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Nitrogen and oxygen dual-doped hollow carbon nanospheres derived from catechol/polyamine as sulfur hosts for advanced lithium sulfur batteries

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ABSTRACT

Although lithium-sulfur batteries are considered as promising high-energy-storage system owing to their high energy density, developing effective materials to host sulfur species on the cathode is still challenging. Herein, an inexpensive and effective carbon precursor, catechol and polyamine is explored to fabricate nitrogen/oxygen dual-doped hollow carbon nanospheres (DHCSs) as sulfur hosts. The group containing nitrogen and oxygen can provide stronger chemisorption for lithium polysulfides than single-doped carbon matrix, which is confirmed by X-ray photoelectron spectroscopy analysis and the theoretical calculation. As a result, the designed sulfur/DHCSs cathode delivers a stable cycling performance remained 851 mAh g^{-1} discharge capacity at 0.2 C with ~0.08% capacity decay per cycle after 200 cycles, revealing its great promise for energy storage application.

1. Introduction

To develop high-energy storage system, much attention has been paid to lithium-sulfur (Li–S) batteries, owing to their high theoretical specific capacity (1675 mAh g^{-1}) and theoretical energy density (2600 Wh kg^{-1}) [1,2]. Moreover, elemental sulfur is environmentally friendly and inexpensive as sulfur is abundant on earth (3%, mass) [3]. In spite of these appealing advantages, there are still some severe problems plaguing the commercial application of Li–S batteries: (1) The high resistance of both sulfur ($\sigma = 5 \times 10^{-30}$ S cm^{-1} at 25 °C) and its discharged products (Li_2S_2/Li_2S). (2) The high dissolution and shuttle effect of polysulfides (Li_2S_x, $3 \leq x \leq 8$) in organic electrolyte. The lithium polysulfides (LiPSs), generated on the cathode, can readily migrate to the anode where they can react with lithium metal to produce insoluble Li_2S and Li_2S_2, causing the loss of active material sulfur. (3) The adverse volume expansion (~80%) of sulfur during discharge and charge. In consequence, Li–S batteries undergo low utilization of active materials, poor rate capability, reduced coulombic efficiency and pronounced capacity fading.

To address the above mentioned issues, much work has been carried out, especially focusing on the sulfur-carbon composites. A major breakthrough is made by Nazar's group through adopting ordered carbon to suppress polysulfide dissolution [4]. Inspired by their pioneering work, various carbon materials with unique structure, including graphene, hollow carbon spheres, carbon nanotube and carbon nanofibers have been reported to confine sulfur species by providing physical confinement [5–8]. However, continuous capacity decay, especially for long cycling is often observed in such sulfur-carbon hybrids. It has been demonstrated that it is due to the poor affinity of non-polar carbon materials with polar LiPSs, leading to continual dissolution of LiPSs into electrolytes [9]. Therefore, physical confinement alone is not enough to encapsulate soluble LiPSs, the strong chemical interaction with LiPSs is needed to effectively confine LiPSs on the cathode [10].

Doping heteroatoms into carbon substrates is a feasible way to adjust the nonpolar property of carbon materials. Along this line, various heteroatoms, such as nitrogen (N), oxygen (O) and boron

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(B), have been reported to modify carbon substrate [11–13]. The doped atoms can trap sulfur species through bonding with positive Li^+ (e.g. $N\cdots Li_2S_n$) or interacting with anion PSs ($Li_2S_n\cdots B$). However, the content of single-heteroatom is generally limited [14]. Thus, dual-doping strategy is proposed to provide enough active sites for chemisorption. It is exciting to find that the dual-doped carbon exhibits improved chemisorption for LiPSs [15–18]. Recently, dual-doped carbon materials are not only limited in Li–S systems, but also in various fields, such as electrocatalysts and supercapacitor [19,20]. However, different precursors with separated steps are normally needed to achieve the incorporation of different atoms, leading heterogeneous distribution of dopants. For example, typical process with air atmosphere oxidation and subsequent nitridation treatment in concentrated HNO_3 is used to obtain N/O co-doped carbon materials [21]. In addition, strict reaction conditions, such as surface active agents or hydrothermal method, are used to fabricate doped carbon materials [18,20]. As carbon precursor plays a vital role on both physical and chemical characteristics of the final obtained carbonaceous materials [22,23], it is important to explore a universal and facile raw materials to prepared heteroatoms-doped carbon. Dopamine, benefited from its ability of virtually self-polymerizing and depositing on virtually any surfaces, has been considered as an effective carbon precursor [24,25]. Our previous work also demonstrated the good coating property of dopamine [26,27]. However, the expensive cost impedes its further practical application. Considering the basic molecular structure of dopamine, it is inferred that separated catechol and polyamine may be utilized to polymerize as the carbon precursor.

Based on this thought, low-cost catechol and polyamine (CPA) is utilized to synthesize N and O dual-doped hollow carbon spheres (DHCSs) as sulfur hosts. It is the first time that the CPA is demonstrated to prepare functional carbon material. There are three main advantages in this work. Firstly, a new carbon precursor is adopted to achieve in-situ doped carbon host. Such carbon precursor can easily form uniform coating layer on the template at room temperature without the requirements of complex equipment or strict reaction conditions, showing its potential application in other field. Most importantly, it is cheaper than dopamine, and equivalent coating ability of CPA as dopamine is found in the experiment. Secondly, N/O dual-doped carbon can be obtained, providing abundance active sites to bond with LiPSs. The influences of co-doping N/O in sulfur-carbon formation and LiPSs adsorption are investigated by the combination of experiment characterization such as X-ray photoelectron spectroscopy (XPS) and theoretical calculation based on first-principle density functional theory (DFT). Thirdly, the conductive carbon with hollow framework can act as a physical confinement to host sulfur species and provide electrochemical reactor at nanoscale to improve sulfur utilization. Benefited from these advantages, the DHCSs, derived from CPA, act as effective hosts for sulfur species, showing a promising application for advanced Li–S batteries.

2. Experimental section

2.1. Sample preparation

2.1.1. Synthesis of SiO_2 spheres

SiO_2 spheres were synthesized according to a slightly modified Stöber method [28]. The typical synthesis process is described as following: Tetraethyl orthosilicate (TEOS) (13.5 mL) was added quickly into a mixture solution of deionized water (70 mL), ethanol (180 mL) and ammonium aqueous (27 mL). After vigorous stirring at room temperature for 3 h, the SiO_2 spheres were isolated by centrifugation and washed using deionized water and ethanol at least three times.

2.1.2. Synthesis of SiO_2@CPA

The as-obtained SiO_2 (0.32 g) spheres were dispersed into deionized water (150 mL) using continuous ultrasonication. Then, catechol (0.3 g) and diethylenetriamine (285 μL) were added to react for 24 h at room temperature. The product was separated by centrifugation and dried in vacuum oven at 80 °C for overnight.

2.1.3. Synthesis of hollow carbon spheres

The carbonization was conducted at 200 °C for 1 h, followed by heating at 700 °C (or 800 °C, or 900 °C) for 3 h with 2 °C min^{-1} in argon atmosphere. Subsequently, the carbonized product was treated with hydrofluoric acid (15%) to remove the SiO_2 template. Finally, the hollow carbon spheres were obtained by centrifugation and dried in freezing dryer. According to the calcination temperatures, the corresponding hollow carbon samples are denoted as DHCSs700, DHCSs800 and DHCSs900, respectively.

2.1.4. Synthesis of carbon/sulfur composites

The melt infiltration is used to impregnate sulfur into the hollow carbon sphere. Both sulfur and as-prepared hollow carbon samples with a certain proportion were mixed via grinding, and then heated at 155 °C for 12 h under argon atmosphere. The obtained composites were designated as S/DHCSs700, S/DHCSs 800 and S/DHCSs900, respectively.

2.2. Cell assembly and electrochemical measurement

The slurry containing 80 wt% as-prepared S/DHCSs, 10 wt% acetylene black and 10 wt% carboxy methyl cellulose (CMC)/styrene butadiene rubber (SBR) (CMC: SBR = 1: 1, mass) was coated onto aluminum foil with doctor blade. After drying at 60 °C overnight in vacuum oven, CR-2032-type coin cells were assembled in an argon-filled glovebox to measure the electrochemical performances. 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (DOL: DME = 1: 1, V/V) was used as electrolyte. The lithium metal foil was used as both counter and reference electrode. The typical sulfur active loading is 1.4 mg cm^{-2} in the cathode. The discharged-charged profiles at different densities from 1.75 V to 2.8 V (vs. Li^+/Li) were conducted on battery system (LAND CT2001A instrument, China). Cyclic voltammetry (CV) curves were obtained on CHI660D at a scan rate of 0.1 mV s^{-1} with voltage range of 1.75–2.8 V. Electrochemical impedance spectra (EIS) were performed on electrochemical workstation (Autolab PGSTAT T302 N) at a frequency range of 0.1 Hz–100 KHz. All electrochemical tests were performed at 25 °C.

2.3. Characterization and measurements

The morphologies of the samples were characterized with scanning electronic microscopy (SEM, HITACHI S-4800) and transmission electron microscope (TEM, TECNAI F30). The crystal structure of all the samples were analyzed with the Rigaku X-ray diffraction (XRD, miniflex600) using Cu-Kα radiation operated at 40 kV and 15 mA. The data were collected in the range from 10° to 60° with scanning speed of 2° min^{-1}. The Raman spectra were performed on Xplora using the 532 nm excitation with the resolution of 1 cm^{-1}. The compositions of the samples were measured on Fourier transform infrared spectrometer (FT-IR, Nicolet IS5 spectrometer). The X-ray Photoelectron spectrum (XPS) was recorded on Qtac-100 Scanning microprobe. The proportion of the element is analyzed with element analysis instrument (Varia-EL-III). The sulfur amount in the composites was determined with