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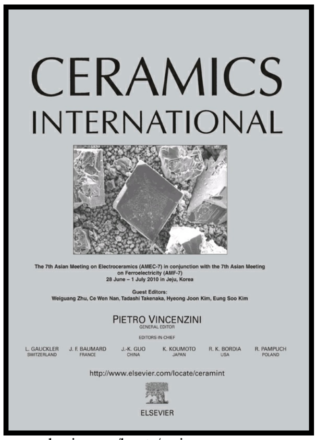

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Improving the electrochemical property of Li-S batteries by using CoS_2 as substrate materials

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Abstract:

Metal sulfide CoS_2 is prepared and used as host materials for Li-S batteries. The CoS_2 particle could immobilize the polysulfide by catalyzing the redox reactions of soluble polysulfide to insoluble polysulfide. Besides, the employment of vapor growth carbon fiber (VGCF) interlayer between CoS_2/S cathode and separator has a positive effect on physically adsorbing polysulfide. Consequently, the chemical and physical adsorption could exist in one Li-S battery system at the same time. As a result, the initial discharge capacity of CoS_2/S composite cathode with VGCF interlayer is 1278 mAh g^{-1} at the rate of 0.1 C. After 200 cycles, the capacity still remains as high as 701 mAh g^{-1}, which is better than the battery without CoS_2, showing excellent electrochemical performance.

Key words:

B. Nanocomposites; C. Electrical properties; E. Li-S batteries; Cobalt disulfide.

1. Introduction

Li–S batteries have been studied for years since sulfur was initiated to be active material [1-4]. Although the gap between practical application and research has become smaller, there are still several questions needed to be solved. Over the past few decades, great deals of articles are connected with carbonaceous materials employed in the sulfur-based cathode and interlayers to enhance the electrochemical property of Li-S batteries [5-10]. However, the research about the employment of metal sulfides in Li-S batteries is relatively rare [11-15], so we explored the application of CoS_2 in Li-S batteries.

Our previously relevant studies have found that VGCF interlayer show the highest electrochemical property in Li-S batteries [16]. However, the conductibility of the positive electrode and the issue of polysulfide (Li_2S_8–Li_2S_4) dissolution still need to be improved. Inspired by these, we suggest a sulfur-based host material of CoS_2 particle with VGCF interlayer in the hope of improving conductivity and cycle performance. With its intrinsic metallic conductivity and catalytic performance [17-19], CoS_2 can not only increase the conductivity of the cathode but also react with Li-S bond of intermediate products. Hence, the correlated chemical reaction about polysulfide on sulfur cathode and anode are both restricted to a great extent. Consequently, the CoS_2/S composite cathode with VGCF interlayer exhibits excellent electrochemical properties and superior cycle stability.

2. Experimental

2.1 CoS_2 /S composites synthesis

Cobalt chloride hexahydrate ($CoCl_2$•$6H_2O$, AR purity (294.413 mg)) and sodium thiosulfate pentahydrate ($Na_2S_2O_3$•$5H_2O$ (310.238 mg)) were dissolved in a mixture of distilled water (10 ml) and ethanol (30 ml) and stirred for 3 h. A homogeneous solution was formed and then was put to autoclave and heated at 160 °C for 24 h in an electric oven. After the reaction was completed, the autoclave was allowed to cool to 20 °C. Finally, the black solid particle was isolated by centrifugation and washed six times with ultrapure water and ethanol (99 %), and then dried in a vacuum oven at 60 °C for 12 h.

CoS_2 /S composites were made through melt-diffusion methods, CoS_2 was adequately milled with sulfur (Alfa Aesar) with a mass ratio of 1:1, 1:3 and 1:5. The composites was heated at 155 ℃ for 12 h in a tube furnace filled with argon gas, the CoS_2 /S mixture were obtained after cooling to 20 °C。

2.2 Characterization

The morphologies and crystal texture of the CoS_2 was characterized by scanning electron microscopy (SEM, Ultra55) and X-ray diffraction (XRD,D8 Advance). Thermal gravimetric analysis (TGA) was conducted applying a TASDT-Q600 analyzer with a heating speed of 10 ℃ min^{-1} under Ar atmosphere. Ultraviolet-Visible spectrum was carried out to verify the dissolved polysulfide species in the electrolyte after 100 cycles.

2.3. Electrochemical measurements

The cathode slurry was prepared by CoS_2 /S composites (70%), conductive carbonblack(20%) and polyvinylidene fluoride (PVDF 10 wt%) binder in N-methyl pyrrolidinone (NMP) solvent. The slurry was then coated onto aluminum foil to make cathode electrode. The areal sulfur loading and the thickness of the cathode electrode is 1.3 mg cm^{-2} and 150 μm, respectively. CR2032 coin-type cells were assembled with cathode electrode, VGCF interlayer, Lithium wafers and commercial separator (Celgard

2400) in glovebox under Ar atmosphere. Bis-(trifluoromethanesulfonly) imide (LiTFSI, 1.0 M) with $LiNO_3$ (0.2 M) dissolved in 1, 3-dioxolane (DOL, J&K) and 1,2-dimethoxyethane(DME, J&K) (v/v, 1:1) was used as electrolyte. The schematic of CoS_2 /S composites cathode with VGCF interlayer of Li-S battery was presented in (Fig.1)

3. Results and discussions

Fig. 2a shows X-ray diffraction patterns of sublimed sulfur, CoS_2 and CoS_2/S composite. The characteristic diffraction peak of prepared CoS_2 exactly matches the standard spectrum of CoS_2 (JCPDS: NO 00-041-1471). From the XRD diffraction pattern of CoS_2/S composite, the characteristic peaks of sublimed sulfur are weakened and the characteristic peaks of CoS_2 are strengthened at 32.3°, 36.3° and 54.9° after being combined with CoS_2, indicating that CoS_2 is uniformly compounded with sublimed sulfur. The sulfur content of CoS_2/S composite was determined by TG analyzer. As seen in Fig. 2b, the weight loss of CoS_2 and CoS_2/S composite before 300 ℃ are 7.6 % and 74 %, respectively. The mass loss of CoS_2 at 100 ℃ is caused by water loss and the weight loss of CoS_2/S composite is consistent with mix ratio by weight. Consequently, the sulfur content of CoS_2/S is 74 %. The morphology of CoS_2 and CoS_2/S composite were shown in Fig 3a. The CoS_2 consists of many smooth small particles with relatively loose particles. However, the shape of CoS_2/S composite is relatively dense (Fig. 3b, 3c), forming a flower-like morphology. The surface of CoS_2/S composite became rough, indicating that elemental sulfur is uniformly attached to the surface of CoS_2, and the corresponding EDX spectrum in Fig. 3d can also prove it. As a base of sulfur electrode, CoS_2 with good electrical conductivity can enhance the conductibility of elemental sulfur, improving the electrochemical stability of Li-S batteries and extending the cycle life.

Fig. 4a exhibits the galvanostatic charge-discharge profiles of CoS_2/S composite cathode with VGCF interlayer and that without CoS_2. The initial discharge capacity of CoS_2/S composite cathode with VGCF interlayer at the rate of 0.1 C is 1278 mAh g^{-1}, which is 187 mAh g^{-1} high than that without CoS_2. The specific capacity of sulfur cathode with VGCF interlayer falls down to 562 mAh g^{-1} after 100 cycles, but the specific capacity of CoS_2/S composite cathode with VGCF interlayer keeps up to 701 mAh g^{-1} even through 200 cycles. The outstanding electrochemical performance of CoS_2/S composite cathode with VGCF interlayer is ascribed to physical absorption of VGCF interlayer to polysulfide and intrinsic metallic conductivity and the reduction reaction of CoS_2, which is in line with the specific discharge plateau at 1.9 V presented in Fig. 4a. Consequently, the CoS_2/S composite cathode with VGCF interlayer exhibits excellent electrochemical properties and longer cycle performance. To explore the optimal ratio of CoS_2 in CoS_2/S composite cathode with VGCF interlayer, various contents of CoS_2 were mixed with sublimed sulfur to research the effect of the CoS_2 amount on cycle stability. Three different ratios of 16.7%, 25% and 50% were studied and their cycle performance were presented in Fig.4c. 25% for CoS_2 shows the best cycling stability, its specific capacity is highest among three ratios after 100 cycles. When the content of CoS_2 is low, it does not play a good role, but when its content is high, the performance of the sulfur cathode is restricted. Therefore, the optimal CoS_2

content in CoS_2/S composite cathode with VGCF interlayer was 25%. Fig. 4d displays the discharge specific capacity of CoS_2/S composite cathode with VGCF interlayer and sublimed sulfur cathode with VGCF interlayer at different electric current density. CoS_2/S composite cathode with VGCF interlayer presented excellent discharge specific capacities of 1399, 1211, 1085, 1015 and 992 mAh g^{-1} at 0.05, 0.1, 0.2 0.5 C and 1 C rates, respectively, while for batteries of sulfur cathode with VGCF interlayer, the homologous specific capacities were all inferior than that of CoS_2/S composite with VGCF interlayer. These results show that Li-S batteries with CoS_2/S composite cathodes with VGCF interlayer have excellent rate performance under different current density conditions.

CV curves of batteries after 100 cycles are shown in Fig. 5a. Further research on the specific capacity contribution of CoS_2 during the reaction of lithium sulfur battery is performed. No significant shift was observed for both the anodic and cathodic peaks even through 100 cycles, manifesting excellent electrochemical stability [20-21]. Unlike the conventional Li-S battery, the CV of CoS_2/S composite cathode with VGCF interlayer find a unusual characteristic peak at around 1.9 V, corresponding to the reaction of CoS_2 with Li^+($CoS_2 + xLi^+ + xe^- \rightarrow Li_xCoS_2$)[22], which is consistent with previous literature[23]. Fig. 5b reveals the impedance comparison between CoS_2/S composite cathode with VGCF interlayer and sulfur cathode with VGCF interlayer after 100 cycles. Significant differences can be seen in the Fig. 5b, both of them are composed of two semicircular regions and a slanted region, which are respectively on behalf of charge transfer resistance (R_{ct}), electrolyte resistance (R_e) and the interfacial resistance (R_i) [24-26]. The interfacial resistance (R_i) and the charge transfer resistance (R_{ct}) of CoS_2/S composite with VGCF interlayer are both smaller than that without CoS_2, which indicates a significant increase in conductivity.

Ultraviolet-Visible spectrum was used to verify polysulfide in electrolyte of CoS_2/S composite cathode with VGCF interlayer [27-30]. The 100 cycled cathodes and VGCF interlayer (charge state) was soaked in the solvent of 1, 3-dioxolane/1, 2-dimethoxyethane (DOL/DME, 1:1, vol) to obtain the solutions. Typical colors of electrolyte were presented in Fig. 6 a, the color of the solution for CoS_2/S composite cathode with VGCF interlayer has no obvious changes even after 100 cycles. In striking contrast, the color for sulfur cathode with VGCF interlayer changed to yellow. According to the UV–Vis absorption spectra of the A and B solutions, there are still many polysulfides remaining in the sulfur cathode with VGCF interlayer shown in Fig.6b. However, there is no polysulfide residue in the CoS_2/S composite cathode with VGCF interlayer, indicating that the CoS_2 indeed has strong reaction for lithium polysulfide.

4. Conclusions

In this paper, CoS_2 particle with good metallic conductivity and catalytic property is used as the sulfur base host material in Li-S battery. As a result, the initial discharge specific capacity of CoS_2/S composite cathode with VGCF interlayer is 1278 mAh g^{-1} at the rate of 0.1 C and the specific capacity keeps up to 701 mAh g^{-1} through 200 cycles. The developed strategy of using CoS_2/S composite cathode with VGCF interlayer is looking forward to enhance the development of Li-S batteries with outstanding electrochemical performance and cycling stability.

Acknowledgement

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Supplementary data

Supplementary data related to this article can be found in supporting information.

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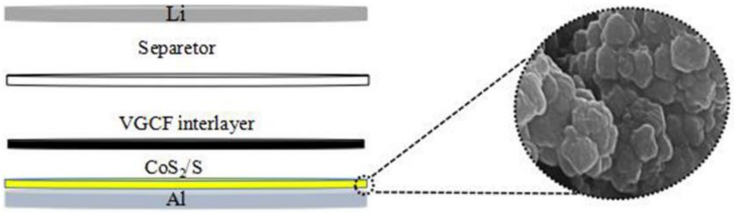

Fig.1. Schematic illustration of CoS_2/S composites cathode with VGCF interlayer in Li-S battery.

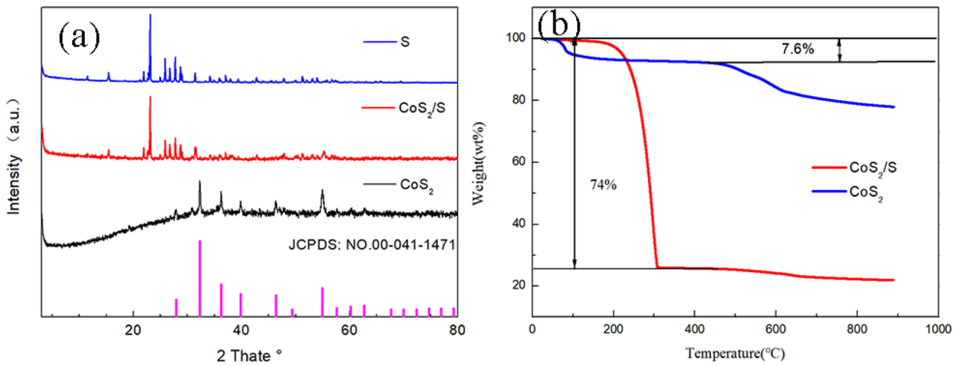

Fig.2. (a) XRD patterns of sulfur, CoS_2 and CoS_2/S composite; (b) TG curve of CoS_2/S composite.

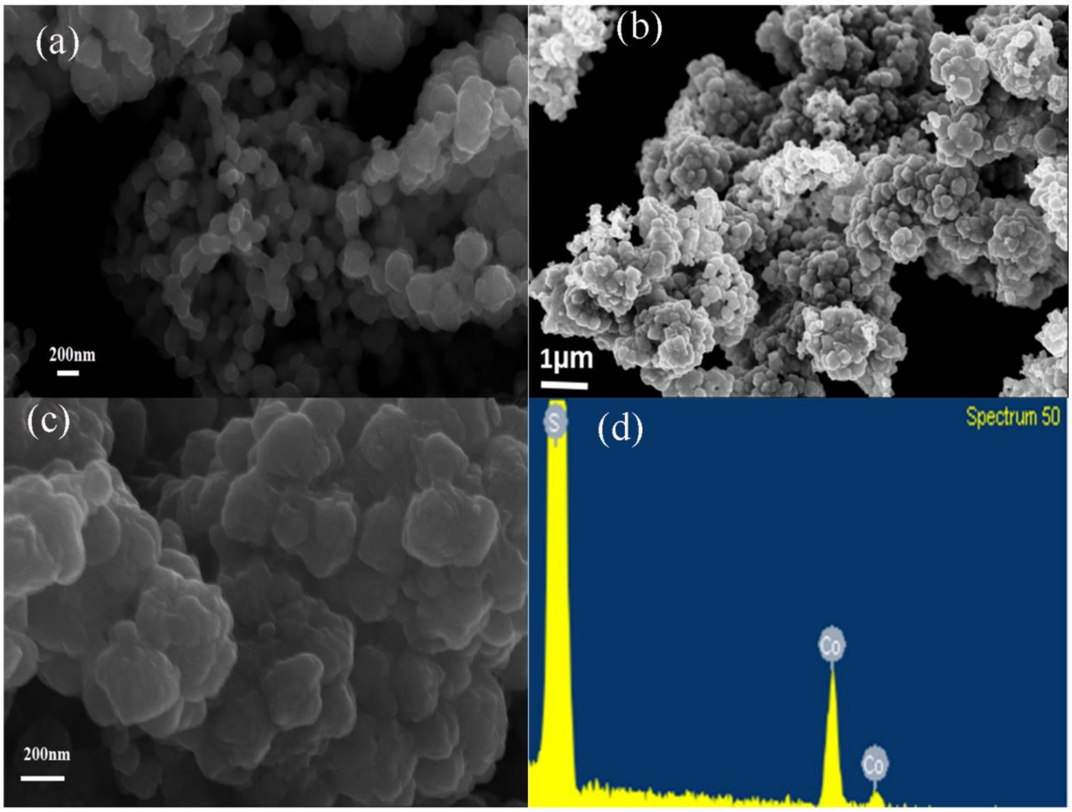

Fig.3. SEM image of (a) CoS_2; (b) CoS_2/S composite; (c) Magnified SEM of CoS_2/S composite; (d) EDX of CoS_2/S composite.

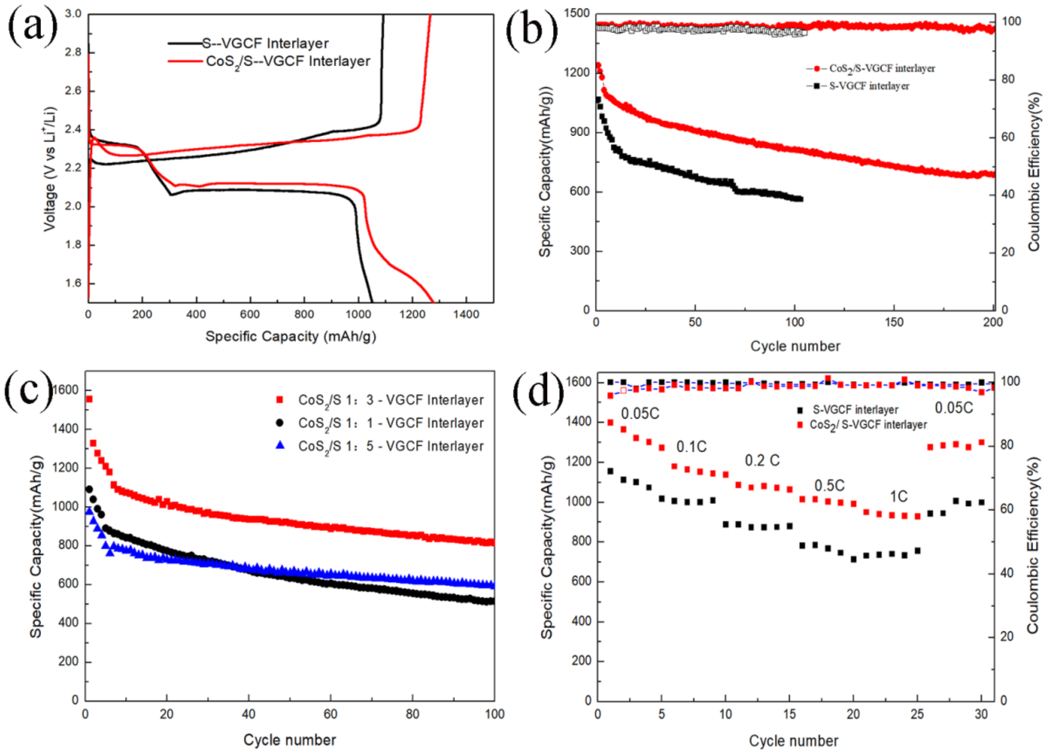

Fig.4 (a) The first discharge-charge profiles; (b) The cycle performances; (c) Cycling performances of the CoS_2/S composite cathode with different CoS_2 content. (d) Rate capability of the CoS_2/S composite cathode with VGCF interlayer from 0.05 C to 1 C.

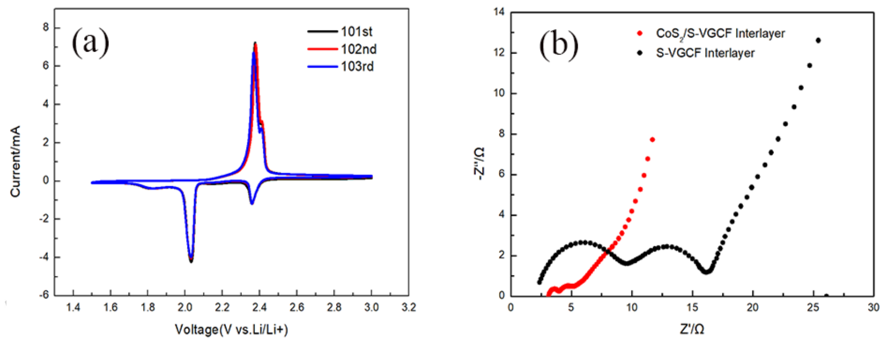

Fig.5 (a) EIS spectra of CoS_2/S composite cathode with VGCF interlayer and sulfur cathode with VGCF interlayer. (b) Cyclic voltammogram profiles.

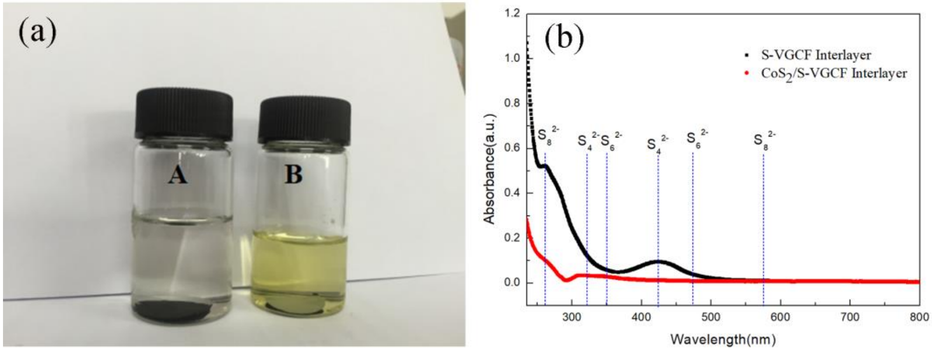

Fig.6. (a) Visible colors of electrolyte for the CoS_2/S composite cathode with VGCF interlayer (A) and Sulfur cathode with VGCF interlayer (B) after 100 cycles in volumetric flasks. (b) the Ultraviolet-Visible spectrum of (A) and (B).