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MoS_2-decorated coaxial nanocable carbon aerogel composites as cathode materials for high performance lithium-sulfur batteries

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ABSTRACT

MoS_2-decorated coaxial nanocable carbon aerogel (MoS_2/CNCA) has been successfully prepared by phenol aldehyde reaction on the substrate of multi-walled carbon nanotube with catalysis of ammonium molybdate followed pyroprocessing with sulfur. The as-prepared samples were characterized by transmission electron microscopy, scanning electron microscopy, thermogravimetric analysis, X-ray powder diffraction, and X-ray photoelectron spectroscopy. The MoS_2-decorated carbon aerogel (CA) with carbon nanotube as fine wire presents narrow distribution of pore size, interconnected structure and high conductance. The MoS_2/CNCA/S composites exhibit improved electrochemical performances as cathode of lithium-sulfur batteries. Especially, the MoS_2-8/CNCA/S composite delivers a discharge capacity of 1343 mAh g^{-1} at 0.2 C with the capacity retention of 81% after 200 cycles. Even at 5 C, the electrode presents high discharge capacity of 723 mAh g^{-1}. These improved results can be attributed to the contribution of entangled network as electronic conductive channel, large surface area, small pore size and special anchoring action of molybdenum disulfide.

1. Introduction

Lithium-sulfur batteries have gained great attraction [1,2] as a promising candidate of next-generation for storage devices. Sulfur cathodes give rise to theoretical gravimetric energy densities of about 2600 Wh kg^{-1} and high theoretical capacity (1675 mAh g^{-1}), which is 3–5 times higher than any present commercial lithium-ion cell [3,4]. Meanwhile, the non-toxicity, cheap and abundance of elemental sulfur provide better opportunity to large-scale practical applications of lithium-sulfur batteries [5,6]. The working principle of Li–S battery is the reaction of lithium with sulfur to form lithium polysulfide (Li_2S_x, $8 \geq x \geq 3$), lithium disulfide, and finally lithium sulfide during the discharge process, with the reverse occurring during the charging process [7,8]. It is multi step reaction mechanism that Li–S battery has suffered some indigenous problems, such as low cycling life, relatively rapid capacity fading, limited rate capability, which hampered the practical application of Li–S battery [9,10]. These issues derive from insulating nature of sulfur and the solubility of reductive polysulfides in organic electrolyte during cycling [3]. The solubility of reductive polysulfides causes a series of problems, including accelerating the consumption of cathode materials by diffusion away from the cathode and the polysulfide shuttle effects [11,12]. Meanwhile, the high reactivity of Li and thus gas generation on cycling result in fast capacity degradation of Li/S batteries [13]. Most recently, many researches have been done to solve the above problems, including the optimization of organic electrolyte or additives [3] and the preparation of sulfur/carbon composites [14].

In suppressing shuttle phenomenon, lithium nitrate provides a good routine at anode by promoting the formation of a SEI film [15]. So lithium nitrate alleviates the shuttle phenomenon, obviously improves the coulombic efficiency, effectively suppress the high reactivity of Li and gas generation [13] and obtains the efficiency of nearly 100% for some charge-discharge cycles. However, the approach only focus on anode and its film in enhancing the coulombic efficiency, this method cannot effectively prevent the degradation of capacity of Li–S battery [16]. To further solve the shuttle problem, we need to comprehensively investigate and research on both anode and cathode. With good coulombic efficiency from passivating treatment of anode, suppressing polysulfide dissolution from cathode becomes a crucial method to solve the problem.

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It is noted that various carbon materials, such as micro/mesoporous-carbons [17,18], graphene [19,20], carbon-tube [16,21] and carbon-nanofiber [22,23], were employed to prevent the shuttle effect of soluble polysulfide and improve capacity and cycling durability for cells [6]. The large surface area and pore volume of carbon matrix are the crucial factors impacting on the electrochemical performance of Li–S battery. The porous carbon matrix constrains sulfur within its pores/channels and inhibits polysulfide diffusing into electrolyte for the adsorption of the porous carbon. For improving electrochemical performance of carbon materials, some metal compounds including V_2O_5 [24], MnO_2 [25], Ti_4O_7 [26] and CeO_2 [27] were incorporated into carbon matrix. But the research not much focuses on the transition metal sulfide.

Carbon aerogel (CA) with 3D network structure presents the relatively large surface area, high porosity and manageable particle size [28] and provides important advantages for CA as cathode matrix. Despite having many studies of CA as matrix, these works mainly focused on the Li-ion batteries. For achieving the function of high conductivity and adsorbability, we design a rational and novel architecture coaxial nanocable carbon aerogel (CNCA) by combining carbon aerogel with wired multi-walled carbon nanotube (MWCNT). For effective anchoring polysulfides, MoS_2-decorated CNCA (MoS_2/CNCA) was further developed. It would probably provide an approach to improve performance of lithium/sulfur battery.

As shown in Scheme 1 of the schematic illustration, MoO_x-CNCA ($x = 2, 3$) were prepared by phenol aldehyde reaction with catalysis of ammonium molybdate on the substrate of MWCNT. MoS_2/CNCA and MoS_2/CNCA/S were obtained from MoO_x-CNCA sulfidation and further sulfur infiltration by pyroprocessing, respectively [29]. The MWCNTs with entangled long rope were soaked in acidic solutions to cut the rope into short and increase oxygen containing groups. And this treatment contributes to improving MWCNT dispersibility [30] and grafting to RF gels [31,32]. The molybdenum disulfide was produced by sulfurization of molybdenum precursor at appropriate temperatures.

We choose CNCA as new matrix for its good electrically conductive, large surface area and porosity property. And sulfur molecule and polysulfide were embedded and adsorbed in pores of the CNCA matrix. The embedding of MWCNT in the CA could help to create networks with better electrical conductivity and flexible buffer to accommodate the volume change during cycling, the delicate design of coaxial nanocable structure for electrode material could provide highly stable electrochemical performance at a high rate in Li–S battery. Meanwhile, transition metal compound provide another opportunity to modify carbon matrix and suppress the loss of polysulfide intermediates. In fact, Zhang et al. [33] used nanosized MoS_2/SnO_2 to modify the carbon matrix and improved electrochemical performance.

As a transition metal sulfide, layered MoS_2 contain copious S atoms on the surface. MoS_2 embedded in CNCA could lead to interactions with the polysulfide and the exposed MoS_2 induce S–S bond breaking, cause the dissociation of the long-chain polysulfide into short chain [34]. So MoS_2 can act as anchor of the soluble polysulfide to improve electrochemical performance of Li–S batteries.

2. Experimental section

2.1. Preparation of CA/S

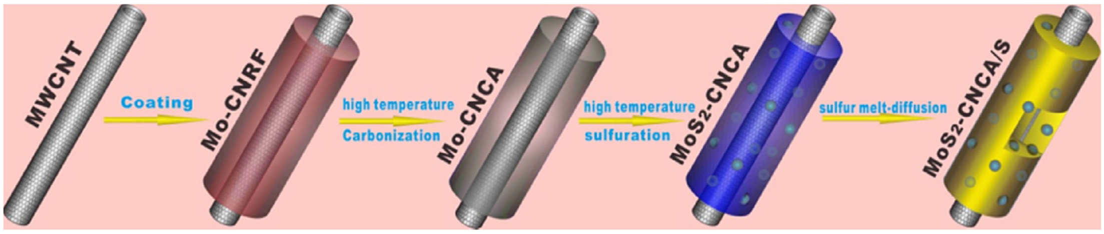
Carbon aerogel was obtained from resorcinol (R)-formaldehyde (F) gel with a mole ratio of 1:2. Ethanolamine (ETA) and sodium dodecyl sulfate (SDS) were used as the catalyst and dispersing agent, respectively. Resorcinol (4.4 g) and sodium dodecyl sulfate ($n_{SDS}/n_R = 1/100$) were dissolved in a mixture solution of ethanolamine ($n_{ETA}/n_R = 1/500$), formaldehyde (8 mL) and water (40 mL) under constant stirring for 40 min. Then, the solution was transferred into a sealed bottle and aged at 80 °C for 48 h. Subsequently, the gel was soaked in acetone and absolute ethyl alcohol about 8 h in turn for replacing water, directly dried at 50 °C in an ambient condition. Finally, CA product was obtained by further carbonizing gel at 800 °C.

The CA/S composites were prepared through a melt-diffusion technique. Typically, the sublimed sulfur and CA at mass ratio of 6:4 were put into 20 mL Tefon-lined stainless steel reactor and kept the temperature at 155 °C for 15 h. The final CA/S was obtained by further treatment at 250 °C for 5 h under argon condition to remove sulfur from the surface of the composites.

2.2. Preparation of MoS_2/CNCA/S

The synthesis process of MoS_2/CNCA was concisely demonstrated in the **schematic 1**. Firstly, MWCNTs with diameter of 10–20 nm (0.25 g) were soaked in 50 mL acid solutions (4:1, VH_2SO_4/VH_2O_2) at room temperature for 24 h. After diluting and filtering, MWCNTs were flushed with deionized water and ethanol until pH neutral. Then, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.0706 g) and SDS ($n_{SDS}/n_R = 1/100$) were dissolved in a solution of formaldehyde(2 mL) and water(5 mL). Sequentially, absolute ethyl alcohol (15 mL) was slowly and successively added into the above solution under constant stirring to become white turbid mixture. Next, the turbid mixture was treated by slowly dropping ammonia until it become transparent. After adding resorcinol (1.1 g) and treated MWCNT into the solution, it was dispersed under supersound for 24 h and then transformed to highly distributed suspension. Then the suspension slurry was transferred into a sealed bottle and aged at 80 °C for 48 h. Subsequently, the obtained deep brown gel was soaked in acetone and absolute ethyl alcohol about 8 h in turn for replacing water, directly dried at 50 °C in an ambient condition and carbonized at 400 °C. Finally, as-prepared carbon and sulfur were mixed at 160 °C for 2 h, heated with a ramp rate of 5 °C min^{-1} and treated at 700 °C for 2 h.

By adjusting amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, we synthesized carbon composites with designed molar ratio of 0.04, 0.08 and 0.12 for molybdenum (Mo)/resorcinol(R) and obtained carbon aerogels with different Mo contents. In this work, four samples with



Scheme 1. Schematic illustration showing the preparation process of MoS_2/CNCA/S.