



3D-hybrid material design with electron/lithium-ion dual-conductivity for high-performance Li-sulfur batteries



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H I G H L I G H T S

- A novel 3D-hybrid Sulfur based composite is proposed.
- EDA-functionalized GO/CNT hybrid (N-GO/CNT) works as 3D conductive frame network.
- Electrons/Li-ions-conductive (dual-functional) SPANI works as the coating layers.
- Remarkable electrochemical performances of S@N-GO/CNT@SPANI were obtained.
- The mechanism of high rate performances was studied.

A R T I C L E I N F O

Article history:

Received 23 September 2016
Received in revised form
12 November 2016
Accepted 18 November 2016

Keywords:

Three-dimensional hybrid
N-GO/CNT framework
Sulfonated polyaniline
Electron/Li-ion conductivity
Confinement effect

A B S T R A C T

We report a novel 3D-hybrid cathode material with three-dimensional (3D) N-GO/CNT framework to load sulfur (77.6 wt %), and sulfonated polyaniline (SPANI) of coating layer. Used as a cathode material, it possesses a high capacity ($1196 \text{ mAh g}^{-1}@0.3 \text{ A g}^{-1}@1.6 \text{ mg cm}^{-2}$), excellent charging-discharging rate ($680 \text{ mAh g}^{-1}@7.5 \text{ A g}^{-1}$) and long-life performance (maintaining 71.1% capacity over 450 cycles), which is mainly attributed to the benefits of excellent electronic/Li-ionic dual-conductivity and confinement effect of the 3D-hybrid N-GO/CNT framework coated by self-doping conducting polymer SPANI. Thus, a 3D sulfur cathode modified with electronic/Li-ionic dual-conduction network can significantly enhance the electrochemical performance and stability, and this novel type of material is very promising for commercial applications that require high energy and power density, long life, and excellent abuse tolerance.

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1. Introduction

Secondary Li-ion batteries play a very important role in energy storage and conversion. However, the currently used cathode materials based on the lithiated transition-metal oxide and phosphate are not able to meet the increasing requirements of electric vehicles, hybrid electric vehicles and other portable electronics owing to limited theoretical specific capacity and energy density [1]. Thus, developing advanced materials as Li-ion cathodes is an urgent task. With substantial merits of extremely high theoretical specific capacity (1675 mAh g^{-1}), superior energy density (2600 Wh kg^{-1}),

widespread availability and environmental friendliness, sulfur has been considered as the most promising candidate as the cathode material for the next-generation rechargeable battery [2–4]. However, several obstacles associated with sulfur electrode materials have hampered their commercialization, including: (i) the insulating nature and insolubility in electrolytes of sulfur species (S , Li_2S and Li_2S_2) impede the full utilization of sulfur and limit specific capacity and rate capability; (ii) the dissolution of polysulfides in electrolytes and subsequent “shutting effect” during cycling cause fast capacity fading; (iii) large volume change in the charge-discharge processes induces the mechanical damage of electrode [5–9].

To address these issues, considerable efforts have been devoted to dealing sulfur with the conductive nanocarbons including carbon nanospheres [5,8], graphene oxide sheets [10–12], carbon nanotubes [6,13,14], and meso-/microporous carbons [15].

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Graphene, a typical two-dimensional carbonaceous material, has now been a good choice to prepare carbon/sulfur composites due to huge surface area and outstanding electronic conductivity. Through the controllable preparation of graphene structure, the composite provides a huge space conductive network that not only improves the electronic conductivity of the electrode but also accommodates volume expansion during cycling. What's more, several researchers found that the introduction of polar chemistry groups (such as $-\text{NH}_2$ [10], $-\text{F}$ [16] and $-\text{PhSO}_3^-$ [17]) are able to trap polysulfides and mitigate the dissolution of polysulfides into electrolytes. Therefore, to fabricate a multi-dimension conductive network functionalized by polar chemistry groups may enhance the comprehensive electrochemical performance of sulfur carbon composites.

Another strategy to overcome the obstacles of sulfur cathode is to modify the surface properties of sulfur-carbon composites with conductive polymer such as polyaniline (PANI) [18], polypyrrole [19], polydopamine [20], Poly (3,4-ethylenedioxythiophene) [21], etc. The coating polymers can efficiently suppress polysulfide dissolution and improve the stability of sulfur cathode during electrochemical cycling because of the strong chemical interactions between polar functional groups and polysulfides. Although these conductive polymers can enhance the conductivity of cathode materials and inhibit diffuse of polysulfides, there still exist some issues such as the low Li^+ conductivity and electronic conductivity depended on the doping condition, constraining the rate performance of cathode composites.

Sulfonated polyaniline (SPANI), a novel self-doped water soluble conducting polymer [22–28], has been widely utilized in fabricating supercapacitor [25] and multilayer hetero-structure light emitting diode devices [29], while no example about SPANI used in rechargeable lithium ion batteries was found. Compared with PANI, which is easy to become insulating for $\text{pH} \geq 3$, SPANI is capable of self-doping without external protonic doping and maintain high activity over a wide range of pH values by introducing a $-\text{SO}_3\text{H}$ group regarded as a strong acid on PANI chain [22]. Moreover, the solubility of SPANI and the good environmental stability is highly improved by the presence of the polar $-\text{SO}_3\text{H}$ groups on the phenyl rings. Especially, previous studies have revealed that $-\text{SO}_3\text{H}$ of SPANI can be translated into non-protonated sodium salt $-\text{SO}_3\text{Na}$ [23], in which case $-\text{SO}_3^-$ is able to serve as the lithium ion transmission sites to own ion conductivity. Based on these, the self-doped SPANI may have the potential use in secondary lithium ion batteries.

Differing from the previous reports about absorption of polysulfides [30,31] or high-rate S cathodes [32,33], this work reported a novel 3D-hybrid material with three-dimensional (3D) N-GO/CNT framework to load sulfur (77.6 wt %), and sulfonated polyaniline (SPANI) of coating layer. By using these novel composites as cathode materials for Li-sulfur batteries, the high capacity (1196 mA h g^{-1} @ 0.3 A g^{-1} / 1.6 mg cm^{-2}), excellent charging-discharging rate (680 mAhg^{-1} @ 7.5 A g^{-1}) and long-life (maintaining 71.1% capacity over 450 cycles), were obtained. These results are mainly attributed to the 3D-hybrid N-GO/CNT framework coated by self-doping conducting polymer SPANI, which owns excellent electronic/Li-ionic dual-conductivity as well as effective confinement effect of polysulfide intermediates. Thus, such a 3D sulfur cathode modified with electronic/Li-ionic dual-conduction network can significantly enhance the electrochemical performance and stability, and this novel type of material is very promising for commercial applications that require high energy and power density, long life, and excellent abuse tolerance.

2. Experimental

Synthesis of GO and N-GO/CNT hybrid: GO was prepared from natural graphite flake (-325 mesh, Alfa Aesar) by a modified Hummers' method using NaNO_3 , KMnO_4 and concentrated H_2SO_4 . In a typical procedure, 50 mg Carboxylic MWCNTs were dispersed in 100 mL distilled water by ultrasonic treatment for 30 min. After that, 100 mg freshly prepared GO was added, and then sonicated for another 1 h. Subsequently, the mixture of the obtained dispersion solution and 200 μL ethylenediamine (EDA) was heated at 75°C for 6 h in a sealed vessel to obtain the N-doped GO/CNT hybrid.

Synthesis of S@N-GO/CNT@SPANI hybrid: Firstly, for the synthesis of S@N-GO/CNT hybrid, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (7.45 g, 30 mmol) was added into fresh N-GO/CNT suspension (the above resultant suspension was diluted to 150 mL) under vigorous stirring, followed by adding HCl (60 mL, 1 M) dropwisely in 1 h. After stirring for 3 h, the products were filtered and washed several times with distilled water until the effluent became neutral. Subsequently, to fabricate S@N-GO/CNT@SPANI hybrid, S@N-GO/CNT hybrid were dispersed in HCl (50 mL, 1 M). After stirring vigorously for 3 h, aniline (0.75 mmol) and metanilic acid (0.75 mmol) were dissolved into above suspension, followed by slowly adding 1.5 mmol of ammonium persulfate (APS) under N_2 gas and stirring for 24 h. The obtained hybrids were filtered and rinsed several times with distilled water, and then dried at 50°C for 24 h in vacuum oven. In contrast, S@N-GO/CNT@PANI hybrid was synthesized in the same method with 1.5 mmol aniline instead of aniline (0.75 mmol) and metanilic acid (0.75 mmol).

Material characterization: The sample structures were characterized with the scanning electron microscopy (ZEISS Supra 55, Oxford X-Max 20, 20 kV) and Transmission electron microscope (HRTEM, JEM-100F, 200 kV) as well as Powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer using $\text{Cu K}\alpha$). Thermogravimetric analysis (TGA) data was collected on a TGA/DSC system at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen flow. Raman spectrum was recorded by iHR 320. The electrical conductivity was measured by a standard four-point probe resistivity measurement system.

Electrochemical measurement: The working electrodes were prepared by mixing a sulfur based-material, carbon black and PTFE in isopropanol with a weight ratio of 6:3:1 through grinding in a mortar. Then the mixtures were pressed into rounds and dried at 60°C for 24 h in the vacuum oven. The 2032 coin-type cells were finally assembled in an Ar-filled glovebox, using pure lithium foil as anode, cell grand 2400 as separator, and 1 M LiTFSI containing 0.3 M LiNO_3 in DOL/DME as electrolyte. The galvanostatic discharge/charge tests were performed at diverse current densities within a cut-off voltage window of 1.5–3.0 V. The cyclic voltammetry (CV) results were conducted by a CHI 660 E electrochemical workstation between 1.5 and 3.0 V. The electrochemical impedance measurements were carried out over the frequency range from 0.1 to 10^5 Hz.

3. Results and discussion

The synthesis scheme of 3D S@N-GO/CNT@SPANI hybrid is shown in Fig. 1. Firstly, GO and carboxylic CNTs were mixed in the deionized water by ultrasonic treatment to obtain homogeneous suspension. The abundant oxygen groups in GO and CNTs react with ammonium in EDA to gain the 3D porous structure of N-GO/CNT hybrid, which can be observed from SEM image (Fig. 1b) and pore structure analysis of N_2 absorption test (Fig. S1). TEM image of the hybrid (Fig. S2) further proves that the undesired GO nano-sheets agglomeration can be physically avoided and a

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