Room Temperature Sodium Sulfur Batteries

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Lithium metal batteries have achieved large-scale application, but still have limitations such as poor safety performance and high cost, and limited lithium resources limit the production of lithium batteries. The construction of these devices is also hampered by limited lithium supplies. Therefore, it is particularly important to find alternative metals for lithium replacement. Sodium has the properties of rich in content, low cost and ability to provide high voltage, which makes it an ideal substitute for lithium. Sulfur-based materials have attributes of high energy density, high theoretical specific capacity and are easily oxidized. They may be used as cathodes matched with sodium anodes to form a sodium-sulfur battery. Traditional sodium-sulfur batteries are used at a temperature of about 300 °C. In order to solve problems associated with flammability, explosiveness and energy loss caused by high-temperature use conditions, most research is now focused on the development of room temperature sodium-sulfur batteries. Regardless of safety performance or energy storage performance, room temperature sodium-sulfur batteries have great potential as next-generation secondary batteries. This article summarizes the working principle and existing problems for room temperature sodium-sulfur battery, and summarizes the methods necessary to solve key scientific problems to improve the comprehensive energy storage performance of sodium-sulfur battery from four aspects: cathode, anode, electrolyte and separator.

room temperature sodium-sulfur battery | shuttle effect | electrode design | separator | electrolyte

1. Introduction

With the development of society and the depletion of natural resources, people have to start using renewable energy to develop low-cost and high-efficiency energy storage devices, such as secondary batteries. The ideal performance characteristics of energy storage devices are high energy density, high power density, long cycle life, low cost and high safety [1]. Among the existing secondary batteries, lithium-ion batteries have been industrialized, but their high cost, low practical energy density (100–200 Wh kg^{-1}) and poor safety performance limit their application [2][3]. In order to meet the energy storage needs of current society, it is necessary to design and develop other batteries with lower cost, longer cycle life and higher energy density and power density.

Sodium is a low-cost alternative to lithium. The content of sodium in the Earth's crust and water is 28,400 mg kg^{-1} and 1000 mg L^{-1}, respectively, which far exceeds the content of lithium. The electrochemical reduction potential of sodium is −2.71 V, which is slightly higher than that of lithium (−3.02 V) [4], and is similar to the standard hydrogen electrode (SHE) potential [5]. When sodium is used as the anode, it can provide a battery voltage greater than 2 V

when matched with an appropriate cathode. The high content, low cost and ability to provide high voltage make sodium an ideal choice for the anode materials of high-energy secondary batteries [6]. Sulfur has the advantages of strong oxidizing property, mature treatment technology, low cost, ready use [7], no toxicity and high capacity (when each atom transfers two electrons [8], the capacity of sulfur is 1.675 mAh g^{-1}) [9], etc. Sulfur has an attractive advantage over lithium as a battery cathode. Compared with lithium-sulfur batteries, sodium-sulfur batteries are a better choice from the perspective of sustainable development and economy, or from the perspective of battery preset performance [10].

The earliest sodium-sulfur battery was constructed in the laboratory of Ford Motor Company, and Kummer and Weber confirmed its feasibility [11]. The battery uses sodium and sulfur as the active materials for the cathodes and anodes, and β-Al_2O_3 ceramics are used as both the electrolyte and the separator. In order to reduce the transmission resistance of sodium ions in the alumina solid electrolyte, it is necessary to ensure that the electrode material is in a molten state, so the working temperature is set at 250–300 °C. Due to the advantages of long service life, high charging efficiency and high energy density, high-temperature sodium-sulfur battery systems have been used in stationary energy storage systems [12]. However, in order to maintain the molten conductive state of the two poles, a high operating temperature is required. The high operating temperature not only causes a loss of electrical energy, but also may cause the failure of the solid electrolyte, which causes explosions and fires due to contact between the cathode and the anode. These problems limit the wide application of high-temperature sodium–sulfur batteries [13].

In order to obviate the above problems, research has been directed toward the development of room temperature sodium-sulfur batteries. The first room temperature sodium-sulfur battery developed showed a high initial discharge capacity of 489 mAh g^{-1} and two voltage platforms of 2.28 V and 1.28 V [14]. The sodium-sulfur battery has a theoretical specific energy of 954 Wh kg^{-1} at room temperature, which is much higher than that of a high-temperature sodium–sulfur battery. Although room temperature sodium-sulfur batteries solve the problems of explosion, energy consumption and corrosion of high-temperature sodium-sulfur batteries, their cycle life is much shorter than that associated with high-temperature sodium-sulfur batteries. For a wider range of applications, its cycle performance needs to be improved [13].

Room temperature sodium-sulfur batteries have the advantages of high safety performance, low cost, abundant resource and high energy density [15][16]. They not only solve the safety problem of high-temperature sodium-sulfur batteries, but also solve the problem of high cost of lithium-ion batteries, and have received widespread attention. Like the lithium-sulfur battery system, room temperature sodium-sulfur batteries also face many problems, such as:

(1) Low conductivity of sulfur (5×10^{-30} S·cm^{-1}) and significant volume expansion (180%) [17]; (2) capacity attenuation caused by the dissolution of intermediate polysulfide in the electrolyte; (3) short circuit caused by sodium dendrites piercing the separator; (4) low utilization rate of the cathode; (5) poor reversibility, etc. [1]. This article will start with a description of the electrochemical reaction mechanism for the room temperature sodium-sulfur battery, and describe the development of room temperature sodium-sulfur battery in recent years in terms of its cathode, electrolyte, separator design and anode protection.

2. Existing Problems and Solutions

Compared with high-temperature sodium-sulfur batteries, room-temperature sodium-sulfur batteries have a higher capacity. However, most reported room-temperature sodium-sulfur batteries still fail to reach one third of the theoretical capacity of sulfur [18][19][20]. This may be due to the following theoretical and technological issues:

(1)Sulfur and sulfide have poor conductivity. During battery cycling, electronic conductivity is very important to the electrodes [21]. However, sulfur (5×10^{-30} $S \cdot cm^{-1}$) and its final recrystallized Na_2S are both semiconductors, lacking inherent high electronic conductivity [22];

(2)The volume expansion of sulfur causes serious changes in structure and morphology [23]. During battery discharge, the volume expansion/contraction of sulfur is a key factor in determining battery capacity. When Na_2S_3 is generated during the discharge process, the volume expansion rate of the sulfur cathode is 36%, for Na_2S_2, the volume expansion rate is 67% and reaches 157% after Na_2S is completely generated [24];

(3)Soluble polysulfide diffuses from cathode the to the anode [6][25]. The inevitable dissolution of Na_2S_x ($4 \leq x \leq 8$) leads to a serious shuttle effect between the cathodes and anode, resulting in poor battery cycle stability and high self-discharge rate;

(4)The formation of needle-like sodium dendrites and deposits [15]. Due to the large difference in size between sodium atoms and sodium ions, sodium easily forms unstable electrodeposited layers and dendrites. Once the dendrites reach a certain length, short circuits will occur [1][2];

(5)Due to the large radius of Na^+, the reaction activity between S and Na is slow, so the conversion of S to Na_2S is incomplete, resulting in low sulfur utilization [26][27][28];

(6)Impedance increases caused by irreversible side reactions [5][29].

Room temperature sodium–sulfur batteries face safety problems caused by the anode sodium dendrites, the insulation problem of the cathode sulfur, the shuttle effect of the intermediate product polysulfide and the loss of active materials caused by its dissolution. Starting from its cathode, electrolyte, anode and separator (Table 1 shows part of the research progress of room temperature sodium–sulfur batteries in the past six years), many methods have been developed to solve these problems:

Table 1. The main research progress of room temperature sodium–sulfur batteries in the past six years.

Publish Date	Reference	Anode	Cathode	Electrolyte	Separator	1st dis. Capacity/mAh/g (C-Rate)	10th dis. Capacity/mAh/g (C-Rate)
2013	Lee et al. [30]	Na-Sn-C comp.	60 wt % S/Hollow C comp. (viz. 56 wt % S) 20 wt % CB 20 wt % PEO	$NaCF_3SO_3$ In TEGDME (4:1 mol %)	-	1200	600
	Hwang et al. [23]	Na	70 wt % S/C–PAN comp. (viz. 32 wt % S) 15 wt % CB 15 wt % PVDF	0.8 M $NaClO_4$ in EC:DMC (1:1)	-	364	-
2013	Xin et al. [31]	Na	80 wt % S/(CNT@MPC) comp. (viz. 32 wt % S) 10 wt % CB 10 wt % PVDF	1 M $NaClO_4$ in PC:EC (1:1 *v*/*v*)	-	1610	1100
2014	Bauer et al. [32]	Na	42.5 wt % S 42.5 wt % C 12 wt % PVDF 3 wt % PTFE (dry)	1 M $NaClO_4$ in TEGDME	Nafion coating on PP separator	400	370
	Zheng et al. [33]	Na	80 wt % HSMC–Cu–S comp. (viz. 50 wt % S) 10 wt % CB 10 wt % CMC (in H_2O)	1 M $NaClO_4$ in EC/DMC (1:1)	-	1000	690
	Yu et al. [34]	Na	60 wt % S 30 wt % CB 10 wt % PVDF	1.5 M $NaClO_4$ 0.3 M $NaNO_3$ in TEGDME	-	900	600
	Yu et al. [35]	Na	MWCNT/Na_2S_6	1.5 M $NaClO_4$ 0.3 M $NaNO_3$ in TEGDME	-	945	535
	Nagata et al. [36]	Na-Sn (15:4.9 mol/mol)	50 wt % S 40 wt % SE 10 wt % AC	P_2S_5 (viz. 71 wt % S)	-	1456	-
				$NaPS_3$ (viz.75 wt % S)		1522	
				Na_3PS_4 (viz.80 wt % S)		1100	

Publish Date	Reference	Anode	Cathode	Electrolyte	Separator	1st dis. Capacity/mAh/g (C-Rate)	10th dis. Capacity/mAh/g (C-Rate)
2015	Kim et al. [37]	Na	60 wt % S/C comp. (viz. 55 wt % S) 20 wt % PVDF 20 wt % Super-P	β-Al_2O_3 (SE)		855	674
				1M $NaCF_3SO_3$ in TEGDME (L)	PP (porous)	350	-
	Kim et al. [38]	Na	SPAN comp. (viz. 41 wt % S)	1M $NaPF_6$ in EC/DEC (1:1 *v*/*v*)	GF	342	260
2016	Wei et al. [25]	Na	MCPS1 (viz. 47 wt % S)	1 M $NaClO_4$ 5 v% SiO_2–IL–ClO_4 in EC/PC	GF	1459	762
	Fan et al. [39]	Na	70 wt % CSCM comp. (viz.18 wt % S 1 g BDTD) 20 wt % AB 10 wt % CMC in C_2H_5OH/H_2O (1:2.5 *w*/*w*)	1 M $NaClO_4$ in EC/DMC (6:4 *v*/*v*)	-	1000	962
	Wang et al. [40]	Na	S/iMCHS comp. (viz.46 wt % S)	1.0 M $NaClO_4$ 5 wt % FEC in PC/EC (1:1 *v*/*v*)	-	1213	430
	Qiang et al. [41]	Na	N,S-HPC/S comp. (viz. 22 wt % S)	1M $NaClO_4$ in EC/PC (1:1 *v*/*v*)	GF/B	400	399
	Yu et al. [42]	Na	Na_2S/AC-CNF comp. (viz. 66 wt % Na_2S)	1.5 M $NaClO_4$ 0.2 M $NaNO_3$ in TEGDME	Na-Nafion membrane	563	658
2017	Yue et al. [43]	Na-Sn-C	Na_3PS_4-Na_2S-C (2:1:1 *w*/*w*) comp.	Na_3PS(SE)	-	869	704
2018	Ye et al. [44]	Na	70 wt % N/S-OMC-5 comp. (viz.20.32 at% N 0.82 at% S) 20 wt % Super-P 10 wt % PVDF	1 M $NaClO_4$ 5 wt % FEC in EC/PC (1:1 *v*/*v*)	-	1742	419
	Lee et al. [45]	Na	S/C-PAA 9:1	1M $NaClO_4$ in PC	GF	623	558
				1M $NaClO_4$ in PC/FEC			

Publish Date	Reference	Anode	Cathode	Electrolyte	Separator	1st dis. Capacity/mAh/g (C-Rate)	10th dis. Capacity/mAh/g (C-Rate)
2019	Xu et al. [46]	Na	80 wt % S@MPCF (6:4 *w*/*w*) 10 wt % Super-P 10 wt % CMCNa	2M NaTFSI in PC/FEC (1:1 *v*/*v*) with 10 mM InI_3	GF/A	1544	1032
	Zhang et al. [47]	Na	70 wt % S@Fe-HC 10 wt % CB 20 wt % CMC	1M $NaClO_4$ in PC/EC (1:1 *v*/*v*) with 5 wt % FEC	GF	945	630
	Li et al. [48]	Na	70 wt % $Te_{0.04}S_{0.96}$@pPAN 20 wt % SuperP 5 wt % SBR 5 wt % NaCMC	1 M $NaClO_4$ in EC/DMC (1:1 *v*/*v*)	-	1816	1015
				1M $NaClO_4$ in DOL/DME (1:1 *v*/*v*) with 10% FEC)		1682	868
	Zhu et al. [49]	Na	60 wt % S/CPAN comp. 40 wt % SE	PEO−NaFSI−1% TiO_2 comp.	-	300	253
	Yan et al. [50]	Na	NiS_2@NPCTs/S	-	-	957	508
	Ma et al. [26]	Na	S@Co/C/rGO	-	-	490	367
	Aslam et al. [51]	Na	S@BPCS (hollow polar bipyramid prism catalytic CoS_2/C as a sulfur carrier)	-	GF	1347	787
2020	Guo et al. [52]	Na	ACC-40S (the carbon–sulfur composite electrode with 40 wt % sulfur loading)	-	GF	1492	1200
	Du et al. [16]	Na	80 wt % rGO/VO_2/S comp. 10 wt % AB 10 wt % PVDF	1 M $NaClO_4$ in TEGDME.	GF	526.2	346

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inhibiting dendrites. Although various carbon-based mesoporous cathode bodies can increase the sulfur utilization rate and thereby increase the initial capacity, the cycle stability is not ideal, especially for long-term cycles. Therefore, in future research, carbon-based materials integrated with metal compounds, such as MOF, metal nitrides and metal oxides, can be further studied to eliminate unnecessary capacity degradation. At the same time, the sulfur equivalent cathode material is also a good choice for sodium–sulfur batteries. In addition, an independent binder-free cathode is also a good research idea. After removing the influence of the binder on the conductivity of the cathode material, the conductivity of the cathode will be improved.

Electrolyte: Tetraethylene glycol dimethyl ether; PAN: Polyacrylonitrile; PEO: Polyethylene oxide; GF: Glass fiber; PVDF: Polyvinylidene fluoride; CB: Carbon black; EC: Ethylene carbonate; DMC: Dimethyl carbonate; PC: Propylene carbonate; CNT: Carbon nanotubes; MPC: Mesoporous carbon; PTFE: Polytetrafluoroethylene; PP: Polypropylene; HSMC: Hierarchical porous carbon; CMC: Carboxymethyl cellulose; MWCNT: Multi-walled carbon nanotubes; SEI: Solid electrolyte interface; AB: Acetylene Black; EEC: Ethylene carbonate; HPC: Hierarchical porous carbon; AC: Activated carbon; OMC: Mesoporous carbon; PAA: Polyacrylic acid; MPCF: Multiporous carbon fibers; NaTFSI: Sodium bis(trifluoromethylthiocarbonyl)imide; SBR: Polystyrene butadiene copolymer; DOL: 1,3 dioxolane; HC: Hollow carbon; rGO: Reduced graphene oxide

The membrane with ion selectivity and physical adsorption will have a good inhibitory effect on the shuttle of polysulfides. Ordinary diaphragms cannot meet these requirements. The surface of the diaphragm must be modified to allow only Na+ to pass through. The modified diaphragm has an excellent capacity retention rate. It is also possible to add an intercalation layer between the diaphragm and the cathode to reduce electrical resistance while suppressing sulfur shuttle. Due to its nanosized frame and pores, the carbon nanofoam sandwich cannot only achieve the above-mentioned purpose, but also can digest volume expansion.

Since sodium dendrites will be generated on the surface of the sodium anode, which will cause a short circuit in the battery, sodium surface protection is necessary. Depositing Al2O3 layer atomic layer or molecular layer on sodium effectively inhibits the formation of sodium dendrites and prolongs the service life of sodium. Among them, MLD Al2O3 coating has better performance. In the future, MLD can be considered as an anode coating technology. In addition, other substances can be combined with sodium to form a composite anode to improve battery performance. The Na2S produced by sodium and some metal sulfides cannot only be used as an artificial SEI membrane to inhibit the growth of sodium dendrites, it can also be used as a 3D host of sodium, digesting the volume changes of sodium and greatly improving the stability of the sodium anode. In addition, it is also an effective idea for composite anodes to manufacture layered nanoboxes and combine the advantages of various hybrid configurations to improve sodium storage performance.

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