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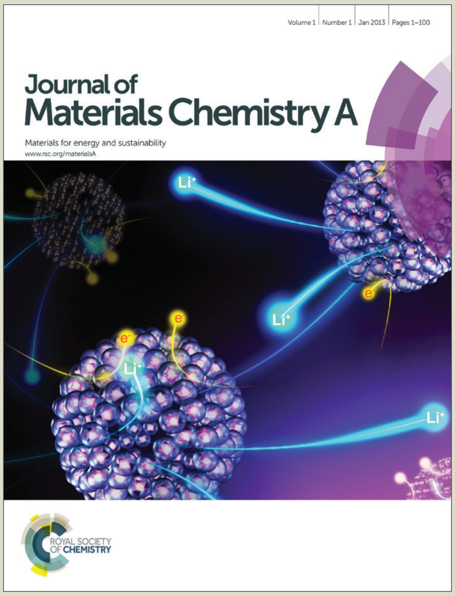

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ARTICLE

Chitosan as a Functional Additive for High-Performance Lithium-Sulfur Batteries

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Chitosan with abundant of hydroxyl and amine groups as an additive for cathode and separator has been proved to be an effective polysulfide trap agent in lithium-sulfur batteries. Compared with common sulfur cathode, the cathode with chitosan shows enhanced initial discharge capacity from 950 to 1145 mAh g^{-1} at C/10. The reversible specific capacity after 100 cycles increases from 508 mAh g^{-1} to 680 mAh g^{-1} and 473 to 646 mAh g^{-1} at rates of C/2 and 1C, respectively. In addition, batteries with separators that are coated with carbon/chitosan layer can exhibit high discharge capacity of 830 mAh g^{-1} at C/2 after 100 cycles and 675 mAh g^{-1} at 1C after 200 cycles with the capacity fading as low as 0.11% per cycle. These studies demonstrate the benefits of using chitosan for not only lithium-sulfur batteries but also potentially other sulfur-based battery applications.

Introduction

Lithium-sulfur battery is one of the appealing candidates for large-scale energy storage devices to meet the energy demands from the emerging electric vehicles and smart energy grids [1,2]. Compared to conventional Li-ion batteries, rechargeable lithium-sulfur batteries have higher theoretical specific capacity of 1672 mAh g^{-1} and theoretical energy density of 2600 Wh kg^{-1} [3]. Moreover the active material of sulfur is nature abundant, low cost (about $ 150 per ton), and non-toxicity [4]. However, there are still several critical issues that hampered the commercialization of lithium-sulfur batteries. The major problem of lithium-sulfur batteries is the dissolution of the lithium polysulfide intermediates (Li_2S_x, $4 < x < 8$) generated during the electrochemical cycle process in the organic liquid electrolyte [5,6,7,8,9]. The soluble polysulfide diffuses out of the cathode and then migrates across the separator into anode where the polysulfide chemically reacts with the metallic lithium to form shorter-chain polysulfide, which leads to the loss of active lithium and the contamination of the whole system. This is the so-called ‘shuttle reactions’, which result in the short cycle life, significant self-discharge, and low columbic efficiency [10].

To trap polysulfide, various strategies have been employed in lithium-sulfur batteries [11]. Porous carbon has been regarded as an useful material to restrain the shuttle of the polysulfide [12,13,14], but the physical barrier and adsorption capability were limited to trap polysulfide in sulfur cathode[15]. Adding functional groups into the host materials can introduce strong chemical binding of sulphur and the discharge products, thus eliminating the polysulfide shuttling. Recently, an *ab initio* simulation study of several functional groups have revealed that both hydroxyl groups and amine groups exhibit strong affinity with Li_2S and lithium polysulfide to minimize their loss into the electrolyte [16]. Furthermore, the combination of the hydroxyl groups with the graphene or the carbon paper has shown a significant improvement in the sulfur utilization and capacity retention [17,18]. Coincidentally, lithium–sulfur batteries showed enhanced performance by bonding two electron-donating amine groups with reduced graphene oxide, and nitrogen-doped carbon composites exhibited strong lithium polysulfide chemisorption for high-performance lithium–sulfur battery [19,20]. These results suggested that hydroxyl groups and amine groups could capture the migrating polysulfide from the cathode during electrochemical reactions. Chemical adsorption or bonding of polysulfide to cathode through hydroxyl groups or amine groups provides a new strategy to suppress the polysulfide shuttle.

This guides us to focus on functional polymer with hydroxyl groups and amine groups because the functional polymer could supply a simple way that used as an additive to improve the performance of the sulfur cathode. Chitosan, a nitrogenous polysaccharide and with abundant of hydroxyl groups and amine groups, shows great hydrophilic properties and has strong affinity with lithium polysulfide to potentially minimize their loss into the electrolyte [21]. Due to its unique molecular structure, chitosan has an extremely high affinity for many classes of dyes, including disperse, direct, reactive, acid, vat, sulfur and naphthol dyes [22]. As for chitosan, it is one of the most plentiful natural biopolymers produced from chitin and is widely used in molecular separation, water treatment and other fields [23]. Moreover, it possesses good

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viscosity that can be considered as an effective electrode binder for lithium-ion batteries [24].

Herein, in this article, we chose chitosan as the polysulfide trapping agent in lithium-sulfur batteries. Its excellence in chemical adsorption capacity of the lithium sulphides and the polysulfide has leaded to much enhanced electrochemical performance. Our results demonstrate that chitosan can be used a highly effective additive for many sulfur-based (Li-S, Na-S etc.) batteries to improve their cycle performance and discharge/charge capacity.

Experimental

Preparation of cathodes

Elemental sulfur (99.5%, analytically grade, Beijing Yili. Corp., China) and acetylene black (AB, Jinpu. Corp., China) were dried at 60 ℃ for 10 h under vacuum before use. Chitosan was purchased from Aladdin, and gelatin (160Bloomg, type B, derived from bovine bones) was used as a binder. The common cathode was prepared by ball-milling the sulfur (63 wt. %), acetylene black (30 wt. %) and gelatin (7 wt. %), and the cathode with chitosan was prepared by ball-milling the sulfur (63 wt. %), acetylene black (30 wt. %), chitosan (3.5 wt. %) and gelatin (3.5 wt. %). Then, both of the two well-mixed slurries were coated onto the Al foil by a doctor blade and dried at 60 ℃ for 10 h under vacuum. The sulfur loading in the cathodes is 1.0-1.5 mg cm^{-2}.

Preparation of the separator coating with chitosan

The carbon/chitosan-coating (C/CTS-coating) separator is prepared by ball-milling acetylene black (80 wt. %), gelatin (10 wt. %) and chitosan (10 wt. %). The obtained slurry was coated onto one side of a Celgard PP separator by doctor blade dried at 60 ℃ for 10 h under vacuum. The weight of the carbon layer was ≈0.2 mg cm^{-2}.

Preparation of Li_2S_6-containg electrolyte

Lithium polysulfide solution with a nominal stoichiometry of Li_2S_6 was prepared by mixing the appropriate ratios of nano-sulfur powder and Li_2S over 24 h.

Electrochemical and microstructural analyses

CR2025 coin-type batteries were assembled in an argon-filled glove box to test the electrochemical performance of the cathode materials with lithium metal as the anode. The electrolyte was 0.6M lithium bis-triuoromethanesulfonylimide (LiTFSI, Beijing Chemical Reagent Research Institute) and 0.4M lithium nitrate in 1, 3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 V:V, ratio, Beijing Chemical Reagent Research Institute). The charge-discharge performances of the batteries were tested with varies rates at a cut-off potential of 1.7-2.8 V under room temperature using LANDCT2001A instrument. The microstructures of the composites were carried out with a field emission scanning electron microscope (SEM，HITACHI S-4800).

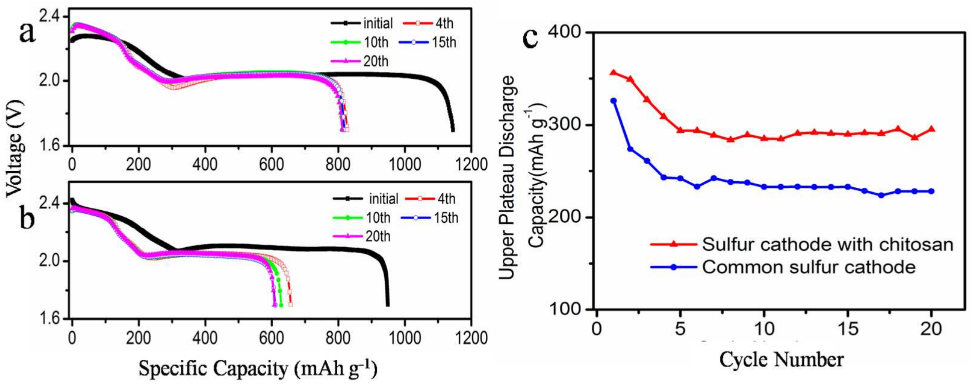

Fig.1 Discharge curves of batteries: a) sulfur cathode with chitosan, b) common sulfur cathode, and c) the upper plateau discharge capacities of batteries with different sulfur cathodes.

Results and Discussion

Chitosan as additive for sulfur cathode

As shown in the Fig.1a and b, the discharge voltage profiles during the initial 20 cycles with different cathodes are compared. They discharged at a rate of C/10 in the first three cycles and C/2 in the next cycles. Fig.1a shows the discharge curves of the batteries utilizing the cathode with chitosan. During the discharge, there are two separate plateaus representing two complete reduction reactions [2]. The upper discharge plateau at 2.3 V corresponds to the reduction reaction from sulfur (S_8) to long-chain polysulfide (Li_2S_x, $4 < x ≦ 8$). The lower discharge plateau at 2.05 V represents the second reduction reaction from long-chain polysulfide to short-chain Li_2S_2/Li_2S [25]. Figure 1a and figure 1b demonstrate that the additive chitosan increases the initial discharge capacity (from 950 mAh g^{-1} to 1145 mAh g^{-1}), attesting to the improved sulfur utilization. And in the following cycles, the overlapping discharge curves of the cathode with chitosan from the 4th cycle to the 20th cycle demonstrate that the polysulfide not only can be immobilized by the chitosan but also can be reactivated, improving stability of the batteries. Moreover, the upper plateau discharge capacities of the cathode with chitosan are better retained than that of the common cathode in Figure 1c.This conform that chitosan can effectively trap the polysulfide and decrease the loss of active material during the discharge-charge process. After adding chitosan into common cathode, the first upper plateau discharge capacity is 356 mAh g^{-1}, approaching 85% of the theoretical value (419 mAh g^{-}

^{1}), indicating that the polysulfide diffusion is limited [26]. After 20 cycles, the cathode with chitosan remains 83% of the original value, while the common cathode only retains 69%. The enhanced upper plateau capacity also demonstrates that chitosan can effectively trap and reactivate the polysulfide.

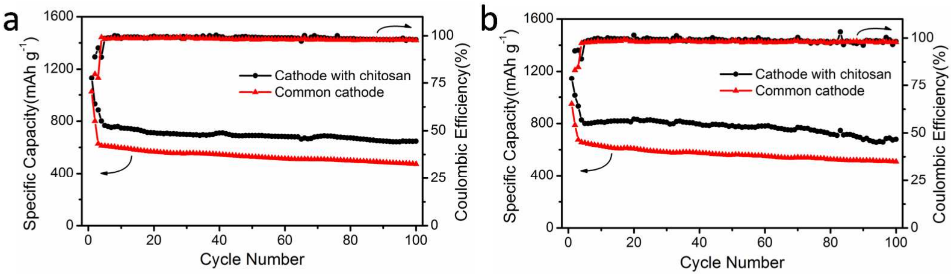

Fig.2 The Cycling performance of sulfur cathode with chitosan and common sulfur cathode at the rate of 1C (a) and C/2 (b).

Fig.2 shows the enhanced discharge capacity and stable recyclability of the cathode with chitosan. All batteries were discharged at rates of C/10 in the first 3 cycles for activating batteries and C/2, 1C in the subsequent cycles. At C/2, the reversible capacity of the cathode with chitosan is 680 mAh g^{-1} after 100 cycles. When the discharge rate increases to 1C, the retained discharge capacity after 100 cycles is 646 mAh g^{-1}, which is close to the capacity at C/2. As a comparison, the common cathode has the discharge capacities of 508 and 473 mAh g^{-1} at rate of C/2 and 1C, respectively, after 100 cycles, indicating that the cathode with chitosan possesses higher reversible capacity and rate performance. The cathodes with chitosan also exhibit the average Columbic efficiency above 98% at various cycling rates after 100 cycles. The above results suggest that adding chitosan into the cathode can suppress the diffusion of polysulfide into the electrolyte and improve the reversible capacity and rate performance.

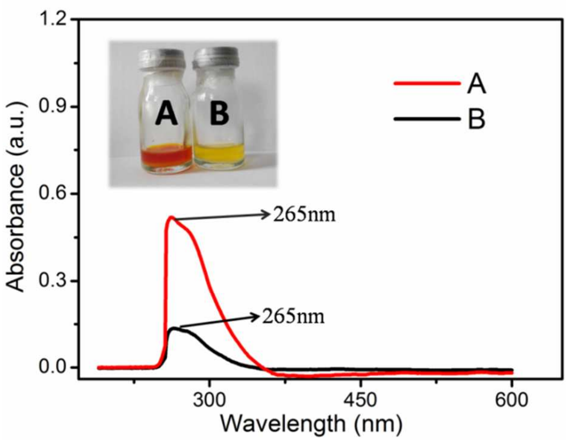

Fig.3 Photographs of solutions of, from left to right: Li_2S_6-containing electrolyte (A), chitosan in Li_2S_6-containing electrolyte (B).

In order to understand the effect of the chitosan on the electrochemical performance of the cathode, a test of its chemical interaction with polysulfide has been performed [27]. As shown in the insert of Fig.3, the two bottles (A and B) contain the same Li_2S_6-based electrolyte. When the chitosan was added into bottle B, the colour of the solution became shallow immediately. This indicates a strong interaction between lithium polysulfide and chitosan. The UV-visual spectroscopy measurements reveal the differences as well, as a decreased peak at 265 nm (assigned to Li_2S_6) on the chitosan-containing electrolyte in bottle B compared to that in bottle A, due to the lower concentration of Li_2S_6 in the electrolyte of bottle B.

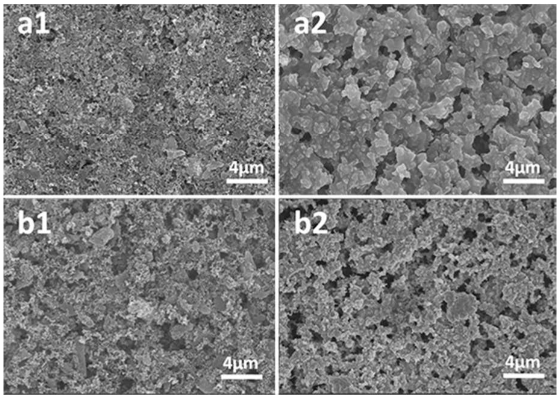

Fig.4 SEM images of the common sulfur cathode (a1) before discharge, (a2) after 50 cycles and the sulfur cathode with chitosan (b1) before discharge, (b2) after 50 cycles.

This observation can explain the improved electrochemical performance in chitosan added Lithium-sulfur battery. It is known that polysulfide easily dissolves into the ether-based solvents during discharge and charge due to the low viscosity of and salvation by the ether-based electrolyte [28]. The hydroxyl groups or amine groups of the chitosan increased the surface hydrophilicity of the cathode with chitosan, which will be beneficial in suppressing the shuttle effect by adsorption of polysulfide. On the discharge/charge of the battery, the migrating of polysulfide will be suppressed and immobilized by the hydroxyl groups or amine groups of the chitosan. The interaction of polysulfide and chitosan should have a clear effect on the electrochemical performance of the batteries, as verified by the added chitosan into the cathode that showed improved stability and capacity retention.

Figure 4 compares the surface morphology from SEM between the common sulfur cathode and cathode with chitosan at different cycles. After adding the chitosan into the sulfur cathode, the top surface of the sulfur cathode with chitosan (b1,b2) coated by a well dispersed layer composed of sulfur and acetylene black, there are not any clusters of sulfur can be found in the SEM images (b2) after 50 cycles [29]. The results reveal that the structure of the sulfur cathode with the chitosan added can still maintain stability before or after cycling, just like the common sulfur cathode.

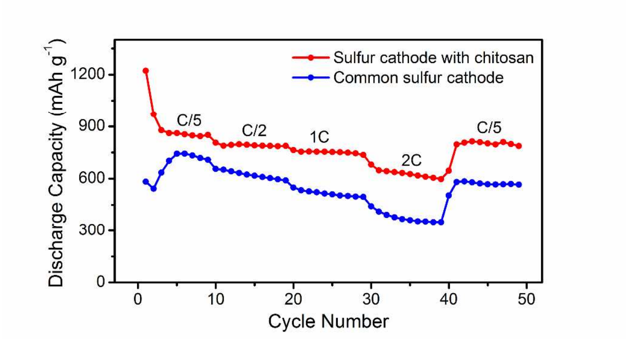

Fig.5 Rate performance of the sulfur cathode with chitosan and common sulfur cathode.

To further confirm the trap of polysulfide with chitosan, the rate performance of the cathode with chitosan has also been investigated. As shown in Fig.5, when increasing the current rate from C/5 to 2C, the discharge capacities of both cathodes were decreased, but the cathode with chitosan possesses higher discharge capacities than the common cathode at all rates. The cathode with chitosan shows a satisfactory specific capacity of 600 mAh g^{-1} at a very high rate of 2C, while the common cathode obtains a low specific capacity of 360 mAh g^{-1}. When the current rate returns from 2C to C/5, the discharge capacities of the sulfur cathode with chitosan can go back to the initial values indicating the stability and improved rate performance of the lithium-sulfur batteries. The results agree with the interaction of polysulfide and chitosan. According to the trap and immobilization of polysulfide, the electrochemical performance has been enhanced after adding chitosan into the common sulfur cathode.

The C/CTS-coating separator

It is verified that chitosan can effectively trap and immobilize the polysulfide and improve the electrochemical performance. Inspired by it, the surface modified separator with chitosan has been prepared. One side of the original Celgard polypropylene separator faced the cathode was coated by carbon and chitosan (C/CTS-coating). The carbon layer serves as an upper current collector for increasing the surface area and conductivity of the cathode region, and the chitosan on the separator can effectively capture and immobilize the polysulfide in the side of the cathode inhibiting 'shuttle effect'.

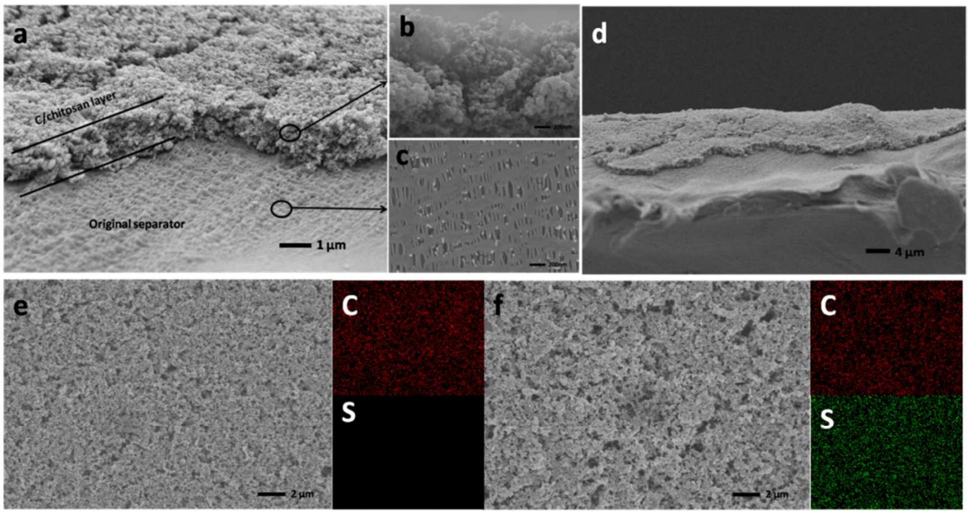

Fig.6 SEM of the observations of (a) and (d) side views of the C/CTS-coating separator, (b) side view of the C/CTS layer and (c) the surface of the original separator. Cross-sectional SEM observation and elemental mapping of the C/CTS-coated separator were obtained (e) before cycling and (f) after 100 cycles at a rate of C/2.

It is noted that common separator has the carbon layer that is ~1.5 μm thick (Fig.6a-d), which is too thin to physically trap the migrating polysulfide [30]. However, the thin carbon/chitosan (C/CTS) layer can efficiently trap the polysulfide by chitosan to chemically suppressing and immobilizing polysulfide. Fig.6e shows the scanning electron microscopy (SEM) and the energy dispersive X-ray spectroscopy (EDX) elemental mapping of the C/CTS-coating separator before cycling. As shown in the insert, the carbon and chitosan are well dispersed on the surface of the original separator leading to a conductive layer. To investigate the effect after adding the chitosan, the SEM and elemental mapping of the C/CTS-coating separator were performed after 100 cycles at a rate of C/2. Results suggest that the active material was trapped by the chitosan as the corresponding EDX elemental mapping shows strong and distinct elemental sulfur signal (marked as green), demonstrating the excellent chemical absorption effects of the chitosan for polysulfide. Moreover the elemental sulfur signal remain uniform, indicating that the trapped polysulfide by chitosan can be re-activated leading no formation of non-conductive agglomerations.

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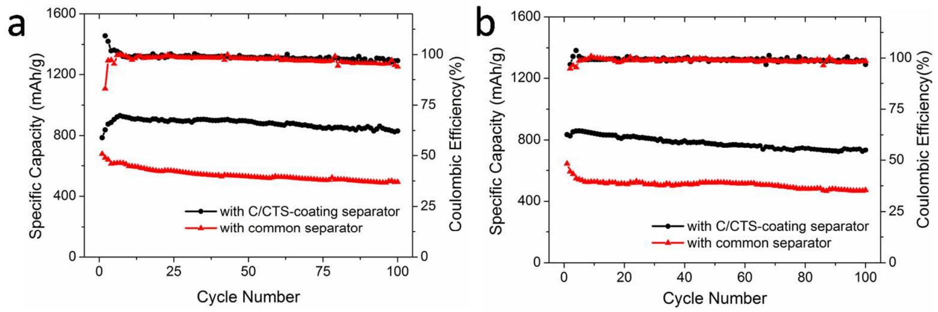

Fig.7 The Cycling performances of the batteries with C/CTS-coating separator and common separator at different rates: (a) C/2 and (b) 1C.

To further demonstrate that the chitosan can intercept and absorb the polysulfide produced during discharge process, cycle performances of the batteries with C/CTS-coating separator at different rates are presented in Fig.7. As shown in Fig.7a and b, the discharge capacities and recyclability of the batteries with C/CTS-coating separator are improved. At a rate of C/2, the batteries with C/CTS-coating separator achieve the reversible capacities of 830 mAh g^{-1} after 100 cycles, with capacity retentions of 89% and the capacity fading as low as 0.11% per cycle. Even cycling at 1C rate, the reversible capacities approach 732 mAh g^{-1} after 100 cycles, which correspond to capacity retention of 88%, and with the capacity fading as low as 0.18% per cycle. Compared with the batteries using C/CTS-coating separator, the batteries with original separator show lower capacities of 680 and 646 mAh g^{-1} at, respectively, C/2 and 1C rates. During the discharge process, some of the yielded polysulfide escaped from the cathode and dissolved into the electrolyte. Then the polysulfide diffuse into the carbon layer of the modified separator and immobilized by the chitosan again on the surface of the separator further improving the utilization of the soluble polysulfide. The improved stable recyclability further confirmed that C/CTS-coating separator can effectively capture and immobilize the active materials.

Conclusions

In summary, we demonstrated that the chitosan is a highly effective additive for lithium-sulfur batteries, improving cycle performance and discharge/charge capacity. Due to its abundant functional groups of hydroxyl and amine which can interact with polysulfide strongly, chitosan can effectively capture and immobilize the polysulfide. The sulfur cathode and the separator with chitosan as an additive show an enhanced reversible capability and cycling performance. After 100 cycles, the sulfur cathode with chitosan shows the reversible specific capacity of 680 mAh g^{-1} and 646 mAh g^{-1} at rates of C/2 and 1C, respectively. The batteries with C/CTS-coating separator exhibit high discharge capacity of 830 mAh g^{-1}at C/2 after 100 cycles and 675 mAh g^{-1} at 1C after 200 cycles with the capacity fading as low as 0.11% per cycle. The modified separator with chitosan as an additive further captures polysulfide and reactivates the trapped active materials. Considering that the chitosan is safe, environmentally friendly and prepared easily, this simple functional additive provides important clues in the development of lithium–sulfur batteries and may be broadly adapted in high-performance lithium-sulfur batteries.

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