Preparation and performance of a sulfur/graphene composite for rechargeable lithium-sulfur battery

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Abstract. The lithium-sulfur (Li-S) battery is a promising electrochemical system that has high theoretical capacity. The sulfur/graphene nanosheets (S/GNS) composite is prepared through thermal reduction between the sulfur (S) and graphene oxide (GO). The morphology and composition of the composite are analyzed by means of x-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopic (EDS) characterization. It is found that the element S distributed uniformly between the layers of GNS. Graphene with a two-dimensional structure of carbon atoms is employed as a conductive and absorbing agent for the S cathode materials of rechargeable Li-S battery. The S/GNS composite cathode shows a specific electrochemical capacity, which is about 1598 mAh g⁻¹ S at the initial discharge and remains above 670 mAh g⁻¹ after 80 cycles.

1. Introduction

Facing the rapid growing energy shortage and global environment problems, the development of Li-ion batteries with high energy-density is in high demand for extending their applications to storing electricity from renewable sources [1]. One of the most promising candidates for storage devices is the Li-S cell. The theoretical specific capacity of S is 1672 mAh g⁻¹, corresponding to a theoretical specific energy of 2600 Wh kg⁻¹ [2]. Furthermore, it possesses obvious advantages of abundant resources, low cost and environmental friendliness.

However, the low electrical conductivity of S and S-containing organic compounds limit active material utilization due to poor electrochemical contacts within the material. Moreover, the dissolution of electrochemical reaction products of polysulfides (Li₂Sₓ, where 1≤x≤8) and the redox shuttle mechanism make capacity faded quickly [3]. To enable operating the Li-S battery, the S cathode material must be well combined with a high conductive and a strong adsorbing agent. Various carbon materials, such as active carbon [4], mesporous carbon [5], and carbon nanotubes [6], have been intensively investigated as additives for Li-S batteries.

Recently, GNS, a two-dimensional structure of carbon atoms with high surface area, superior electrical conductivity, chemical stability, and mechanical properties, has attracted high attention for
use of energy storage applications [7]. In a recent report by Wang et al., S was melted and coated on the GNS, which shows an improved capacity [8]. Furthermore, in another report, researchers synthesized a graphene-sulfur composite material by synthesizing submicrometer sulfur particles coated with PEG containing surfactants and GNS. The composite showed high specific capacity with relatively good cycling stability as the cathode for Li-S batteries [9].

Herein, we used a facile and low-cost methodology to the large-scale synthesis of S/GNS composite, wherein the GO was used instead of GNS which is easy to be prepared, and S as a reducing agent will be reduce GO to GNS through thermal process. Meanwhile, melted S can be homogeneously distributed between the layers of GNS to take advantage of the fact that S interacts strongly with carbon. The lyophilized method can also keep a high surface area of the composite.

2. Experimental

2.1. Materials Synthesis and characterization

The GO was made by a modified Hummers method [10], and then mixed with elemental S (Aladdin Reagent, AR) in the weight ratio of 1:5, with the mixture designated S/GO. The S/GO was ultrasonicated for 30 min to get a uniform suspension and then lyophilized it. The mixture was held at 423 K for 4 h under argon gas protection to allow the melted elemental S to infiltrate into the layers of GNS. Then, the temperature was increased to 573 K and held for 2 h, reduced GO to GNS.

The microstructure analyses were characterized using XRD measurements being performed on a Rigaku-Dmax 2500 diffractometer with Cu Kα radiation. SEM was performed on a field emission Hitachi S-4800 instrument.

2.2. Electrochemical measurements

The working cathode slurry was prepared by mixing 80 wt.% composite with 10 wt.% acetylene black (Hong-xin Chemical Works) and 10 wt.% polyvinylidene fluoride (PVDF, DuPont Company, 99.9%) binder in N-methyl-2-pyrrolidinone (NMP, Aladdin Reagent, AR) solvent. A sulfur cathode slurry containing 50 wt. % S, 40 wt.% carbon black, and 10 wt.% PVDF binder was also prepared in the same way to compare with the working cathode. The slurries were coated onto Al foil current collector using doctor’s blade. It was dried in a vacuum oven at 333 K for 24 h and then pressed. Subsequently, the electrode was cut into disks with a diameter of 12 mm. Coin-type cells of 2025 were assembled in an Ar-filled glove box with H2O and O2 content below 1 ppm, with Li foil as anode, 1 M LiPF6 EC/DMC (v/v, 1:1) as electrolyte. The charge/discharge performances were tested between 1.2 V and 3 V, using LAND CT2001A multi-channel battery testing system at room temperature. The electrochemical impedance response (EIS) measurements were carried out with a BioLogic VMP3 station.

3. Results and discussion

3.1. The structure characterization

Figure 1. SEM images of (a) elemental S powder, (b) GNS and (c) S/GNS composite.
Figure 1 shows the SEM images of element S, GNS and their composites prepared through reduction. The bare S power consists of microsized particles (Figure 1a). Figure 1b shows the GNS reduced by decomposition at 573 K for 4 h under argon gas protection. After heat treatment of S/GO, the microsized S particles melted and coated uniformly on the GNS sheets (Figure 1c).

To verify the composition of our S/GNS composite, we carry out EDS mapping/imaging of the material. Chemical mapping confirms that the bright particles in the SEM image (Figure 2a) are element C (Figure 2c, carbon mapping), with element S being coated on the GNS sheets uniformly (Figure 2d, S mapping). EDS spectrum captured for the region shown in Figure 2b also shows the existence of S.

![Figure 2. EDS characterization of S/GNS composite. (a) SEM image of GNS coated S particles. (b) EDS spectrum captured for the region shown in (a). (c) EDS mapping of the carbon region shown in (a). (d) EDS mapping of the S region shown in (a).](image)

![Figure 3. XRD patterns of elemental S and S/GNS composite.](image)
Figure 3 shows the XRD patterns for the S powder and S/GNS composite. Elemental S exhibits several sharp peaks from 10 to 60 degree, indicating its good crystal state. For the S/GNS composite with a low S content of 22 wt.%, the characteristic peaks of crystal S are not detectable, which suggests that S becomes amorphous and homogeneously distributed in the composite.

3.2. Electrochemical performance of the S/GNS

Figure 4 shows the discharge curves of the S and S/GNS composite vs. Li/Li+. The discharge curves represent a typical characterization of Li-S batteries. The discharge curves show two plateaus based on the voltage profile. The detailed mechanisms for oxidation and reduction of S, polysulfides and Li sulfide during discharge-charge were already reported. The upper plateau is well known as the change from elemental S to the higher order Li polysulfides (Li$_2$S$_n$, 8>$n$>2). The lower plateau is caused by the reduction of the higher order Li polysulfides to lower order Li sulfides (Li$_2$S$_2$, Li$_2$S). Calculated from the S content (22 wt.%), the initial discharge specific capacity of the working cathode is about 1598 mAh g$^{-1}$, the utilization of electrochemically active S is 95.6% assuming a complete reaction to the product of Li$_2$S. In contrast, the initial discharge specific capacity of the S cathode is about 1094 mAh g$^{-1}$.

![Figure 4. First discharge curves of the S and S/GNS composite electrodes](image1)

![Figure 5. Discharge capacities vs cycle number for S and S/GNS composite electrodes](image2)

The cycling performance of the S/GNS composite electrode is compared to that of the pure S, as shown in Figure 5, being cycled at a constant current density of 160 mAh g$^{-1}$. The discharge specific capacity of the composite electrode drops from initial 1598 mAh g$^{-1}$ to 670 mAh g$^{-1}$ after 80 cycles, which shows a good cyclic stability. The initial capacity of the S/GNS electrode is higher than that of the pure S electrode and the cycling stability of the S/GNS composite is also improved.

EIS is also invited to investigate the differences of electrochemistry of the two electrodes. Nyquist profiles are illustrated in Figure 6. The simplified equivalent circuit on the upper-right is used to interpret the measured data. It can be see from the figure that all the Nyquist plots of cathodes are composed by a semicircle at high frequencies relating to the contact resistance and charge transfer resistance, and a short inclined line in low frequency regions due to the ion diffusion within the cathode. The semicircle in S/GNS electrode is much smaller than the S electrode, because GNS can provide a better electron and ionic conductivity network.
4. Conclusions
A S/GNS composite with layered structure is prepared by thermal treatment with a mixture of elemental S and GO, the GO can be well reduced to GNS and elemental S is coated uniformly onto the GNS through heat treatment. The S/GNS composite shows a specific capacity, which is about 1598 mAh g⁻¹ S at the initial discharge and remains above 670 mAh g⁻¹ even after 80 cycles. GNS can provide a better electron and ionic conductivity network in the composite and can also contain the polysulfides effectively. The S/GNS composite is a promising cathode material for rechargeable Li-S battery.

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