Hollow TiO$_2$ spheres hosts as efficient polysulfide adsorbents for high-performance lithium-sulfur batteries

Jinguo Zhao$^{1}$ and Heng Chen$^{1,3}$

$^1$ Department of Mechanical and Electrical Technology, Xi’Jing University, Shaanxi Xi’an 710123, People’s Republic of China
$^2$ Research and Development Center of Intelligent Control Technology, School of Science, Xi’Jing University, Xi’an 710123, People’s Republic of China
$^3$ Shaanxi Engineering Research Center of Controllable Neutron Source, School of Science, Xi’Jing University, Xi’an 710123, People’s Republic of China

E-mail: zhaojinguo@126.com

Keywords: electric vehicles, lithium-sulfur batteries, capacity fading, cycle performance

Abstract

Lithium-sulfur batteries are one of the most promising energy storage systems due to their high specific capacity and energy density. They are promising candidates for the electric vehicles. However, the severe shuttle effect of the soluble polysulfide inhibits the application of the lithium-sulfur battery. Therefore, hollow TiO$_2$ spheres (HTOS) are synthesized and used as host materials for the element sulfur. For the as-prepared S@HTOS composites, the presence of TiO$_2$ could not only restrain the shuttle effect of the polysulfide, but also the hollow sphere structure is beneficial of the structural stability. As a result, the as-prepared S@HTOS composite electrode shows high initial specific capacity and superior cycle stability.

1. Introduction

With the increasing pollution of the environment caused by car tail gas, developing electric vehicles has become a hot topic for the government all over the world [1-4]. In the component of the electric vehicles, the most important part is the energy storage system [5-7]. Among various energy storage systems, lithium-sulfur batteries have drawn much attention due to their high specific capacity (1675 mAh g$^{-1}$) and high energy density (2600 Wh Kg$^{-1}$) [8-10]. During the past decades, many researchers have devoted themselves to develop high performance lithium-sulfur batteries [11]. Great achievements have been obtained via designing perfect cathode materials and modifying the separators [12-15]. However, the poor cycle stability still inhibits the application of lithium-sulfur batteries.

On the one hand, the insulation nature of sulfur and excess dissolution of polysulfides in the electrolyte usually cause low active material utilization. On the other hand, the dissolved polysulfides can repeatedly shuttle and corrode the electrode structures, leading to weak cycle stability [16-18]. Therefore, it is urgent for the researchers to find ways to solve the problems. In fact, most reported works could hardly deal with the two issues at the same time [19, 20]. As a result, the bad electrochemical performance still exists in the lithium-sulfur batteries. To achieve this goal, the most promising method is designing a host material, which could enhance the electronic conductivity [21]. Meanwhile, this host material could provide chemical adsorption for the soluble polysulfide [22]. Among various materials, metal oxides have been employed as the host materials for sulfur in many reports, demonstrating superior electrochemical performance [23]. Cui used yolk-shell Sulphur-TiO$_2$ composites as cathode materials for the lithium-sulfur batteries with capacity decay of 0.033% per cycle after 1000 cycles [24]. Besides, other TiO$_2$-based composites were reported as cathode materials for the lithium-sulfur batteries, demonstrating superior electrochemical performance [25, 26].

Based above theme, in our work, we developed and used hollow S@TiO$_2$ spheres composites (HTOS) via solution method as cathode materials for the lithium-sulfur batteries. Compared with other reported TiO$_2$-based cathode materials, the as-prepared S@HTOS composites could not only restrain the shuttle effect of the polysulfide, but also the metal oxide TiO$_2$ could enhance the electronic conductivity. Moreover, the hollow sphere structure is beneficial for the structural stability, restraining the volume change of sulfur during
electrochemical process. As a result, the as-prepared S@HTOS composite electrode shows high initial specific capacity and superior cycle stability.

2. Experimental

2.1. Preparation of HTOS

20 ml titanium isopropyl alcohol was dissolved into 30 ml ethanol. Then, 1.2 ml ammonia was added into above mixture under stirring. After that, 10 ml hydrochloric acid was added into for reacting 30 min. Finally, the precipitate was washed and dried at 80 °C to prepare HTOS.

2.2. Preparation of the S@HTOS composites

Typically, the element sulfur was prepared by using chemical reaction method. 1.8 g sodium thiosulfate was dissolved into 30 ml ethanol. Then, 20 ml Titanium isopropyl alcohol and 1.2 ml ammonia were added into above solution under stirring. Finally, 10 ml hydrochloric acid was added into for reacting 30 min. The as-prepared S@HTOS composites were obtained at 155°C for 12 h for ensuring the uniform distribution of sulfur.

2.3. Materials characterization

The morphology of as-prepared S@HTOS composite was characterized by scanning electron microscope (EM-30 AX) and transmission electron microscope (JEM-2010HR). The structure of the S@HTOS composites was obtained by using x-ray diffraction (D8 Advance). The content of sulfur in the S@HTOS composite was tested by using thermogravimetric analysis (TA Q600). X-ray photoelectron spectroscopy (Thermo ESCALAB 250Xi) was used to judge the chemical valence of S@HTOS composites.

2.4. Electrochemical measurements

The electrochemical performance of the S@HTOS composites is tested by using Coin 2032 half battery. Typically, the electrode slurry was prepared by mixing S@HTOS composites, carbon black and polyvinylidene fluoride with ratio of 90:5:5. N-methyl pyrrolidone was used as solvent. After that, the electrode slurry was coated uniformly on the surface of Al film. Then, the as-prepared electrode film was dried at 60 °C for removing solvent. The sulfur loading of the as-prepared electrode is about 2.1 mg cm$^{-2}$. The electrolyte consists of 1.0 M LiTFSI in (DOL:DME = 1:1) with 1.0 %LiNO$_3$. The electrolyte/sulfur (E/S) mass ratio is 5:1. The package of half 2032 battery was completed in the glove box filled with Ar. The constant discharge/charge curves and rate performances were tested on battery tester (LAND CT 2001A). Electrochemical impedance spectra was obtained by using electrochemical station (CHI 660E).

2.5. Adsorption measurements

Polysulfide (Li$_2$S$_n$) solution was prepared by mixing Li$_2$S and sulfur into DME with molar ratio of 1:5 at room temperature followed by vigorous magnetic stirring. Then, the S@HTOS composites are added into the solution to observe the color change.

3. Results and discussions

Figure 1 (a) shows the TEM image of TiO$_2$ samples. It can be seen that the TiO$_2$ samples exhibit hollow spheres structure. The diameter of the hollow TiO$_2$ spheres is about 80–100 nm [27]. Figure 1(b) shows the TEM image of the S@HTOS composites. It can be observed that the as-prepared S@HTOS composites display similar hollow sphere structure with the HTOS. This could confirm the uniform immersion of element sulfur into the hollow sphere structure of HTOS [28]. The uniform distribution could ensure the steady capacity release for the S@HTOS composites as cathode materials for lithium–sulfur batteries. Furthermore, corresponding EDX element mappings was conducted for the S@HTOS composites. As shown in figures 1 (c)–(f), it can be clearly seen that the elements Ti, O and S are uniformly distributed in the whole hollow sphere structure of the S@HTOS composites [29].

To determine the crystal structure of the samples, XRD was conducted for the sulfur, HTOS and S@HTOS composites. As shown in figure 2(a), the HTOS shows typical rutile structure of TiO$_2$, showing same diffraction peaks with other literatures [30, 31]. The pure sulfur samples exhibits typical orthorhombic structure of sulfur. Finally, the as-prepared S@HTOS composites display similar diffraction peaks with the pure sulfur samples. The only difference is the intensity of the diffraction peak [32]. The S@HTOS composites shows weaker diffraction peak than the pure sulfur. This could further confirm the uniform distribution of sulfur into the hollow sphere structure of HTOS. To obtain the sulfur content in the S@HTOS composites, TG analysis was conducted for the S@HTOS composites. As shown in figure 2(b), the mass loss of the S@HTOS composites is about 80%.
Therefore, the sulfur content in the S@HTOS composites is 80%. This sulfur content is used for the calculation of specific capacity for the lithium-sulfur battery.

Figure 3(a) shows the XPS of Ti 2p for the S@HTOS composites. For Ti 2p, it can be seen that there are two peaks at 454.2 eV and 463.9 eV, respectively. These two peaks are related to the Ti 2p_{3/2} and Ti 2p_{1/2}, respectively. Moreover, there is one peak at 457.8 eV, which is ascribed to the presence of the Ti-O chemical bond [33]. To further investigate the chemical relationship between Ti and polysulfide, ultraviolet spectrum was tested for the pure sulfur and S@HTOS composites. As shown in figure 3(b), for the pure sulfur sample, there is still strong absorbance at 282 nm, which is caused by the presence of polysulfide. In terms of the S@HTOS composites, it can be seen that the absorbance becomes weaker even disappearing by using S@HTOS composites. This result proves that the S@HTOS composites could adsorb the soluble polysulfide [34]. To confirm the efficient inhibition of soluble polysulfide, the as-prepared S@HTOS composites were added into the Li_2S_6 solutions. As shown in inset figure 3(b), the pristine Li_2S_6 solution shows yellow color. After the addition of S@HTOS composites after 12 h, the solution becomes colorless clarification.

The constant discharge and charge profiles of the S@HTOS were test at 0.1 C for 100 cycles. As shown in figure 4(a), the as-prepared S@HTOS composite cathode shows initial specific capacity of 1396 mAh g^{-1} at
0.1 C. The specific capacity remains at 928 mAh g\(^{-1}\) after 100 cycles. This demonstrates that the S@HTOS composites have high specific capacity and superior cycle performance. Besides, it can be observed that the discharge curves display two voltage platforms at 2.3 V and 2.1 V, respectively. This is attributed to the electrochemical transformation from sulfur to polysulfide and Li\(_2\)S finally. Figure 4(b) shows the constant discharge and charge curves of the pure sulfur and S@HTOS composites at 0.2 C. It can be seen that the initial specific capacity for the S@HTOS composites is 1112 mAh g\(^{-1}\). While the specific capacity for the pure sulfur is only 956 mAh g\(^{-1}\). The as-prepared S@HTOS composites exhibit much higher specific capacity than the pure sulfur. The presence of metal oxides HTOS could improve the conductivity of the sulfur.

The cycle performance of the samples was tested at 0.5 C for 300 cycles. As shown in figure 5(a), the S@HTOS composites show initial capacity of 918 mAh g\(^{-1}\) at 0.5 C. The capacity remains at 716 mAh g\(^{-1}\) after 300 cycles with capacity retention of 78%. However, for the pure sulfur, its capacity fades rapidly with the improvement of the cycle numbers. In all, the S@HTOS composites exhibit excellent cycle stability, which is ascribed to the efficient inhibition of soluble polysulfide. The chemical bond Ti-S confirms the chemical absorption between HOTS and polysulfide. As a result, the utilization ratio of the active materials could be improved. Figure 5(b) compares the rate capability of the pure sulfur and S@HTOS composites at various current densities from 0.1 C to 2 C. It can be clearly observed that the S@HTOS composites display higher rate performance than the pure sulfur. Even at high current density of 2 C, the specific capacity of the S@HTOS composites could remain at 698 mAh g\(^{-1}\), demonstrating superior rate capability. While the pure sulfur suffers from severe capacity fading with the increase of the current densities from 0.1 C to 2 C.

To prove the structural stability of the S@HTOS composites, SEM image of S@HTOS was tested after 300 electrochemical cycles. As shown in figure 6(a), the S@HTOS composites still keep the hollow sphere structure without structural collapse. This has direct influence on the perfect cycle stability of the S@HTOS composites.
Moreover, corresponding element mappings of the Ti, O and S for the S@HTOS composites after 300 cycles were conducted. As shown in figures 6 (d)–(g), it can be seen that the elements Ti, O and S are still uniformly distributed into the whole S@HTOS composites.

Figure 5. (a) Cycle stability of the sulfur and S@HTOS electrode at 0.5 C. (b) Rate capability of the sulfur and S@HTOS electrode at various current densities from 0.1 C to 2 C.

Figure 6. (a) SEM image of S@HTOS after 300 cycles. (b)–(e) Corresponding element mappings of the Ti, O and S for the S@HTOS composites after 300 cycles.

Figure 7. EIS of the pure sulfur and S@HTOS electrode before cycle.

Moreover, corresponding element mappings of the Ti, O and S for the S@HTOS composites after 300 cycles were conducted. As shown in figures 6(d)–(g), it can be seen that the elements Ti, O and S are still uniformly distributed into the whole S@HTOS composites.

Figure 7 shows the electrochemical impedance spectra for the pure sulfur and S@HTOS electrode. The spectra display a semicircle in the high frequency region and an inclined line in the low-frequency range,
respectively. The semicircle corresponds to the charge transfer resistance on the electrode [36]. The smaller semicircle represents more superior electronic conductivity of the S@HTOS composites electrode.

4. Conclusions

In conclusion, the hollow S@HTOS composites are successfully prepared and employed as cathode materials for lithium-sulfur batteries. The as-prepared S@HTOS cathode shows high specific capacity of 1396 mAh g\(^{-1}\) at the current density of 0.1 C, which is much higher than the pure sulfur electrode. Besides, the S@HTOS cathode delivers specific capacity of 716 mAh g\(^{-1}\) after 300 cycles at the current density 0.5 C. Even at high current density of 2 C, the specific capacity still remains at 698 mAh g\(^{-1}\), indicating superior rate capability. The excellent electrochemical performance is attributed the hollow structure of S@HTOS, which could enhance electronic conductivity and inhibit the dissolution of polysulfide.

Acknowledgments

This study was funded by Shaanxi Key Research and Development Plan (2018GY-091).

ORCID iDs

Jinguo Zhao https://orcid.org/0000-0002-9004-5848

References

[1] Dai S J, Feng Y, Wang P, Wang H, Liang H G, Wang R F, Linkov V and Ji S 2019 Electrochim. Acta 321 134678
[2] Walle M D, Zhang M Y, Zeng K, Li Y J and Liu Y N 2019 Appl. Surf. Sci. 497 143773
[3] Yan Y, Xie J C, Zhao Y, Zhang Y, Cui N, Li C and Hao C 2019 J. Alloy Compd. 805 733
[4] Zhang L, Wu B, Li Q F and Li J F 2019 Appl. Surf. Sci. 484 1184
[5] Fan L L, Deng N P, Yan J, Li Z H, Kang W M and Cheng B W 2019 Chem. Eng. J. 369 874
[6] Qi M L, Liang X Q, Wang F, Han M S, Yin J H and Chen M H 2019 J. Alloy Compd. 799 345
[7] Zeng S B, Li X, Guo F, Zhong H and Mai Y H 2019 Electrochim. Acta 320 134571
[8] Kim M S, Kim M S, Do V D, Xia Y Y, Kim W and Cho W 2019 J. Power Sources 422 104
[9] Li S P, Han Z L, Hu W, Peng L F, Yang J Q, Wang L H, Zhang Y Y, Shan B and Xie J 2019 Nano Energ. 60 153
[10] Cheng H, Cai N and Wang M 2019 Solid State Ionics 337 12
[11] Wu L, Wang Z F, An C H and He G 2019 J. Alloy Compd. 806 881
[12] Qi W T, Wu W J, Cao B Q, Zhang Y and Wu Y C 2019 Int. J. Hydrogen Energy. 44 20257
[13] Wang C N, Sun L S, Wang X X and Wang L M 2019 Carbon 153 691
[14] Zhang W, Zhang J F, Zhao Y and Wang X 2019 Mater. Lett. 255 126595
[15] Zha C Y, Wu D H, Zhang T K, Wu J H and Chen H Y 2019 Energ. Storage Mater. 17 118
[16] Xu H F, Shi Y Z, Yang S B and Li B 2019 J. Power Sources 430 210
[17] Kim J H, Byun D J, Kim H S, Choi W C and Kim S O 2019 J. Power Sources 427 165
[18] Lu H, Chen Z, Yuan Y, Du H L, Liu J L, Liu X, Hou Z Z, Zhang K, Fang J and Qu Y H 2019 J. Electrochem. Soc. 166 A2453
[19] Li Y D, Wang Q, Zheng D G, Li W P and Wang J X 2019 J. Alloy Compd. 787 982
[20] Shen C, Andrei P and Zheng J F 2019 Electrochim. Acta 6 134948
[21] Liu G X, Feng K, Cui H T, Li J, Liu Y Y and Wang M 2020 Chem. Eng. J. 381 122652
[22] Wang K, Li W Y, Ye W K, Yin W H, Chai W W, Qu Y, Rui Y C and Tang B H 2019 J. Alloys Compd. 793 16
[23] He J R and Manthiram A 2019 Energ. Storage Mater. 20 55
[24] Seh Z W, Li W Y, Cha J J, Zheng G Y, Yang Y, Mcdowell M T, Hsu P C and Cui Y 2013 Nat. Commun. 4 1–6 https://www.nature.com/articles/ncomms3237
[25] Zhao Y, Zhu W, Chen G Z and Cairns E J 2016 J. Power Sources 327 447
[26] Li G J, Yu L, Hu H, Zhu Q C, Wang Y Y and Yu Y 2016 Electrochim. Acta. 212 59
[27] Wang C N, Liu X J, Wang R F, Linkov V and Ji S 2019 J. Alloy Compd. 807 151672
[28] Chen A, Liu W F, Hu H, Chen T, Ling B L and Liu K Y 2018 J. Power Sources 400 23
[29] Liu N, Wang L, Zhao Y, Tan T Z and Zhang Y G 2018 J. Alloy Compd. 769 678
[30] Wang J, Fu C M, Wang X F, Yao Y M, Sun M L, Wang L N and Liu T X 2018 Electrochim. Acta 292 568
[31] Park G D, Lee J Y, Piao Y Z and Kang Y C 2018 Chem. Eng. J. 355 600
[32] Zhang Y C, Jiang Y, Qi Z Y, Zhong X W and Yu Y 2018 Energy Storage Mater. 12 37
[33] Wang Y G, Lu Y, Luo R J, Zhang Y G, Guo Y, Yu Q H, Liu X M, Kim J K and Luo Y S 2018 Ceram. Int. 44 16265
[34] Zhang P G, Zhang C Y, Xue A J, Li C, Song J M and Shen Y H 2016 J. Mater. Sci. 51 3448