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Nitrogen-doped graphene nanosheets/sulfur composite as lithium–sulfur batteries cathode

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ABSTRACT

Lithium–sulfur batteries have been receiving unprecedented attentions in recent years due to their exceptional high theoretical capacity and energy density, low cost and environmental friendliness. Yet their practical applications are still hindered by short cycle life, low efficiency and poor conductivity which are mainly caused by the insulating nature of sulfur and dissolution of polysulfides. Here, a nitrogen-doped graphene nanosheets/sulfur (NGNSs/S) composite was synthesized via a facile chemical reaction deposition. In this composite, NGNSs was employed as a conductive host to entrap S/polysulfides in the cathode part. The NGNSs/S composite delivered an initial discharge capacity of 856.7 mAh g^{-1} and a reversible capacity of 319.3 mAh g^{-1} at 0.1 C with good recoverable rate capability.

1. Introduction

Recently lithium–sulfur (Li–S) batteries are becoming one of the most attractive next-generation lithium batteries. As one of the most abundant, low-cost and environmental friendly elements on earth, sulfur has a theoretical capacity and energy density of 1675 mAh g^{-1} and 2600 Wh kg^{-1} (vs. 272 mAh g^{-1} and 387 Wh kg^{-1} for $LiCoO_2$), respectively, which are much higher than typical commercial lithium-ion battery cathodes such as $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$ [1,2]. However, low active material utilization, capacity degradation, poor Coulombic efficiency and poor cycle life are the challenges of Li–S cells using sulfur cathodes. During the electrochemical reaction, both sulfur and its discharge product Li_2S have high electrical resistivities [3]. Moreover, dissolution of polysulfides in the electrolyte and precipitation of polysulfides on the electrodes result in the so-called shuttle effect [4], which leads to the decrease of the active mass utilization during discharge process and strain field which degrades the cycle life [5–7]. It was also reported that volume expansion and crack formation of the sulfur electrodes take place during cycling which could lead to the failure of batteries [8]. In recent years, intensive efforts have been exerted in improving Li–S batteries by developing sulfur composite cathode materials (such as sulfur/carbon materials composite [9–13], sulfur/conductive polymers composite [14–17] and sulfur/metal oxide additives composite [18–20]), modifying electrolytes to manipulate the solubility of polysulfides (such as changing lithium salt and solvent [21,22], employing polymer electrolyte [23], adding electrolyte additive [24] and using polysulfides containing electrolyte [25,26]), and designing various cell configurations (such as placing carbon-based interlayer [27–30], coating modification of separator [31–33], fabricating lithium metal free anode [34], and binder or metal current collector free cathode [35–37]).

Graphene, a two-dimensional (2D) crystalline allotrope of carbon, has been considered as a promising conductive matrix for Li–S batteries due to its superior electrical conductivity, high specific surface area and excellent chemical tolerance. Graphene/sulfur composites with different structures such as graphene-wrapped sulfur particles [38–41] or sandwich type composites [42–44] have been reported. However, these close-type structures only provide physical barriers by which polysulfides dissolution in the electrolyte is hardly prevented in long term cycling and constrain Li^+ transporting across graphene in the lateral direction. Chemical adsorption of sulfur and polysulfides by the host is another attractive strategy to effectively eliminate the polysulfide dissolution. Several studies have been reported on the chemical interactions between functional group (e.g. oxygen group or hydroxyl group) on graphene and polysulfides which are beneficial to the enhancement of polysulfides immobilization [45,46]. Nitrogen- (N-) doping by introducing nitrogen groups and generating the extrinsic defects on carbon lattice is proved to be an effective way to improve the electrochemical performance of electrodes [47–54]. There are

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three major types of N-doped groups: pyridinic-N, pyrrolic-N and graphitic-N [55]. It has been found that these N-doped active sites can adsorb Li^+ and also serve as tunnels for Li^+ transportation [56]. Recently, several studies have been reported on developing N-doped graphene/sulfur (NG/S) composite for Li–S batteries. X. Wang et al. synthesized two types of NG/S composite: pyridinic-N enriched and pyrrolic-N enriched, respectively. Pyridinic-N has been proved to contribute more efficiently on confining the diffusion of soluble polysulfides [57]. In another work, C. Wang et al. reported a NG/S composite with 3D structure. The NG with the pyridinic-, pyrrolic- and graphitic-N groups exhibited a better performance comparing to undoped graphene, which was attributed to the 3D conductive network and reactive N functional groups [58]. Y. Qiu et al. further studied the role of N-doping in immobilizing polysulfides and compared the binding energies for primitive-, pyridine- and pyrrole-graphene with atomic Li and polysulfides by a computational method. It has been revealed that the enhancement is mainly due to the ionic attractions between N and Li cations, instead of N and S anions [59]. All the work above so far has been successfully introduced basic N functional groups in the NG sheets. It has to be noted that the performance of NG can be determined by several factors, such as the type of N functional groups, the N content in the NG, and structure and morphology of NG induced by N-doping, indicating more studies related to NG/S composites need to be further addressed.

In order to study the contribution of other N-doped functional groups, in this work, we have successfully synthesized the N-doped graphene nanosheets with amino-N and pyridine-N-oxide functional groups. The N-doped graphene nanosheets/sulfur (NGNSs/S) composite was prepared and evaluated as cathode materials in Li–S batteries. At 0.1 C, the NGNSs/S composite exhibited discharge capacities of 857 mAh g^{-1} and 319.3 mAh g^{-1} at the first and 20th circles, respectively. It is suggested that the NGNSs provided a conductive matrix with high surface area and high conductivity and N functional groups facilitated immobilization of the polysulfides.

2. Experimental

2.1. Synthesis of NGNSs

NGNSs were synthesized from natural flake graphite, as reported in our previous work [55,60]. First, graphite oxide was obtained by the oxidation of natural graphite in a modified Hummers method [55]. The graphene nanosheets (GNSs) were obtained by the thermal exfoliation of graphite oxide at 1050 °C for 30 s under nitrogen atmosphere. NGNSs were produced by treating the pristine GNSs at the mixed gas of ammonia and argon at 900 °C for 5 min [60].

2.2. Synthesis of NGNSs/S composite

NGNSs/S composite was synthesized by a facile chemical reaction deposition method [58]. The procedures are as illustrated in Fig. 1a. First, a 0.04 M $Na_2S_2O_3$ solution was prepared by dissolving 1.58 g $Na_2S_2O_3$ in 250 ml distilled water, followed by magnetic stirring for 30 min. Next, the as-synthesized 0.4 g NGNSs were dispersed in the $Na_2S_2O_3$ solution to produce composite. The mixture was under sonication for 1 h and it was continuously stirred. Then, 20 ml 10 M hydrochloric acid was dropped into the solution. After stirring for 24 h to let the reaction proceed completely, the product was filtered and washed with distilled water several times to eliminate salt products as well as until pH reached 7 and finally dried in a vacuum oven at 60 °C for 24 h. GNSs/S composite was synthesized by the same procedures as NGNSs/S composite. Pure S particles were obtained via the same chemical reaction route as described above and in the chemical Eq. (1) as below [61]:

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2\uparrow + H_2O + S\downarrow \quad (1)$$

2.3. Characterization

The microstructure and morphology characterization of obtained NGNSs, S particles and NGNSs/S composite was carried out by using a JEOL FE6330 field-emission scanning electron microscope (SEM). The nitrogen contents of NGNSs were determined by XPS analysis with a Kratos Axis Ultra Al (α) X-ray photoelectron spectroscopy at 14 kV. The crystal structures of the products were examined by X-ray diffraction (XRD) on a Siemens D5000 X-ray diffractometer via Cu Kα radiation between 10° and 90° at a scan rate of 2°/min. The surface area was characterized by nitrogen adsorption/desorption isotherms at 77 K using a Tri-Star II Micromeritics and calculated by Brunauer–Emmett–Teller (BET) measurement. Detailed surface information of NGNSs was obtained by using a JASCO Fourier transform-infrared spectrometer (FTIR)-4100. The weight percentage of sulfur in the composite was determined by thermogravimetric analysis (TGA) conducting on a SDT Q600 at a heating rate of 5 °C/min from room temperature to 400 °C under nitrogen protection.

2.4. Electrochemical measurement

Electrochemical characterization was carried out in CR2032-type coin cells. The NGNSs/S working electrodes were constructed from 80 wt.% NGNSs/S composite, 10 wt.% poly(vinylidene difluoride) (PVDF) binder, and 10 wt.% Carbon black in an N-methyl-2-pyrrolidinone (NMP) solution. GNSs/S, sulfur particles and NGNSs working electrodes were also prepared and evaluated as control samples. The well mixed slurry was uniformly casted onto aluminum foil current collectors and the electrodes were dried in a vacuum oven at 60 °C for 12 h. The coin cells were assembled in an argon-filled glove box with lithium metals as the counter and reference electrodes and Celgard 2400 polypropylene film was used as separator. The electrolyte was a 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1, v/v) with 1 wt.% $LiNO_3$ mixed solution. The cyclic voltammetry (CV) data were collected with a biologic VMP3 potentiostat at a scan rate of 0.1 mV s^{-1} at 1.0–3.0 V (vs. Li/Li^+). Galvanostatic charge/discharge cycling profiles of the cells with constant current densities and rate capability at various current densities were conducted at a cut-off potential of 1.0–3.0 V (vs. Li/Li^+) on a Neware BTS-610 instrument. Electrochemical impedance spectroscopy (EIS) was conducted on the VMP3 in the frequency range from 100 kHz to 0.1 Hz with an input AC voltage amplitude of 10 mV. All the electrochemical tests were performed at room temperature.

3. Results and discussion

3.1. Characterization

The SEM results of S particle, NGNSs and NGNSs/S composite are compared in Fig. 1b–d. It can be seen in Fig. 1b that irregular shaped sulfur particles formed by precipitation of chemical reaction are in the particle size of several microns. Fig. 1c displays the morphology of NGNSs which was randomly orientated agglomerate of planar sheets. Fig. 1d shows the morphologies of NGNSs/S composite at different magnifications. It can be observed that the sulfur particles are pretty homogenously mixed with the NGNSs together (Fig. 1d inset). Fig. 1e shows the TEM image of NGNSs, in which the 2D layered structure of NGNSs can be observed.

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