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Hongqiang Wang

University of Wollongong, hw571@uowmail.edu.au

Sha Li

University of Wollongong, sl739@uowmail.edu.au

Dan Li

University of Wollongong, danli@uow.edu.au

Zhixin Chen

University of Wollongong, zchen@uow.edu.au

Hua-Kun Liu

University of Wollongong, hua@uow.edu.au

See next page for additional authors

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TiO₂ coated three-dimensional hierarchically ordered porous sulfur electrode for the lithium/sulfur rechargeable batteries

Abstract

A three-dimensional (3D) hierarchically ordered mesoporous carbon-sulfur composite slice coated with a thin TiO₂ layer has been synthesized by a low-cost process and investigated as a cathode for the lithium-sulfur batteries. The TiO₂ coated carbon sulfur composite thin slice works as a binder-free cathode without any current collectors for lithium-sulfur batteries. The hierarchical architecture provides a 3D conductive network for electron transfer, open channels for ion diffusion and strong confinement of soluble polysulfides. Meanwhile, TiO₂ (titanium dioxide) coating layer could further effectively prevent the dissolution of polysulfides and also improve the strength of the entire electrode, thereby enhancing the electrochemical performance. As a result, after TiO₂ coating, the electrode demonstrates excellent cycling performance, with a discharge capacity of 608 mAh/g at 0.2 C current rate and 500 mAh/g at 1 C current rate after 120 cycles, respectively.

Keywords

coated, three, dimensional, hierarchically, ordered, porous, sulfur, electrode, rechargeable, lithium, batteries, tio2

Disciplines

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Authors

Hongqiang Wang, Sha Li, Dan Li, Zhixin Chen, Hua-Kun Liu, and Zaiping Guo

TiO₂ coated three-dimensional hierarchically ordered porous sulfur electrode for the lithium/sulfur rechargeable batteries

Hongqiang Wang^a, Sha Li^a, Dan Li^a, Zhixin Chen^c, Hua Kun Liu^a, Zaiping Guo^{a,b,c,*}

^a Institute for Superconducting & Electronic Materials, University of Wollongong, NSW 2522, Australia
Email: zguo@uow.edu.au

^b Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, College of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, P.R. China

^c School of Mechanical, Materials & Mechatronics Engineering, University of Wollongong, NSW 2500, Australia.

ABSTRACT: A three-dimensional (3D) hierarchically ordered mesoporous carbon-sulfur composite slice coated with a thin TiO₂ layer has been synthesized by a low-cost process and investigated as a cathode for the lithium-sulfur batteries. The TiO₂ coated carbon sulfur composite thin slice works as a binder-free cathode without any current collectors for lithium-sulfur batteries. The hierarchical architecture provides a 3D conductive network for electron transfer, open channels for ion diffusion and strong confinement of soluble polysulfides. Meanwhile, TiO₂ coating layer could further effectively prevent the dissolution of polysulfides and also improve the strength of the entire electrode, thereby enhancing the electrochemical performance. As a result, after TiO₂ coating, the electrode demonstrates excellent cycling performance, with a discharge capacity of 608 mAh/g at 0.2 C current rate and 500 mAh/g at 1 C current rate after 120 cycles, respectively.

Keywords: 3D architecture, binder-free, ordered mesoporous structure, mass production

1. Introduction

Rechargeable lithium ion batteries (LIBs) have achieved great development during the past decades as power sources for various portable devices such as laptops, smart phones and electric vehicles [1-4]. However, the specific energy of the commercialized lithium ion batteries will become insufficient for the future electric vehicles due to the low capacity of conventional electrode materials. Therefore, new electrode materials with higher gravimetric and volumetric capacity should be developed. Sulfur, as one of the most abundant elements on the earth, can offer ultra-high energy density (theoretically 2567 Wh kg⁻¹) and high theoretical specific capacity (1675 mAh·g⁻¹), making it a very promising cathode candidate for the next generation batteries [5-8]. The Li-S battery system may suffer, however, from

several disadvantages, including the low conductivity of sulfur and lithium sulfide [9] as well as the large volume changes of sulfur particles during charge and discharge processes. A more significant challenge that needs to be overcome is the high solubility of the intermediate lithium polysulfides in organic electrolytes. The soluble polysulfides can diffuse from the cathode and react with the lithium anode to generate insoluble lower-order polysulfides in the form of Li_2S or Li_2S_2 , resulting in the precipitation of these species on the surface during cyclic processes [10,11]. These issues lead to the low utilization of sulfur, which is the active material, low coulombic efficiency of the sulfur cathode, and fast capacity fading [12-15].

There are two basic strategies to address this problem in terms of designing nanostructured sulfur cathodes. One is to constrain the sulfur or lithium polysulfide within a framework by using host materials, such as various types of porous carbon [16,17], hollow carbon spheres [13,18], carbon nanotubes [19,20], graphene [21,22], graphene oxide [23,24], and conductive polymers [25,26]. An alternative route is to build a physical barrier to prevent soluble polysulfides from dissolving in the organic electrolyte by forming a thin film to act as a coating on the surface of the active material. Such barrier materials include polymers [27,28] and metal oxides such as TiO_2 [29], Al_2O_3 [30], SiO_x , and VO_x [31]. Compared with a polymer coating, a metal oxide coating layer could almost completely block out-diffusion of the polysulfides and enhance the strength of the entire electrode to withstand structural damage during long cycle testing.

Herein, we employ 3D hierarchical porous carbon slice (C) as an improved confined matrix for high-level sulfur impregnation. 3D porous nanostructured carbon is highly desirable for high-performance electrode materials, as it can not only provide a continuous electron pathway to ensure good electrical contact, but also facilitates the transport of ions and electrolyte. Additionally, the well-developed 3D structure with macropores and ordered interconnected mesopores can encapsulate a large amount of sulfur, provide a large specific surface area, and facilitate fast ion transport, thus enhancing the electrochemical performance of electrodes. In order to trap the dissolved polysulfides more effectively, a TiO_2 layer was further coated on the surface of the as-prepared porous carbon-sulfur composite to obtain carbon-sulfur- TiO_2 composite (Fig.1). The as-prepared TiO_2 coated carbon-sulfur composite slice could be used as cathode directly without further electrode preparation process, therefore, no inert weight, i.e. binders and metal substrate, is included in the electrodes.

2. Experimental

2.1. Synthesis of hierarchical porous-structured carbon

The ordered mesoporous carbon-silica composite slice with macroporous architecture were synthesized through an evaporation-induced coating and self-assembly method using foam as template, as described by Zhao et al [32]. The foam was cut into thin slice (as displayed in Fig. S1 (left)) to prepare carbon-silica composite slice. Afterwards, the obtained thin slice was put into boiling 2 mol/L NaOH solution for 2 h to remove the silica to obtain the hierarchical porous carbon slice (as showed in Fig. S1 (right)).

2.2. Fabrication of TiO₂ coated porous carbon-sulfur composite electrodes

The as-prepared carbon slice and sulfur were mixed together in a weight ratio of 3:7 and heated to 160 °C in a sealed stainless steel autoclave for 24 h to facilitate sulfur diffusion into the carbon host. Then, the composite was heated at 200 °C and kept for 10 minutes under flowing argon gas (50 cm³s⁻¹) to vaporize the sulfur deposited on the outside surface of the composite (with the sample at this stage denoted as C-S). After that, titanium diisopropoxide bis(acetylacetonate) was used as the titanium precursor to coat a TiO₂ layer on the surface of the C-S composite slice according to a previous report²⁵ to obtain C-S-TiO₂ slice (denoted as C-S-TiO₂).

2.3. Characterization

The crystal phases of the resulting materials were analyzed by powder X-ray diffraction (XRD, MMA GBC, Australia). Thermogravimetric analysis (TGA) was carried out to determine the sulfur content with a TGA/differential scanning calorimetry (DSC) type instrument (METTLER TOLEDO, Switzerland) at a heating rate of 10 °C min⁻¹ from room temperature to 500 °C under argon atmosphere. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. The pore size distributions were derived from the adsorption branches of the isotherms based on the Barrett–Joyner–Halenda (BJH) model. The morphologies of the samples were investigated by field-emission scanning electron microscopy (FESEM; JEOL JSM-7500FA). Transmission electron microscope (TEM) images were collected on a JEOL 2011 200 kV instrument. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a VG Scientific ESCALAB 2201XL instrument using aluminum K α X-ray radiation.

2.4. Electrochemical measurement

The C-S and C-S-TiO₂ composite thin slices can be as a binder-free electrode for lithium-sulfur batteries that does not require any current collectors. Coin-type (CR2032) cells were assembled in an argon-filled glove box. The electrolyte used was 1 M lithium bis(trifluoromethanesulfonyl)imide in a solvent mixture of 1,3-dioxolane (DOL):

dimethoxyethane (DME) (1:1, v/v) containing LiNO_3 (1 wt%). The coin cells were galvanostatically charged-discharged between 1.5 and 3.0 V (vs. Li/Li^+) by using a cell test instrument (CT2001A, LAND, China).

3. Results and discussion

A scanning electron microscope (SEM) image in Fig. 2 shows that the carbon slice is a 3D interconnecting network composed of prism-shaped struts with macropores about 300 μm in diameter. Thermogravimetric (TG) curves of the C (inset in Fig. 2) displays a weight loss of 96 wt% from 400 to 650 $^{\circ}\text{C}$, indicating that the content of carbon is up to 96% and nearly all the silica has been removed from the carbon-silica composite.

As shown in Fig. 3(a), the X-ray diffraction (XRD) pattern of the carbon exhibits low-intensity and broad peaks, which reveal a typical amorphous structure. The pure elemental sulfur has various diffraction peaks, corresponding to an orthorhombic structure. As for the C-S and C-S- TiO_2 composites, some diffraction peaks of the elemental S are visible, although the intensities become distinctly lower and some diffraction peaks even disappear, which suggests good dispersion of the S within the mesoporous carbon hosts [33]. The sulfur content in the C-S and C-S- TiO_2 composites was determined by thermogravimetric analysis (TGA) conducted under argon atmosphere (as shown in Fig. 3(b)). The amount of sulfur in the C-S and C-S- TiO_2 composites is 60 wt% and 53 wt%, respectively.

The nitrogen adsorption-desorption isotherms of the C, C-S, and C-S- TiO_2 composites are shown in Fig. 4(a) to confirm the pore structures. The isotherms of C and the C-S composite are type IV isotherms with hysteresis at relative pressure above 0.4, which is characteristic of mesopores. Note that the insertion of sulfur leads to a significant decrease in the pore volume (from 1.26 to 0.33 cm^3/g) and Brunauer-Emmett-Teller (BET) surface area (1564 to 487 m^2/g for C and C-S composite, respectively). Meanwhile, the pore size (Fig. 4(b)) also shows a strong decrease from 7 nm to 4.5 nm, suggesting that a large portion of the pores are filled with sulfur. The C-S- TiO_2 sample, however, does not exhibit a typical isotherm, indicating that the TiO_2 layer almost completely covers the surface of the C-S composite.

Well-developed ordered mesostructure can be observed for the C sample, and the pore size estimated from the transmission electron microscope (TEM) image (Fig. 5(a)) is less than 8 nm, in good accordance with the value from the N_2 sorption isotherms. Moreover, compared to the C, the contrast and the pore size of the C-S composite are obviously decreased, and no significant amount of bulk sulfur on the external surface is detected (Fig. 5(b)). This indicates

that sulfur is homogeneously embedded in the mesopores of the sample due to the intense capillary forces. As for the C-S-TiO₂ composite, the mesopores are not as clear as those in the C and the C-S composite due to the TiO₂ coating on the surface of the C-S composite, resulting in a nearly complete lack of differentiation of the mesoporous composite (Fig. 5(c)). The scanning TEM (STEM) (Fig. 5(d)) and corresponding elemental mapping images of the C-S-TiO₂ composite demonstrate that the TiO₂ coating layer is evenly distributed on the surface of the C-S composite, which is also in good agreement with the results from the N₂ sorption isotherms.

X-ray photoelectron spectroscopy (XPS) was used to further confirm and characterize the TiO₂ coating layer on the surface of the C-S composite electrode (as displayed in Fig. S2). Three peaks positioned at 288.3, 284.9, and 283.7 eV are observed from the C1s spectrum, which could be attributed to the C=O, C-O, and C=C/C-C groups [34,35], respectively, indicating that C still retains some oxygen-containing groups from the carbonization process of the carbon precursor. The S 2p spectrum exhibits two peaks at 164.8 and 163.7 eV, corresponding to the resolved S 2p_{1/2} and S 2p_{3/2} peaks. Additionally, two peaks at 460.8 and 454.8 eV corresponding to Ti 2p_{1/2} and Ti 2p_{3/2} are shown in the Ti 2p spectrum, demonstrating the presence of Ti⁴⁺ [36]. As the penetration depth of XPS is about 10 nm, it is likely that the possible elemental sulfur signal is from places where the TiO₂ layer is thinner than 10 nm. The XPS results together with the TEM images and N₂ sorption isotherms results reveal that most of the surface area of the C-S composite is covered with a TiO₂ layer less than 10 nm in thickness.

The cycling performance of the C-S and the TiO₂ coated composite electrodes at current rates of 0.2 C and 1 C is shown in Fig. 6(a). The initial discharge capacity is up to 1168 and 1111 mAh/g for the C-S composite cathode at the 0.2 C and 1 C rates, while the TiO₂ coated electrode delivers a corresponding discharge capacity of 1128 and 1076 mAh/g, respectively, which is slightly lower than for the C-S composite cathode due to the poor conductivity of the TiO₂ layer. This can be seen from the electrochemical impedance spectra (EIS) of the C-S and C-S-TiO₂ electrodes, as shown in Fig. S3. The resistance of the C-S-TiO₂ electrode is much higher than that of the C-S electrode, resulting in lower initial discharge capacity. In contrast, it is obvious that the TiO₂ coated sample shows superior cycling performance in the long run. In the beginning, the capacities of the two samples are almost the same, however, the gap become more and more significant, especially after 20 cycles, as shown in Fig. 6(a). The discharge capacity at the 120th cycle can reach 608 mAh/g at 0.2 C and 500 mAh/g at the 1 C rate for the TiO₂ coated electrode, while the C-S composite cathode only exhibits

corresponding capacities of 450 and 370 mAh/g, respectively. This means that the mesopores of C can trap the polysulfides for a short time, but only a real capping layer can confine the polysulfides in the carbon matrix over a long span of time. Another important aspect that contributes to the stable cycling performance is that the TiO_2 layer can effectively integrate the individual components in the electrode into a whole system and enhance the strength of the entire electrode to withstand structural damage during cycling. It is noted that specific capacity of the electrode without any binders and metal substrate in our study could be comparable with that using binders and substrate in previous report [21, 23-25]. This suggests that the polysulfides are better trapped inside the carbon matrix due to the TiO_2 layer that is coated on the surface of the C-S composite.

The rate capability of the C-S and the TiO_2 coated composite electrodes at different current rates, ranging from 0.2 C to 5 C, is shown in Fig. 6(b). Compared with the C-S electrode, after TiO_2 coating, the rate performance is obviously improved, especially at high current rates. The discharge capacity at the second discharge cycle for the C-S- TiO_2 composite cathode is 1142 mAh/g at the current rate of 0.2 C, which is slightly lower than that of the C-S composite. Nevertheless, the discharge capacity for the C-S- TiO_2 electrode remains as high as 889, 770, 714, 677, and 650 mAh/g, as the current density is increased to 0.5, 1, 2, 3, and 5 C, respectively, which is much higher than the performance of the C-S composite, as shown in Fig. 6(b). Fig. 6(c) and (d) display the discharge/charge voltage profiles of C-S and C-S- TiO_2 electrodes at various rates, in which two plateaus at around 2.0 and 2.3 V are observed in the discharge process, which are typical characteristics of sulfur-carbon cathodes. Compared with previous report [13,18,37], rate capabilities (in table 1) for TiO_2 coated samples are higher. On the one hand, 3D porous hierarchical structure could support rapid electronic/ionic transport and improve electrochemical kinetics. On the other hand, a possible reason is that the TiO_2 works as an effective coating that helps to maintain the integrity of the electrode during charge and discharge processes. Together with the 3D hierarchically ordered porous carbon, it provides a real barrier to effectively trap polysulfides and minimize the dissolution of the polysulfides, thus reducing the loss of active mass in the cathode, and enhancing the electrochemical performance.

4. Conclusions

In summary, we have fabricated a 3D hierarchically ordered porous carbon-sulfur composite cathode, TiO_2 layer has been further introduced on the surface of C-S composite to help trap the dissolved polysulfides and enhance the strength of the entire electrode, which leads to notably improved performance for the lithium-sulfur battery, especially over long cycling and

at high rates. Furthermore, the 3D hierarchically ordered porous carbon slice can be mass produced in a simple way at low cost and carbon sulfur composite thin slice could work as a binder-free cathode without any current collectors for lithium-sulfur batteries, which makes our S-based electrode highly promising for practical application in lithium-sulfur batteries.

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Table 1. Rate performance of Lithium-sulfur cathodes with different nanostructures

different nanostructures	0.1 C	0.2 C	0.5 C	1 C	2 C	3 C	5 C
TiO ₂ coated 3D hierarchically porous architecture [this study]	—	1142	889	770	714	677	650
porous hollow carbon-sulfur composites [13]	—	1150	970	750	600	450	820
sulfur in double-shelled hollow carbon spheres [18]	1080	820	550	350	—	—	—
graphene-based sandwich-type architecture [37]	—	1146	856	743	502	—	—

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FIGURES

Fig.1 Pictorial representation of the structure of C-S-TiO₂ composite.

Fig. 2. SEM image of as-prepared carbon. Inset shows the TG curve of C under air atmosphere to determine the content of carbon.

Fig. 3. (a) XRD patterns of C, S, C-S, and C-S-TiO₂ composites, and (b) TG curves of C-S and C-S-TiO₂ composites under argon atmosphere.

Fig. 4. (a) N₂ sorption isotherms and (b) pore-size distributions of C and C-S composite.

Fig. 5. TEM images of (a) C, (b) C-S composite, (c) C-S-TiO₂ composite, and (d) STEM image of C-S-TiO₂ and corresponding elemental mapping images of C, S, and Ti.

Fig. 6. (a) Cycling performances of C-S and C-S-TiO₂ electrodes at current densities of 0.2 C and 1 C; (b) rate capabilities of C-S and C-S-TiO₂ electrodes; discharge/charge voltage profiles of (c) C-S and (d) C-S-TiO₂ electrodes at various rates.