

Is overprotection of sulfur cathode good for Li-S batteries?

Tian Gao,^{‡a} Jie Shao,^{‡b} Xingxing Li,^a Guobin Zhu,^a Qiujuan Lu,^a Yuyao Han,^a Qunting Qu,^{*a} and
Honghe Zheng^{*a}

^aCollege of Physics, Optoelectronics and Energy & Collaborative Innovation Center of Suzhou
Nano Science and Technology, Soochow University, Suzhou, Jiangsu 215006, China

^bCollege of Chemistry, Chemical Engineering and Material Science, Soochow University, Suzhou,
Jiangsu 215006, China

E-mail: qtqu@suda.edu.cn; hhzheng@suda.edu.cn

[‡] The authors contribute equally to this work.

Experimental details

Preparation of electrospun carbon nanofibers paper: 1.5 g of PAN was dissolved into 15.5 ml of DMF through vigorous stirring at 60 °C for about 6 h. The electrospinning of the above solution was carried out at a working voltage of 1-20 kV. The flow rate and needle tip-to-plate collector distance were fixed at 1 mL h⁻¹ and 15 cm, respectively. The as-spun PAN nanofibers paper was heated from room temperature to 250 °C at a heating rate of 1 °C/min and then stabilized at 250 °C for 1 h in air. At last, the nanofibers were carbonized at 1000 °C for 2 h.

Preparation of C/S and sulfur cathodes: The C/S composite was first prepared by heating the mixtures of carbon black and sulfur with a weight ratio of 6/4 at 155 °C in a vacuum container for 3 h and then under the flow of Ar gas for 10 h. The C/S cathode disks were prepared through the conventional preparation procedures of electrode disks in Li-ion batteries. Briefly, the slurry composed of C/S active material, carbon black, and poly(vinylidene fluoride) (PVDF) binder with a weight ratio of 6/3/1 dispersed in N-methylpyrrolidone was spread onto aluminum foil and dried in a vacuum oven at 60 °C for 24 h. Thus the mass loading of sulfur in the final C/S cathode is about 24%. The sulfur cathode was prepared through the same procedures using pure untreated sulfur as the active material.

Electrochemical Testing: CR2032-type coin cells were assembled for electrochemical testing. Li foil was used as the counter and reference electrodes. 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 0.1 M LiNO₃ dissolved in 1,3-dioxolane and 1,2-dimethoxyethane (volume ratio: 1/1) were used as the electrolyte. All the electrolyte components are purchased from Sigma-Aldrich Co. All the discharge/charge tests were carried out at a constant current rate of 0.2 C.

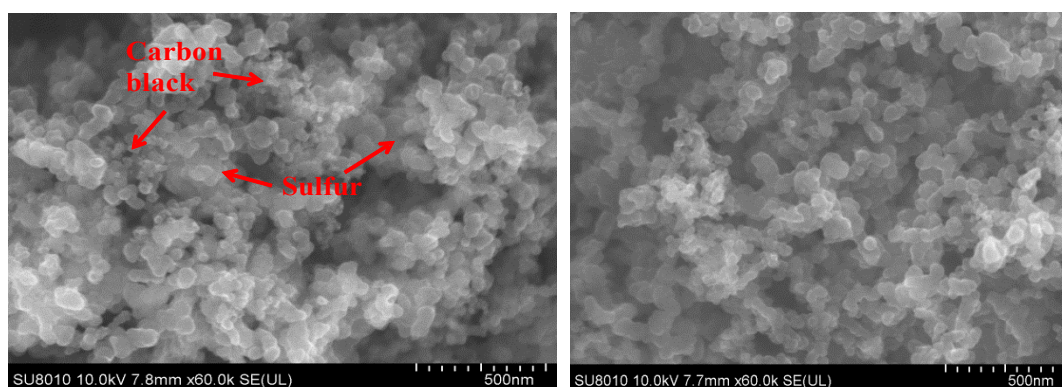


Figure S1 SEM images of C/S composites (left) before and (right) after thermal treatment.

It can be seen that the physically mixed C/S composite exhibits separate aggregates of sulfur and carbon black particles. After thermal treatment, sulfur is uniformly covered on the surface of carbon black nanoparticles.

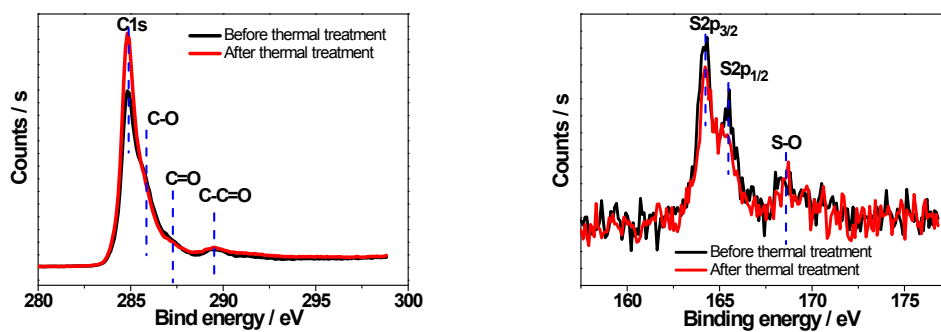


Figure S2 C1s and S2p XPS spectra of C/S composites before and after thermal treatment.

No significant changes are observed for the C1s and S2p binding energies of C/S composites before and after thermal treatment. Nonetheless, it is observed that the relative intensity ratio of peak S2p to C1s greatly decreases after thermal treatment, which can be attributed to the decreased particles size of sulfur when being uniformly covered on carbon and the reduced crystallinity of sulfur after thermal treatment.

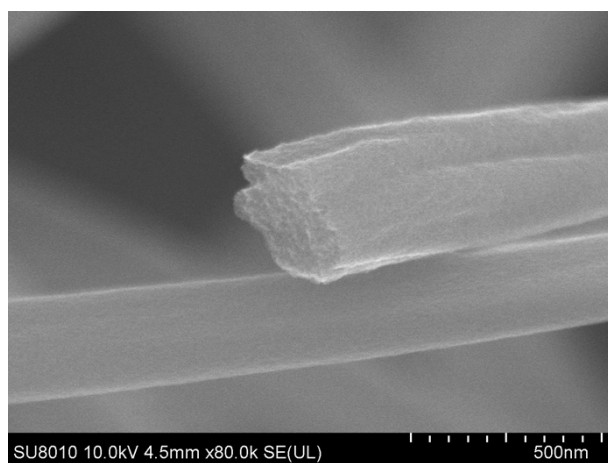


Figure S3 SEM image of as-prepared carbon nanofibers at high magnification.

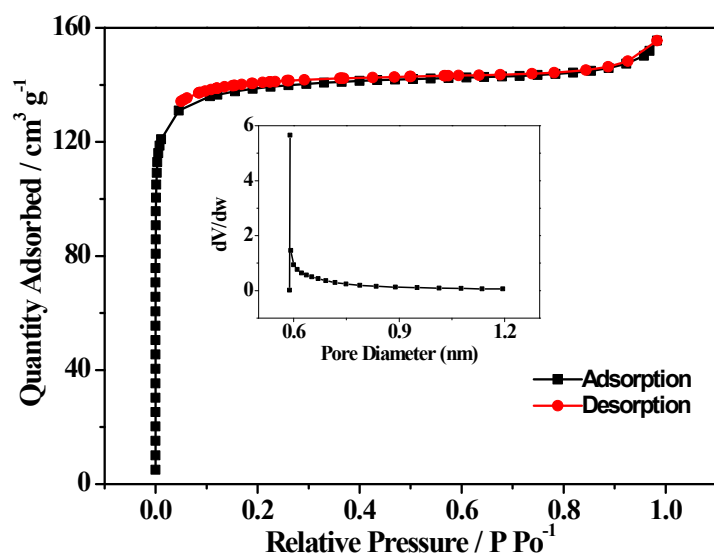


Figure S4 N₂ adsorption/desorption isotherms and the corresponding pore-size distribution of as-prepared carbon nanofibers paper.

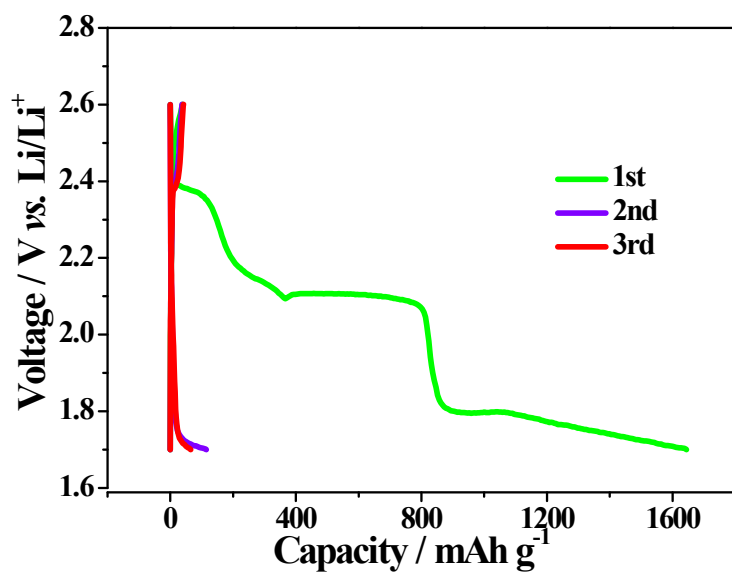


Figure S5 The initial three discharge/charge curves of C/S cathode-based Li-S cell in the presence of carbon interlayer tested in another parallel experiment.

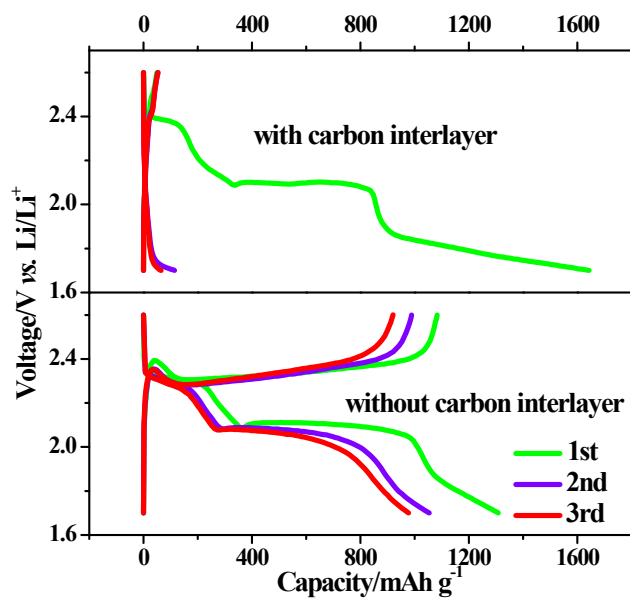


Figure S6 The initial three discharge/charge curves of mesoporous carbon CMK-3/S cathode based Li-S cells in the presence and absence of carbon interlayer.

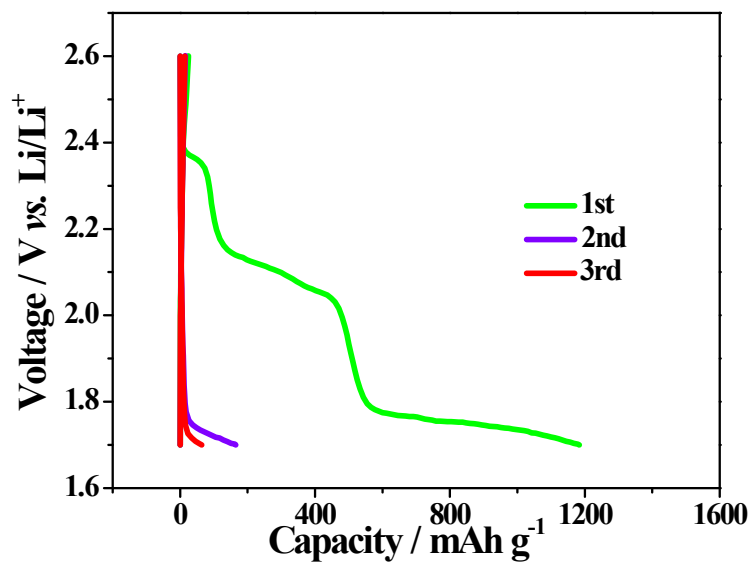


Figure S7 The initial three discharge/charge curves of activated carbon/S cathode-based Li-S cell in the presence of carbon interlayer.

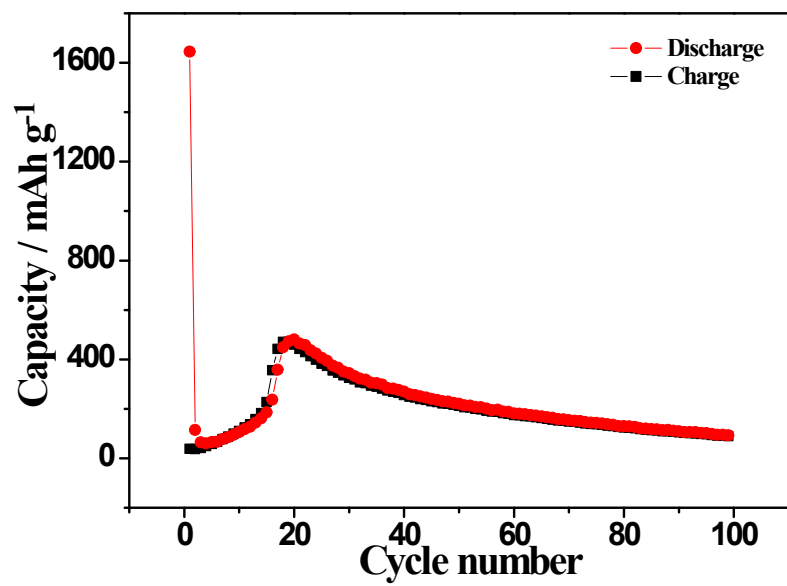


Figure S8 The cycling performance of mesoporous carbon CMK-3/S cathode-based Li-S cell in the presence of carbon interlayer.

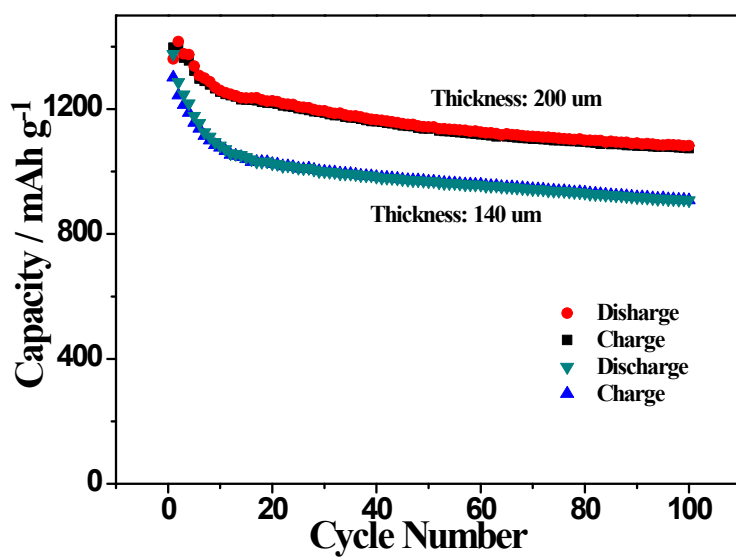


Figure S9 Influence of carbon paper thickness on the cycling performance of sulfur-based cathodes.

The sulfur-based cathode is composed of sulfur, conductive carbon, and binder with a weight ratio of 6/3/1. Two carbon papers with the thickness of 140 μm and 200 μm were used as the interlayers, respectively. The 200 μm-thick carbon interlayer presents better performance than the 140 μm one, suggesting that more polysulfides can be restrained with the increase of carbon interlayer thickness.

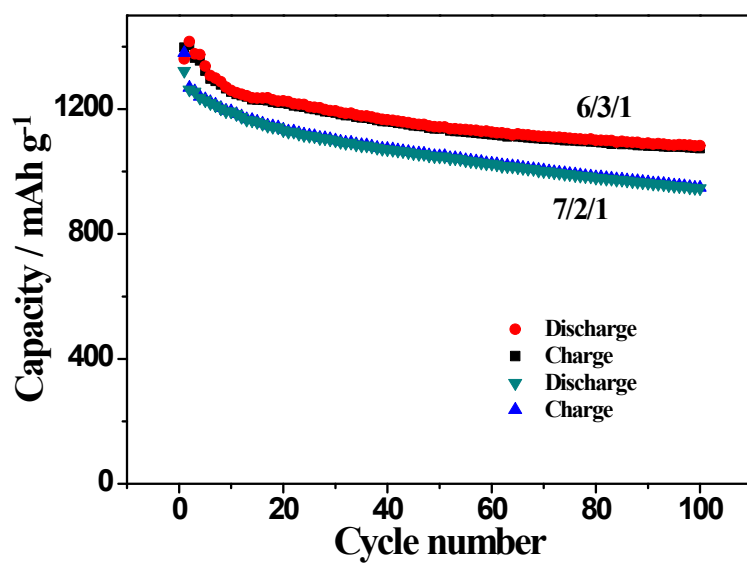


Figure S10 The cycling performance of sulfur cathode-based Li-S cells with different cathode composition. Carbon interlayers with a thickness of 200 μm are used.

The sulfur-based cathode with a weight ratio of 6/3/1 (sulfur/conductive carbon/binder) presents better performance than the one with a ratio of 7/2/1.

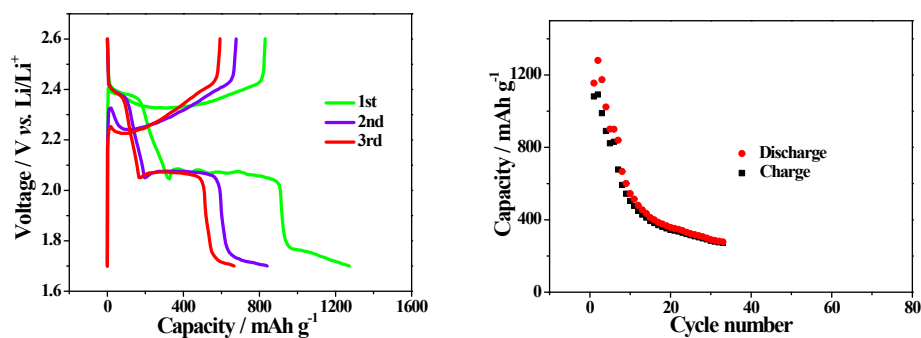


Figure S11 The initial three discharge/charge curves (left) and long-term cycling performance (right) of another C/S cathode-based Li-S cells in the presence of carbon interlayers.

Besides the C/S cathode shown in the main article, we prepared another thermally treated C/S composite containing 70% of sulfur and fabricated it into an electrode using a weight ratio of 7/2/1 (C/S composite/conductive carbon/binder), equaling to the sulfur loading of 49% in the final electrode. We found that this cathode can be effectively cycled in the presence of carbon interlayer. It is reasonable to assume that there may be a small amount of unprotected sulfur or polysulfides due to the decreased carbon content. However, the capacity and cycling performance of this electrode is unsatisfactory.

Based on our present results, the optimal electrochemical performance is obtained for the sulfur-based cathode with an electrode composition of 6/3/1 in the presence of 200 μm -thick carbon interlayer.