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Flower-like nitrogen-oxygen-doped carbon encapsulating sulfur composite synthesized via in-situ oxidation approach

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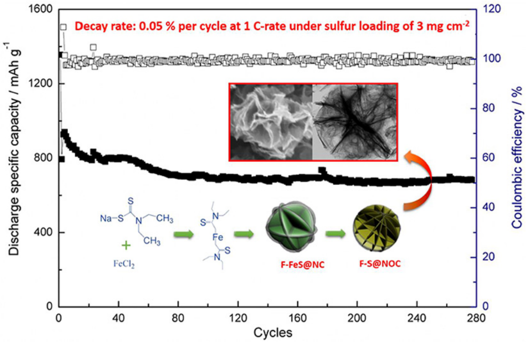
HIGHLIGHTS

- A nitrogen-oxygen-doped carbon coated sulfur composite gained by in-situ oxidation.
- A sulfur-containing organic ferro-compound as the only raw material.
- Rich nitrogen/oxygen functional groups distributed on carbon frame.
- Unique flower-like structure assembled by two-dimensional petal unit.
- Space restriction, chemical bonding combined with fast electrochemical kinetics.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium sulfur battery, with higher gravimetric energy, is regarded as one of the promising next-generation energy storage devices. However, rapid capacity fading and poor rate capability under higher loading hinder its practical applications. Despite the encouraging progress achieved, the cost-effective solutions are still need to be sought for. Herein, a flower-like nitrogen-oxygen-doped carbon coated sulfur (F-S@NOC) composite was synthesized from a low-cost sulfur-containing organic ferro-compound, through a facile calcination and an in-situ oxidation process. The unique flower configuration is constructed by two-dimensional flake petal unit that not only expose more polar nitrogen/oxygen-containing functional groups for anchoring the dissolved intermediates of lithium polysulfides (LiPSs), but also facilitate improved electrochemical reaction kinetics since fast electron/Li^+ transfer. Therefore, F-S@NOC demonstrates excellent electrochemical performances that a decay rate of 0.05% per cycle at 1C, and a high initial areal capacity of 4.49 mAh cm^{-2} at 0.2C, are obtained respectively under the sulfur loading of 3 and 4.6 mg cm^{-2}.

1. Introduction

Lithium sulfur (Li-S) batteries, with great potential as next generation energy storage device, have attract increasing attention, owing to high theoretical specific capacity (1675 mAh g^{-1}), abundance and lower cost of element sulfur [1–4]. However, the inherent insulation of sulfur, the shuttle effect resulted from the dissolution of the intermediates, and the material microstructure collapse caused by severe volumetric variation during cycling, all lead to rapid capacity decay and low active material utilization, which significantly hamper the

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practical applications of Li-S batteries [5–7].

To overcome these abovementioned hurdles, extensive efforts have been devoted to optimizing the cathode materials by structure design and the introduction of polar-philic components. Owing to the various and controllable micromorphology, carbon-based materials, such as porous/hollow carbon sphere [8–13], carbon nano-tube/fiber [14–17], and graphene-based carbon materials [18–21], demonstrate prominent spatial limitation to the intermediates of lithium polysulfides (LiPSs), which greatly extends the cycle life of Li-S battery. Whereas, ultimate physical confinement of sulfur also reduces the transfer rate of Lithium ion at the same time. Recent studies have shown that polar host can effectively anchor the dissolved LiPSs via forming strong chemical bonds with them. Hence, a great deal of polar-philic inorganic composites [22–25], like oxides [26–32], metal sulfides [33–36], carbides [37–40], nitrides [41–43], are widely investigated as the hosts of sulfur. However, besides the lowered electron conductivity and limited specific surface area compared with the carbon-based materials, the introduction of these composites inevitably leads to complicated preparation, low yield and high cost.

Comparatively, the functionalization of the carbon-based material, through the introduction of polar functional groups, could enable them the moderate chemical adsorption capabilities to bond with the ionized LiPSs nearby, without lowered conductivity or increased cost involved at the same time. Hence, the sulfur/carbon composites, carrying with various nitrogen, oxygen and phosphorous containing functional groups, have been subsequently reported [44–48]. The two-dimensional carbon frames with more exposed polar-philic reaction active sites are regarded to be good both for mass transfer and for chemical adsorption. In this work, we developed a modified single-source-decomposition to synthesize a nitrogen-doped carbon coated ferrous sulfide (FeS@NC) composite that exhibits a two-dimensional nano-sheet presence, assembling to the unique flower shape. The flower-shaped FeS (F-FeS), as the sulfur source and structure template, was in-situ oxidized to sulfur inside of the carbon shell. Moreover, oxygen-containing functional groups were introduced, for the reason that iodine was adopted as the oxidation agent during the in-situ oxidation process. Therefore, the obtained sulfur was encapsulated in nitrogen-oxygen-doped carbon (NOC) framework, which totally cloned the morphology of the F-FeS@NC, presenting the morphology of an assembled flower shape. The particular tow-dimensional petal unit of nitrogen-oxygen-doped carbon coated sulfur (S@NOC) composite enabled the larger contact surface area between the active sulfur and the conductive frame, providing more electron transmission paths. Moreover, the thin carbon shell also facilitated the fast Lithium ion (Li^+) transfer. In the other hand, two-dimensional carbon matrix exposed more polar-philic nitrogen/oxygen-containing functional groups, enabling quick and efficient anchoring of the generated LiPSs, which could greatly suppress the LiPSs diffusion towards the anode metal lithium. The anchoring effect, combined with fast transfer of electron and Li^+, guaranteed the superior electrochemical reaction kinetics on the two-phase interface, advancing smooth conversion of the intermediates from liquid to solid state. Hence, the LiPSs loss was greatly inhibited, which led to the improved cycling stability.

2. Experimental

2.1. Synthesis of flower-like nitrogen-doped carbon coated FeS (F-FeS@NC)

8.5 g of Sodium diethyl dithiocarbamate and 6.3 g of $FeCl_2$ were dissolved in 50 ml deionized water, then stirred for 30 min. The obtained black precipitation of iron (II) diethyl dithiocarbamate was separated and washed by centrifugation with deionized water and ethanol for several times. 2 g of iron (II) diethyl dithiocarbamate was heated in a tube furnace to 750 °C at 5 °C min^{-1} under argon gas. After 2 h elapsed, the product was cooled to room temperature to obtain the F- FeS@NC.

2.2. Synthesis of flower-like nitrogen-oxygen-doped carbon coated sulfur (F-S@NOC) composite

200 mg of as-prepared F-FeS@NC was dispersed in 80 ml solution of ethanol and deionized water (v:v = 1:1), followed by the addition of 200 mg of $FeSO_4 \cdot 7H_2O$ and 1.8 g of I_2. After 30 min, 300 mg of $Fe_2(SO4)_3$ was added to the solution under vigorously stirring at 25 °C for 24 h. The product of F-S@NOC was washed by ethanol and deionized water, and collected by filtration before drying at 60 °C. 2 g of iron (II) diethyl dithiocarbamate was calcined to obtain about 450 mg F-FeS@NC that is further in-situ oxidized to get approximate 150 mg F-S@NOC composite.

2.3. Synthesis of flower-like nitrogen/oxygen-doped carbon (F-NOC)

The obtained F-S@NOC was heated at 500 °C for 24 h under low pressure to remove the sulfur inside. And the obtained black powder is F-NOC.

2.4. Synthesis of sulfur/flower-like nitrogen/oxygen-doped carbon composite (S/F-NOC)

The S/F-NOC composite was prepared by loading sulfur in the F-NOC frame, through melt-diffusion method.

2.5. Material characterization

The crystal phases of all the products were analysed using X-ray diffraction with Cu kα radiation (D/max-RB, Rigaku). Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) measurements were carried out by heating to 600 °C at a scanning rate of 5 °C min^{-1} under nitrogen atmosphere. Transmission electron microscopy images and HAADF images were obtained using FEI Tecnai F20 field emission scanning transmission electron microscope (STEM) operated at 300 keV. The energy dispersive X-ray (EDX) analysis measurement was made in the F30 using an Oxford detector. Scanning electron microscopy (SEM) was performed with a JSM-7800F. N_2 adsorption/desorption isothermals were collected by a gas adsorption analyzer (ASAP-2020). The specific surface areas and pore-size distribution were calculated using Brunauer-Emmett-Teller (BET) and Density Functional Theory (DFT) methods, respectively. XPS measurements were carried out on an ESCALAB250 X-ray photoelectron spectrometer using monochromatic Al kα (1486.6 eV) radiation. UV–Visible spectra were recorded with a Hitachi U-3900 spectrometer in the range of 300–700 nm, using the standard electrolyte (1M LiTFSI in 1:1 DME/DOL solution with 5 wt% $LiNO_3$) as the reference. Raman spectra were collected by a Jobin Yvon LabRam HR800 micro-Raman system at room temperature.

2.6. Electrochemical measurement

To prepare the working electrodes, the prepared F-S@NOC composite was mixed with Super P, Carboxymethylcellulose sodium (CMC) and styrene butadiene rubber (SBR) with a mass ratio of 80:10:4:6 in deionized water to form a homogeneous slurry. The slurry was casted onto a carbon coated Al foil with sulfur loading of about 2.5 mg cm^{-2}. To improve the Li^+ diffusion in the electrode, 1 wt% of NH_4HCO_3, as the pore-forming agent, was added into the slurry when fabricate the high loading electrode. Then, the electrode was cut into round disks with a diameter of 12 mm followed by vacuum drying at 60 °C overnight. The 2032-type coin cells were assembled in an argon-filled glove box using lithium foil as the counter electrode and Celgard 2325 membrane as separator. The electrolyte was a solution of 1 M LiTFSI in a mixture of DME and DOL (1:1, v/v) containing 5 wt% of $LiNO_3$. The electrolyte/sulfur ratio of 20 μL/mg is employed. Galvanostatic cycling was carried out using a Neware Battery Measurement System (Neware,