Improving electrochemical performance of lithium-sulfur battery with a conductive polymer-coated sulfur cathode

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Low sulfur utilization, poor cycle life, and the security problems caused by Li metal anode are main drawbacks to hinder the practical application of lithium-sulfur battery. Here we report a facile modification for traditional sulfur cathode to achieve high capacity and considerably improved cycle life. By coating a commercially-purchased conductive polymer PEDOT:PSS onto the surface of pristine sulfur electrode, significant enhancement is achieved in both sulfur utilization and capacity retention. With this strategy, gravimetric energy densities of the cell with modified S cathode are estimated to 1113 Wh kg⁻¹ based on the total composition of electrode. The PEDOT:PSS film not only serves as a soft buffer to restrict the polysulfides immigrating to lithium anode, suppress mechanical stress and sustain a stable electrode, but also provides more active surfaces to capture and reutilize the polysulfides.

Introduction

An urgent demand for electric vehicles (EVs) arises with increasingly serious energy and environmental issues, which promotes rapid development of rechargeable batteries with high energy density worldwide. Among all redox couples of rechargeable batteries, lithium-sulfur couple has a very high theoretical energy density of 2600 Wh kg⁻¹ or 2800 Wh L⁻¹ based on a two-electron complete reaction: \( \text{S}_8 + 16\text{Li}^+ + 16e^- \rightarrow 8\text{Li}_2\text{S} \). Much higher than those of traditional lithium-ion batteries (LIBs). In addition, sulfur has advantages of low cost, environmental benignity and nontoxicity. Thus, lithium-sulfur battery is considered as a promising candidate for next-generation high energy storage system.

Although there are many advantages of lithium-sulfur battery, successful application is still hindered by low sulfur utilization and rapid capacity fading. The problems are mainly caused by the insulating nature of sulfur and the final discharge product (Li₂S), and the dissolution of long-chain polysulfides generated during discharge-charge process. In addition, the volume expansion of sulfur during the lithiation process is as large as 80% due to the density difference between sulfur and Li₂S, which also results in structure collapse of the cathode and degradation of battery performance. Besides, the safety and engineering difficulties related to Li metal anode are also tough challenges.

Lots of efforts have been devoted to overcoming above problems, especially with the influx of nanotechnologies, great progress has been achieved in the field of lithium-sulfur battery in recent years. One of the most important strategies is to impregnate sulfur onto various carbon structures. By constraining the growth of sulfur nanofiller within the pores of the conductive porous carbon matrix, the conductivity of sulfur electrode can be greatly improved, and the dissoluble loss of sulfur in the liquid electrolyte can also be restrained, leading to a remarkably improved electrochemical performance. In this way, some nano-architected sulfur composites have been reported to exhibit specific capacity over 1000 mAh g⁻¹ or show excellent cyclability up to hundreds of times.

But, almost all the capacity data reported in lithium-sulfur batteries were calculated only based on the mass of sulfur. In fact, a large fraction of carbon is used to enhance the conductivity and suppress the dissolution of polysulfides, thus the S content in the whole cathode is always less than 50%. Since the carbon matrix can hardly contribute the capacity to the sulfur cathode, the volumetric energy density for lithium-sulfur batteries is difficult to exceed the traditional LIBs except...
on the condition that S loading is high enough (> 70%). However, little attention has been paid to this point. On the other hand, fabrication of the nano-architected sulfur composites usually requires complicated procedures, involving high-temperature process and corrosive acid for template removal. Such procedures may greatly limit the manufacturability of S cathode. Therefore, it is highly desirable to develop a simple and scalable approach to fabricate S cathode with high overall capacity over long-term cycling.

Polymers also have been used to couple with S for their abundant controllable morphologies and physical and chemical properties, but unlike carbon materials which are widely used as sulfur supporters, polymers have been used mostly as coating layers for S or S/C materials. For example, with a simple PEG-coating, Ji et al. reported that a stable capacity of CMK-3/S composite can be improved from 900 mA h g\(^{-1}\) to over 1100 mA h g\(^{-1}\). Cui et al. also has reported a conductive polymer wrapped CMK-3/S composite. With PEDOT:PSS coating, the CMK-3/S composite showed a high initial reversible capacity of 1140 mA h g\(^{-1}\) and a good cyclability with a decay of 15% per 100 cycles. While in these two unique designs, the preparation of CMK-3 is elaborate, and the subsequent combination with sulfur needs to melt and infuse S into the carbon matrix, which are not suitable for large-scale production.

Here we proposed a modified S cathode prepared via a very simple method. Commercially-purchased poly(3,4-ethylenedioxythiophene:poly(styrenesulfonate) (PEDOT:PSS) aqueous solution was pasted onto a pristine S electrode by a conventional blade method. The PEDOT:PSS film was not only served as a soft buffer to restrict polysulfides immigrating to lithium anode, suppress mechanical stress and sustain a stable electrode, but also provides abundant active surfaces to capture and reutilize the polysulfides, as shown in Fig. 1. Such a super-simple modification for sulfur cathode can give a largely improved stability for the lithium-ion delithiation process. Since the PEDOT:PSS layer is very thin and light, which occupies less than 5 wt.% of the total electrode, there is no obvious negative effect on the total gravimetric or volumetric capacities of sulfur cathode. Moreover, unlike the previous reports in which the polymers are coated on S or S/C particles, here the conductive PEDOT:PSS is coated on the S electrode, which successfully avoid the widely-used top-down route to melt and infuse S into the matrix. Therefore the PEDOT:PSS-modified sulfur cathode can be directly prepared by the present Li-ion battery production line.

Results and discussion
The SEM images in Fig. 2 reveal the morphology change of the S electrode before and after PEDOT:PSS coating. The pristine S cathode displays a rough surface with well-dispersed S particles (Fig. 2a). After PEDOT:PSS coating, the electrode surface becomes smooth and dense (Fig. 2b). From Fig. S1, we can see that the surface of PEDOT:PSS-coated S cathode is also pretty uniform in low magnification. Fig. 2c gives a contrast from a sulfur electrode partly covered by PEDOT:PSS film, which clearly shows that the PEDOT:PSS film is tightly coated on the S cathode surface. XPS measurement was carried out to further confirm the existence of PEDOT:PSS film. Fig. 3 shows the S 2p peak of pristine S cathode pure PEDOT:PSS film and the PEDOT:PSS-coated S cathode. The pristine S cathode shows two characteristic peaks of element sulfur at 164.0 and 165.2 eV. For pure PEDOT:PSS, four peaks can be fitted: the two peaks located at higher binding energy of 168.7 and 167.5 eV are assigned to PSS, while the other two at 165.3 and 163.8 eV are attributed to PEDOT. The PEDOT:PSS-coated S cathode exhibits similar characteristic peaks to the pure PEDOT:PSS, but the two peaks located at lower binding energy displays higher relative intensity due to the overlap of elemental S and S in PEDOT. As XPS is a surface detective method with a detective depth around 10 nm, it can be speculated that this additional PEDOT:PSS layer is quite thin. It can be inferred that negative effect on gravimetric and volumetric capacities of the sulfur cathode should be very small.

The electrochemical properties of sulfur cathodes with and without PEDOT:PSS coating were investigated with coin cells. All the cells were assembled and sealed in the same condition. Fig. 4a and 4b shows CV curves of the first 3 cycles for the sulfur cathodes without and with PEDOT:PSS coating. Both curves show two distinct reduction peaks and one oxidation peak, which agrees well with the typical CV characteristics of sulfur cathode. The two peaks at 2.25 and 2.05 V correspond to the reduction of S8 to higher-order polysulfides (Li2Sx, 4 < x < 8), and then to Li2Sx (x = 1, 2). The intense oxidation peak at about 2.5 V should be assigned to the oxidation of Li2Sx (x = 1, 2) to high-order lithium polysulfides or elemental sulfur[16, 18, 31]. After PEDOT:PSS coating, the position of two reduction peaks are virtually unchanged, indicating that PEDOT:PSS makes no difference with the redox reactions of sulfur. Fig. 4c and 4d show the discharge-charge profiles at different cycles. All the profiles display two discharge plateaus. For the PEDOT:PSS-coated S cathode, a capacity increase and a discharge plateau rise occur at the second discharge compared with the initial one, indicative of a remarkable activation process, which is due to the penetration of electrolyte through the additional PEDOT:PSS film. In the following cycles, the two discharge plateaus stabilize at 2.25 and 2.05 V, which agrees with the cathode without PEDOT:PSS coating, demonstrating that the inhibition effect only exists in the initial discharge process.

Fig. 5a shows their cycling performances at 0.2 C. The PEDOT:PSS-coated S cathode delivers a reversible specific capacity as high as 1061 mAh g⁻¹, while the pristine S cathode is only 867 mAh g⁻¹. After 100 cycles, the coated cathode still maintains a capacity up to 638 mAh g⁻¹, whereas the pristine one only keeps 275 mAh g⁻¹. As shown in Fig. 5b, the PEDOT:PSS-coated S cathode also exhibits a greatly enhanced rate capability. Its discharge capacities are 1189, 891, 768, 646 and 585 mAh g⁻¹ at 0.1, 0.2, 0.5, 1 and 2 C, respectively. Even the current density is tuned back to 0.1 C after 50 cycles, a capacity of 790 mAh g⁻¹ is still attained. As a comparison, the pristine S cathode exhibits a much poorer rate capability, whose capacities are 747, 514, 405, 264 and 194 mAh g⁻¹ at 0.1, 0.2, 0.5, 1 and 2 C, respectively.

The significant improvement in the electrochemical performance confirms the “trap and reutilization” effect of the PEDOT:PSS film (Fig. 1). For the pristine S cathode, during the repeated lithiation-delithiation process, the dissolved
polysulfides may mostly transfer between cathode and anode (Fig. 1a), leading to shuttle effect, active material loss and capacity decay. After coating, the PEDOT:PSS film serves as a soft buffer to restrict the diffusion of polysulfides into the electrolyte, so the shuttle effect can be largely alleviated. Meanwhile, the trapped polysulfides can be further reduced/oxidized due to the electric conductivity of PEDOT:PSS. In addition, this ductile film can also relieve the volume change and strengthen the connection between the insulated S/Li$_2$S particles and Super-P conductor. All these factors help PEDOT:PSS-coated S cathode to achieve a much higher discharge capacity and considerably improved cyclability. To gain insight into the protection mechanism of PEDOT:PSS coating, the morphology evolution of the electrodes before and after cycling was investigated, as shown in Fig. 6. For the pristine S electrode, clear S particles are observed in the fresh cathode (Fig. 6a), but after 50 cycles the particles greatly aggregate (Fig. 6b), implying a serious redistribution of active materials upon cycling. For the PEDOT:PSS-coated S cathode, it still keeps a smooth and dense surface after 50 cycles (Fig. 6d), which is quite similar to the fresh one (Fig. 6c). The “trap” effect of PEDOT:PSS can be also visually proved by checking the disassembled cells after 100 cycles (the insets of Fig. 6b and 6d). The inside of the pristine sulfur cell became yellow in the ether electrolyte, but
no color change was observed in the PEDOT:PSS-coated S cathode.

In order to provide more valuable data for practical application, the capacity density and energy density were calculated based on the total composition of sulfur cathode and the corresponding lithium-sulfur batteries with the model proposed by Gao et al.\textsuperscript{28}. For the purpose of simplicity, only the mass and volume of active material, carbon, binder and conductive polymer were considered. The detailed calculation process is described in the supporting information. The energy densities of the typical LiCoO\textsubscript{2} cathode and LiCoO\textsubscript{2}-graphite battery were also calculated based on the same model to get a quick understanding of the general situation. As shown in Fig. 7a, the PEDOT:PSS-coated S cathode displays a gravimetric energy density of 1319 Wh kg\textsuperscript{-1}, much higher than that of the pristine S cathode (1004 Wh kg\textsuperscript{-1}) and the LiCoO\textsubscript{2} cathode (521 Wh kg\textsuperscript{-1}). When it couples with lithium anode, the corresponding battery demonstrates gravimetric energy densities of 1113 Wh kg\textsuperscript{-1}, much higher than those of the traditional LiCoO\textsubscript{2}/graphite battery (362 Wh kg\textsuperscript{-1}). But, the sulfur system does not show advantage in the volumetric energy density, the PEDOT:PSS-coated S cathode displays a volumetric energy density of 739 Wh L\textsuperscript{-1}, which is much lower than that of the LiCoO\textsubscript{2} cathode (1669 Wh L\textsuperscript{-1}). When coupled with lithium anode, the gap narrowed, but the volumetric energy density is still lower than that of the LiCoO\textsubscript{2}/graphite battery. Obviously, the main advantage of lithium-sulfur system is its high gravimetric energy density. Fig. 8 and Table S1 also give a rough comparison of specific capacity and energy density (calculated based on the overall cathode) between the PEDOT:PSS-coated S cathode and some typical nano-architected sulfur-based composite cathodes (based on mesoporous carbon\textsuperscript{15, 37}, microporous carbon\textsuperscript{25, 26}, graphene\textsuperscript{24, 38}, hollow structured sulfur\textsuperscript{21} and polysulfide mediator materials\textsuperscript{39, 40}). Through this feasible method, the PEDOT:PSS-coated S cathode achieves a high gravimetric energy density of the cathodes (1319 Wh kg\textsuperscript{-1}), which is much better than the cathodes based on the micro/meso porous carbon and comparable to those of the cathodes based on graphene, hollow structured sulfur and polysulfide mediator materials.

Conclusions

A great and repeatable improvement of electrochemical performance of lithium-sulfur battery has been achieved by coating a conductive PEDOT:PSS film on the surface of pristine sulfur electrode. Due to the “trapping and reutilization” effect of PEDOT:PSS film, the cathode delivers a specific capacity as high as 1061 mAh g\textsuperscript{-1}. After 100 cycles, the PEDOT:PSS-coated S cathode can still maintain a specific discharge capacity of 638 mAh g\textsuperscript{-1}, much higher than those of the pristine S cathode (275 mAh g\textsuperscript{-1}). The gravimetric energy densities of the cell with the modified S cathode are estimated to 1113 Wh kg\textsuperscript{-1} based on the total composition of electrode. It is noted that the polymer layer is coated on the S electrode rather than the S particles, which is meaningful for industrial operability. With this strategy, we believe that we can further improve the electrochemical performance of lithium-sulfur battery by addressing the thickness of coating layer and employing different polymer layers.

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Notes and references

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