05C. In the future, the research direction will focus on smaller pore size and high sulfur loading rate. The price of raw materials is also considered by researchers. The sulfur positive electrode derived by sugar is a good example to obtain cheap positive electrode.

4.1.5. Sulfur-Bi$_2$S$_3$@C composite materials

Because of the unique structure of the Bi_2S_3 composite materials, it not only slows the dissolving of polysulfide, but also maintains the integrity of electrode. It ensures the excellent cycle stability. The composite of Bi_2S_3 which coated by graphite nanoplate has been prepared by Li et al. [31] This composite material is prepared by precipitation method and ball milling. This method is simple, scalable and high energy. The Bi_2S_3 particles are coated by amorphous carbon, it results in the increasing of electronic conductivity and prevents the dissolving of polysulfide during the cycle processes. The Bi_2S_3 particles wrapped in the graphite nanoplate can be used as the protective layer to prevent the polysulfide dissolve into liquid electrolyte. The initial capacity can reach 550 mAh g_{sul}^{-1}, after cycling for 100 times, the capacity retention is 69%. The results show the sulfur-microporous carbon composite materials are high density and have the advantage of excellent cycling performance. It can be the good choice for the Na/S batteries to achieve the excellent electrochemical performance. Owing to the unique structure of Bi_2S_3, the Bi_2S_3 without carbon independent served as positive electrode; however, the Na/S battery show poor cycle performance because of the low electronic conductivity. In the future, the research direction will focus on the Bi_2S_3 working well in Na/S batteries without carbon.

4.1.6. Covalent sulfur based carbonaceous materials

In 2016, Lu et al. reported the covalent sulfur based carbonaceous materials being selected in RT-Na/S batteries, which was realized by pyrolysis of sulfur powder and thiophene derivative at 500 °C [32]. This covalent sulfur effectively prevent the formation of sodium polysulfide (Na_2S_n, $4 \leq n \leq 8$), solved the problem of dissolution of polysulfide; on the other hand, when cycling during charge/discharge process, this covalent sulfur is reversible in these carbonaceous materials. As shown in Fig. 3a, there are no distinct platform between 2.0 V and 2.2 V in the process of discharge, suggesting no formation of Na_2S_n ($4 \leq n \leq 8$) during cycling. Furthermore, the Raman spectra of S−S stretch (466 cm^{-1}) at the different states which are pristine, fully sodiated and fully desodiated showed in Fig. 3b. When the state at fully sodiated, it is clear that the peak is disappeared because of the formation of Na_2S, and recovered when the state at fully desodiated, implying the S−S bond have excellent recoverability. Besides, Fig. 3c exhibits the XPS curve of high-resolution S 2p when at the state of fully sodiated, the peak of S 2p3/2 and the S 2p1/2 shifted to the lower energy compared with the pristine materials, indicating the lower oxidation state of S atoms, this is mainly due to the strong interaction between Na^+ and S atom. Thus, it can conclude that in the process of sodiation, the covalent sulfur has reaction with Na^+ and form Na_2S; while in the process of desodiation, the covalent sulfur return from S^{2-}. Based on this condition, with the sulfur content of 18%, the covalent sulfur based materials exhibits the reversible capacity higher than 1000 mAh g_{sul}^{-1} and long cycling stability even after cycling for 900 times with capacity attenuation at the rate of 0.053% per cycle.

The sulfur-carbonaceous composite materials are the widely used for positive electrode in Na/S batteries. There are many different types of carbon matrix. Every matrix of carbon has their own advantages in morphology and electrochemical performance. In this review, we focus on graphene, mesoporous carbon hollow nanospheres, carbon nanofibers, microporous carbon, Bi_2S_3@C and covalent sulfur based carbonaceous. The graphene help achieving the evenly distributions of sulfur and high loading rate of sulfur. In the internal of the mesoporous carbon hollow nanospheres, there is enough area to contain the sulfur and allow the volume change of sulfur. The shell of the mesoporous carbon hollow nanospheres play the role of highly conductive grid to transfer the sulfur and electrons. Carbon nanofiber is the better choice for flexible positive electrode can be used in Na/S batteries. Because the advantages of interconnected conductive network and excellent structural stability. Microporous carbon have the effect on reduce the shuttle effect, due to the limitation of microporous carbon on sulfur. The special structure of Bi_2S_3 composite material lead to excellent cycling performance. It can not only slow down the dissolution of
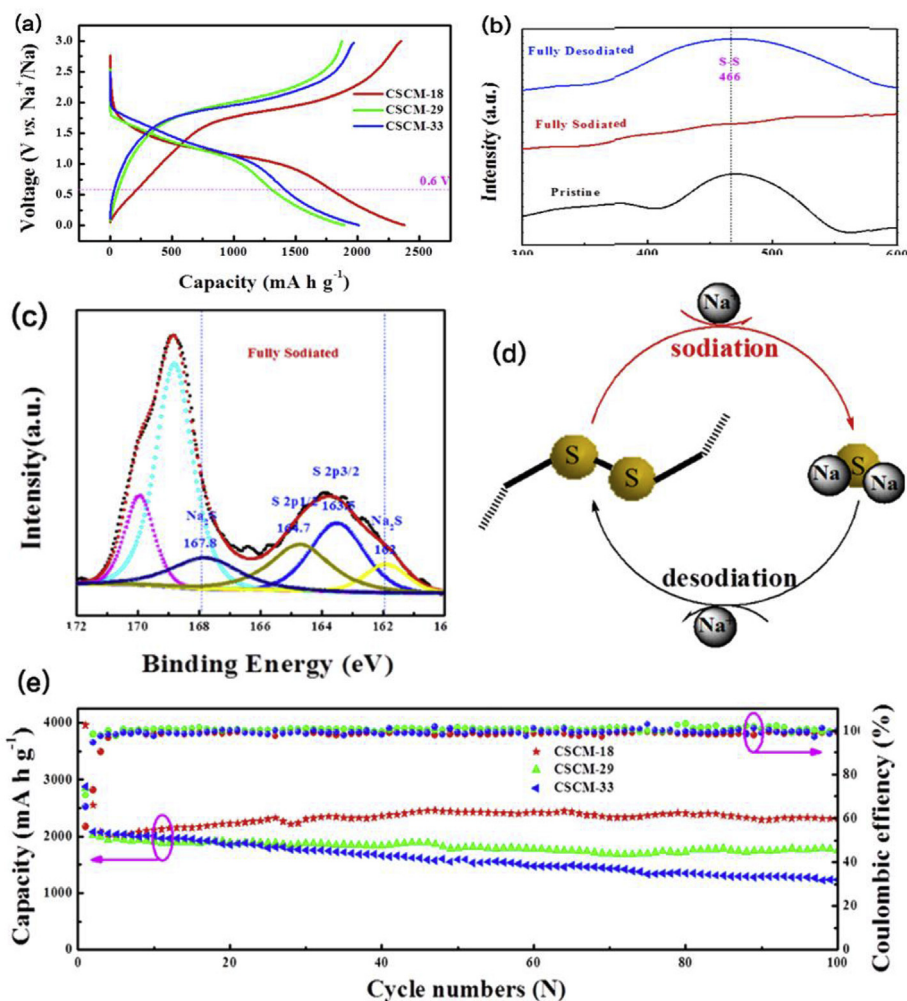
Fig. 3. (a) The typical profiles of discharge/charge of the CSCM-18, CSCM-29 and CSCM-33 when the current density is $100\,mA\,g^{-1}$. (b) The ex-situ Raman spectra of CSCM-18 at different states which are pristine, fully sodiated and fully desodiated. (c) The curve of XPS of CSCM-18 when fully sodiated. (d) The proper mechanism of the sodiation and desodiation in the CSCM. (e) When cycling at the current density of $100\,mA\,g^{-1}$ and the voltage between 0.01 and 3.0 V, the cycling stability of CSCM-18, CSCM-29 and CSCM-33 [32].

polysulfides, but also keep the integrity of electrodes. The most popular effect of covalent sulfur is preventing the formation of sodium polysulfide and result in solving the problem of dissolution of polysulfides.

Although the commonly used loading method ensure the intimate contact between sulfur and carbonaceous materials, it have the disadvantages of low sulfur loading rate. The common method to loading sulfur into carbonaceous materials need to be improve and result in high loading rate of sulfur.

4.2. Sulfurized polyacrylonitrile

In 2013, Choi et al. synthesized the C-PANS compound which was obtained through thermal treatment of PAN (produced by a process of electrospinning) and sulfur mixture (Fig. 4a and b), the PAN made up by sulfur species bonding π-conjugated ring structures covalently that exists in small molecular, and cyclization of the −CN groups in PAN polymer is used to form the bonding (Fig. 4c) [33]. Extra sulfur in the composite is uniformly dispersed and stabilized. This C-PANS (31 wt%) exhibited excellent cycling performance with the maintained capacity of $153\,mAh\,g_{sul}^{-1}$ after cycling for 500 times at 1 C (Fig. 4d). Meanwhile, the EDS mapping

of the cycled sodium negative electrode further demonstrated that sulfur element was not detected in the negative electrode of Na/S battery (Fig. 4e and f), indicating that C-PANS nanofibers can effectively suppress dissolution of sodium polysulfides. Afterwards, Ahn et al. prepared the new flexible positive electrode (not includes the conductive additive, binder and current collector) with the sulfurized polyacrylonitrile (PAN) nanofiber web, this flexible positive electrode can be bended to 180 °C without fraction [34]. Compared with the former work, the electrons move through the SPAN and the SPAN web works well in this flexible positive electrode, and can also avoid the drawbacks of the former work like physical separation of active material from the current collector. It showed an initial capacity of $604\,mAh\,g_{ele}^{-1}$ at 0.01 C, and a revisable capacity of $266\,mAh\,g_{ele}^{-1}$ after cycling for 200 times and the coulombic efficiency is nearly 100%. So it can be considered as the cheap and flexible positive electrode for the Na/S batteries.

The enhanced performance of Na/S batteries due to the using of sulfurized polyacrylonitrile positive electrode, this positive electrode could lead to chemical binding between frameworks of sulfur and carbon; moreover, it also inhibits the dissolution of polysulfides and show the better electrochemical performance.
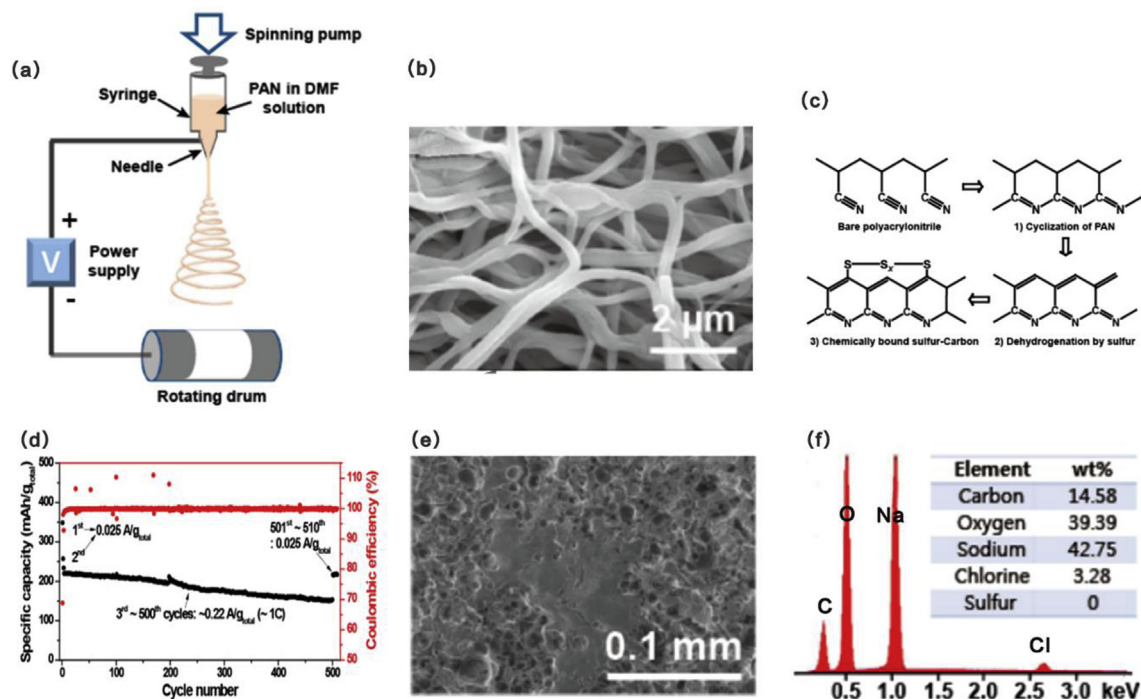
Fig. 4. (a) The PAN nanofibers produced by the process of electrospinning. (b) An image of SEM of the c-PANS NFs. (c) The diagram of structural changes during the processes of carbonization and sulfurization of c-PANS. (d) Capacity retention and Coulombic efficiencies of c-PANS NFs. In the first two cycles and final ten cycles, the sample was cycled at 0.1 C ($0.025\ A/g_{total}$), however, from the cycle 3 to 500, it was cycled at 1 C ($0.22\ A/g_{total}$). (e) An SEM image of the surface of the sodium metal counter electrode after cycling for 500 times. (f) Elemental information for the area of (e) [33].

4.3. Na$_2$S positive electrode

As demonstrated before, the possible solution could meet safety issue of the Na/S battery depends on the low temperature all-inorganic solid-state Na/S battery, as a result of the flammability of the electrolyte and the constitution of sodium dendrites can be effectively avoided.

The Na$_2$S/carbon nanotube fabric positive electrode was used in RT-Na/S batteries by Manthiram et al. [35] MWCNT fabrics is spreaded by the multi-walled carbon nanotube (MWCNT) which is wrapped by particles of Na$_2$S. This distinct positive electrode structure could help the ion and electron transporting. The cells (~55 wt % Na$_2$S in the electrode) can maintain capacities of 560 mAh g_{ele}^{-1} and 380 mAh g_{ele}^{-1}, respectively, after cycling at the rates of C/10 and C/3 for 50 times. This Na$_2$S/MWCNT positive electrode could works well with non-sodium negative electrodes, it could solve the safety issues of Na-metal negative electrodes.

Wang et al. reported a new method to produce the Na$_3$PS$_4$−⊕ Na$_2$S−C nanocomposite positive electrode, this positive electrode can be used in all-inorganic solid-state Na/S batteries to solve the problem of resistance between electrode and electrolyte interfacial [36]. The homogeneous distribution of the positive electrode materials ensure high conductivity and enough interface contact. At 50 mA g_{sul}^{-1}, this nanocomposite positive electrode transfers the high initial discharge capacity of 869.2 mAh g_{sul}^{-1}. This battery has the better cycling performance and rate performance than other all-inorganic solid-state Na/S batteries.

Most Recently, Wang et al. synthesized the composite positive electrode of Na$_2$S−Na$_3$PS$_4$-CMK-3 for LT all-inorganic solid-state Na/S battery [37], which was innovatively realized by the melting-casting and then have the process of stress release annealing-precipitation (Fig. 5a and b). As reported, the initial casting−annealing process makes the closely contact between Na$_3$PS$_4$ solid electrolyte and the CMK-3 mesoporous carbon in the conductive matrix of mixed ionic/electronic, at the same time, the solid electrolyte species in situ precipitated Na2S active in the process of annealing ensures the interfacial contact among the Na$_2$S, CMK-3, Na$_3$PS$_4$ without residential stress, which significantly improves the electrochemical performance and reduces the interfacial resistance. As a result, this Na$_2$S−Na$_3$PS$_4$-CMK-3 based positive electrode shows a stable cycling performance and the reversible capacity is 810 mAh g_{sul}^{-1} after cycling for 50 times (50 mA g_{sul}^{-1}) (Fig. 5c and d). The raw materials of Na$_2$S−Na$_3$PS$_4$-CMK-3 with the advantages of low-cost and simple preparation threw a new direction for the further development of advanced LT-Na/S batteries at industrial scale.

4.4. Polymeric sulfur positive electrode

Polymer electrodes are widely used in other rechargeable batteries [40,41], however, it less used in Na/S batteries. Owing to the sulfur in S-rich copolymer electrode have a strong chemical binding with polymer framework, it is a better way to limit the Na polysulfides in positive electrode. This method results in inhibition of dissolution of polysulfides into electrolyte. This research method is still in the early stage, the reports of it are less. Recently, Wang et al. [39] reported poly(S-pentaerythritol tetraacrylate (PETEA))-based positive electrode used in RT-Na/S battery. The Fig. 6a shows the preparation processes of copolymer electrode and quasi-solid-state Na/S Battery. This battery shows better electrochemical performance. The initial discharge capacity can reach 877 mAh g_{ele}^{-1} at the cycle rate of 0.1C (Fig. 6b). From the determination of thermos gravimetric analysis, the sulfur content in this positive electrode is 97.1 wt% (Fig. 6c). Analyse from the result of NMR and X-ray photoelectron spectroscopy (Fig. 6d and e), the strong covalent C−S bonds was formed in this poly(S-PETEA) copolymer. When the S-
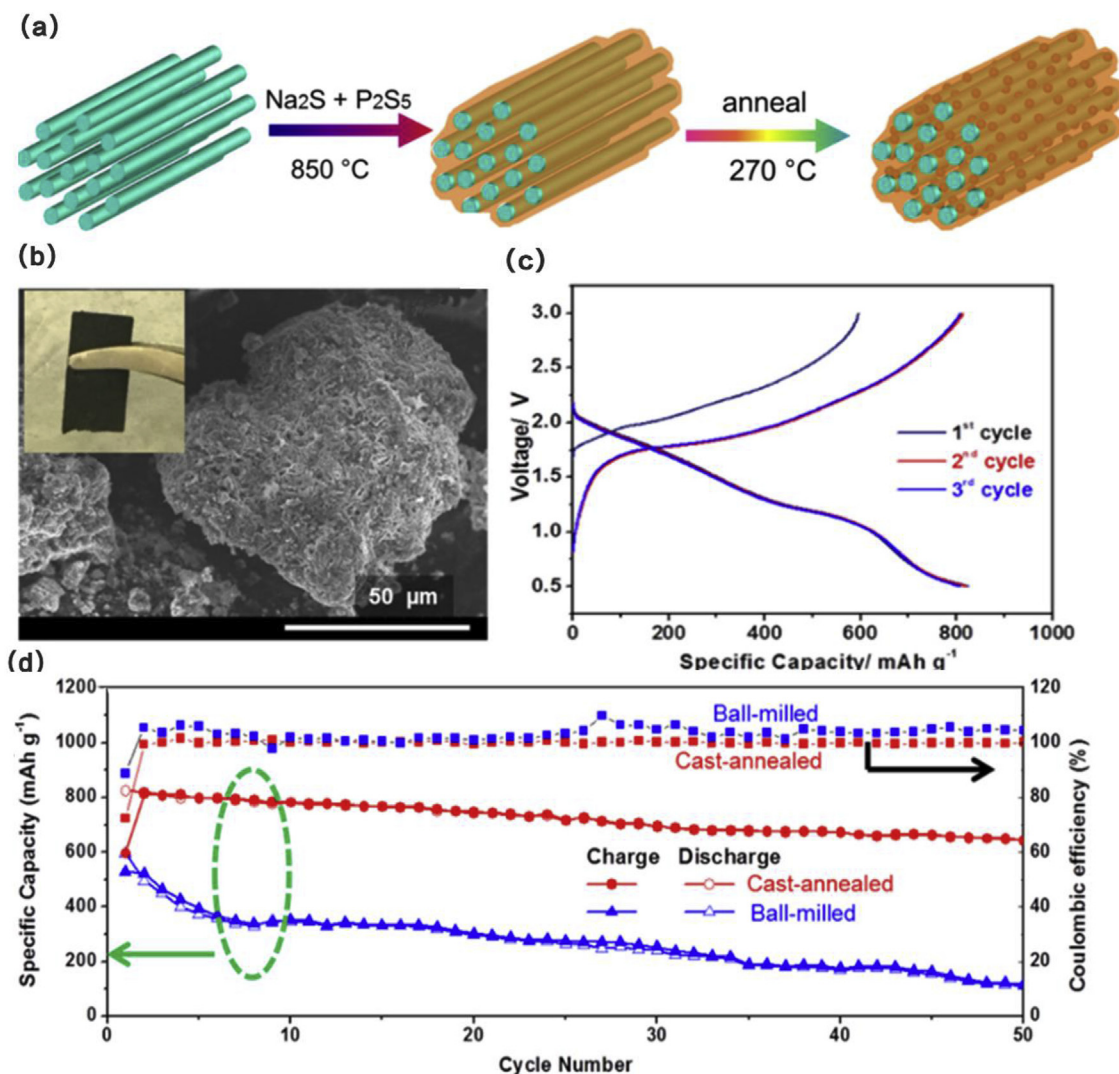
Fig. 5. (a) Schematic diagram of the production processes of Na$_2$S-NPS-C composite positive electrode which prepared by cast annealed. (b) The optical image of cast-annealed Na$_2$S-NPS-C nanocomposite which prepared in the (a). (c) The different electrochemical performances between the Na$_2$S-NPS-C composite which prepared by ball milled and Na$_2$S-NPS-C nanocomposite positive electrodes which prepared by cast annealed in ASNSB which was tested at 60 °C to be ranging around 0.5 and 3 V. When the positive electrodes cycling at 50 mA g^{-1}. First three curves of charge–discharge of Na$_2$S-NPS-C composite which prepared by ball milled. (d) Cycling properties of Na$_2$S-NPS-C composite which prepared by ball milled and Na$_2$S-NPS-C nanocomposite positive electrodes which prepared by cast annealed at 50 mA g^{-1} currently [37].

PETEA composite with mesoporous carbon host, the product obtained show the enhanced performance and further help for the inhibition of dissolution polysulfides into electrolyte, this means the polymeric sulfur fully limit by the mesoporous carbon. Analyse from the curve of cyclic voltammetry (Fig. 6f), the embedding of polymer matrix in the poly(S-PETEA) both play the role of intrinsic binder and chemically limitation of Na polysulfides. In this report, they combine the polymeric sulfur and GPE, the surface of the Na negative electrode is smooth because of the reduction of Na dendrite. The sulfur content on the Na negative electrode is low because of the inhibition of shuttle effect (Fig. 6g). Owing to the safety issues, the solid state Na/S batteries is popular in the recent years. This battery solves the problem of poor cycle performance. In the future, the Na/S battery which using this type of positive electrode will focus on improve the initial discharge capacity. In the future, the polymer positive electrode will be better used in the high-Performance all-plastic full battery. Zhang et al. give us a good example of how to use the polymer electrode in all-plastic full battery [42].

4.5. Sulfur-equivalent positive electrode materials

The sulfur-equivalent materials represent the sulfur-containing compounds that not include the elemental sulfur but have a comparable electrochemical performance and without the generation of polysulfides. The Na/S battery system based on this positive electrode solves the problem of polysulfide dissolve in the organic electrolyte. The idea of amorphous MoS$_3$ used as the positive electrode in RT-Na/S is attempted by Lu et al. (Fig. 7a) [38]. Because amorphous chain-like MoS$_3$ has high sulfur content and its one dimensional chain can promote the fast diffusion of Na$^+$ ions and has more open sites toward their active storage. The authors utilized 1 M NaClO$_4$ in EC/DEC with 8 vol % FEC as the electrolyte. The initial discharge capacity is 460 mAh g$_{MoS3}^{-1}$ at 23 mA g^{-1} and followed by the 428 mAh g$_{MoS3}^{-1}$ (Fig. 7b). Even when cycled at 0.45 A g^{-1}, the discharge capacity can retain at 180 mAh g$_{MoS3}^{-1}$ after cycling for 1,000 times, and its Coulombic efficiency still keep at ~100% (Fig. 7c). These results are superior to that of other reports about Na/S battery. Fourier-transformed EXAFS of MoS$_3$ further
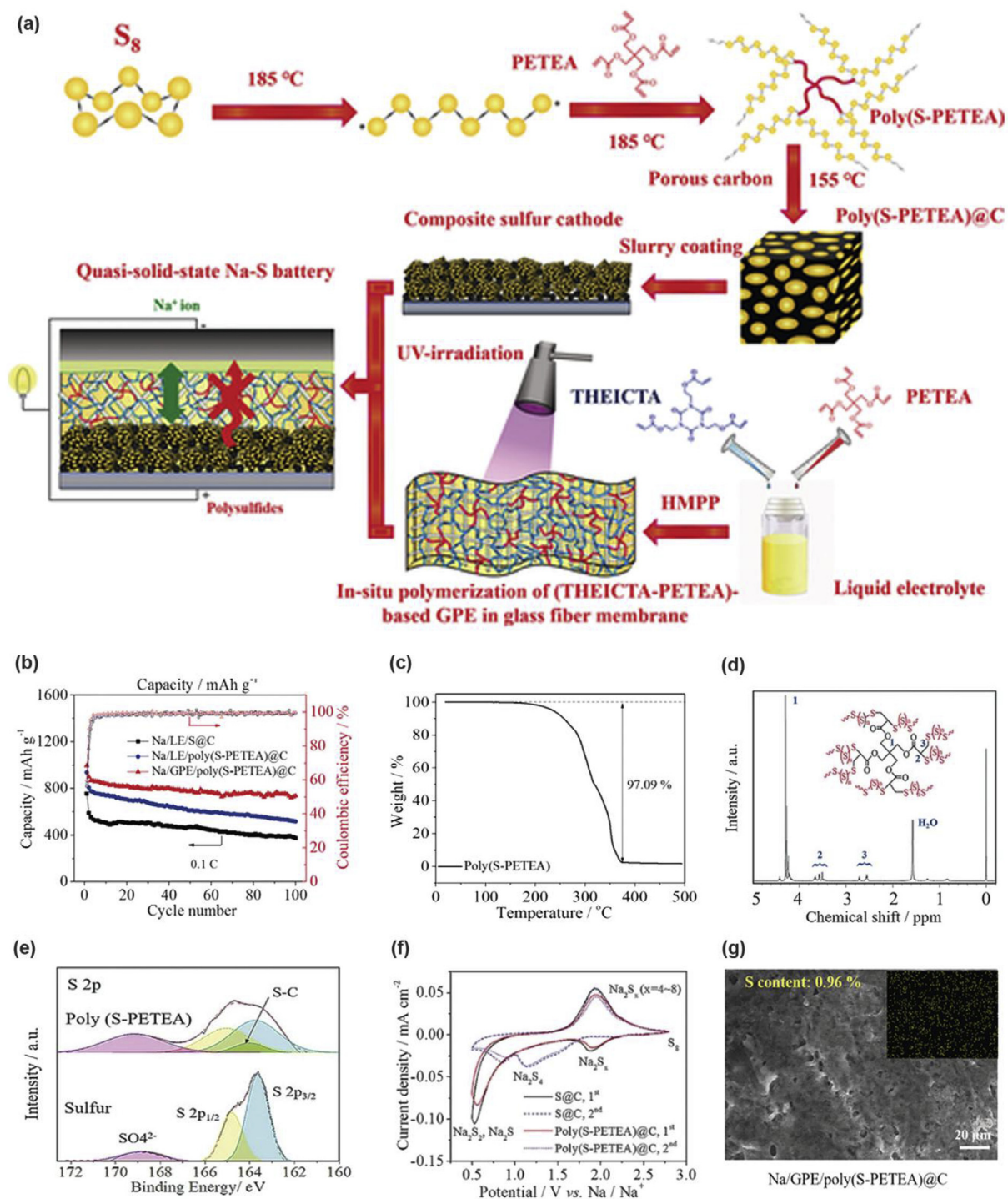
Fig. 6. (a) The preparation processes of quasi-solid-state Na/S battery. (b) The capacity and coulombic efficiency of the positive electrode and battery when cycling at 0.1C. (c) TGA curve of poly(S-PETEA). (d) The curve of NMR of poly(S-PETEA). (e) The curve of XPS of sulfur and poly(S-PETEA). (f) The curve of CV of Na/S battery. (g) The Na/S battery cycle at 0.1C for 100 times [37].

confirmed that the sodiation and desodiation of MoS_3 did not cause distinct Mo—S bond breaking or Mo—Mo bond formation (Fig. 7d). There was no Li_2S or metallic Mo, Na_2S, or polysulfide detected as the reaction intermediate or final product. And the S K-edge XANES spectrum further demonstrated that the reduction of sulfur was probably due to stronger interaction between Na and S (Fig. 7e and f). This work innovatively solved the problem of polysulfide dissolve in RT-Na/S battery.

Owing to the safety issues and shutte effect, researchers start to give up using element sulfur as positive electrode, the great potential sulfur-equivalent materials are aroused the interest of researchers. The first advantage of sulfur-equivalent materials is eliminating the security risks of sulfur; moreover, the second advantage is working well with carbonate electrolyte at 55 °C.

From these articles, although the method of sulphide mixture is easy and effective, owing to the mechanical mixing of sulfur and
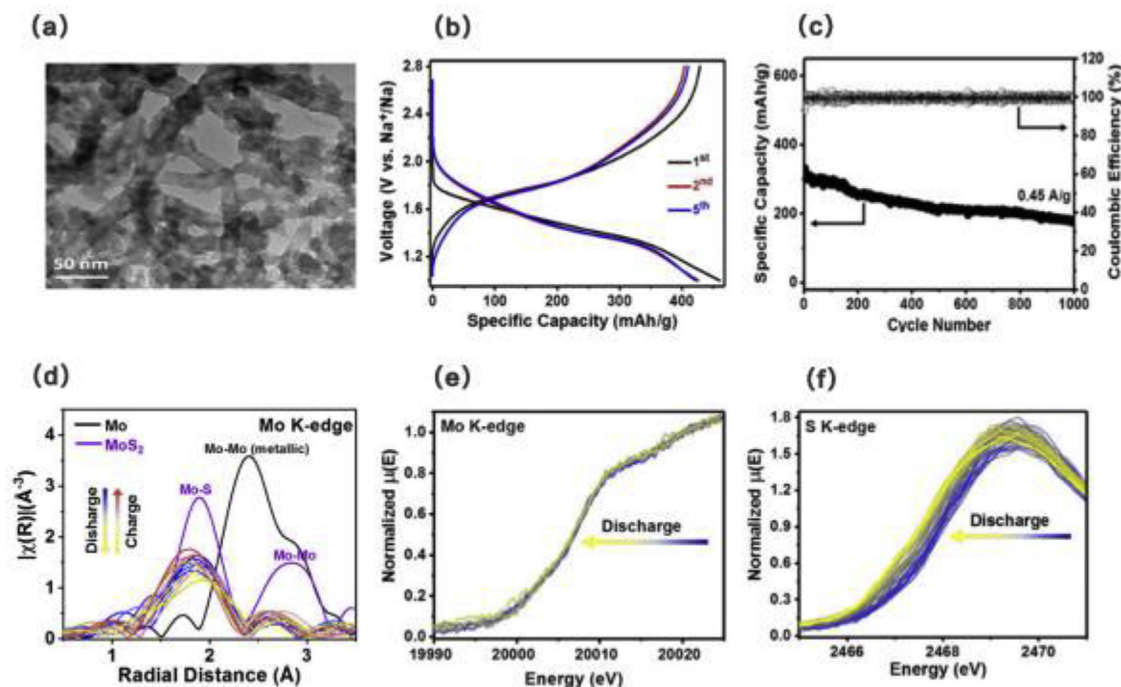
Fig. 7. (a) TEM image of MoS₃. (b) The curves of galvanostatic charge and discharge at 23 mA/g. (c) Cycling stability of a high-loading electrode (6.9 mg cm⁻²) at 0.1 mA/cm² for the first several cycles and then at 0.5 mA/cm². (d) Comparing Fourier-transformed Mo K-edge EXAFS spectrum among MoS3, MoS2 and metallic Mo during lithiation and delithiation. (e) Evolution of Mo K-edge XANES spectrum during lithiation. (f) Evolution of S K-edge XANES spectrum during lithiation [30].

conductive additives lead to poor contact, the normal sulphide mixture positive electrode has the disadvantage of poor electrochemical performance. The mechanical mixing also leads to low capacity. The capacity reduce rapid during the cycles. Owing to the using of sodium sulfide and sodium polysulfide could instead of sulfur, it could lead to the using of sodium-free negative electrode. The safety of sodium-sulfur batteries can be improved. In the future, the $Na_2S/AC-C$-based nanocomposites are widespread concern. The reports about $Na_2S/AC-CNF$ nanocomposite positive electrode and $Na_3PS_4-Na_2S-C$ nanocomposite positive electrode are good examples to relieve the shuttle effect and increase the utilization of active sulfur substances. The sulfur-carbonaceous composite positive electrodes are the widely used positive electrodes in sodium-sulfur batteries. The different carbonaceous matrices have different advantages. The macropores can make sure the excellent contact between electrolytes and active materials. The micropores are easily fixed with active materials. The graphene and carbon nanofibers have the distinct carbon structure. They all can show the excellent conductivity and electrochemical performance. In the future, the researches might mainly focus on flexible positive electrodes. The carbon nanofibers and polyacrylonitrile are good raw materials to synthesize flexible positive electrodes. The report about $S_{1-x}Se_x$ @ carbon nanofibers is the good example to make flexible positive electrode, this positive electrode also could inhibition of polysulfide shuttle effect.

5. Electrolytes

The mainly purpose of using electrolytes are inhibiting the shuttle effect and extrusion of sodium polysulfides. The widely used electrolytes in Na/S batteries are solid-state electrolyte, ether-based electrolyte, carbonate-based electrolyte and ionic-liquid-based electrolyte. Each type of the electrolyte has their own advantages and disadvantages. The mainly advantage of solid-state or

polymer electrolyte is safe. The ether-based electrolytes are used to improve the ion transport between electrodes and electrolytes. Carbonate-based electrolyte and ionic-liquid-based electrolyte are in the early stage of research; however, the better performance is over than solid-state electrolyte and ether-based electrolyte.

5.1. Polymer/solid-state electrolyte

At early stages, owing to the safety performance of solid-state electrolyte, the researchers develop many solid-state electrolytes. However, this type of electrolyte shows low capacity and poor cycle performance because of the immense interfacial resistance between electrode and electrolyte [51]. For example, the Na/S battery which uses the poly (ethylene oxide) (PEO) polymer electrolyte, after ten cycles, the discharge capacity reduce seriously (from 505 mAh g_{sul}^{-1} to 166 mAh g_{sul}^{-1}) [52]. The SiO_2-poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) served as the gel polymer electrolyte, the discharge capacity also reduce greatly (from 165 mAh g_{sul}^{-1} to 21 mAh g_{sul}^{-1}) [43]. The first liquid electrolyte solution is 1 M NaTf in a 1:1 EC and PC, then mix the EC and PC with f. The conductivity of this gel polymer could reach the highest value of 4.1×10^{-3} S■cm⁻¹. The electrochemical potential window could be 4 V. This working voltage range is enough for the electrolyte for sodium batteries. The result of TGA shows no weight loss of gel electrolyte of EC:PC-NaTf-(PVdF-HFP) in the temperature range from room temperature to 420 °C, this means the good thermal stability.

In the most recent three years, many new solid and polymer electrolytes are developed which could improve these problems. Wang et al. [36] demonstrated that nanocomposites $Na_3PS_4-Na_2S-C$ can be both used as the positive electrode and electrolyte of all-inorganic solid-state Na/S batteries (ASSBs). As for details, the highly ionic conductive Na_3PS_4 can work as either solid electrolyte or active material (catholyte) once mixed with electronic

conductive carbon, resulting in an intrinsic superior interfacial contact between electrode and electrolyte. The effectively improvement of the capacity due to the nanocomposite positive electrode which contained nanosized Na_2S. The nanocomposite positive electrode includes nanosized Na_2S, Na_3PS_4, and carbon which are homogeneous distribution in it and it ensures a high mixed (ionic and electronic) conductivity and an interfacial contact sufficiently. This report also showed at the environment of room temperature, the activation energy of Na_3PS_4 is 0.45 eV and the ionic conductivities is 1.09×10^{-4} S∎cm^{-1}. The evenly mixed of sulfur active materials, solid electrolyte and carbon could lead to better electrochemical performance. The high initial discharge of this positive electrode and electrolyte can reach 869.2 mAh g$_{sul}^{-1}$ at 60 °C (50 mA g$_{sul}^{-1}$) (Fig. 8a and b). The practical applications of the all-inorganic solid state Na/S batteries which have the advantages of safe and high-energy will be promoted by the proposed electrode design.

A new mixed electrolyte was developed by Ahn et al. [44] This mixed electrolyte was made up of β-alumina solid electrolyte and tetraethylene glycol dimethyl ether (TEGDME) electrolyte. The liquid electrolyte is 1 M $NaCF_3SO_3$ in TEGDME. The β-alumina solid electrolyte was chosen as a separator owing to it is easy to be commercialized and showed the stability with TEGDME electrolyte, shuttle effect and the extrusion of sodium polysulfides can be prevented by using an optimized amount of TEGDME electrolyte. The widely voltage range is between 1 and 3 V. this electrolyte could prevent the moving of sodium polysulfide. More than cycling for 104 times, owing to the leakage of the TEGDME, there is no loss of the sodium polysulfide. The initial discharge capacity of this Na/S battery is 855 mAh g$_{ele}^{-1}$ (1/64C) at room temperature. It also can show a discharge capacity of 521 mAh g$_{ele}^{-1}$ at the 104th discharge. However, the problems of low conductivity and high thickness of this solid electrolyte still need to be further considered.

Deepak Kumar reported the ionic liquid based gel electrolyte [45]. The ionic liquid based gel film is incorporation with EC/PC. The electrolyte is also the EC:PC-NaTf-(PVdF-HFP). He utilized the Hg−Na as negative electrode, sulfur composite materials as positive electrode. In the report, we could find out the ionic conductivity of this electrolyte is 8.4×10^{-3} S∎cm^{-1}. We use the formula of $t_{Na^+} = \frac{I_0}{I_s}\left(\frac{\Delta V - I_0 R_0}{\Delta V - I_s R_s}\right)$ to calculate the sodium-ions transport number,
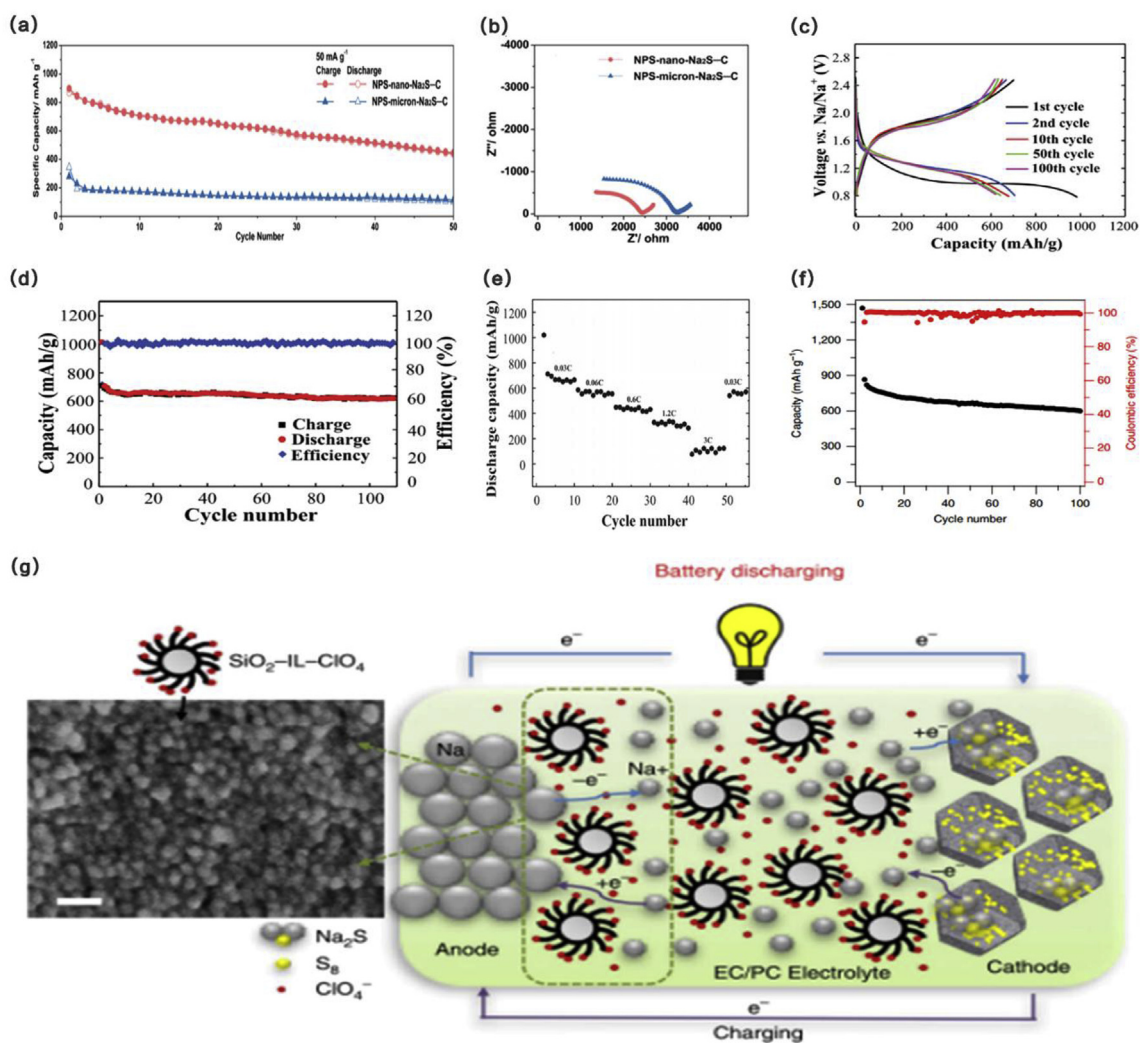

Fig. 8. (a) Cycling performance of composite of NPS-micron-Na_2S−C and nanocomposite positive electrodes of NPS-nano-Na_2S−C at a current of 50 mA g^{-1}. (b) Impedance profiles the ASSBs using composite of NPS-micron-Na_2S−C and nanocomposite positive electrodes of NPS-nano-Na_2S−C [28]. (c) Discharge/charge voltage profiles of the HSMC-Cu-S composite positive electrode in RT-Na/S battery during the 1st, 2nd, 10th, 50th and 100th cycle. (d) Cycling performance and Coulombic efficiency of the composite positive electrode of HSMC-Cu-S in RT-Na/S battery. (e) Rate performance of the composite positive electrode of HSMC-Cu−S composite positive electrode at different rate between 0.03 and 3 C [37]. (f) The ratio among Capacity, Coulombic efficiency and cycle numbers. (g) Schematic diagram of the Na/S battery during galvanostatic cycling [39].

the value of gel polymer electrolyte film is 0.19. The report also showed the electrochemical stability window of gel electrolyte is between −2.3 V and 2.3 V. The result shows the initial discharge capacity of Na/S battery which using this electrolyte is 267 mAh g_{sul}^{-1}. This gel polymer which including NaTf/EMITf/EC-PC can endure temperature less than 90 °C. It can be the better transmitter for Na$^+$ ion, because cathodic deposition and anodic oxidation of sodium are facile at Na/gel electrolyte interface. Owing to these advantages of gel polymer electrolyte, it can be the better substitution of liquid electrolyte [45].

Wang et al. reported a new electrolyte which is (PETEA-tris[2-(acryloyloxy)ethyl] isocyanurate (THEICTA))-based gel polymer electrolyte. This electrolyte solve the problem of poor cycling performance which exist in other Na/S batteries which using polymer and solid state electrolytes. The electrolyte reported in this paper have the advantages of high ionic conductivity, safety and stability. It could not only stable the interface between Na electrode and electrolyte, but also limit the Na polysulfides. Ionic conductivity is the important aspect to evaluate the performance of polymer electrolyte, the ionic conductivity of this electrolyte could reach 3.85×10^{-3} S cm^{-1} at 25 °C. This electrolyte shows better performance also because of the high Na ion transference number, it could reach 0.34. This battery could stable for 300 h when cycle at the current density of 0.1 mA cm^{-2}, it means that uniform Na deposition have the stable interface of Na/GPE.

Kandagal et al. forecasted a new solid electrolyte Na$_{10}$GeP$_2$S$_{12}$ from the perspective of theoretical prediction [46]. They determine the decomposition reaction energies and phonons, then they established a thermodynamically stable structure of Na$_{10}$GeP$_2$S$_{12}$.4.7 mS cm^{-1} is the estimated conductivity of this electrolyte at room temperature, this value is higher than other solid electrolytes like β-alumina and Na$_3$Zr$_2$Si$_2$PO$_{12}$ [36,45]. It also identified that the reason for its thermodynamic stability and the lower activation barrier for the diffusion of Na-ions is soft Na/S phonon modes. Besides, the calculated electronic bandgap of this structure is around 2.7 eV, which guarantees a wide electrochemical window for the safety operation of Na/S battery. This work lay a solid foundation for the experimental research on the Na$_{10}$GeP$_2$S$_{12}$ electrolyte and discuss about the reason of this electrolyte advantageous over other electrolytes which used commonly in many different aspects, for example, cost, easy to prepare, mechanical stability and safety.

Although this type electrolyte shows the advantage of safety, the problems of low capacity and poor cycle performance need to be solved in the future. The new electrolyte Na$_{10}$GeP$_2$S$_{12}$ which reported in this review give the research direction for the further research. The high ions conductivity and wide electrochemical window are the goals for solid electrolyte to achieve in the future.

5.2. Ether-based electrolyte

For the result of excellent ion transport between the electrodes and a liquid electrolyte is necessary. Ether-based electrolyte like the EC/DMC, PC and TEGDME is one of this type electrolyte used in Na/S battery [19,53]. Since they are excellent solvents for sodium polysulfides that form in RT-Na/S battery during cycling, it always leads to the "polysulfide shuttle", which means polysulfides that inevitably dissolve out of the positive electrode rather than effectively confinement, shuttle to the negative electrode and involve in the redox reaction on the negative electrode. This phenomenon directly causes the loss of active materials, the corrosion of sodium negative electrode and restricting the cycling performance. For example, Ahn et al. pointed out the Na/S battery which using the TEGDME as liquid electrolyte [47]. Although the conductivity of the electrolyte is enhanced compared with the polymer electrolyte, the

discharge capacity seriously reduces from 538 mAh g_{sul}^{-1} to 240 mAh g_{sul}^{-1} after 10 cycles. To overcome the shuttle effect of polysulfide in the ether-based electrolyte, Pint et al. synthesized the microporous carbon host, in which sulfur molecules stored in are limited to the sizes S$_{2-4}$, successfully avoiding the situation of ether-based electrolyte form high-order polysulfide during cycling [30]. The electrolyte of this Na/S battery is NaPF$_6$ in tetraglyme. This strategy improves the sulfur utilization and avoiding the dissolution of polysulfide in electrolyte. So the cycling stability being improved to some extent but the rapid capacity decay still existed in the first several cycles. For instance, when the battery cycle at 0.1 C, a rapid reduction of capacity retention in the first 20 cycles, the reduction rate is 60%, the capacity reduces at the speed of 0.1% per cycle stably in the following cycles. The voltage window of this electrolyte is between 0.5 and 2.7 V. This voltage range is widely for Na/S batteries. Hassoum et al. first time used the trifluoromethanesulfonate (NaCF$_3$SO$_3$) in triethylene glycol dimethyl ether (TREGDME) as the electrolyte for Na/S battery [75]. The result showed this electrolyte could work well with the cathode which combining multiwalled carbon nanotubes and sulfur. The initial capacity was around 500 mAh g_{sul}^{-1} and nearly 100% coulombic efficiency could be maintained after 10 cycles, the average voltage was 1.7 V. Therefore, the expected practical energy was 140 Wh kg^{-1}. They also used $t^+ = \frac{Iss(\Delta V - I_0 R_0)}{I_0(\Delta V - IssRss)}$ to calculate the sodium transference. The result showed the t$^+$ of this battery was 0.72, indicating the small resistance and fast electrochemical process at the electrode and electrolyte interlayer. The ionic conductivity of sulfur was 3×10^{-3} S cm^{-1} at room temperature. This value showed the TREGDME- NaCF$_3$SO$_3$ solution is suitable as the adequate electrolyte for low-resistance Na/S batteries. In the future, the research will continue focus on preventing the polysulfide shuttle, the microporous carbon is the better example to improve this problem, the composite materials of microporous and sulfur work well with ether-based electrolyte; however, the new problem of rapid capacity decay in the first several cycles need to be solved in the future.

5.3. Carbonate-based electrolyte

The advantages of the carbonate-based electrolyte are wide electrochemical stability and high ionic conductivity [54,55]. Meanwhile, it also contributes the formation of a stable SEI on the negative electrode, which can alleviate the negative electrode corrosion due to the polysulfide shuttle effect. But this type of solvents is sensitive through nucleophilic attack which using the way of reduction of solubility polysulfides [56–58], which means reduced-solubility polysulfides have a reaction with the carbonate-based electrolyte irreversible in RT-Na/S batteries, this phenomenon always causes rapid capacity degradation.

The commonly used carbon-based electrolytes in RT-Na/S battery are NaClO$_4$ in EC/DMC and NaClO$_4$ in EC/PC [49,55,59,60]. For example, Zheng et al. used the NaClO$_4$ in PC/EC and FEC as electrolyte, sulfur loaded mesoporous carbon as positive electrode. Owing to the preparation problems during the sulfur loading in HSMC-Cu composite material, the HSMC-Cu−S composite material shows the BET specific surface area is 100 m^2 g^{-1} and the pore volume is about 0.1 cm^3 g^{-1} [48]. This defect limits the reaction area for the redox conversion. However, this electrolyte works well with the HSMC-Cu−S positive electrode, which can relieve this problem to a certain extent. The HSMC-Cu−S positive electrode in Na/S batteries only show one charging and discharging plateau at nearly 0.8 V, when the happening of reaction: S$_8$ + Na → Na$_2$S$_n$ (n > 4). When the loading rate of sulfur is 50 wt %, the initial capacity of this battery is around 1000 mAh g_{ele}^{-1}, the capacity is maintained at

610 mAh g_{ele}^{-1} after cycling for 110 times at 0.03C (Fig. 8c, d and e). Wang et al. demonstrated that sulfur accommodated in the PAN-based positive electrode materials can perfectly match with the NaClO$_4$ in EC/DMC electrolyte [49]. This electrolyte helps the sulfur accommodated in the composite positive electrode showing the excellent electrochemical reversibility. This carbonate-based electrolyte also solves the problem of sodium dendrite. The Na/S battery which using this PAN-based positive electrode containing 45 wt % sulfur. The specific capacity of this battery is 655 mAh g_{sul}^{-1} in the first cycle. It also can achieve 500 mAh g_{sul}^{-1} after 18 cycles. From the first cycle to 18th cycle, we cannot find obvious voltage plateau during the processes of charge and discharge, the average voltage of charge and discharge are 1.8 V and 1.4 V.

However, it needs to mention that profiles of charge/discharge of the batteries with the carbonate based electrolyte show great difference with that of ether-based electrolytes. These carbonate-based electrolytes exhibit continuously decreasing profiles in the discharging process, and majority capacity is achieved below 1.5 V, to be compared with ether-based electrolyte, it is better to suggest a different reaction mechanism.

The commonly method of using carbonate-based electrolyte in RT-Na/S is learn from the successfully applications in Li/S batteries. The research of carbonate-based electrolyte is at the early stage. The problem meet by researchers is clear, which are formation of polysulfide and rapid capacity attenuation.

5.4. Ionic-liquid-based electrolyte

The advantages of ionic liquid are excellent thermal stability, low volatility, non-flammability, excellent cycle performance, durability and wide electrochemical potential window [61–63]. But the discharge capacity and rate capability of ionic-liquid batteries are not as good as the organic electrolyte batteries. Owing to these reasons, some researchers think the ionic-liquid-based electrolyte is not beneficial to use at room temperature [64,65]. The researchers obtain a big success when they use the ionic liquid electrolyte for LIBs. This electrolyte shows stable thermal at 242 °C. The batteries show the excellent cycle performance and improvement rate capacity. Electrolyte which based on propylpiperidinium have better conductivity and effective in inhibition battery short circuit [66]. The lifetime of these batteries could improve 10000-fold than before. Only 11 w % of SiO$_2$-PP-TFSI in a PC-LiTFSI host lead to ten-fold increase of battery lifetime [67].

Nowadays, the combination of ionic-liquid electrolyte and liquid carbonate electrolyte is also the research hotspot to achieve stable electrodeposition and prevent dendrite formation on the negative electrode. Wei et al. reported the new liquid carbonate electrolyte including the ionic liquid 1-methyl-3-propylimidazolium-chlorate tethered to SiO$_2$ nanoparticles. From the analysis of spectroscopic, they find out the nanoparticles constitute a sodium-ion conductive film on the negative electrode, the conductive film could help to stable deposition of the sodium [50]. SiO$_2$–IL–ClO$_4$ particles serves as the important role to ensure stability during the charge and discharge. They do the electrochemical test to compare the electrolyte containing SiO$_2$–IL–ClO$_4$ particles with the electrolyte which was not containing. The result shows when the voltage reach 4 V, the electrolyte displays a better performance. When the voltage increases to 4.5 V, the electrolyte which containing SiO$_2$–IL–ClO$_4$ particles still stable. The SiO$_2$–IL–ClO$_4$ particles mainly play two important roles, the first one is the ionic liquid forms a SEI layer stably on the surface of the sodium mental, it leads to the limit contact with electrolyte and prevents the occurrence of electrochemical side reactions. Second, the SiO$_2$ particles serve as the anchor points for ClO$_4^-$ anions, it also serves as the supporting electrolyte to reduce electric field. As shown in Fig. 8g, on the side

of negative electrode, during the processes of discharge, the sodium atoms loss electrons and become into sodium ions. On the side of positive electrode, the sodium ions which diffusion from negative electrode reaction with sulfur and become into Na$_2$S. During the processes of charging, the reserve reactions happened on both sides of negative electrode and positive electrode. The result showed this battery can stable cycling at the rate of 0.5 C. They can reach the reversible capacity of 600 mAh g_{sul}^{-1} and 100% coulombic efficiency after cycling for 100 times (Fig. 8f). In the future, owing to the excellent electrochemical performance of mixture electrolyte of carbonate-based electrolyte and ionic-liquid-based electrolyte, and it is at the early development stage. In 2019, a new carbonate free ionic-liquid-based electrolyte is reported by Kumar and Kanchan. This report for the first time pointed out that the poly(vinylidinefluoride-co-hexafluoropropyline) (PVdF-HFP) in 1-ethyl 3-methyl imidazolium trifluoromethanesulfonate (EMITf) could serve as the electrolyte for Na/S battery [76]. The electrochemical working window could be increased to 4.8 V and the electrical conductivity offered by this electrolyte was 5.7×10^{-3} S cm^{-1}. This result was better than other solid polymer electrolytes [77,78]. Based on this electrolyte, the initial capacity of the battery was around 240 mAh g_{sul}^{-1}. Although the discharge capacity does not all depend on electrolytes, stable electrolytes could provide a safe environment for Na/S batteries. The research in the future will focus on this type of electrolyte and improve the discharge capacity and rate capacibility.

From these articles, we can know the electrolyte is important part to meet the problem of polysulfide migration in sodium-sulfur batteries. The polysulfide can easily dissolve in TEGDME-based electrolytes, but it cannot dissolve in EC/PC-based electrolytes. The solid and polymer electrolytes show the excellent performance of safety. However, it still needs to be improving in the performance of low capacity and poor cycling. In the future, the researches may focus on solving these problems to improve the capacity and cycle performance. The report about the mixture electrolyte of beta-alumina and TEGDME is a good attempt. Although the ether-based electrolytes have the advantages of excellent electrochemical performance, non-flammable and high stability, the ether-based electrolytes show low capacity and high speed of polysulfide dissolving in it. When using the carbonate-based electrolytes, the carbonates might have the reaction with polysulfide, it could lead to higher capacity and long cycle life, and the carbonate-based electrolytes also have the advantages of electrochemical stability and high ionic conductivity. The reports about the ionic-liquid-based electrolytes are less. However, the ionic-liquid-based electrolytes show the advantages of excellent thermal stability, low volatility, non-flammability and excellent cycle performance. In the future, the discharge capacity and rate capability can improve by mix the carbonate electrolytes and ionic-liquid-based electrolytes. The report about the new liquid carbonate electrolyte including the ionic liquid 1-methyl-3-propylimidazolium-chlorate tethered to SiO2 nanoparticles is the good example to make the mixture electrolytes.

6. Separator

The main actions of separator are either ensuring the guidance of sodium-ions or inhibition the shuttle of polysulfide, preventing the polysulfide migrating to negative electrode and producing the inactive substances at the surface of negative electrode, which have the effect on the cycling performance of the batteries. At the start, the β-alumina serves as both electrolyte and separator in Na/S battery. But the β-alumina cannot prevent the shuttle of polysulfide. Nowadays, the most widely used separators are polypropylene and glass fiber separators [17,47,68]. However, either the

polypropylene separator or glass fiber separator cannot meet the requirements of favouring the sodium-ion transfer and inhibiting the polysulfide shuttle together. For the purpose of improvement in specific capacity and cycling stability, many workers from the perspective of surface modification, make the functionalized membranes.

For example, In the 2014, Kaskel et al. first reported the RT-Na/S battery which used the sodiated Nafion-coated polypropylene membrane [69]. A porous polypropylene membrane coated by the

sodiated Nafion lead to either combined sufficient sodium ion conductivity or reduced polysulfide permeation. So compared with the uncoated separator, after cycling for 20 times, the capacity of discharge increases from 200 mAh g_{sul}^{-1} (polypropylene separator) to 350 mAh g_{sul}^{-1} (sodiated Nafion-coated separator) with the growth rate of 75%.

Afterwards, Manthiram et al. compared the Celgard separator and sodiated-Nafion membrane separator for RT-Na/S battery (Fig. 9a) [70]. When the dimensions of pore in the micrometer scale,
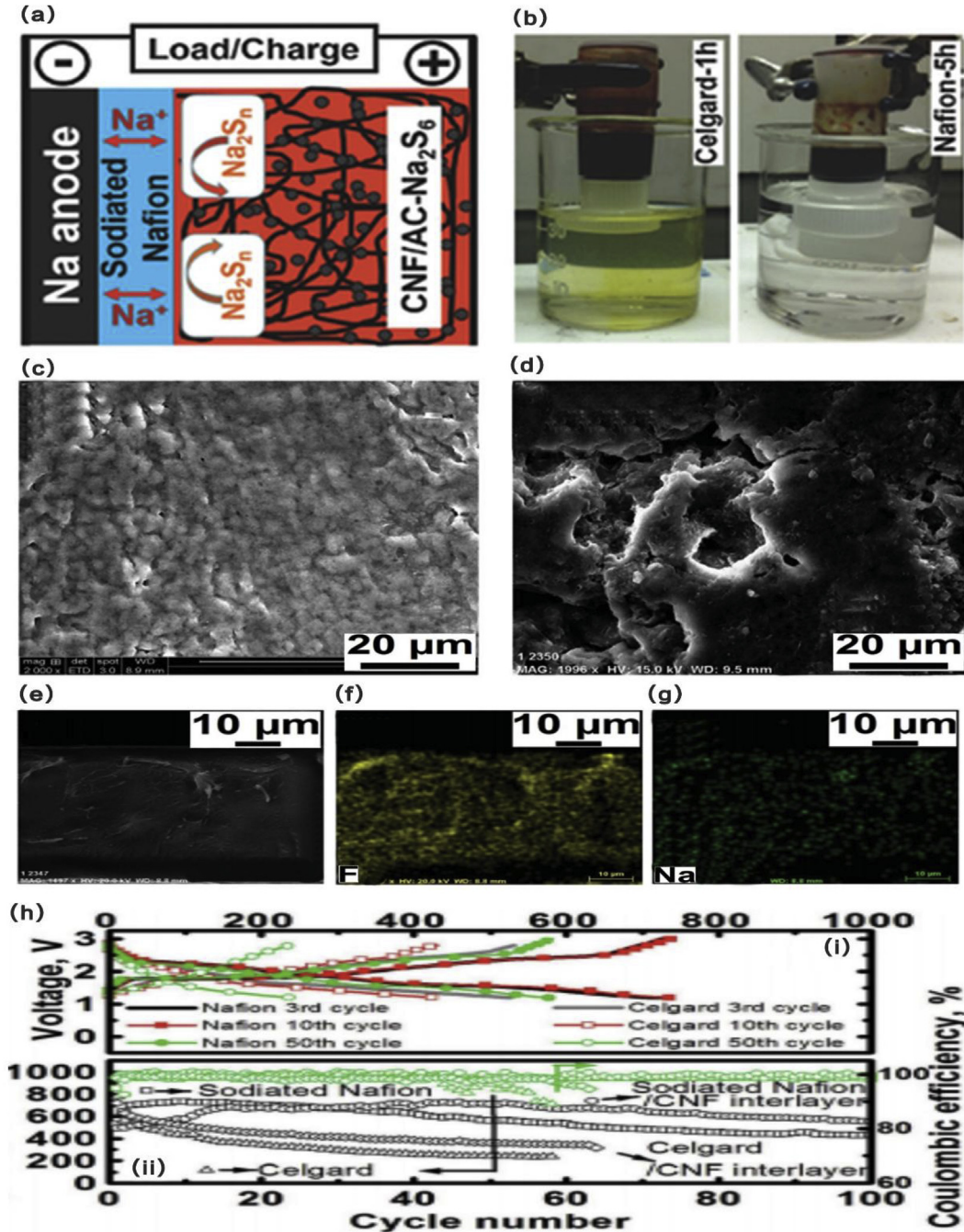

Fig. 9. (a) Schematic of a RT-Na/S battery which using the separator of sodiated Nafion membrane. (b) Polysulfide diffusion test of the Celgard separator after 1 h and Polysulfide diffusion test of the sodiated Nafion membrane after 5 h. (c) SEM image of the negative electrode of pristine sodium. (d) SEM image of the sodium negative electrode after 100 cycles in the sodium polysulfide cell which using the separator of Sodiated Nafion. (e) SEM cross-sectional image of a sodiated Nafion membrane after cycling for 100 times in the sodium polysulfide cell which using the separator of Sodiated Nafion. (f) EDS Element mapping of the Nafion membrane which is cycled along the cross-section in the area of (e). (g) EDS elemental (sodium) mapping of the cycled Nafion membrane along the cross-section, the area is shown in (e). (h_i) When cycle at the rate of C/5, profiles of Charge/discharge of the cells which using the different separators of Sodiated Nafion and Celgard at different cycles. (h_{ii}) Discharge capacities and Coulombic efficiencies changed by different cycle numbers in the different cells which using different separators of Sodiated Nafion, CNF-interlayered Sodiated Nafion, Celgard and CNF-interlayered Celgard at the rate of C/5 [70].

the separators of porous Celgard are easily permits the dissolved polysulfide species migrate from the positive electrode to the sodium metal negative electrode and results in the shuttle effect. As shown in Fig. 9b, after almost half an hour of rest, the colour of the TEGDME solvent changed from colourless to light yellow. On the other hand, the sodiated Nafion membrane effectively blocked the diffusion of polysulfide species. Despite 5 h of rest, the colour of TEGDME solvent noticed to remain unchanged. In addition, analyse

the SEM/EDX image of the Nafion membrane which is being cycled, we can see the distribution of the sodium ions (Na$^+$) across the cross section of the membrane does not demonstrate a clear change after cycling (Fig. 9c–g) compared with the newly sodiated sample, confirming the well-kept Na$^+$ conductive environment in the Nafion membrane. Based on this condition, the discharge capacity of the Na/S battery increase from 500 mAh g$_{sul}^{-1}$ (Celgard separator) to 750 mAh g$_{sul}^{-1}$ (sodiated-Nafion membrane) (Fig. 9h). They also
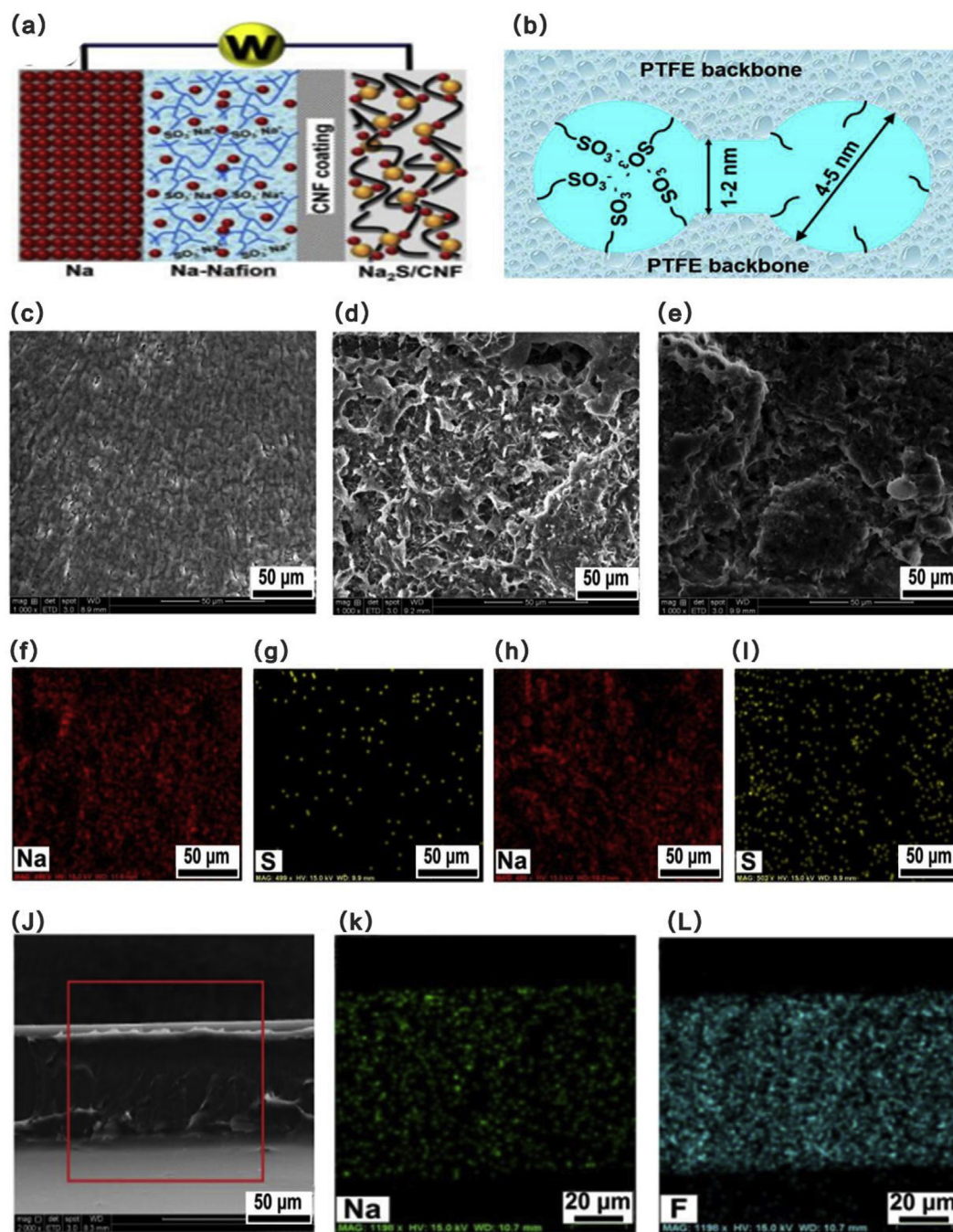

Fig. 10. (a) Schematic of a cell which using the separator of Na-Nafion/AC−CNF coating. (b) Architecture of Nafion membrane. (c) SEM image of an negative electrode of pristine Na. (d) SEM image of Na negative electrode which was cycled for 100 times in the sodium cell which using the separator of Na-Nafion/AC−CNF coating. (e) SEM image of an negative electrode of Na which was cycled after 50 times in the sodium cell which include the separator of Celgard/AC−CNF coating. (f) Sodium and (g) sulfur EDS element mappings of the Na negative electrode which was cycles after 100 times in the sodium cell which using the separator of Na-Nafion/AC−CNF coating. (h) Sodium and (I) sulfur EDS element mappings of the Na negative electrode which was cycled after 50 times in the sodium cell which using the separator of Celgard/AC−CNF coating. (j) SEM cross-section image of the Nafion membrane after cycle for 100 times from the sodium cell which using the separator of Na-Nafion/AC−CNF coating. (k) Sodium and (L) fluorine EDS element mappings of the Nafion membrane which is being cycled in the area of (j) [71].

further showed the sodiated-Nafion membrane can work well with the positive electrodes of carbon nanofiber fabrics and active carbon. The conductivity of ions of the sodiated Nafion membrane is $2.7 \times 10^{-5} \, \text{S cm}^{-1}$, after cycling for 100 times, the reversible capacity is maintained at 550 mAh g_{ele}^{-1}.

Then Manthiram et al. further utilized the Sodium-Nafion membrane which coated by carbon as the separator (Fig. 10a) [71]. The report showed the conductivity of sodium ion in the sodium-Nafion membrane to be ranging around $2 \times 10^{-5} \, \text{S cm}^{-1}$ and $3 \times 10^{-5} \, \text{S cm}^{-1}$. The author deeply explained that the Nafion membrane includes a hydrophobic region which composed of a poly-(tetrafluoroethylene) backbone, a hydrophilic ion-cluster regions (the size is about 40—50 Å, as shown in Fig. 10b) and the $-SO_3-$ serves as fixed-charge sites and transferable cations (e.g., Na^+ in the Na-Nafion) and plays the role of counter-ions. Connecting these hydrophilic clusters are the hydrophilic channels of 10—20 Å diameters, so it provides Na^+-ion conductive path, but prevents the passage of the polysulfides to the negative electrode. The Na-Nafion which coated by carbon used as an upper-current-collector, due to its excellent conductivity, it enhances electrochemical use of the positive electrode active materials Na_2S. After cycles, author also confirmed the Na-ions are scattered in the cycled membrane homogeneously, showing a simple path of Na^+-ion diffusion which maintained during cycling of the battery. Moreover, by comparing the cycled sodium negative electrode, it can see that the degradation of surface in the sodium negative electrode with Celgard membrane worsen than that of Na-Nafion/AC—CNF coating separator (Fig. 10c-l), suggesting the separator which coated by Na-Nafion/AC—CNF can effectively mitigate the polysulfide shuttle to the negative electrode. The result is the battery with proposed separator exhibits superior performance to that of other separators. In the future, the separator can be produced to thinner and help to reach higher ionic conductivity. The sodiated Nafion membrane can be used to help the Na/S batteries achieve higher energy density and cycle performance.

Recently, Demir-Cakan et al. reported the new research about Al_2O_3-Nafion membrane [72]. The Al_2O_3-Nafion membrane can help preventing the polysulfide shuttle between the negative electrode and positive electrode. The Al_2O_3 serves as the adsorbent to entrap the polysulfide ions, at the same time, the Nafion membrane can cation selectivity which allows immigrant of Na^+ cations and repels polysulfide anions because of the sulfonic groups with negatively charged. Comparing with the batteries which do not have membrane and only use Nafion membrane, owing to the wetting of membrane by electrolyte, the initial capacity of Na/S battery with the Al_2O_3-Nafion coating is lower in the first 10 cycles. But there is an improvement in the following cycling performance. After cycling for 100 times, the discharge capacity can keep stable at 250 mAh g_{sul}^{-1} (0.1 C). However, it needs to mention the low capacity enhancement is effected by the low diffusivity and high insulating nature of Al_2O_3. So the additive materials which have the advantages of good conductive and high polysulfide adsorption capabilities is appealing for the high performance Na/S battery.

7. Conclusion

In this review, we compared the working mechanisms of HT-Na/S battery, IT-Na/S battery and RT-Na/S battery. The critical factors (positive electrodes, separators, electrolytes) associated with the leap in the performance of Na/S batteries have been deeply discussed from the latest reported achievements and advances.

The researches of Na/S batteries mainly focus on improving the conductivity of sulfur and preventing the occurrence of shuttle effect. Although various carbon based mesoporous positive electrode hosts can improve the sulfur utilization that lead to a high

initial capacity, the cycling stability is not ideal especially for the long-term cycling. Therefore, in the future research, the carbon based materials integrated with the metal compounds, such as MOFs, metal nitrides, metal sulphides, and metal oxides, etc. could be further studied to eliminate the unnecessary capacity fading. Meanwhile, sulfur-equivalent positive electrode materials that not include the elemental sulfur but have a comparable electrochemical performance and without the generation of polysulfides are also good choices for Na/S batteries. The MoS_3 which we reported in this review is a good example of application of sulfur-equivalent positive electrode material. On the other hand, electrolytes are critical factor to affect the performance of the Na/S batteries. The performance of carbonate-based electrolyte shows relatively higher capacity and a difference voltage profiles that without the distinct platforms. The combine of ionic-liquid-based electrolyte and carbonate-based electrolyte are proved to be the better option. Solid electrolytes are, of course, one of the good choice to eliminate the dissolving of the intermediates of the reaction between Na and S. However, the solid electrolytes for the Na/S batteries are currently not satisfactory. Moreover, the safe feature of solid electrolyte profits the its overwhelming safety advantage it in the practical application of Na/S battery. Therefore, it must be one of the hottest research topic. Furthermore, advanced surface modification still needs to be explored to make the functionalized separator that can either migrate the Na^+ cations or repels polysulfide anions without increasing the interface resistance, for the purpose of optimizing the performance of batteries and additionally remedying the limitation of positive electrode and electrolyte in the performance of Na/S battery.

Conflicts of interest

The authors declare no conflict of interest.

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