SPECIAL TOPIC: Graphene Oxides towards Practical Applications

Multifunctional V_3S_4 -nanowire/graphene composites for high performance Li-S batteries

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ABSTRACT Lithium sulfur (Li-S) batteries have been regarded as a promising next-generation energy storage system with high theoretical specific capacity and energy density, but still facing challenges. In order to make Li-S batteries more competitive, combination of trapping sites and electrocatalytic properties for polysulfides is an effective way to improve the battery performance. In this study, we prepare a type of multifunctional V_3S_4 -nanowire/graphene composites (V_3S_4 -G) by uniformly dispersing V_3S_4 nanowires on the graphene substrate. This structure contributes to the sufficient exposure of multifunctional V_3S_4 active sites which can anchor polysulfides and accelerate reaction kinetics. Thus, the Li-S batteries based on the multifunctional V_3S_4 -G sulfur cathode deliver a stable cycling performance and good rate capability. Even at sulfur loading of 3 mg cm^{-2} , the V_3S_4 -G sulfur cathode possesses a low capacity decay rate of 0.186% per cycle at 0.5 C.

Keywords: Li-S batteries, V_3S_4 -G, trapping sites, electrocatalytic properties

INTRODUCTION

With the growing demand for energy storage devices with high energy density, lithium sulfur (Li-S) batteries have been regarded as a promising new generation battery system possessing both high specific capacity and energy density [1,2]. In addition, sulfur as the active material of cathode has abundant resources and low cost, which makes Li-S battery more competitive [3]. However, there are some issues that impede the commercialization of Li-S batteries. For instance, both of the sulfur and the reaction product Li_2S are electronic and ionic insulation so that

the Li-S battery has limited utilization of active materials [4–6]. Besides, the volume change of sulfur during the cycle process leads to the pulverization of the electrode and damages the cathode structure [7,8]. Moreover, the lithium polysulfides, produced during the charge and discharge process, can dissolve in the ether-based electrolytes traveling through the separator [9]. The dissolved lithium polysulfides can react with the lithium metal anode resulting in low coulombic efficiency and fast capacity decay [10–12].

To date, there have been large amounts of studies focusing on the aspects of the electrode structure, the membrane design and the use of novel types of binders to improve the battery performance [13–17]. As for the Li-S batteries, the reasonable design of the cathode framework is the critical factor to promote the development of such high energy storage system. The carbon materials with high conductivity and high specific surface area are suitable to act as the sulfur host to encapsulate sulfur and buffer the volume change [18–23]. However, the non-polar carbon-carbon bond has weak affinity with lithium polysulfides and the “shuttle effects” cannot be restricted effectively [24,25]. The improvement of the Li-S battery performance should consider the construction of chemical trapping sites to anchor lithium polysulfides. The inorganic materials with polar surface can interact with lithium polysulfides strongly to restrain the loss of active materials [26–31]. For instance, the vanadium-based materials can anchor lithium polysulfides tightly and improve the redox kinetics [32–34]. Because of such synergistic effects, the Li-S batteries exhibit stable cycling

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performance. Even though the utilization of inorganic materials can improve the cycling stability of Li-S battery, the limited specific surface area of those substrates have an adverse effect on the increase of areal sulfur loading [35]. In order to address this issue, constructing inorganic materials-carbon based composites is an effective method, which can not only improve the conductivity and accommodate the elemental sulfur, but also provide strong chemical interaction sites for polysulfides. The utilization of carbon nanotubes threaded hollow Co_3S_4 nanoboxes and NiS nanoparticles distributing on carbon hollow spheres as cathode can contain sulfur and suppress the diffusion of lithium polysulfides [36,37]. According to these studies, it can conclude that the reasonable design of sulfur cathode should combine all the features including high conductivity, enough void space to accommodate the sulfur and strong chemical interactions with lithium polysulfides.

Herein, inspired by the above studies, we prepared a type of V_3S_4 -nanowire/graphene composites (V_3S_4 -G) as multifunctional sulfur host for high performance Li-S batteries. Because of the electrostatic interaction between the polyaniline and the graphene oxide (GO), the precursors of the V_3S_4 -G can distribute uniformly on the surface of GO. After heat treatment, the V_3S_4 nanowires are uniformly dispersed on the surface of graphene without obvious agglomeration. Compared with other reported studies which have utilized vanadium sulfide/graphene composites in Li-S batteries, the V_3S_4 -G with unique porous nanowire structure possesses higher specific surface which is favorable to high sulfur loading content reaching 78 wt% [38,39]. Meanwhile, such structure of the V_3S_4 -G contributes to the full exposure of multifunctional V_3S_4 active sites which have strong adsorption ability to lithium polysulfides and can accelerate electrochemical reaction kinetics to enhance the utilization of active materials. Owing to the advantages of V_3S_4 in anchoring and catalyzing lithium polysulfides, the multifunctional V_3S_4 -G cathode can achieve outstanding battery performance. At sulfur loading of 3 mg cm^{-2} , the Li-S batteries with multifunctional V_3S_4 -G cathode perform a stable cycling performance with a low capacity decay rate of 0.186% per cycle at 0.5 C and good rate capability.

EXPERIMENTAL SECTION

Preparation of GO

The synthesis process of GO was similar to the modified Hummer's method [40]. Briefly, 1 g of graphite was

mixed with 0.5 g NaNO_3 in 23 mL of concentrated sulfuric acid and stirred for 24 h. In the next step, the mixture was kept in an ice bath with the addition of 3 g of KMnO_4 power below 5°C . Then the mixture was heated and stirred for 2 h. After that, 45 mL of deionized water was added to the obtained mixture under vigorously stirring. 10 mL 30% H_2O_2 was poured into 140 mL of deionized water and the resulting solution was poured into the above mixture. Then 300 mL 10% HCl was used to wash the sediment in the container. Finally, the sediment was washed with deionized water for several times, and then freeze-dried.

Preparation of V_2O_5 -W

The V_2O_5 nanowires (160 mg) which were synthesized according to the reported method were dispersed in 80 mL of deionized water and sonicated for 20 min [41]. 1.0 g of Pluronic F127 was dissolve in 3 mL ethanol followed by sonication until the solution became clear. Then the above solutions were mixed. After that, 80 μL of aniline and 0.4 mL of concentrated HCl were added to 20 mL of water, which was poured into the mixture of V_2O_5 nanowires and Pluronic F127. After 6 h stirring, the obtained green sediment was collected by centrifugation and washed with deionized water for thrice. Then the sediment was freeze-dried. The dry green powder was annealed at 800°C for 2 h under the atmosphere of Ar/H_2 to obtain V_2O_5 -W.

Preparation of V_3S_4 -W

The synthesis process of V_3S_4 -W was similar to that of V_2O_5 -W, except that the green precursor was annealed at 800°C for 2 h under the atmosphere of Ar/H_2 with the crucible containing sulfur powders in front of it.

Preparation of V_3S_4 -G

GO (100 mg) and 160 mg of V_2O_5 nanowires were dispersed in 80 mL of deionized water followed by sonication for 20 min. 1.0 g of Pluronic F127 was dissolved in 3 mL of ethanol followed by sonication until the solution became clear. Then the above solutions were mixed together. After that, 80 μL of aniline and 0.4 mL of concentrated HCl were added into 20 mL water. The resulting solution was poured into the mixture of GO/ V_2O_5 nanowires and Pluronic F127. After 6 h stirring, the obtained green sediment was collected by centrifugation and washed with deionized water for thrice. Then the sediment was freeze-dried and the obtained green powder was annealed at 800°C for 2 h under the atmosphere of Ar/H_2 with the crucible containing sulfur powders in

front of it.

Polysulfide adsorption test

The Li_2S was mixed with sulfur powder under a molar ratio of 1:5 dissolving in 1,2-dimethoxyethane to get Li_2S_6 solution with a concentration of 1 mol L^{-1} . Then the concentrated Li_2S_6 solution was diluted to 1 mmol L^{-1} and the V_2O_3 -W, V_3S_4 -W and V_3S_4 -G were added into the diluted Li_2S_6 solution and kept statically.

Materials characterization

The scanning electron microscopy (SEM) images were carried out by a field-emission scanning electron microscope (Merlin Compact, ZEISS). The transmission electron microscopy (TEM) images were characterized by an FEI Tecnai T20 at 200 kV. The X-ray diffraction (XRD) analysis and the X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Rigaku DMAX-2400 X-ray diffractometer equipped with Cu K α ($\lambda = 1.5405 \text{ \AA}$) radiation and monochromatized Al K α radiation (Axis Ultra DLD, Kratos Analytical Ltd.) respectively. The Brunauer-Emmett-Teller (BET) measurement was utilized to analyze the specific surface area. The sulfur loading content was investigated by thermogravimetric analysis (TGA) under N_2 atmosphere (Q600 Simultaneous DSC-TGA). The UV-2550 was utilized to perform the ultraviolet/visible absorption spectra before and after adding V_2O_3 -W, V_3S_4 -W and V_3S_4 -G powder into the Li_2S_6 solution respectively.

Electrochemical characterization

The sulfur composite was prepared by mixing V_2O_3 -W, V_3S_4 -W or V_3S_4 -G with sulfur under a mass ratio of 1:4 at 155°C for 12 h. Then the working electrode was prepared by mixing the sulfur composite, Ketjen black, and polyvinylidene fluoride (PVDF) with the mass ratio of 7.5:1.5:1 pasted on carbon cloth. The areal sulfur loading mass of the working electrode was above 1 mg cm^{-2} . The CR-2032 coin cells were assembled by using lithium metal as counter electrode and 1 mol L^{-1} lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 2 wt% LiNO_3 in the solution of 1,2-dimethoxyethane and 1,3-dioxolane with the volume ratio of 1:1 as the electrolyte. The Bio-logic VSP multichannel potentiostatic-galvanostatic system was utilized to perform cyclic voltammetry (CV) in the voltage range of 1.8–2.8 V vs. Li^+/Li at a scan rate of 0.1 mV s^{-1} . The cycling performance of the Li-S batteries was characterized by LAND CT 2001A in the voltage range of 1.8–2.8 V vs. Li^+/Li .

Assembly of symmetrical cell

The V_2O_3 -W, V_3S_4 -W and V_3S_4 -G were used as electrodes to assemble symmetrical cell without addition of sulfur respectively. The material and the PVDF binder were mixed under a weight ratio of 3:1. The electrolyte in the symmetrical cells contained 0.5 mol L^{-1} Li_2S_6 , 1 mol L^{-1} LiTFSI and 2 wt% LiNO_3 in the solution of 1,2-dimethoxyethane and 1,3-dioxolane with the volume ratio of 1:1. The Bio-logic VSP multichannel potentiostatic-galvanostatic system was utilized to perform CV of symmetrical cells in the voltage range of -0.7 – $0.7 \text{ V vs. Li}^+/\text{Li}$ at a scan rate of 3 mV s^{-1} . The Bio-logic VSP multichannel potentiostatic-galvanostatic system was also used to perform the electrochemical impedance spectroscopy (EIS) tests of the symmetrical cells between 1 mHz to 1 MHz with the amplitude of 5 mV.

Theoretical analysis

The density functional theory (DFT) calculations were utilized to calculate the adsorption binding energy between vanadium materials (V_2O_3 and V_3S_4) and Li_2S_6 implemented in the Vienna *ab initio* Simulation Package (VASP) [32,42]. The exchange correlation energy was described by Perdew-Burke-Ernzerhof functional and the cutoff energy of the plane wave basis was set at 400 eV [43]. The k -point mesh $1 \times 2 \times 3$ was carried out for V_2O_3 and V_3S_4 . The following equation was utilized to define the adsorption binding energy as $E_a = E_t - E_h - E_s$, where E_t was the total energy of the vanadium materials after adsorbing Li_2S_6 , E_h was the energy of the isolated vanadium material (V_2O_3 or V_3S_4) and E_s was the energy of the isolated Li_2S_6 molecule.

RESULTS AND DISCUSSION

The synthesis of graphene-based vanadium composites is presented in Fig. 1. Briefly, the aniline *in situ* polymerizes on the V_2O_5 nanowires forming polyaniline coated nanowires (PANI-N) in Fig. 1a. Meanwhile, the resulting nanowires are dispersed on the surface of GO simultaneously as shown in Fig. S1. The preparation of the V_3S_4 -G is shown in Fig. 1b, which is under the atmosphere of Ar/H_2 with the crucible containing sulfur powders. The H_2 acts as a reagent reacting with sulfur gas in high temperature to obtain H_2S which keeps sulfuration progressing successfully [44,45]. The XRD pattern of V_3S_4 -G is displayed in Fig. S2. The diffraction peaks located at 34.8° , 44.5° , and 45.3° confirm that we have successfully synthesized V_3S_4 (PDF#73-2026) after annealing. Without GO, we can still get the V_2O_3 (PDF#71-0342) or V_3S_4 (PDF#73-2026) with crystalline features, as displayed in

Figure 1 (a) The illustration of the synthetic procedure for V_3S_4 -G. (b) The synthesis method to prepare V_3S_4 -G in the furnace.

Fig. S3.

According to the SEM images of V_3S_4 -G in Fig. S4, the nanowires are dispersed on the flake-like graphene sheets. Comparison with the V_3S_4 -G, V_2O_3 -W and V_3S_4 -W show some larger particles, as shown in Fig. S5. The TEM images reveal that the V_2O_3 -W and V_3S_4 -W have similar structures, as shown in Fig. 2a, b. Without GO, the agglomeration of nanoparticles in V_2O_3 -W and V_3S_4 -W cannot be entirely avoided and the nanowires also tend to be agglomerated. As for the V_3S_4 -G in Fig. 2c, the nanoparticles are uniformly dispersed on the nanowires which are scattered on the wavy surface of the graphene sheets without agglomeration. The elemental mappings in Fig. 2d show the distribution of sulfur, vanadium and carbon element in the V_3S_4 -G. Therefore the existence of graphene sheets contributes to the uniform dispersion of V_3S_4 nanowires. In addition, the Pluronic F127 acts as the template and its effect was investigated as well. Without Pluronic F127, the nanoparticles will agglomerate and unevenly distribute as shown in Fig. S6. However, other samples with Pluronic F127 have smaller nanoparticles with more even distribution on the nanowires.

The nitrogen adsorption-desorption isotherms and pore size distribution curves of V_2O_3 -W, V_3S_4 -W, and V_3S_4 -G are displayed in Fig. 2e, f. Both of V_2O_3 -W and V_3S_4 -W have limited specific surface area and pore volume as exhibited in Table S1. However, it is worth noting that the specific surface area and pore volume of V_3S_4 -G are larger for the addition of graphene sheets. Meanwhile, the mesopores in the V_3S_4 -G are more available to accommodate sulfur compared with the V_2O_3 -W and V_3S_4 -W which only have limited specific surface area and lack

of porous structure. The XPS result in Fig. S7 displays that the V_2O_3 -W contains the elements of C, O, N and V. As for the XPS survey spectra of V_3S_4 -W and V_3S_4 -G in Fig. S8, both of them show the presence of elemental peaks including C 1s, N 1s, O 1s, V 2p and S 2p. Compared with the XPS survey spectrum of V_3S_4 -W, the C 1s peak in V_3S_4 -G XPS survey is more distinct. The XPS measurement is a surface analysis and the presence of graphene sheets where the V_3S_4 nanowires are dispersed has an influence on the intensity of C 1s peak.

The abilities of V_2O_3 -W, V_3S_4 -W and V_3S_4 -G to adsorb lithium polysulfides were investigated by polysulfide adsorption test as shown in Fig. 3a. After adding materials into the Li_2S_6 solution, the polysulfides solution which contains V_2O_3 -W powders completely fades and the color of solutions containing V_3S_4 -W and V_3S_4 -G also becomes almost clear. The ultraviolet/visible spectra display that the concentrations of polysulfides all decline after adding V_2O_3 -W, V_3S_4 -W and V_3S_4 -G. In addition, the V_2O_3 -graphene composites (V_2O_3 -G) can also interact with lithium polysulfides strongly, as shown in Fig. S9. Thus, all of the results indicate that the affinity between the materials and lithium polysulfides is strong and the presence of V_2O_3 and V_3S_4 can strengthen the interaction with lithium polysulfides. Moreover, we explored the chemical interactions of the materials including V_2O_3 -W, V_3S_4 -W and V_3S_4 -G with lithium polysulfides by XPS measurements. After putting V_2O_3 -W powders into the polysulfide solution, the high resolution of Li 1s spectrum (Fig. 3b) can be deconvoluted into two peaks corresponding to the presence of Li-O and Li-S bonds [46,47]. In the high resolution V 2p spectrum of V_2O_3 -W, the V

Figure 2 The TEM images of (a) V_2O_3 -W, (b) V_3S_4 -W, and (c) V_3S_4 -G. (d) The elemental mapping of V_3S_4 -G. (e) Nitrogen adsorption-desorption isotherms, and (f) pore size distributions of the V_2O_3 -W, V_3S_4 -W, and V_3S_4 -G.

$2p_{1/2}$ and V $2p_{3/2}$ have shifted to lower binding energy after adsorbing lithium polysulfides as shown in Fig. S10. Correspondingly, the presence of thiosulfate and polythionate in the S 2p spectrum of the V_2O_3 -W/ Li_2S_6 (Fig. S11) can further confirm the strong interactions between V_2O_3 -W and lithium polysulfides [48]. Thus, the formation of Li-O bonds and the change of V 2p spectrum confirm that the V_2O_3 -W can anchor polysulfides effectively. In Fig. S12, the peaks of C-S and V-S can be observed in both of V_3S_4 -W and V_3S_4 -W/ Li_2S_6 S 2p spectra [49]. In addition, the new peaks located at 164.5 and 163.0 eV in the S 2p spectrum of V_3S_4 -W/ Li_2S_6 are attributed to the existence of carbon-bonded bridging sulfur species (S_B -C) and terminal sulfur atoms (S_T), respectively [24,50]. Compared with the S 2p spectrum of lithium polysulfides reported, the peak of S_T shifts to higher binding energy confirming that the V_3S_4 -W has strong affinity with lithium polysulfides [24,50]. Meanwhile, the shift of V^{2+} and V^{3+} peaks to lower binding energy can also be observed in V 2p spectra of V_3S_4 -W (Fig. S13) and V_3S_4 -G (Fig. 3c). The above XPS results can evidence the strong interactions between V_3S_4 and lithium polysulfides. In addition, the binding energy of V_2O_3 and V_3S_4 with lithium polysulfides was investigated by density functional theory (DFT) as shown in Fig. 3d, e.

The binding energy between V_2O_3 and Li_2S_6 is 3.93 eV forming O-Li and V-S bonds. However, the binding energy between V_3S_4 and Li_2S_6 is 1.20 eV forming S-Li and V-S bonds. These results confirm that the V_2O_3 has better affinity with lithium polysulfides, which is attributed to the stronger polar surface of metal oxides than that of metal sulfides. Though the binding energy between V_3S_4 and Li_2S_6 is lower, the V_3S_4 can also anchor lithium polysulfides tightly which has been proved by polysulfide adsorption tests. Thus, on the basis of the experimental and theoretical results, both of the V_2O_3 and V_3S_4 can be the trapping sites to restrain the migrant of lithium polysulfides, while the V_2O_3 can anchor polysulfides more effectively.

In order to investigate the catalytic properties of V_2O_3 -W, V_3S_4 -W and V_3S_4 -G for lithium polysulfides, the symmetrical cells were assembled with the identical material as both working and counter electrodes. The CV measurements were taken to evaluate the catalytic properties of each material in symmetrical cells. The results of CV tests for the symmetrical cells without any addition of lithium polysulfides in its electrolyte are shown in Fig. 4a. On the basis of these CV curves, the contribution of capacitive current can be neglected [51]. When the electrolyte containing lithium polysulfides is utilized in the

Figure 3 (a) The ultraviolet/visible absorption spectra of Li_2S_6 solution before and after adding $\text{V}_2\text{O}_3\text{-W}$, $\text{V}_3\text{S}_4\text{-W}$ and $\text{V}_3\text{S}_4\text{-G}$. The inset photograph displays the Li_2S_6 solution and the Li_2S_6 solution after adding $\text{V}_2\text{O}_3\text{-W}$, $\text{V}_3\text{S}_4\text{-W}$ and $\text{V}_3\text{S}_4\text{-G}$. (b) The high resolution of Li 1s spectrum of the $\text{V}_2\text{O}_3\text{-W}/\text{Li}_2\text{S}_6$. (c) The high resolution of V 2p spectrum of the $\text{V}_3\text{S}_4\text{-G}$ before and after putting into lithium polysulfide solution. The top and side view about the adsorption of Li_2S_6 on (d) the V_2O_3 (104), and (e) the V_3S_4 (112).

symmetrical cells, the electricity has increased significantly in the second cycle of CV profiles in Fig. 4b, which means that all the materials ($\text{V}_2\text{O}_3\text{-W}$, $\text{V}_3\text{S}_4\text{-W}$ and $\text{V}_3\text{S}_4\text{-G}$) can promote the conversion of lithium polysulfides [52–54]. Comparing the catalytic property of $\text{V}_2\text{O}_3\text{-W}$ with that of $\text{V}_3\text{S}_4\text{-W}$, the CV profile of $\text{V}_3\text{S}_4\text{-W}$ has larger current indicating that the $\text{V}_3\text{S}_4\text{-W}$ can facilitate the transformation of lithium polysulfides more effectively. Furthermore, the redox peaks of $\text{V}_3\text{S}_4\text{-G}$ in the CV profile are more conspicuous in comparison with those of $\text{V}_3\text{S}_4\text{-W}$, which suggests that the $\text{V}_3\text{S}_4\text{-G}$ has the best electrocatalytic performance to accelerate the conversion of lithium polysulfides among the materials. In addition, the EIS was utilized to investigate the charge transfer resistance of $\text{V}_2\text{O}_3\text{-W}$, $\text{V}_3\text{S}_4\text{-W}$ and $\text{V}_3\text{S}_4\text{-G}$ in the symmetrical cells. In Fig. 4c, the minimum charge transfer resistance of $\text{V}_3\text{S}_4\text{-G}$ suggests that the conversion process of lithium polysulfides can be effectively improved corresponding to the results of CV tests in the symmetrical cells [55,56]. Thus, it can be deduced that the

favorable affinity and improved reaction kinetics for lithium polysulfides of the $\text{V}_3\text{S}_4\text{-G}$ can deliver a good performance in the following electrochemical measurements.

The sulfur loading content of $\text{V}_3\text{S}_4\text{-G}/\text{S}$ is 78 wt% investigated by TGA tests as shown in Fig. 4d. The sulfur loading content of $\text{V}_2\text{O}_3\text{-W}/\text{S}$ and $\text{V}_3\text{S}_4\text{-W}/\text{S}$ is 83 and 80 wt%, respectively (Fig. S14). Meanwhile, the uniform dispersion of sulfur on the $\text{V}_3\text{S}_4\text{-G}/\text{S}$ is identified by elemental mapping in Fig. S15. We can also find that the dispersion of sulfur element is approximately consistent with the vanadium element suggesting that the sulfur is infiltrated into the vanadium sulfide nanowires. The second cycle of CV curves of $\text{V}_2\text{O}_3\text{-W}/\text{S}$, $\text{V}_3\text{S}_4\text{-W}/\text{S}$, and $\text{V}_3\text{S}_4\text{-G}/\text{S}$ are displayed in Fig. S16. In the CV results, the Li-S battery with $\text{V}_3\text{S}_4\text{-W}/\text{S}$ cathode has cathodic peaks located at 2.01 and 2.29 V, while the battery with $\text{V}_2\text{O}_3\text{-W}/\text{S}$ has cathodic peaks situated at lower potential. Considering the similar structure of both $\text{V}_2\text{O}_3\text{-W}$ and $\text{V}_3\text{S}_4\text{-W}$, we can speculate that the V_3S_4 can improve the

Figure 4 (a) The CV curves of the symmetrical cells without Li_2S_6 (LiPs represent the lithium polysulfides). (b) The second cycle of CV curves of symmetrical cells containing Li_2S_6 . (c) EIS spectra of the symmetrical cells with Li_2S_6 electrolyte. (d) The sulfur loading content of V_3S_4 -G/S. (e) The cycling performance at 0.3 C, and (f) rate capability ranging from 0.3 to 3 C of the V_2O_3 -W/S, V_3S_4 -W/S, and V_3S_4 -G/S.

reaction kinetics more effectively. It is worth noting that the cathodic peaks of the V_3S_4 -G/S cathode have the largest potential suggesting that the V_3S_4 -G can further accelerate the conversion of lithium polysulfides. The presence of the graphene substrates in the V_3S_4 -G is beneficial to avoiding the agglomeration of nanowires leading to much more exposure of active sites. Thus, the kinetics of the Li-S batteries with V_3S_4 -G/S cathode can be further improved.

The cycling performance and rate capability of each material were evaluated by the following measurements. The initial discharge capacity of V_3S_4 -G/S is 1370 mA h g^{-1} , while both of V_2O_3 -W/S and V_3S_4 -W/S have lower discharge capacity of 970 and 1001 mA h g^{-1} respectively at 0.3 C in Fig. 4e. After 100 cycles, the discharge capacity of V_3S_4 -G/S still remains at 936 mA h g^{-1} maintaining better performance, while the discharge capacity of V_2O_3 -W/S or V_3S_4 -W/S decreases to 695 or 707 mA h g^{-1} respectively. Meanwhile, the rate performances of V_2O_3 -W/S, V_3S_4 -W/S, and V_3S_4 -G/S are displayed in Fig. 4f with the current density ranging from 0.3 to 3 C. In comparison with V_3S_4 -W/S and V_2O_3 -W/S cathodes, the V_3S_4 -G/S delivers the superior rate capability with the discharge capacity of 1278, 974, 876, 806, and 741 mA h g^{-1} at the current density ranging from 0.3

to 3 C. It can also find that the V_2O_3 -W/S and V_3S_4 -W/S have similar discharge capacity at low current densities. However, when the current density increases to 1 and 2 C, the discharge capacity of V_3S_4 -W/S is much higher, which means the V_3S_4 -W can improve the reaction kinetics more effectively corresponding to the results of the symmetrical cells and the CV tests. The improved battery performance of V_3S_4 -G/S means that the presence of graphene sheets with the even distribution of active sites for lithium polysulfides is favorable to keep cycling performance stable and enhance the kinetics for Li-S batteries.

On the basis of above discussion, the existence of the multifunctional V_3S_4 which can adsorb lithium polysulfides and accelerate their conversion is beneficial to improving the battery performance. More importantly, those multifunctional active sites are supposed to be fully exposed so that the battery performance can be further improved. With the presence of graphene substrates, the V_3S_4 nanowires can uniformly distribute without agglomeration. As a result, the active sites which act as both polysulfides trapping sites and electrocatalysts can be sufficiently exposed in the V_3S_4 -G (Fig. 5a). When sulfur loading mass of the V_3S_4 -G/S raises to 3 mg cm^{-2} (V_3S_4 -G/S-3), the first three cycles of the V_3S_4 -G/S-3 CV curves in Fig. 5b are almost overlapping which suggests the good

Figure 5 (a) The interactions between V₃S₄-G and lithium polysulfides. (b) The first three CV curves of the V₃S₄-G/S-3. (c) The cycling performance of the V₃S₄-G/S-3 at 0.5 C.

cycling stability at high sulfur loading mass. As for the cycling performance of V₃S₄-G/S-3 in Fig. 5c, the initial capacity of V₃S₄-G/S-3 is 1024 mA h g⁻¹ displaying a low capacity decay rate of 0.186% per cycle after 200 cycles at the current density of 0.5 C. Moreover, the Li-S batteries based on the V₃S₄-G cathode also perform well compared with several reported studies (Table S2). Meanwhile, the V₃S₄-G/S-3 also delivers the superior rate capability with the discharge capacity of 1157, 937, 769, and 598 mA h g⁻¹ at the current density of 0.3, 0.5, 1, and 2 C, respectively (Fig. S17). Thus, the V₃S₄-G/S-3 can achieve favorable cycling and rate performance in the condition with large sulfur loading mass owing to the presence of multifunctional parts with both trapping sites and electrocatalytic properties for lithium polysulfides.

CONCLUSIONS

In summary, we synthesized a type of multifunctional V₃S₄-G as sulfur host. With the presence of graphene sheets, the agglomeration can be avoided and the specific surface area of V₃S₄-G can be increased to 220.0 m² g⁻¹.

Furthermore, on the basis of experimental and theoretical analyses, the V₃S₄ can act as trapping sites to restrain the migrant of lithium polysulfides with a binding energy of 1.20 eV by forming V-S and S-Li bonds. The V₃S₄-G also possesses electrocatalytic properties to accelerate the conversion of lithium polysulfides. With the sufficient exposure of multifunctional active sites in V₃S₄-G, the V₃S₄-G/S delivers a high initial capacity of 1370 mA h g⁻¹ at the current density of 0.3 C and good rate capability with high discharge capacity of 741 mA h g⁻¹ at 3 C. When the sulfur loading mass increases to 3 mg cm⁻², the Li-S batteries based on the multifunctional V₃S₄-G cathode also deliver a stable cycling performance with a low capacity decay rate of 0.186% per cycle at 0.5 C for 200 cycles. As a consequence, this study provides a promising approach to prepare a multifunctional sulfur cathode with trapping sites for polysulfides and enhanced kinetics for high-performance Li-S batteries.

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- 1 Rosenman A, Markevich E, Salitra G, *et al.* Review on Li-sulfur battery systems: An integral perspective. *Adv Energy Mater*, 2015, 5: 1500212
- 2 Fang R, Zhao S, Sun Z, *et al.* More reliable lithium-sulfur batteries: Status, solutions and prospects. *Adv Mater*, 2017, 29: 1606823
- 3 Tang T, Hou Y. Multifunctionality of carbon-based frameworks in lithium sulfur batteries. *Electrochem Energy Rev*, 2018, 1: 403–432
- 4 Yuan H, Huang JQ, Peng HJ, *et al.* A review of functional binders in lithium-sulfur batteries. *Adv Energy Mater*, 2018, 8: 1802107
- 5 Liang J, Sun ZH, Li F, *et al.* Carbon materials for Li-S batteries: Functional evolution and performance improvement. *Energy Storage Mater*, 2016, 2: 76–106
- 6 Luo R, Yu Q, Lu Y, *et al.* 3D pomegranate-like TiN/graphene composites with electrochemical reaction chambers as sulfur hosts for ultralong-life lithium-sulfur batteries. *Nanoscale Horiz*, 2019, 4: 531–539
- 7 Rehman S, Guo S, Hou Y. Rational design of Si/SiO₂@hierarchical porous carbon spheres as efficient polysulfide reservoirs for high-performance Li-S battery. *Adv Mater*, 2016, 28: 3167–3172
- 8 Wei Seh Z, Li W, Cha JJ, *et al.* Sulphur-TiO₂ yolk-shell nanoarchitecture with internal void space for long-cycle lithium-sulphur batteries. *Nat Commun*, 2013, 4: 1331
- 9 Tang T, Hou Y. Chemical confinement and utility of lithium polysulfides in lithium sulfur batteries. *Small Methods*, 2019, 3: 1900001
- 10 Rehman S, Khan K, Zhao Y, *et al.* Nanostructured cathode materials for lithium-sulfur batteries: progress, challenges and perspectives. *J Mater Chem A*, 2017, 5: 3014–3038
- 11 Seh ZW, Sun Y, Zhang Q, *et al.* Designing high-energy lithium-sulfur batteries. *Chem Soc Rev*, 2016, 45: 5605–5634
- 12 Li T, Bai X, Gulzar U, *et al.* A comprehensive understanding of lithium-sulfur battery technology. *Adv Funct Mater*, 2019, 29: 1901730
- 13 Hencz L, Chen H, Ling HY, *et al.* Housing sulfur in polymer composite frameworks for Li-S batteries. *Nano-Micro Lett*, 2019, 11: 17
- 14 Xiang H, Chen J, Li Z, *et al.* An inorganic membrane as a separator for lithium-ion battery. *J Power Sources*, 2011, 196: 8651–8655
- 15 Chen X, He W, Ding LX, *et al.* Enhancing interfacial contact in all solid state batteries with a cathode-supported solid electrolyte membrane framework. *Energy Environ Sci*, 2019, 12: 938–944
- 16 Chen H, Ling M, Hencz L, *et al.* Exploring chemical, mechanical, and electrical functionalities of binders for advanced energy-storage devices. *Chem Rev*, 2018, 118: 8936–8982
- 17 Li G, Wang C, Cai W, *et al.* The dual actions of modified polybenzimidazole in taming the polysulfide shuttle for long-life lithium-sulfur batteries. *NPG Asia Mater*, 2016, 8: e317
- 18 Fang R, Li G, Zhao S, *et al.* Single-wall carbon nanotube network enabled ultrahigh sulfur-content electrodes for high-performance lithium-sulfur batteries. *Nano Energy*, 2017, 42: 205–214
- 19 Rehman S, Tang T, Ali Z, *et al.* Integrated design of MnO₂@carbon hollow nanoboxes to synergistically encapsulate polysulfides for empowering lithium sulfur batteries. *Small*, 2017, 13: 1700087
- 20 Yang W, Yang W, Song A, *et al.* 3D interconnected porous carbon nanosheets/carbon nanotubes as a polysulfide reservoir for high performance lithium-sulfur batteries. *Nanoscale*, 2018, 10: 816–824
- 21 Gu X, Tong C, Lai C, *et al.* A porous nitrogen and phosphorous dual doped graphene blocking layer for high performance Li-S batteries. *J Mater Chem A*, 2015, 3: 16670–16678
- 22 Fang R, Chen K, Yin L, *et al.* The regulating role of carbon nanotubes and graphene in lithium-ion and lithium-sulfur batteries. *Adv Mater*, 2019, 31: 1800863
- 23 Bai X, Wang C, Dong C, *et al.* Porous honeycomb-like C₃N₄/rGO composite as host for high performance Li-S batteries. *Sci China Mater*, 2019, 62: 1265–1274
- 24 Xia Y, Fang R, Xiao Z, *et al.* Confining sulfur in N-doped porous carbon microspheres derived from microalgae for advanced lithium-sulfur batteries. *ACS Appl Mater Interfaces*, 2017, 9: 23782–23791
- 25 Zhou W, Xiao X, Cai M, *et al.* Polydopamine-coated, nitrogen-doped, hollow carbon-sulfur double-layered core-shell structure for improving lithium-sulfur batteries. *Nano Lett*, 2014, 14: 5250–5256
- 26 Zhong Y, Xia X, Deng S, *et al.* Spore carbon from *aspergillus oryzae* for advanced electrochemical energy storage. *Adv Mater*, 2018, 30: 1805165
- 27 Li Z, He Q, Xu X, *et al.* A 3D nitrogen-doped graphene/tin nanowires composite as a strong polysulfide anchor for lithium-sulfur batteries with enhanced rate performance and high areal capacity. *Adv Mater*, 2018, 30: 1804089
- 28 Zhang L, Chen Z, Dongfang N, *et al.* Nickel-cobalt double hydroxide as a multifunctional mediator for ultrahigh-rate and ultralong-life Li-S batteries. *Adv Energy Mater*, 2018, 8: 1802431
- 29 Zhang Z, Wu DH, Zhou Z, *et al.* Sulfur/nickel ferrite composite as cathode with high-volumetric-capacity for lithium-sulfur battery. *Sci China Mater*, 2019, 62: 74–86
- 30 Song Y, Zhao S, Chen Y, *et al.* Enhanced sulfur redox and polysulfide regulation via porous VN-modified separator for Li-S batteries. *ACS Appl Mater Interfaces*, 2019, 11: 5687–5694
- 31 Wang M, Song Y, Sun Z, *et al.* Conductive and catalytic VTe₂@MgO heterostructure as effective polysulfide promotor for lithium-sulfur batteries. *ACS Nano*, 2019, 13: 13235–13243
- 32 Song Y, Zhao W, Kong L, *et al.* Synchronous immobilization and conversion of polysulfides on a VO₂-VN binary host targeting high sulfur load Li-S batteries. *Energy Environ Sci*, 2018, 11: 2620–2630
- 33 Guo T, Song Y, Sun Z, *et al.* Bio-templated formation of defect-abundant VS₂ as a bifunctional material toward high-performance hydrogen evolution reactions and lithium-sulfur batteries. *J Energy Chem*, 2020, 42: 34–42
- 34 Song Y, Zhao W, Wei N, *et al.* In-situ PECVD-enabled graphene-V₂O₃ hybrid host for lithium-sulfur batteries. *Nano Energy*, 2018, 53: 432–439
- 35 Wang Y, Huang X, Zhang S, *et al.* Sulfur hosts against the shuttle effect. *Small Methods*, 2018, 2: 1700345
- 36 Chen T, Zhang Z, Cheng B, *et al.* Self-templated formation of interlaced carbon nanotubes threaded hollow Co₃S₄ nanoboxes for high-rate and heat-resistant lithium-sulfur batteries. *J Am Chem Soc*, 2017, 139: 12710–12715
- 37 Ye C, Zhang L, Guo C, *et al.* A 3D hybrid of chemically coupled nickel sulfide and hollow carbon spheres for high performance lithium-sulfur batteries. *Adv Funct Mater*, 2017, 27: 1702524
- 38 Zhu X, Zhao W, Song Y, *et al.* In situ assembly of 2D conductive vanadium disulfide with graphene as a high-sulfur-loading host for lithium-sulfur batteries. *Adv Energy Mater*, 2018, 8: 1800201
- 39 Cheng Z, Xiao Z, Pan H, *et al.* Elastic sandwich-type rGO-VS₂/S composites with high tap density: structural and chemical cooperativity enabling lithium-sulfur batteries with high energy density. *Adv Energy Mater*, 2018, 8: 1702337

- 40 Yin H, Zhang C, Liu F, *et al.* Hybrid of iron nitride and nitrogen-doped graphene aerogel as synergistic catalyst for oxygen reduction reaction. *Adv Funct Mater*, 2014, 24: 2930–2937
- 41 Zhou F, Zhao X, Yuan C, *et al.* Vanadium pentoxide nanowires: Hydrothermal synthesis, formation mechanism, and phase control parameters. *Cryst Growth Des*, 2008, 8: 723–727
- 42 Kresse G, Furthmüller J. Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput Mater Sci*, 1996, 6: 15–50
- 43 Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. *Phys Rev Lett*, 1996, 77: 3865–3868
- 44 Liu Q, Yao W, Zhan L, *et al.* V_3S_4 nanoparticles anchored on three-dimensional porous graphene gel for superior lithium storage. *Electrochim Acta*, 2018, 261: 35–41
- 45 Xu Z, Zhang Y, Wang Y, *et al.* Flower-like nanostructured V_3S_4 grown on three-dimensional porous graphene aerogel for efficient oxygen reduction reaction. *Appl Surf Sci*, 2018, 450: 348–355
- 46 Li G, Lei W, Luo D, *et al.* 3D porous carbon sheets with multidirectional ion pathways for fast and durable lithium-sulfur batteries. *Adv Energy Mater*, 2018, 8: 1702381
- 47 Ye Z, Jiang Y, Qian J, *et al.* Exceptional adsorption and catalysis effects of hollow polyhedra/carbon nanotube confined CoP nanoparticles superstructures for enhanced lithium-sulfur batteries. *Nano Energy*, 2019, 64: 103965
- 48 Liang X, Kwok CY, Lodi-Marzano F, *et al.* Tuning transition metal oxide-sulfur interactions for long life lithium sulfur batteries: The “goldilocks” principle. *Adv Energy Mater*, 2016, 6: 1501636
- 49 Liu Y, Sun Z, Sun X, *et al.* Construction of hierarchical nanotubes assembled from ultrathin V_3S_4 @C nanosheets towards alkali-ion batteries with ion-dependent electrochemical mechanisms. *Angew Chem Int Ed*, 2020, 59: 2473–2482
- 50 Pang Q, Tang J, Huang H, *et al.* A nitrogen and sulfur dual-doped carbon derived from polyrhodanine@cellulose for advanced lithium-sulfur batteries. *Adv Mater*, 2015, 27: 6021–6028
- 51 Lin H, Yang L, Jiang X, *et al.* Electrocatalysis of polysulfide conversion by sulfur-deficient MoS_2 nanoflakes for lithium-sulfur batteries. *Energy Environ Sci*, 2017, 10: 1476–1486
- 52 Wei N, Cai J, Wang R, *et al.* Elevated polysulfide regulation by an ultralight all-CVD-built ReS_2 @N-doped graphene heterostructure interlayer for lithium-sulfur batteries. *Nano Energy*, 2019, 66: 104190
- 53 Yang W, Yang W, Dong L, *et al.* Enabling immobilization and conversion of polysulfides through a nitrogen-doped carbon nanotubes/ultrathin MoS_2 nanosheet core-shell architecture for lithium-sulfur batteries. *J Mater Chem A*, 2019, 7: 13103–13112
- 54 Zhang Y, Xu G, Kang Q, *et al.* Synergistic electrocatalysis of polysulfides by a nanostructured VS_4 -carbon nanofiber functional separator for high-performance lithium-sulfur batteries. *J Mater Chem A*, 2019, 7: 16812–16820
- 55 Yuan H, Peng HJ, Li BQ, *et al.* Conductive and catalytic triple-phase interfaces enabling uniform nucleation in high-rate lithium-sulfur batteries. *Adv Energy Mater*, 2019, 9: 1802768
- 56 Chen G, Song X, Wang S, *et al.* Two-dimensional molybdenum nitride nanosheets modified Celgard separator with multifunction for Li-S batteries. *J Power Sources*, 2018, 408: 58–64

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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多功能 V_3S_4 纳米线/石墨烯复合材料在高性能锂硫电池中的应用

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摘要 具有高理论比容量与能量密度的锂硫电池被认为是一种颇具前景的新一代能量储存系统, 但其目前仍面临一定挑战. 将多硫化物的吸附位点与电催化性能相结合, 是提升电池性能的有效方法. 在本工作中, 我们将一种 V_3S_4 纳米线均匀分布在石墨烯基底上得到了多功能 V_3S_4 纳米线/石墨烯复合材料(V_3S_4 -G). 该材料的结构有助于暴露 V_3S_4 活性中心, 从而锚定多硫化锂并提升其反应动力学. 基于该多功能 V_3S_4 -G硫正极的锂硫电池表现出稳定的循环性能与良好的倍率性能. 即使在硫的负载量达到 3 mg cm^{-2} 时, 在 0.5 C 的电流密度下, 该 V_3S_4 -G硫正极仍然保持低的容量衰减速率(每圈0.186%).