Effects of sulfur carriers with different morphologies on performances of lithium–sulfur battery

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ABSTRACT

Nowadays, energy storage systems have been considered as an effective way to meet the urgent demand for portable electronic products and electric vehicle industry, which requires the development of power sources that can provide high capacity as well as high safety, resulting in an increase on secondary batteries with excellent performances and non-pollution. Lithium-sulfur (Li-S) battery is considered as one of the most promising candidate batteries due to its high theoretical energy density, low cost and non-toxicity. Despite many advantages associated with Li–S battery, it is hard to be applied to commercial-scale production owing to its shuttle effect, insulating nature, agglomeration of sulfur, polysulfide dissolution and fast capacity decay during charge–discharge process. To meet these challenges, numerous characteristics of sulfur electrode have been designed, such as sufficient space to accommodate sulfur volume expansion, small dimensions of active material to avoid pulverization, and appropriate electrolyte additives to minimize the shuttle effect. According to previous studies, morphology of sulfur carriers has an important effect on electrochemical performances of Li–S battery. This review mainly aims at present status of different morphological sulfur carriers including carbon, metallic oxide, organic polymer and their composites, then summarizes their advantages, unresolved problems and common synthesis methods, respectively. At last, development and future prospects of Li–S battery are also presented.

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1. Introduction

Rapid development of lithium-ion batteries (LIBs) has been achieved since its commercialization in 1990. However, low energy density (less than 300 Wh kg^{-1}) is a main factor limiting its use in some emerging applications such as electric vehicles and large-scale grids [1]. The demand for higher specific capacity drives urgent search for new systems over current technology. Li–S battery has become one of the most promising candidates for energy storage systems owing to its specific capacity (for sulfur cathode is 1675 mAh g^{-1} and Li anode is 3860 mAh g^{-1}) as high as five times of commercial graphite [2–4]. Moreover, sulfur is abundant in nature [5,6]. Therefore, Li–S battery has become a research hotspot and achieved some gratifying achievements in modern electronic devices [7–11].

Although there are many advantages associated with Li-S battery, sulfur cathode suffers from three fatal deficiencies. Firstly, electronic conductivity of sulfur and its reaction products are poor (for sulfur is 5×10^{-30} S cm^{-1} at 25 °C) during electrochemical process, leading to low utilization of active materials and bad cycle performance [12]. Secondly, the shuttle effect in the charge–discharge process is caused by polysulfide dissolution, which means the polysulfide dissolves into organic electrolyte in forms of soluble polysulfide ions of S^{2-}_n ($n = 1$,

2, 4, 6, 8), and side reactions happen between S^{2-}_8, S^{2-}_6, S^{2-}_4, S^{2-}_2, and S^{2-}, thus leading to low coulombic efficiency, high self-discharge rate and short cycle life of cells [13,14]. Thirdly, for the sulfur cathode, a large volume expansion from S to Li$_2$S (about 76%) happens, which forms "dead sulfur" easily, resulting in electrode pulverization and fast capacity decay [15–17].

In the past five years, extensive progress of the sulfur cathode has been ongoing to improve its cycle performance, including electrolyte composition optimized [18–22], lithium anode protected [23–27] and cathode modified by different carriers, etc., but one of the most effective strategies is still to select suitable sulfur carriers. In these reports, the effects of different morphological carriers on the electrochemical performances of Li–S battery were studied systematically, such as carbon [28–30], metallic oxide [31,32], organic polymer [33–35] and their composites. In this paper, we not only summarize the preparation methods and electrochemical performances of sulfur carriers with different morphologies, but also discuss their advantages and limitations. Finally, future development prospects of Li–S battery are also presented.

2. Carbon material

Carbon materials are used as the sulfur carrier due to their excellent electronic conductivity, high stability and rich source, furthermore, can act as a buffer to accommodate the volume change of active materials in the charge–discharge process [36,37]. However, those properties are

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decided by their morphologies, such as specific surface area, pore volume and density [38–40]. To improve specific capacity and cycle performance of Li–S battery, carbon carriers with different morphologies have been developed, including amorphous, one-dimensional (1D), two-dimensional (2D), three-dimensional (3D), porous spherical and core-shell structure.

2.1. Amorphous carbon

Amorphous carbon (AC) includes carbon black (CB), acetylene black (AB), ordinary conductive carbon black (OCCB), super conductive carbon black (SB) and so on, and was widely investigated as sulfur host due to its simple synthesis process. Their carbon atoms order in short-range but disorder in long-range due to amorphous structure of these carbon materials. Though a number of particles agglomerate during the synthesis process, it is noticeable that a certain amount of pores is existent in AC. Some physical properties of AC such as specific surface area, pore volume and agglomeration degree can strongly influence the electrochemical performances of Li–S battery.

For some AC carriers, most sulfur is adsorbed on their surface but a small part of sulfur is impregnated into micropores due to the influence of Van Edward force. Rosenman et al. reported a Li–S cell which achieved a reversible capacity of over 500 mAh g^{-1} after 1000 cycles using disordered micro-porous carbon powders as sulfur matrix [41]. Li et al. synthesized a multiple pore size AC that had a bimodal pore system concentrated at about 1.6 nm and 14.1 nm as the sulfur carrier. This sulfur cathode exhibited a discharge capacity of 795 mAh g^{-1} after 100 cycles at a current density of 800 mA g^{-1} [42].

To explore the relationship between AC structure and its electrochemical properties, some comparative tests between Ketjen Black (KB) and AB were carried out by Zheng et al. The results showed that high surface area of AC improved utilization ratio of active sulfur, and decreased loaded current density per gram of cathode material during the electrochemical reactions. The initial discharge capacities of KB/S and AB/S were 1253 and 1004 mAh g^{-1} at 0.2C, respectively, indicating similar sulfur utilization ratio in carbon matrix. When the current density increased to 0.5C, the discharge capacities of KB/S and AB/S after 200 cycles had obvious difference, which was caused by high specific area or porous structure of KB and low surface or nonporous structure of AB [43]. The AB was also taken as the sulfur carrier by Tan et al. and showed high initial discharge capacity of 1610 mAh g^{-1} at 0.05 mA cm^{-2} and retained 69% of the value after 100 cycles, which benefited from the specific area of 54.66 m^2 g^{-1} and pore volume of 0.21 cm^3 g^{-1} [44]. Meanwhile, Jeong et al. constructed four types of sulfur cathodes using EC-600JD, Printex XE-2, Cabot BP-2000 and SB, respectively. Only little differences of the properties were observed in low current and middle voltage but obvious performance differences happened at high rate, which suggested that electrochemical behaviors were decided by the surface area and porous volume of different carbon materials [45].

The electrochemical performances of sulfur powders can be enhanced obviously via AC matrix, but the commercialization of Li–S battery has been gravely hindered owing to its low sulfur utilization and rapid capacity fading in the charge–discharge process. The shuttle effect that soluble polysulfide ions are dissolved in organic electrolyte is the first reason, which results in losing a lot of active materials. What is worse is that the pores of AC will be coated by insulated Li$_2$S$_2$ and Li$_2$S, leading to the separation of internal sulfur and the electrolyte, thus limiting electrochemical reactions. The second weakness is that contact resistance will increase during the charge–discharge process due to particles far from metal collector, which results in serious electrode polarization. Compared to AC, 1D carbon has high aspect ratio, excellent electronic conductivity and only extends in one direction, which can reduce polarization effectively. Therefore, 1D carbon has attracted increasing attention recently.

2.2. 1D carbon

1D carbon has aroused much attention attributed to its low density, excellent softness and high tensile strength. Moreover, intimate contact between sulfur and 1D carbon can improve fast electron and lithium ion transport in the electrode, and provide a large number of high active reactive points for the electrochemical process. As typical 1D carbon materials, carbon nanofibers (CNFs) and carbon nanotubes (CNTs) have attracted considerable attention in Li–S battery.

CNFs are regarded as an essential sulfur carrier due to their tunable structure. Zhang et al. prepared CNFs with about 40 nm diameter by confined nanospace pyrolysis method as the sulfur matrix. While 27 wt% sulfur deposited on the surface, the discharge capacity of CNFs/S after 50 cycles retained about 950 mAh g^{-1} at 0.1C [46].

In order to increase sulfur loading on the CNFs, a longitudinally opened vapor-grown CNFs with a porous structure was obtained by simple KOH activation. When the specific surface area of CNFs increased to 40.4 m^2 g^{-1} and its pore volume rose to 0.16 cm^3 g^{-1}, CNFs/S composite reached 57 wt% sulfur content and delivered a discharge capacity of 408 mAh g^{-1} after 80 cycles at 0.2C [47]. While Wang et al. prepared a novel 1D ordered mesoporous CNFs (OMCF) with interwoven nanostructure (as shown in Fig. 1) via electrospinning technique. The CNFs host exhibited a high specific surface area of 1345 m^2 g^{-1} and a large pore volume of 1.21 cm^3 g^{-1}, which loaded the sulfur of 63 wt% content. At 0.3C, the CNFs/S cathode displayed a capacity of 690 mAh g^{-1} even after 300 cycles [48].

Despite excellent properties in above-mentioned CNFs/S, most sulfur exposures on the surface, leading to the loss of active sulfur (S^2 − x, 4 ≤ x ≤ 8) during the charge–discharge process. Therefore, CNFs were replaced by CNTs in order to improve the electrochemical performances of sulfur cathode. In CNTs/S electrode, sulfur can be loaded not only on the surface but also inside internal channels, which can reduce active materials loss effectively. Liu et al. fabricated CNFs with inner diameter about 10 nm and outer diameter about 15 nm for sulfur scaffold by nano-agglomerated fluidized bed technology. The hierarchical CNTs/S coaxial nanocables with 50 wt% sulfur content exhibited an initial discharge capacity of 1020 mAh g^{-1} at 0.5C and the capacity loss rate was only 0.14% per cycle for later 140 cycles. These results showed excellent electrochemical performances for Li–S battery [49]. Kim et al. prepared CNTs/S using sulfur infiltrated vertically CNT array, where the CNTs with a wall thickness of 15 nm but average outer diameter of 50 nm were grown via chemical vapor deposition (CVD) process. At 3.2C, the Li–S cells showed an average capacity of ~400 mAh g^{-1} and stable working over 150 cycles at 90 °C, suggesting high temperature stabilization of as-prepared sulfur cathode [50]. However, smooth and closed surface of the CNTs prevent Li$^+$ entering center. Wu et al. reported a mesohollow and microporous CNTs prepared by a coaxial electrospinning with polyacrylonitrile (PAN) and polymethylmethacrylate (PMMA) as outer and inner spinning solutions followed by a carbonization strategy. As-prepared CNTs had outer diameter of 300–400 nm but tunnel size of 30–60 nm. The hollow structure was constructed because inner PMMA fibers were decomposed at high temperature without any solid residual. Moreover, wall pores with 6–8 nm formed when the gas escaped from the inside in the decomposition process. The discharge capacity of CNTs/S electrode was 715 mAh g^{-1} after 70 cycles at 0.1C, corresponding to 88% of initial capacity caused by fast lithium ion transfer path on wall pores [51].

Obviously, "dead sulfur" on the surface of CNTs/S composite is less than that of CNFs/S composite. However, the sulfur in the CNTs/S exists in forms of "sulfur column" inside tunnels, showing low electrochemical reaction activity. Some efforts have been tried to further improve the utilization ratio of active sulfur. Zhao et al. encapsulated multi-wall carbon nanotubes (MWCNTs) into hollow CNTs through a step-by-step strategy to obtain a sulfur cathode (as shown in Fig. 2). A tube-in-tube structured carbon nanomaterial (TTCN) was used to accommodate sulfur and exhibited outstanding electronic conductivity property. After