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Free-standing sulfur cathodes composited with carbon nanorods arrays for Li-S batteries application

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Sulfur is an attractive active material for lithium batteries in terms of its high specific capacity and energy density. Despite main advantages, lithium sulfur (Li-S) batteries still suffer from great challenges with serious capacity decay and awful rate performance due to severe "shuttle effect" and mass loss of active materials. Herein we report a free-standing carbon-sulfur cathodes by anchoring sulfur into 3D carbon nanorods arrays. Binder-free and integrated characteristics are realized. Sulfur infuses into interspaces among arrays and trapped by the interconnected carbon arrays. The assembled cells exhibit initial discharge specific capacity of 1050 mAh g^{-1} at 0.2 C and 892 mAh g^{-1} at 2.0 C, companied by an outstanding coulombic efficiency of 98% after 200 cycles at 0.2 C. The obtained S-C cathode also shows excellent rate capacity with low capacity fade. The proposed new S-C architecture may pave the way toward construction of novel S-Li batteries.

1. Introduction

On account of the energy crisis and increasing requirements of electronic devices/vehicles, traditional batteries cannot meet the growing demand of large-volume energy storage [1–3]. Advanced lithium ion batteries (LIBs) with high capacity [4,5] and energy density [6–8] are highly desirable. Currently, rechargeable lithium-sulfur (Li-S) batteries are regarded as compelling candidates for their high specific capacity (1675 mAh g^{-1}) and high theoretical energy density (2600 Wh kg^{-1}), about 6 times larger than traditional batteries, as well as low cost and environment friendly feature [9]. However, their extensive application is still restrained by drawbacks of fast capacity degradation, poor coulombic efficiency, low active material utilization and poor cycle lifetime [10,11]. The above problems may due to the insulating instinct of sulfur and dissolution of intermediate lithium polysulfides products (Li_2S_x, $4 \leq x \leq 8$), which lead to "shuttle effects" between cathode and anode with loss of active sulfur and suppression of deep lithiation [12,13]. All these weaknesses ultimately deteriorate the electrochemical performances during charge/discharge process at different cycling rates [14,15]. Hence, to circumvent above disadvantages, it is urgent to explore new structure [16,17] and novel technology to encapsulate sulfur in cathode [18,19].

In recent years, nanoengineered carbon materials have become new research hotspots to address above issues, owing to high specific surface area and high porosity. Lots of carbon materials mainly including carbon black [20,21], carbon nanocoils [22], carbon nanotubes (CNT) [23,24], carbon nanofibres [25,26], porous carbon spheres [27,28], graphene [29,30] are acting as hosts to accommodate sulfur while improving ionic/electronic conductivity simultaneously. For instance, Chen et al. [29] adopted self-assembled graphene oxide with simultaneous deposition of sulfur, and demonstrated volumetric capacity of 233 mAh cm^{-3} at 0.5 C and only 0.18% per cycle capacity fade was found. Ma et al. [24] reported CNT-PEI-S hybrids and displayed quite high capacity (ca. 1000 mAh g^{-1}) at 0.5 C and capacity retention exceeded 90% at different current rates. All these results demonstrate that porous carbon materials are excellent conductive matrixes and stabilizer for S cathode.

Recently, free-standing S-C cathode is attractive because of good electrical connection with the current collector and binder/additive-free characteristics [31]. To date, there is no report about anchoring S into the self-supported carbon nanorods arrays as well as their application for Li-S batteries. In the present work, we design/fabricate S composites with 3D carbon nanorods arrays with high mass loading of S (80.55%). The interspaces of carbon nanorods are sheltered by each other leaving abundant paths to penetrate ions/electrons and suppress the polysulfides shuttle.

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Enhanced capacity and rate cycling stability are verified due to the judicious designed S-C architecture.

2. Experimental

2.1. Synthesis of 3D ZnO nanorods arrays template

ZnO nanorods arrays template was prepared via a facile hydrothermal process. Briefly, 2.38 g $Zn(NO_3)_2 \cdot 6H_2O$ and 1.12 g Hexamethylenetetramine was dissolved in 80 mL deionized water. The mixture was thoroughly stirred for a while to form a clear solution Then, it was transformed into a 100 mL Teflon liner with nickel foam as the substrates. After heating at 95 °C for 6 h, the sample was washed and dried at 60 °C for 2 h to form ZnO nanorods arrays.

2.2. Synthesis of 3D carbon nanorods arrays (CNAs)

In a typical synthesis, 1.44 g glucose was dissolved in 80 mL water followed by homogeneous magnetic stirring. Then the solution was pulled down into Teflon line with nickel foam supported ZnO nanorods arrays, and kept 180 °C for 1.5 h in oven. After heating process, nickel foam supported CNAs were washed and dried at 60 °C for 2 h. The sample was heated at 800 °C with a flow of Ar gas (100 sccm) for 2 h to form carbon nanorods arrays. During the hydrothermal process, the pH value of glucose solution changed from 6 to 3, and the ZnO template was etched during the formation of carbon nanorods arrays.

2.3. Synthesis of CNAs/S composite electrode

The composite cathode was prepared via a solution-based method. Sulfur counting as ca. 2 mg cm^{-2} of composite was dissolved into moderate CS_2 solution with ultra-sonication for 10 min. S/CS_2 solution was then dipped onto the surface of nickel foam supported CNAs. The treated sample was then dried at 50 °C to evaporate CS_2. Finally, sulfur was infused into the carbon basement by sealing composite in Teflon liner heating at 155 °C for 12 h in oven, followed by cooling down to room temperature.

2.4. Cells fabrication and electrochemical measurements

The free-standing cathode was manufactured by cutting pre-prepared CNAs/S composites into small square slices of 1 cm × 1 cm. Coin-type half-cells were then assembled in a vacuum glove box filled with protection gas of Ar. The electrolyte was selected as 1 M lithium bis(trifluoromethanesulfonyl)imide and 0.1 M lithium nitrate ($LiNO_3$) in 1,3-dioxolane (DOL) and 1,2-dimethoxy-ethane (DME) (v:v = 1:1). The working electrodes (CNAs/S composites) and the anodes (pure lithium foil) were assembled into CR2025 coin-type cells, inserting a polypropylene film (Celgard 2400) between them. Electrolyte was then dropped between cathode and separator with 15–20 μL per cell. Relevant electrochemical measurements were performed using a LAND battery program-control test system (Wuhan, China). The cycling tests and cyclic voltammetry (CV) measurements were galvanostatically in the fixed voltage range of 1.7-2.8 V versus Li/Li$^+$ at 25 °C at different charge/discharge rates (0.1 C, 0.2 C, 0.5 C, 1.0 C, 2.0 C and 5.0 C) with CHI660D electrochemical workstation at a scan rate of 0.1 mV s^{-1}. PARSTAT MC multi-channel electrochemical workstation is conducted to test electrochemical impedance spectroscopy (EIS) with amplitude of 5 mV at the frequency range from 0.01 mHz to 10 mHz.

2.5. Material analysis

The microstructure and morphology of samples were characterized using scanning electron microscope (SEM, Hitachi S-4800) and transmission electron microscope (TEM, JEOL JEM200CX) at an acceleration voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded on X'Pert PRO instrument operated at 40 KV and 30 mA with Cu Kα radiation from angle 10° to 80°. Thermogravimetric analysis (TGA) measurement was tested by Netzsch-STA449C thermal analyzer in air from room temperature to 800 °C at a heating rate of 10 °C min^{-1}. The Raman spectrum was scanned from 0 to 3500 cm^{-1} using 325 nm laser wavelengths on an argon Renishaw inVia laser Raman spectroscopy (Laber Raman Series, HR–800) using 325 nm laser wavelengths. X-ray photoelectron spectroscopy (XPS) was selected as characterizing the bonded structure of samples, using an ESCAL 220i-XL electron spectrometer with a monochromated Al–K X-ray radiation source in a base pressure of 10^{-7} Pa.

3. Results and discussion

The fabrication process of CNAs/S composites is shown in Fig. 1. The 3D ZnO nanorods arrays (Fig. 1a) act as a template to synthetize carbon nanorods arrays. Then, sulfur is impregnated into CNAs via solvent removal through drying forming CNAs/S with homogenous distribution of sulfur among surface and gap of CNAs via 155 °C heating.

The as-synthesized ZnO composed of nanorods exhibits a three-dimensional porous structure with ZnO diameter of ca. 50–100 nm (Fig. 2a). ZnO nanorods networks are uniformly distributed on the surface of nickel foam (Fig. 2b). After hydrothermal process of glucose, the pH of solution changes from 6 to 3. The ZnO template will be etched by acid intermediate products with —COOH and —OH groups, leaving carbon nanorods arrays [32]. Carbon nanorods keep basic appearance with cylinder outline as well as wider diameter ca. 100–200 nm (Fig. 2c and d). The surfaces of nanorods are a bit rougher and maintain original excellent distribution (Fig. 2d). After infusing process, sulfur is well-proportioned wrapped outside CNAs composites after 155 °C sublimation. The existence of small sulfur particles can be an

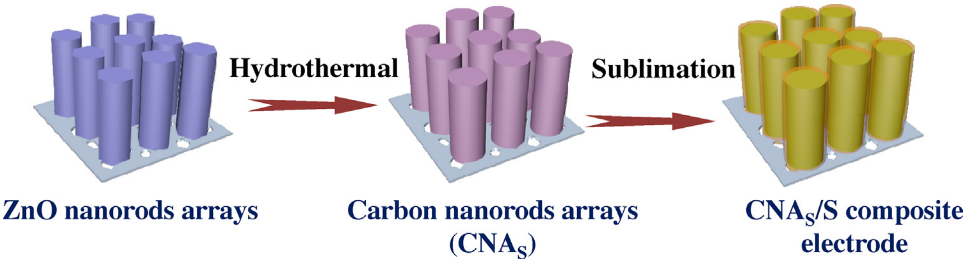

Fig. 1. Design and preparation of CNAs/S composite integrated cathode. (a) ZnO nanorods arrays. (b) Carbon nanorods arrays (CNAs) structure. (c) CNAs/S composite electrode.