Edge sulfurized graphene nanoplatelets via vacuum mechano-chemical reaction for lithium–sulfur batteries

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ABSTRACT

Lithium–sulfur batteries have great potential for high energy applications due to their high capacities, low cost and eco-friendliness. However, the particularly rapid capacity decay owing to the dissolution and diffusion of polysulfide intermediate into the electrolyte still hamper their practical applications. And the reported preparation procedures to sulfur based cathode materials are often complex, and hence are rather difficult to produce at large scale. Here, we report a simple mechano-chemical sulfurization methodology in vacuum environment applying ball-milling method combined both the chemical and physical interaction for the one-pot synthesis of edge-sulfurized grapheme nanoplatelets with 3D porous foam structure as cathode materials. The optimal sample of 70%S–GnPs-48 h (ball-milled 48 h) obtains 13.2 wt% sulfur that chemically bonded onto the edge of GnPs. And the assembled batteries exhibit high initial discharge capacities of 1089 mAh/g at 0.1 C and 950 mAh/g at 0.5 C, and retain a stable discharge capacity of 776 mAh/g after 250 cycles at 0.5 C with a high Coulombic efficiency of over 98%. The excellent performance is mainly attributed to the mechano-chemical interaction between sulfur and grapheme nanoplatelets. This definitely triggers the currently extensive research in lithium–sulfur battery area.

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1. Introduction

Compared with the current commercialized cathode materials based on transition metal oxides and phosphates, sulfur has recently received noteworthy attention for lithium–sulfur batteries (LSBs) due to its high theoretical capacity (1675 mAh/g) and energy density (2600 Wh/kg). Thus, together with its advantages of low cost, simplicity and eco-friendliness, makes sulfur to be the most promising cathode material for practical applications [1,2]. However, sulfur-based cathode materials are still faced with many challenges before large-scale production such as: (a) poor electrical conductivity of sulfur; (b) large volume and morphology changes of sulfur electrodes over lithiation and (c) dissolution and diffusion of the polysulfides intermediate into the electrolyte, which lead to particularly rapid capacity decay and low Coulombic efficiency [3,4]. Over these years, extensive efforts have been paid to solve the above-mentioned problems by encapsulating sulfur with various carbon hosts, such as porous carbon [5–7], conducting polymers [8–10], carbon nanotubes [11–15] and graphene

derivatives [16–23]. Recently, the group of Yi Cui [24] applied hollow carbon nanofibers to improve the cyclic stability, which exhibits improved capacity of 1180 mAh/g at 0.2 C and capacity retention of 80% after 300 cycles at 0.5 C; the group of Yunhui Huang [25] presented an order meso–microporous core–shell carbon material as cathode which shows a capacity of 837 mAh/g at 0.5 C after 200 cycles with a capacity retention of 80%. The group of A. Manthiram [26] applied a sulfur-muti-wall nanotube cathode by a binder/current collector-free fabrication procedure, which exhibits high capacities of 1352 mAh/g at 1 C and 1012 mAh/g at 4 C. Meanwhile, other more materials have been applied to LSBs such as copper-stabilized sulfur–microporous carbon (maintain 600 mAh/g after 500 cycles at 100 mA/g) [27], nanoarchitecture graphene/CNT@porous carbon (809 mAh/g at 10 C with low decay rate of 0.12% per cycle) [28], and 3D interconnected carbonaceous multiscale-cellular foams (maintain 800 mAh/g at 150 mAh/cm³ after 50 cycles) [29]. Although many improvements have been made to develop high-performance LSBs, sulfur-based cathode materials are still faced with manifold challenges. As a monolayer carbon material, graphene exhibits excellent performance such as superior electronic conductivity, high surface area and outstanding mechanical properties, making it an optimal material for high performance LSBs. Recently, the group of Hongjie Dai [30] reported a

sulfur–graphene material synthesized by wrapping poly(ethylene glycol) coated sulfur particles with oxidized graphene sheets. Chen and co-workers [31] designed a graphene-based porous carbon material for the immobilization of sulfur. However, all of the reported physical or chemical procedures for S–graphene cathode materials are often complex and even environmentally harmful, and hence are impractical for large-scale produce [32,33]. Therefore, it remains challenging to design a new process for the preparation of S–graphene composites.

Here, we designed a simple, low-cost, eco-friendly ball-milling method applied vacuum mechano-chemical interaction for large-scale preparation of S–GnPs cathode materials. This method is effective to exfoliate the graphite to be layered GnPs, and high content of sulfur (as high as 13.2 wt%) is edge-selectively functionalized to GnPs accompanying with a uniformly adsorption on/within the GnPs, which results to a 3D porous foam structure through self-assembling effect. In this architecture, GnPs acts as conductive intensifier and the polysulfide reservoir to improve the cathode performance. Furthermore, the optimal ball-milling time was studied for S–GnPs preparation. When used for LSBs, the as-prepared S–GnPs materials exhibit excellent electrochemical performance and practical significance.

2. Experimental

2.1. Synthesis of S–graphene nanoplatelets (GnPs)

Predetermined amounts of commercial graphite and pure sulfur were placed into a steel jar with stainless steel balls and the jar was kept in vacuum environment. Thereafter, the jar was fixed in a planetary ball-mall machine (QM-3SP04, Nanjing) and agitated at 500 rpm for settled time. Finally, the resultant powders were obtained and denoted as 70%S–GnPs-xh (x represents the ball-milling time). The 70%S–GnP-xh samples were further Soxhlet extracted with carbon disulfide (CS_2) to remove physically adsorbed sulfur to produce the samples denoted as 70%S–GnPs-xh-CS_2 for characterization. Meanwhile, the GnPs-48 h sample was prepared by the same ball-milling procedure as those for the 70%S–GnPs samples at 48 h without sulfur.

2.2. Characterization methods

The morphology of 70%S–GnPs was characterized by scanning electron microscopy (SEM, Quanta 400/INCA/HKL) equipped with a Centurio EDS detector. Transmission electron microscope (TEM) images were tested on a probe-corrected JEOL ARM200F operated at 300 kV. The phase identification of 70%S–GnPs-xh samples was carried out by powder X-ray diffraction (XRD) applied an Empyrean X-ray generator. The sulfur contents of the 70%S–GnPs-xh samples were determined by thermogravimetric analysis (TGA, TA instruments 2000) under nitrogen with a temperature ramp of 10 °C/min. The element analyses (EA) were performed on the instrument of Element Analyzer (Elementar Analysensysteme GmbH). The samples were oxidized and translated into gaseous substance under high-temperature. The gases were then detected upon entering into the detector. X-ray photoelectron spectroscopy (XPS) measurements were operated on VG Scientific ESCALAB 2201 XL instrument applied aluminum $K\alpha$ X-ray radiation. Raman spectra were measured using a Raman spectrometer (Lab RAM HR, Horiba JobinYvon SAS).

2.3. Electrochemical measurements

The electrochemical characterizations of the as-prepared samples were carried out by R2025 coin cells using lithium metal as the anode and Celgard 2500 film as separator. The electrodes were fabricated by uniformly blending 80 wt% active materials (70%S–GnPs-xh or 70%S + 30%GnPs-48 h) with 10 wt% of carbon black (Super P, Timcal) and 10 wt% of polyvinylidene fluoride (PVDF) binder. N-methyl-2-pyrrolidone (NMP) was used as the solvent for the mixture. The obtained working electrodes were cut into circular disks with a diameter of 14 mm. The coin cells with sulfur loading of ~1.4 mg/cm^2 were assembled in an Ar-filled glove box using 1 M lithium bis-trifluoromethanesulfonylimide (LiTFSI) in 1,3-dioxolane (DOL)/dimethoxyethane (DME) (1:1, v/v), including 0.1 M LiNO$_3$ as the electrolyte. And it is 50 μL of electrolyte that was added per coin cell. Discharge–charge measurements were carried out in a voltage range of 1.7–2.8 V at different current densities by a NEWARE battery tester. The capacities are calculated based on the mass of sulfur (~1.4 mg/cm^2) in the cathode materials. Then 1 C corresponds to 1675 mA/g. Electrochemical impedance spectroscopy (EIS) was carried out by the Solartron1255 B frequency response analyzer coupled with a Solartron 1287 electrochemical interface in the frequency range from 100 MHz to 0.1 Hz with an applied voltage of 5 mV. The electronic conductivity was carried out using a four-point probe meter (SDY-4, China)

3. Results and discussion

3.1. Structure and morphology

The schematic representation of 70%S–GnPs-xh materials preparation applied a mechano-chemical method. Briefly, 70 wt% sulfur and 30 wt% commercialized graphite were placed into a steel jar sealed under vacuum to rotate at 500 rpm for 24, 48, 72 or 96 h in turn. The vacuum environment contributes to reduce the doping of oxygen to GnPs and improves the bonding content of sulfur. The resultant products are denoted as 70%S–GnPs-xh (x represent the ball-milling time). Furthermore, the as-prepared 70%S–GnPs-xh samples were Soxhlet extracted with carbon disulfide (CS_2) solvent to physically remove the sulfur that unbounded to GnPs, and the final products are designed as 70%S–GnPs-xh-CS_2. Compared with 70%S–GnPs-48 h, the GnPs-48 h sample was prepared without sulfur under the same conditions (see Fig. 1). **Q5**

The scanning electron microscope (SEM) images of the 70%S–GnPs samples under different ball-milling times from 24 to 96 h are shown in Fig. 2. All the samples exhibit large particles of ~2–30 μm for S–GnPs composites. Detailed examination for the sample of 70%S–GnPs-48 h-CS_2 was imaged with TEM. It is observed that the 70%S–GnPs-48 h-CS_2 sample reveals a clearly morphology of 3D porous foam structure forming from self-assembling of the sulfur functionalized GnPs material (Fig. 3(a)). As expected, the monolayer or multilayer structures of GnPs flakes are clearly obtained in Fig. 3(b) and (c), indicating that the mechano-chemical method is effective to exfoliate the graphite to be layered GnPs. Fig. 3(d) is the high angle annular dark field (HAADF) STEM images for layered structure of 70%S–GnPs-48 h-CS_2 and the energy dispersive X-ray (EDX) was carried out (Fig. 3(e)) at point 1 and point 2 from Fig. 3(d) to measure the distribution of sulfur. It can be proved that the sulfur content around the edge is much higher than that on the inside of mono-layered or multi-layered GnPs, indicating that sulfur is mainly chemically bonded to the edge of GnPs with the formation of C–S bonds and oxygen containing functional groups. The introduction of oxygen is mainly owing to the translation of certain active sulfur and carbon into functional groups by means of spontaneous reaction with oxygen in air after opening the ball-milling jar. The introduced oxygen-containing groups in GnPs can immobilize sulfur and improve the capacity retention in the cathode due to the weak binding between the polysulfides and the oxygenated framework [34–37]. The energy dispersive spectroscopic (EDS) mapping for 70%S–GnPs-48 h-CS_2 was further carried out as shown in Fig. S1. Carbon, sulfur and oxygen