

In-situ synthesis of sulfur-TiO₂ hollow shell materials for high-performance lithium-sulfur batteries

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Abstract. Lithium-sulfur batteries with higher energy density are highly attractive, but the practical applications have been greatly affected by their poor cycle performance. Despite much effort has been devoted to design the structure of sulfur cathode to suppress polysulfide dissolution, relatively little emphasis has been placed on in-situ immobilizing the sulfur atoms. Herein, we demonstrate a new approach of in-situ immobilizing the sulfur atoms into the TiO₂ host, in which, the polysulphides can localized in the cathode side and efficiently reused during cycling due to the novel S-TiO₂ hollow shell structure. The battery based on the well-designed S-TiO₂ cathode can deliver a discharge capacity of 601 mA h g⁻¹ at 0.5 C after 100 cycles. The good electrochemical performance could be attributed to the homogeneous dispersing of sulfur in the TiO₂ host in the in-situ formation process, and the hollow structure of the S-TiO₂ materials. The economical and simple strategy to overcome the polysulfide dissolution issues provides a commercially feasible way for the construction of lithium-sulfur batteries.

1. Introduction

Rechargeable batteries with superior performance are very attractive and important in advanced energy storage systems [1]. In a wide variety of cathode materials, sulfur as an abundant and nontoxic element can deliver a theoretical specific capacity of 1675 mA h g⁻¹. Therefore, Li-S batteries have attracted increasing interest in recent years and been considered as one of the most prospective candidates for the next generation Li-ion battery [2].

Despite of the considerable advantages, there are still many issues in blocking the Li-S battery's commercialization process, such as, the insulating nature of the sulfur and the final discharge product lithium sulfides, and the sulfur cathode proceeds through multiple steps and involves a series of intermediate products (Li₂S_x, x=8, 6, 4, and 2) during discharging. The dissolved high order species can diffuse and react with metal lithium, then the low order products can diffuse back to the cathode side, which called "shuttle effect" [3]. To tackle the drawbacks mentioned above of Li-S batteries, many approaches have been developed on structure design of the cathode electrode, and different approaches always have their own advantages and limitations, also rapid capacity fading during



cycling has not completely avoided, especially the high cost and the complexity of the synthesis process prevent their large-scale applications.

As is well-known, $\text{Na}_2\text{S}_2\text{O}_3$ which always used as sulfur precursor in many researches can be reduced to form sulfur particles in the acid solution according to reaction formula (1) [4]. However, little work focus on the in-situ modification in this reaction process. Moreover, when the $\text{Ti}(\text{SO}_4)_2$ is dissolved in water, hydrogen ions will be released and anatase TiO_2 which can bind favourably with polysulphide anions due to hydrophilic Ti–O groups and surface hydroxyl groups can be formed after hydrolysis reaction (reaction formula (2, 3)) [5]. As the result, the two reaction can occur at the same time, and sulfur particles can in-situ dispersed in the TiO_2 structure. In view of its advantages, herein, we report a facile and effective method for in-situ modifying the sulfur cathode and suppressing the shuttle effect in lithium-sulfur batteries by synthesizing S- TiO_2 hollow core-shell composites. The sulfur can in-situ dispersed in the TiO_2 networks, which may shorten the migration pathway of lithium ions as well as a trap for dissolved polysulfides.



2. Experimental section

2.1. Sample preparation

S- TiO_2 hollow core-shell composites were synthesized by slowly adding concentrated $\text{Ti}(\text{SO}_4)_2$ (0.133 g, 100 mL) to an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (1.033 g, 100 mL). After reaction in ice-water bath for 2 h, the S- TiO_2 hollow core-shell composites were washed by centrifugation and then the as-synthesized S- TiO_2 composites dried under vacuum overnight.

2.2. Characterization and electrochemical measurements

Powder XRD patterns were collected on a Bruker D8 Advance diffractometer using Cu K α irradiation ($\lambda = 1.5406 \text{ \AA}$) and the morphology were obtained by a Hitachi s-4800 high resolution scanning electron microscope coupled with a BRUKER QUANTAX EDS spectrometer.

The cathode electrodes used in the experiments was prepared by mixing S- TiO_2 hollow core-shell particles, super P and polytetrafluoroethylene (PTFE) binder at a 7:2:1 mass ratio. Then the as-prepared cathode was dried in a vacuum oven at 60°C for 24 h. After that, CR2320 coin cells were assembled in a glove box filled with argon using lithium metal as the counter electrode. The electrolyte was 1, 3-dioxolane and 1, 2-dimethoxyethane (1:1 in volume) with 1 M lithium LiTFSI and 0.1M LiNO_3 and the separators was Celgard 2320. Cycling was carried out between 1.7 and 2.8 V on a Neware multi-channel battery tester at room temperature.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of the as-prepared S- TiO_2 hollow shell composite, sulfur and TiO_2 . The peaks of crystalline sulfur and TiO_2 (JCPDS No. 21-1272) clearly indicated that the composition of S- TiO_2 composite. The broadening peaks of the TiO_2 anatase demonstrates that the resulting TiO_2 host are very small indicating good dispersion of sulfur within the TiO_2 host.

The SEM images of S- TiO_2 hollow shell composite are shown in Figure 2. It can be clearly identified that the S- TiO_2 composite is globular, and the typical diameter of it is in range of 500 nm – 1 μm . Moreover, from Figure 2c, the morphology of the S- TiO_2 composites is truly hollow shell structure and the rough shell of hollow shell can be clearly observed from the Figure 2d, which is

conducive to the contact between cathode materials and electrolyte. To further determine the distribution of different element in the S-TiO₂ composites, the results of element mappings were obtained for the composites. Figure 3b-3d show the element mappings for oxygen, sulfur and titanium based on the SEM image which shown in Figure 3a. The element mappings result of oxygen, sulfur and titanium from Figure 3 demonstrate a very similar intensity distribution, which testifying that sulfur and TiO₂ are uniformly distributed, and since the in-situ formation of the sulfur in the metatitanic acid, the sulfur is tightly bonded with TiO₂ in the S-TiO₂ composites. Consider to the TiO₂ possess hydrophilic Ti-O groups and surface hydroxyl groups [4, 6], which can bind with polysulphide anions, hence when the S-TiO₂ hollow shell composite used as cathode materials in Li-S battery, the specific capacity of the Li-S battery would be raised.

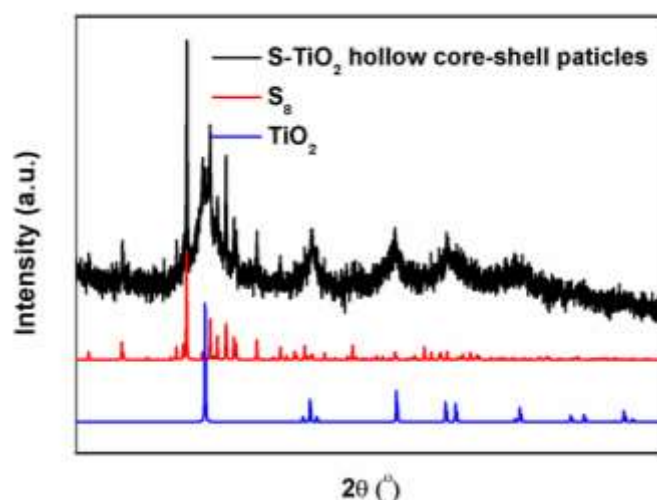


Figure 1. X-ray diffraction pattern of elemental sulfur, TiO₂, and S-TiO₂ hollow core-shell composites.

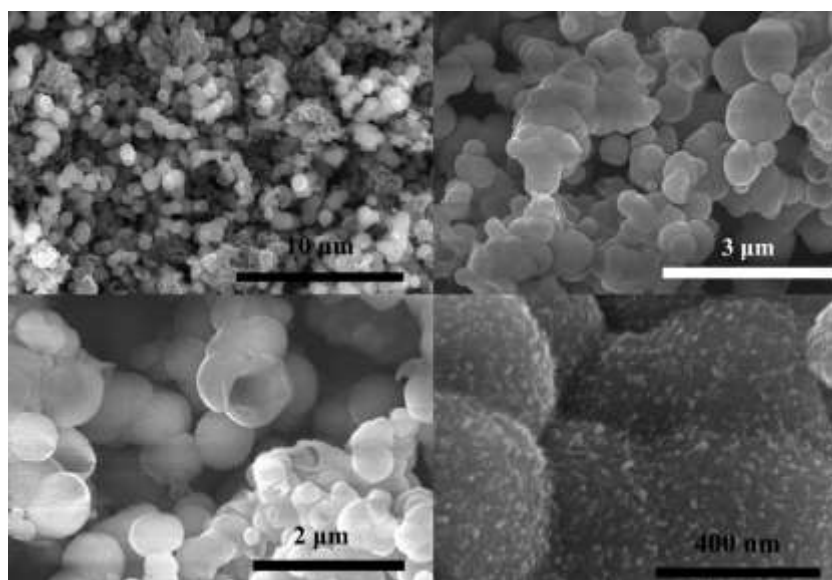


Figure 2 SEM images of as prepared S-TiO₂ hollow shell composites at different magnification scale.

Cycling performance of the S-TiO₂ hollow shell composites cathode are presented in Figure 4, and the capacity result in this experiment was calculated based on sulfur mass. The sulfur content was obtained to be ~52 wt% in the hollow shell nanostructures according to the TGA measurement. Figure

4 shows the cycling performance of S-TiO₂ hollow shell composites cathode at a current rate of 0.5 C (1C = 1675 mA g⁻¹). An initial discharge capacity of 848 mA h g⁻¹ was observed, even after 100 cycles, 601 mA h g⁻¹ discharge capacity was also achieved. Meanwhile, the average coulombic efficiency in the 100 cycles reaches about 96%. The good charge and discharge stability can be assigned to the in-situ formation of the sulfur which have great dispersion in the TiO₂ hosts. In addition, TiO₂ which possess hydrophilic Ti-O groups and surface hydroxyl groups can tightly interact with sulfur, effectively preventing the diffusion of polysulfide anions and minimizing the “shuttle effect” [4, 6].

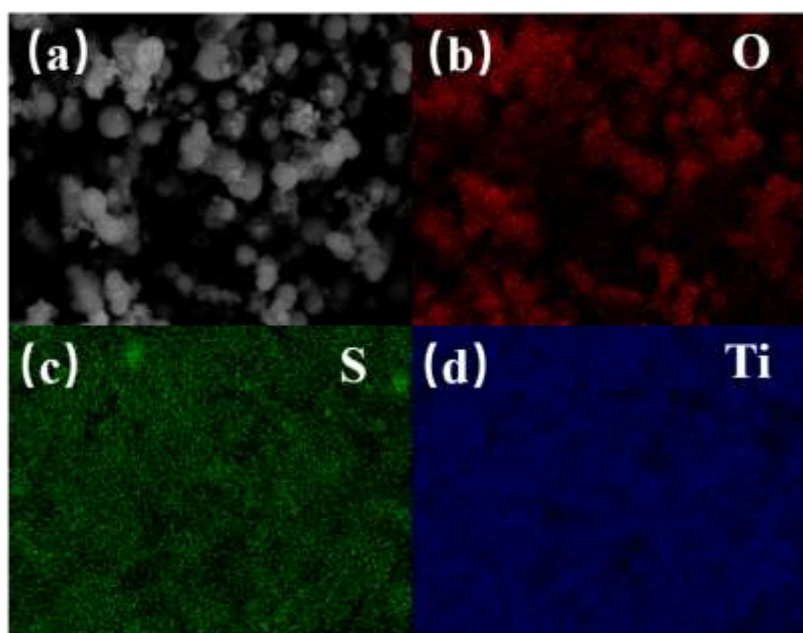


Figure 3 X-ray diffraction patterns of elemental sulfur, TiO₂, and S-TiO₂ hollow shell composites.

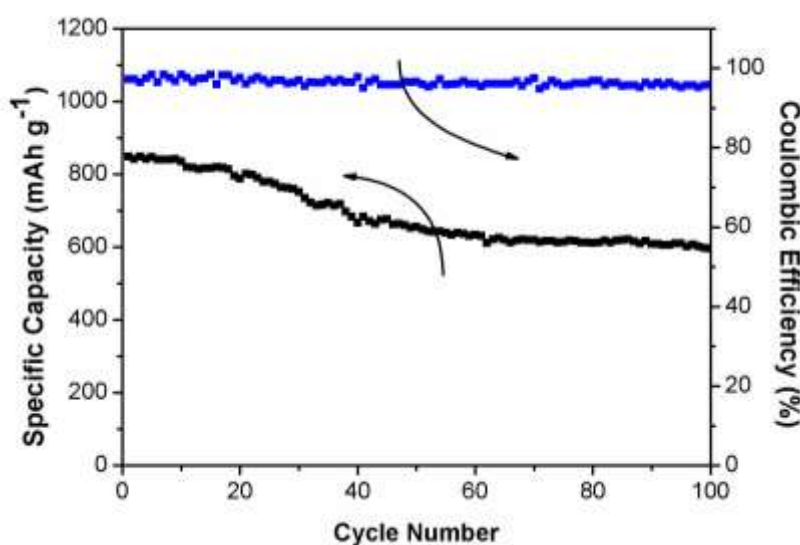


Figure 4 Cycling performances of S-TiO₂ hollow shell composites cathode.

4. Conclusion

In summary, a novel S-TiO₂ hollow shell composites cathode which consisted of small dimension TiO₂ and homogeneously distributed sulfur, has been successfully fabricated by an in-situ co-hydrolysis strategy. The S-TiO₂ hollow shell composite shows good cycling stabilities due to the in-situ sulfur formation in the TiO₂ hosts, which displays the 601 mA h g⁻¹ at 0.5 C after 100 cycles. This result demonstrates that the TiO₂ hosts play an important role in preventing the dissolution of the polysulphide anions to the electrolyte and minimizing the “shuttle effect”. Furthermore, this novel synthetic method provides an excellent choice to the future cathode design of Li-S batteries.

Acknowledgments

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