

Preparation and Electrochemical Performance Analysis of TiO₂/TiC@S Cathode Material for Lithium-sulfur Batteries

Yeli Yan^{1, a}, Haodong Yin^{1, b}, Fanghao Li^{1, c}, Zhibin Wang^{1, d} and Peibo Shi^{1, e}

¹School of Maritime, Shandong Jiaotong University, Weihai 264200, China

^aLyer1210@126.com, ^b290450002@qq.com, ^c772749373@qq.com,

^dwzb1786297922@163.com, ^e1014418900@qq.com

Abstract

In order to solve the problems of volume change and poor conductivity of sulfur electrode during charging and discharging of lithium-sulfur batteries, a solution method was proposed to prepare TiO₂/TiC@S composite electrode materials by sol-gel and hot-melt methods. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analyzer (TGA) and other characterization techniques were used to study and analyze the microscopic morphology, synthesis, and sulfur loading content of the prepared materials. At the same time, the adsorption capacity of LiPSs was studied by UV-Vis absorption spectroscopy, and the electrochemical properties of the materials were tested by constant current charge-discharge and cyclic voltammetry curves. The results show that the surface of TiO₂/TiC@S composites is loose and porous, the particles are evenly distributed, and the sulfur is effectively combined with the matrix material, which can effectively ensure the conductivity of the electrode material. The high adsorption capacity of TiO₂/TiC composites for LiPSs can effectively reduce the "shuttle effect" of lithium-sulfur batteries and improve the discharge specific capacity and cycle performance of the batteries. At 0.2 C, the initial capacity is as high as 847.90 mAh·g⁻¹ (1 C=1675 mAh·g⁻¹), and it remains at 411.51 mAh·g⁻¹ after 500 cycles, and its capacity retention rate reaches 48.53%, showing that Good long cycle performance.

Keywords

Lithium-sulfur batteries; TiO₂/TiC, Positive electrode material; Titanium carbide; Titanium dioxide.

1. INTRODUCTION

Lithium-sulfur batteries are considered to be very promising electrochemical energy storage devices due to their high specific capacity (1675 mAh·g⁻¹) and high energy density (2600 mAh·g⁻¹) [1]. Sulfur resources in nature are abundant and low cost, and discarded lithium-sulfur batteries have less toxic pollution to the environment and are easy to recycle. However, the commercial application of lithium-sulfur batteries is still affected by the following problems [2]: (1) The density of sulfur element and Li₂S is quite different, and a drastic volume change will occur during mutual conversion; (2) The electrical conductivity of sulfur electrode is very low. These problems will lead to the gradual loss of active material sulfur in lithium-sulfur batteries, resulting in rapid capacity decay, reduction in Coulomb efficiency, and possibly more serious self-discharge. Therefore, how to improve the conductivity of the active material, reduce the volume change during the conversion process, and obtain a sulfur cathode with higher energy density is the core issue to improve the performance of lithium-sulfur batteries. Therefore,

reasonable and effective structural design of sulfur cathode is the technical key to improve the performance of lithium-sulfur batteries [3].

To solve the above problems, functional materials such as conductive porous carbon [4], carbon nanotubes [5], metal oxides [6], and transition metal carbides [7] are used as sulfur host materials to improve the conductivity of lithium-sulfur batteries and alleviate the volume expansion effect. For example, Liu [8] has demonstrated through studies that conductive and polar titanium carbide can not only chemisorb lithium polysulfides through titanium-sulfur (Ti-S) coordination, but also optimize the lithium sulfide (Li_2S) precipitation mechanism for better oxidation reduction reaction. Cengiz E C [9] synthesized TiO_2 nanofibers with mesoporous structure by electrospinning and heat treatment, which can effectively improve the electrical conductivity of the composites and promote the utilization of sulfur, thereby improving the electrochemical performance.

In this paper, $\text{TiO}_2/\text{TiC}@S$ composite electrode materials synthesized by sol-gel method and hot-melt method were used as cathode materials for lithium-sulfur batteries. The electrochemical performance of $\text{TiO}_2/\text{TiC}@S$ as a cathode material for lithium-sulfur batteries were analyzed by physical and electrochemical characterization.

2. EXPERIMENTAL SECTION

2.1. Instruments and Reagents

Tetrabutyl titanate, titanium carbide, sublimed sulfur, lithium nitrate, tetrahydrofuran, polyvinylidene fluoride (PVDF) and N-methylpyrrolidone (NMP) were all analytically pure, purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.; Hydrochloric acid (36%) and anhydrous ethanol were purchased from Yantai Shuangshuang Chemical Co., Ltd.; Electrolyte (battery grade) was purchased from Shanghai Songjing New Energy Technology Co., Ltd.; Acetylene black (battery grade) was purchased from Denka, Japan.

Fourier transform infrared spectroscopy (FTIR) (IRAffinity-1S WL, Shimadzu, Japan) was used to scan the range of $400\text{--}4000\text{ cm}^{-1}$ in wavelength to characterize the types and approximate contents of functional groups contained in the composites. The morphology of the composite was observed by scanning electron microscope (SEM, Sigma 300). Ultraviolet-visible (UV-vis) spectra were collected using an ultraviolet spectrophotometer (UV-1800, Shimadzu, Japan) to analyze the LiPSs adsorption capacity of the samples. The battery was charged and discharged using a battery test system (CT-4008T-5 V 10 mA, Shenzhen Kejingzhida) with a voltage range of 1.6~2.8 V. The instrument used for the cyclic voltammetry (CV) test was the CHI660D electrochemical workstation produced by Shanghai Chenhua Instrument Co., Ltd. The scanning rate of CV was $0.1\text{ mV}\cdot\text{s}^{-1}$, $0.2\text{ mV}\cdot\text{s}^{-1}$, $0.5\text{ mV}\cdot\text{s}^{-1}$, and the voltage range of 1.6~2.8 V.

2.2. Preparation of TiO_2/TiC Composites

TiO_2/TiC composites were prepared by sol-gel method [10]. Add 3 mL of distilled water to 5 mL of absolute ethanol, add hydrochloric acid dropwise to adjust the pH to 3, and stir vigorously to obtain mixed solution A. Take 10 mL of anhydrous ethanol in a conical flask, slowly drop 1 mL of tetrabutyl titanate into the conical flask under magnetic stirring, and add 0.2 mL of glacial acetic acid dropwise, stir for 10 min to make it evenly mixed, it was slowly added dropwise to solution A with a dropper while stirring continuously for 30 min to obtain a TiO_2 sol solution.

Weigh a certain amount of titanium carbide and add it to the prepared TiO_2 sol solution, stir and disperse it into a suspension, and let it stand for 24 h. The suspension was suction filtered and washed 2-3 times with absolute ethanol, and the solid was collected and dried in a drying oven to constant weight. The composite material was placed in a muffle furnace, heated to 250°C at a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ at room temperature, kept at a constant temperature for 60 min, and

then continued to heat up to 500°C for 2 h. After waiting for the muffle furnace to cool to room temperature naturally, the TiO₂/TiC composite material can be obtained.

2.3. Preparation of TiO₂/TiC@S Cathode Materials

The TiO₂/TiC@S cathode material was prepared by hot melt method [11]. According to the ratio of TiO₂/TiC and sublimation sulfur at a mass ratio of 1:1, they were ground in an agate mortar for 30 min, and then placed in a vacuum drying oven for 15 h at 155°C. After cooling, grinding and sieving can obtain sulfur supported TiO₂/TiC (TiO₂/TiC@S) cathode material.

2.4. Thermogravimetric Testing of TiO₂/TiC@S

The sulfur content in the TiO₂/TiC@S cathode material was measured by a Perkin Elmer thermogravimetric analyzer (nitrogen atmosphere with a gradient of 10 °C·min⁻¹).

2.5. Lithium Polysulfide Adsorption Experiment

Lithium polysulfide adsorption experiments were carried out on TiC and TiO₂/TiC composites [12]. Li₂S₆ was prepared by adding a solution of Li₂S and sublimed sulfur in a ratio of 1:6 to tetrahydrofuran, and then stirring with a magnetic stirrer for 10 h. The solvent is 1 mol·L⁻¹ electrolyte, and the electrolyte consists of lithium bistrifluoromethanesulfonimide (LiTFSI) and ethylene glycol dimethyl ether (DME)/1,3-dioxolane (DOL) (V(DME) : V(DOL)=1:1), and 1% (mass fraction) lithium nitrate was added. Before the adsorption test, the same mass (20 mg) of TiC and TiO₂/TiC composites were vacuum dried at 70°C for 12 h. The TiC and TiO₂/TiC composites were then dispersed into glass bottles of Li₂S₆ solution (5 mL, 1 mM), stirred for 10 min, and then left to stand for 24 h. After the samples were precipitated, the color change of the solution was observed. Ultraviolet-visible (UV-vis) spectra were collected on the supernatant of the above solutions using an ultraviolet spectrophotometer to analyze the LiPSs adsorption capacity of the samples.

2.6. Assembly of the Battery

The above synthesized TiO₂/TiC@S composite electrode material, acetylene black, and binder PVDF were mixed uniformly with solvent NMP in a mass ratio of 7:2:1, coated on aluminum foil, and dried in an oven at 80°C for 6 h. Subsequently, it was cut into 12 mm diameter discs as working electrodes and transferred to a glove box for later use.

The assembly of the CR2032 coin cell was carried out in a glove box filled with high-purity argon, and the water and oxygen content in the glove box were all below 0.5 μL/L. TiO₂/TiC@S was used as the positive electrode material, pure lithium sheet (size of Φ16 mm×0.6 mm) was used as the negative electrode material, and Celgard 2400 polypropylene was used as the separator. The electrolyte is lithium bis-trifluoromethanesulfonimide (LiTFSI) and ethylene glycol dimethyl ether (DME)/1,3-dioxolane (DOL) (V(DME): V(DOL)=1:1), and add 1% (mass fraction) of lithium nitrate. The amount of battery electrolyte was 50 μL. The assembly sequence is negative electrode shell→lithium sheet→electrolyte solution→diaphragm→electrolyte solution→positive electrode plate→gasket→shrapnel→positive electrode shell. Finally, the button battery was sealed with a sealing machine and left for 24 h.

3. RESULTS AND DISCUSSION

3.1. Characterization and Analysis of TiO₂/TiC@S Composites

The synthesis process principle of TiO₂/TiC@S cathode material is shown in Figure 1. The TiO₂/TiC composite material was prepared at high temperature by the sol-gel method, and then the TiO₂/TiC@S composite electrode material was prepared for lithium-sulfur battery after sulfur loading by the hot-melt method.

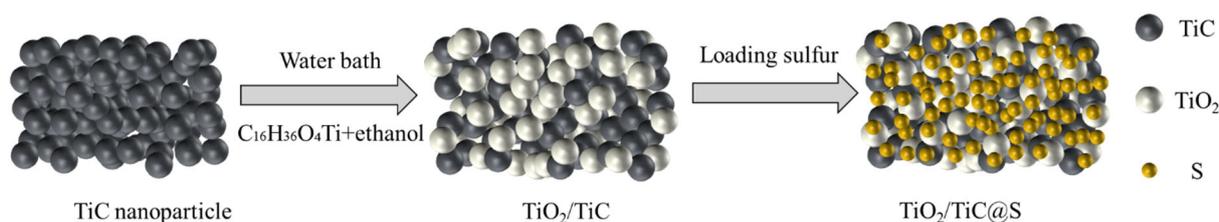


Figure 1. Schematic diagram of the preparation process of $\text{TiO}_2/\text{TiC}@S$ composites

The infrared spectra of TiO_2/TiC and $\text{TiO}_2/\text{TiC}@S$ are shown in Figure 2. The curve has a characteristic absorption peak of TiO_2 at 939 cm^{-1} , which is caused by vibration due to the existence of Ti-O bonds on the surface of TiO_2 . There is a TiC absorption peak at 1051 cm^{-1} , which is mainly due to the stretching vibration caused by the Ti-C bond. The existence of these functional groups indicates that the structural integrity of the composite matrix material has not been destroyed. Compared with the TiO_2/TiC composite matrix material, the infrared spectrum of the $\text{TiO}_2/\text{TiC}@S$ composite electrode material has one more absorption peak at about 1234 cm^{-1} , which is mainly caused by the C=S stretching vibration, which proves that S is successfully loaded on the matrix material. Moreover, the structural integrity of the composite electrode material is not damaged.

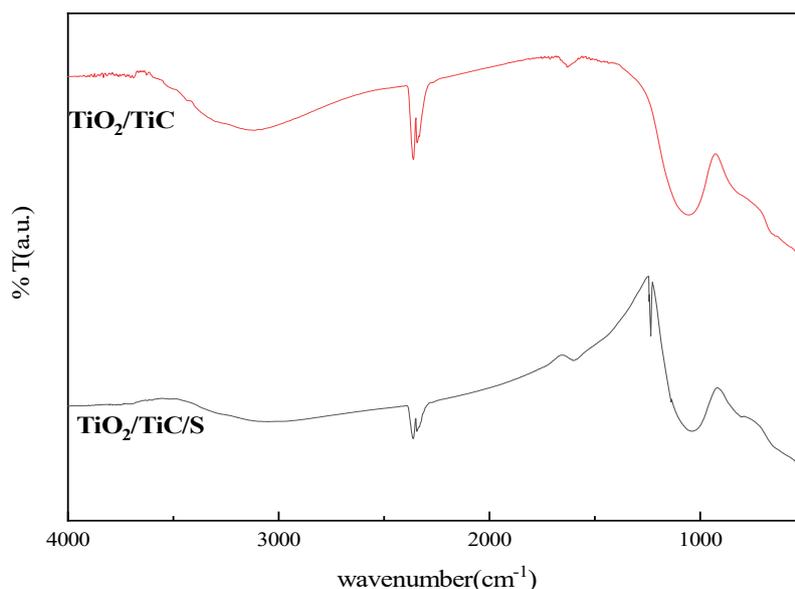


Figure 2. Infrared spectra of TiO_2/TiC and $\text{TiO}_2/\text{TiC}@S$

The scanning electron microscopes of TiO_2/TiC and $\text{TiO}_2/\text{TiC}@S$ composites are shown in Figure 3. It can be observed from Figure 3a. that after high temperature sintering, the bulk TiC surface has obvious coating and small particles, which indicates that the TiO_2/TiC composite can be successfully prepared by the sol-gel method. It can be observed from Figure 3b. that the morphology of the $\text{TiO}_2/\text{TiC}@S$ composite is different from that of the TiO_2/TiC matrix material, with irregular shape and no cracks, which indicates that sulfur has been loaded on the matrix material. Through surface analysis, it can be seen that the surface of the material is loose and porous, and the particle distribution is uniform, which can effectively alleviate the volume expansion problem caused by the charging and discharging of lithium-sulfur batteries. In addition, the surface of the TiO_2/TiC composite matrix material is not covered by a large amount of sulfur, so that the sulfur and the matrix material are effectively combined, which can ensure the conductivity of the electrode material.

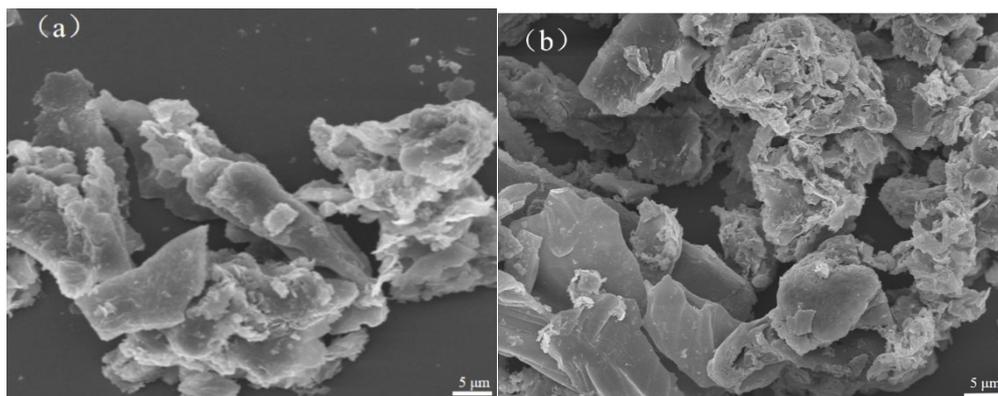


Figure 3. (a) SEM image of TiO_2/TiC . (b) SEM image of $\text{TiC-TiO}_2/\text{S}$.

Thermal analysis (TGA) tests were performed on the $\text{TiO}_2/\text{TiC@S}$ composites. As shown in Figure 4, the temperature between 100°C and 400°C is always related to the sulfur content of the material. Therefore, the sulfur content of $\text{TiO}_2/\text{TiC@S}$ can be measured from the TGA curve Huasheng to be 49.5%, which is close to the theoretical value (50%, mass fraction). It shows that the sulfur is basically filled into the pores of the material. This is consistent with the previous SEM analysis results, indicating that the sulfur loading was successful.

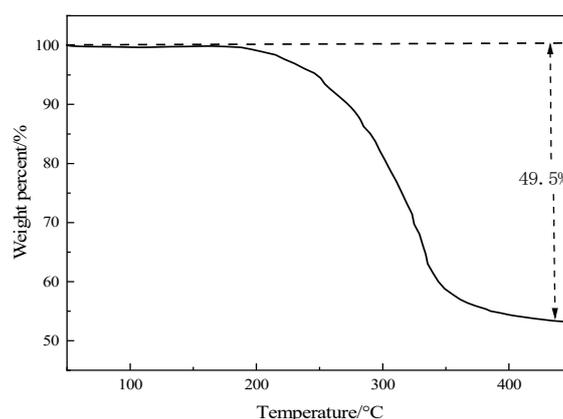


Figure 4. Thermogravimetric analysis curve of $\text{TiO}_2/\text{TiC@S}$

3.2. Adsorption Effect of TiO_2/TiC Composites on Lithium Polysulfides

In lithium-sulfur batteries, the strength of the interaction between the matrix material and the polysulfide plays a key role in suppressing the shuttle effect, which can effectively reduce the volume expansion problem during charging and discharging. To investigate the adsorption capacity of the prepared materials for lithium polysulfides, the adsorption experiments of lithium polysulfides were carried out on TiC and TiO_2/TiC composites. As shown in Figure 5a, the solution of adding TiO_2/TiC composites was almost colorless and transparent after 24 h, which intuitively indicated the best adsorption capacity for LiPSS. In contrast, the TiC -added solution remained yellow. The concentration difference of Li_2S_6 in solution after adsorption was further analyzed by UV-vis absorption spectrum, as shown in Figure 5b. The pristine Li_2S_6 solution has a strong absorption phenomenon in the visible light range of 390-500 nm. Compared with the pristine Li_2S_6 solution and the Li_2S_6 solution exposed to TiC , the absorption peak intensity of the Li_2S_6 solution exposed to the TiO_2/TiC composite was the weakest, indicating the least amount of residual Li_2S_6 in its supernatant. This result indicates that the TiO_2/TiC composite has the highest adsorption capacity for LiPSS, which is consistent with the previous direct observation.

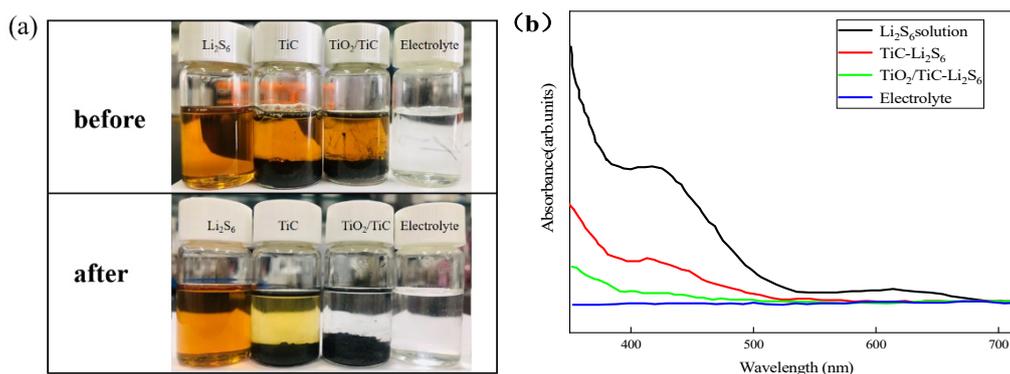


Figure 5. Adsorption experiments of lithium polysulfides (a) Optical image of Li₂S₆ static adsorption test; (b) UV-vis absorption spectra corresponding to each sample after adding TiC and TiO₂/TiC composites for 24 h.

3.3. Electrochemical Performance Analysis

In this study, the electrode reactions were analyzed by cyclic voltammetry. The TiO₂/TiC@S composites were scanned at scan rates of 0.1 mV·s⁻¹, 0.2 mV·s⁻¹ and 0.5 mV·s⁻¹ to obtain the cyclic voltammetry curves of the TiO₂/TiC@S composites, as shown in Figure 6. When the scanning speed is 0.1 mV·s⁻¹ at the potential of 2.4 V and 2.1 V, two reduction peaks appear in the composite electrode material of TiO₂/TiC@S. The first reduction peak is the conversion of S to Li₂S₈, and the second reduction peak is the conversion of Li₂S₈ to Li₂S₂ and Li₂S. In addition, the potential and shape of the redox peaks changed greatly with increasing scan rate. This is because the as-prepared TiO₂/TiC@S has excellent reversibility, good electron conduction and lithium-ion diffusion speed. In addition, the oxidation and reduction peak widths are small, even at high scan rates, the redox peak potentials still do not change much, and the oxidation and reduction peak potentials hardly change with the increase of scan rate. This indicates that the material is more excellent in charge transfer rate, reversibility and electrochemical reaction stability when used as a cathode material active material for lithium-sulfur batteries.

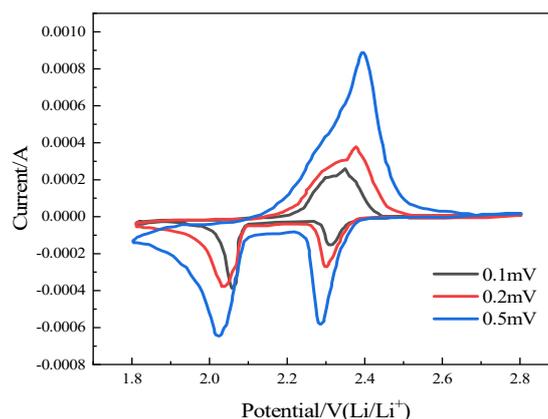


Figure 6. Cyclic voltammety curves of composite electrode materials with different scan rates

The specific capacity of the battery was analyzed by the constant current charge-discharge test, and the initial charge-discharge curves and cycle performance curves at different current rates (1 C=1675 mA·g⁻¹) and 0.2 C rate of the TiO₂/TiC@S cathode material were obtained, as shown in Figure 7. The TiO₂/TiC@S cathode material has a specific discharge capacity of 875.39 mAh·g⁻¹ at 0.1 C rate, 778.73 mAh·g⁻¹ at 0.2 C rate, and 712.52 mAh·g⁻¹ at 0.5 C rate. the discharge voltage plateau does not change significantly, and the TiO₂/TiC@S composite electrode material

has good discharge performance. This is because the $\text{TiO}_2/\text{TiC}@S$ composite electrode material has good internal structure and electrical conductivity. At a charge-discharge rate of 0.2 C, the capacity retention rate was 48.53% after 500 charge-discharge cycles. At this time, the S element was evenly distributed in the middle of the matrix material. This indicates that the $\text{TiO}_2/\text{TiC}@S$ composite electrode material ensures the stability of the electrochemical reaction and can effectively suppress the shuttle effect of polysulfides.

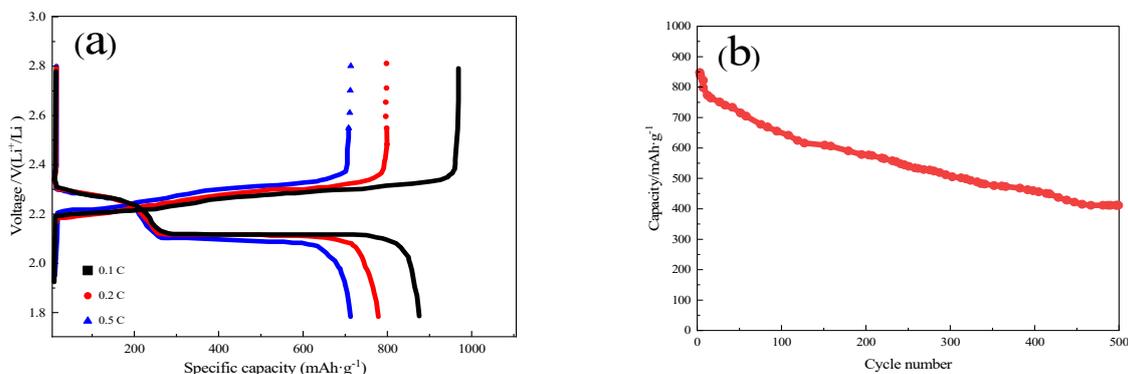


Figure 7. Charge-discharge curves at different current rates and cycle performance curves at 0.2 C rate

4. CONCLUSION

To improve the electrochemical performance and cycle life of lithium-sulfur batteries, a sulfur-supported TiO_2/TiC composite ($\text{TiO}_2/\text{TiC}@S$) was synthesized by sol-gel method and hot-melt method for lithium-sulfur battery cathode. It can be seen from SEM that the surface of $\text{TiO}_2/\text{TiC}@S$ material is loose and porous, and the particle distribution is uniform, which can effectively prevent the phenomenon of volume expansion. It is found by FTIR and TGA that sulfur is effectively combined with TiO_2/TiC material and has a high loading capacity. Combined with the results of polysulfide adsorption experiments, the TiO_2/TiC composite has a high adsorption capacity for LiPSs, which can effectively suppress the shuttle effect. Electrochemical analysis shows that the initial capacity of $\text{TiO}_2/\text{TiC}@S$ composite electrode material is as high as $847.90 \text{ mAh}\cdot\text{g}^{-1}$ ($1 \text{ C}=1675 \text{ mAh}\cdot\text{g}^{-1}$) at 0.2 C, and remains at $411.51 \text{ mAh}\cdot\text{g}^{-1}$ after 500 cycles, and its capacity retention rate reaches 48.53%, showing good long-cycle performance. This work further confirms the potential of the composite of TiO_2 materials and titanium carbide materials with excellent electrical conductivity as sulfur host materials and provides a way to develop high-performance sulfur cathode materials.

ACKNOWLEDGMENTS

This work was funded by; Introduction and Education Plan of Young Creative Talents in Universities of Shandong Province (500076); Demonstration Base of Joint Cultivation of Graduate Students in Shandong Province; Shandong Provincial Higher Educational Science and Technology Foundation, China (KJ2018BBA015).

REFERENCES

- [1] G. Zhou, H. Chen, Y. Cui: Formulating energy density for designing practical lithium-sulfur batteries, *Nature Energy*, Vol. 7 (2022) No.4, p.312-319.
- [2] S. Ohno, W. G. Zeier: Toward Practical Solid-State Lithium-Sulfur Batteries: Challenges and Perspectives, *Accounts of Materials Research*, Vol. 2 (2021) No.10, p.869-880.

- [3] Y. Cao, H. Wu, G. Li, et al: Ion selective covalent organic framework enabling enhanced electrochemical performance of lithium-sulfur batteries, *Nano Letters*, Vol. 21 (2021) No.7, p.2997-3006.
- [4] S. Y. Lee, Y. Choi, J. K. Kim, et al: Biomass-garlic-peel-derived porous carbon framework as a sulfur host for lithium-sulfur batteries, *Journal of Industrial and Engineering Chemistry*, Vol. 94 (2021) No.1, p.272-281.
- [5] M. Zheng, Y. Chi, Q. Hu, et al: Carbon nanotube-based materials for lithium-sulfur batteries, *Journal of Materials Chemistry A*, Vol. 7 (2019) No.29, p.17204-17241.
- [6] Y. Yang, Y. Wang, Y. Xia, et al: Balancing Anchoring and Diffusion for Screening of Metal Oxide Cathode Materials in Lithium-Sulfur Batteries, *The Journal of Physical Chemistry C*, Vol. 125 (2021) No.44, p.24318-24327.
- [7] Z. Pourali, M. R. Yaftian, M. R. Sovizi: Li₂S/transition metal carbide composite as cathode material for high performance lithium-sulfur batteries, *Materials Chemistry and Physics*, Vol. 217 (2018) No.1, p.117-124.
- [8] H. Liu, Y. Li, P. Zeng, et al: Multiple roles of titanium carbide in performance boosting: mediator, anchor and electrocatalyst for polysulfides redox regulation, Vol. 7455 (2021) No.12, 130744.
- [9] E. C. Cengiz, R. Demir-Cakan: TiO₂ embedded hydrothermally synthesized carbon composite as interlayer for lithium-sulfur batteries, *Journal of Solid State Electrochemistry*, Vol. 24 (2020) No.10, p.2469-2478.
- [10] W. Zayani, S. Azizi, El-Nasser K S, et al: Electrochemical behavior of a spinel zinc ferrite alloy obtained by a simple sol-gel route for Ni-MH battery applications, *International Journal of Energy Research*, Vol. 45 (2021) No.4, p.5235-5247.
- [11] X. Zhou, X. Ma, C. Ding, et al: A 3D stable and highly conductive scaffold with carbon nanotubes/carbon fiber as electrode for lithium sulfur batteries, *Materials Letters*, Vol. 251 (2019) No.4, p.180-183.
- [12] X. Hong, R. Wang, Y. Liu, et al: Recent advances in chemical adsorption and catalytic conversion materials for Li-S batteries, *Journal of Energy Chemistry*, Vol. 42 (2020) No.1, p.144-168.