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Full Length Article

MnS decorated N/S codoped 3D graphene which used as cathode of the lithium-sulfur battery

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ABSTRACT

A scale-upable MnS nanocrystal decorated N/S codoped graphene nanocomposite (MNSG) for Li-S batteries has been readily synthesized through hydrothermal process and followed by thermal treatment under N_2. Sulfur is loaded into nanohybrid to produce an outstanding Li-S battery cathode through integrating the advantages and avoiding the disadvantages of graphene and MnS. The optimized cathode can deliver a higher capacity of 756 m Ah g^{-1} at 0.5 C (1 C = 1675 mA g^{-1}) after 200 cycles and can retain 73% of the initial capacity, which indicates a potential applicable cathode material for lithium-sulfur batteries.

1. Introduction

The rapid depletion of fossil fuels and increasing environmental pollution issues are major stimulating forces for developing clean energy technologies. Renewable energy sources, such as solar, wind and tide are attractive solution in this issue. However, efficient utilization of these intermittent resources requires efficient and economical energy storage systems, among which advanced rechargeable batteries are the most suitable option. However, it is recognized that traditional lithium-ion batteries (LIBs) are approaching their theoretical energy density limits [1–3], which are not capable to fulfill the specific energy requirements in these special application fields.

Lithium sulfur (Li-S) batteries are considered as one promising candidate for next-generation LIBs due to their low cost and high theoretical specific capacity (1675 mAh g^{-1}) and energy density (2600 Wh kg^{-1}) [4,5]. However, practical applications of Li-S batteries are highly hindered by the low electrical conductivity of sulfur and the shuttling effect of polysulfides during cycling, which lead to low capacity and poor durability [6–8]. Much efforts have been made to overcome these issues [9–12], among which the employing doped carbon as supportor materials is an efficient way to suppress shuttle effect and improve the conductivity of sulfur cathode simultaneously [13–15]. 2D graphene possesses outstanding performance due to high electrical conductivity and large surface area, which may help it to wrap around sulfur particles to build a conducting network resulting in larger capacity and better rate performance. However, earlier study confirmed that these nonpolar carbon-based materials possesses weak interaction with polar Li_2S_n species, which can still lead to graduate capacity fading upon long-term cycling [16–18].

Besides the carbon materials, Intrinsical polar metal oxides whose surface have strong interact with polar polysulfide, have been widely used to fabricate the sulfur-based cathodes, such as TiO_2 [19], Ti_4O_7 [20], MnO_2 [21], $NiFe_2O_4$ [22], and Nb_2O_5 [23]. Recently, metal sulfides (CuS [24], Co_9S_8 [25], CoS_2 [26], TiS_2 [27], FeS_2 [28] and NiS2 [29,30]) have also been introduced into the cathode to improve the electrochemical activity of sulfur-based electrodes. Compared with metal oxides, metal sulfides cannot only provide strong interaction with polar polysulfide but also provide more activation sites for redox reactions of polysulfide during cycling, which would be due to accelerated charge transfer through higher conductive matrixt [29]. Furthermore, there would be a tendency to immobilize polysulfide through the interaction with metal sulfides rather than metal oxides [31].

In this paper, N/S codoped graphene and polar MnS nanocrystals are combined together through hydrothermal process and followed thermal treatment under N_2, which is employed as an effective host for preparing sulfur cathode. This approach will integrate the advantages and avoid the disadvantages of graphene and

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MnS through synergetic effect to produce an outstanding Li-S battery, such as high electronic conductivity of N/S-GO to reach high capacity and great rate performance; MnS as functional absorbents to suppress the shuttle effect of polysulfide to improve battery's durability.

2. Experimental section

2.1. Synthesis of the MNSG and NSG composite

Graphene oxide (GO) was prepared according to an improved Hummer's method reported by Marcano et al. [32]. Firstly, 100 mg of GO was dispersed in 50 mL of ethylene glycol to form a GO dispersion, and then 60 mg (1 mmoL) urea, 38 mg (0.5 mmoL) thiourea and 19.7 mg (0.1 mmoL) $MnCl_2{\cdot}4H_2O$ were added to this dispersion under stirring for 30 min. The mixture was transferred into an autoclave and hydrothermally treated at 180 °C for 12 h. MnS decorated N/S codoped graphene aerogel was obtained and then freeze-dried for 72 h in a vacuum lyophilizer. Finally, the dry aerogels were calcined at 600, 750, 900 °C for 3 h in N_2 atmosphere resulting in the formation of MnS decorated N/S codoped three-dimensional graphene (MNSG-T). For a comparison, N, S codoped three-dimensional graphene (NSG-T) was also prepared by similar procedures without the addition of $MnCl_2{\cdot}4H_2O$.

2.2. Synthesis of the S/MNSG and S/NSG composite

To uniformly distribute sulfur in the MNSG composite, 0.7 g sulfur was dissolve in 15 mL of CS_2. 0.3 g MNSG composite was completely soaked in the CS_2 solution for several minutes, and then dried out at 45 °C. Finally, the S/MNSG composite is heated at 155 °C in a sealed flask for 12 h, and then treated at 200 °C for 2 h to obtain the uniform S/MNSG composite. S/NSG is also prepared by similar procedures.

2.3. Synthesis of the of Li_2S_6 solution

Sublimed S and Li_2S in a molar ration of 5:1 were added into 30 mL of anhydrous tetrahydrofuran (THF) at the same time, then aged at 50 °C for 24 h and homogeneous 5 mM Li_2S_6 solution was obtained.

2.4. Material characterization

The structures and morphologies of obtained composites were characterized with X-ray diffraction (XRD, X'Pert PRO MPD, Holland), field emission scanning electron microscopy (FE-SEM) (Hitachi S-4800, Japan), and transmission electron microscopy (TEM, JEM-2100UHR, Japan). The functional groups in the samples were studied by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALab250Xi). The weight ratio of sulfur in the composite was determined by thermogravimetric analysis (TGA, STA 409 PC Luxx, Germany).

2.5. Electrochemical measurements

In a standard electrochemical measurement, the S/MNSG, S/NSG samples were mixed thoroughly with polyvinylidene fluoride (PVDF) and carbon black (with the weight ratio of 8:1:1). The powders were then dispersed into N-methylpyrrolidone (NMP) solvent and stirred for 24 h at room temperature, then uniformly coated onto an Al foil and dried at 60 °C for 12 h in a vacuum chamber. CR2032 coin-type batteries were assembled with lithium metal as reference electrodes inside an Ar-filled glove box (MBraun, Unilab), with the oxygen and water content below 1 p.p.m. A Celgard 2400 polypropylene membrane was used as the separator. The electrolyte was 1.0 M lithium bis-trifluoromethanesulfonylimide (LiTFSI) in a mixed solvent of 1, 3-dioxolane and 1, 2-dimethoxyethane (DOL/DME, 1:1, v/v) with 1 wt% $LiNO_3$. The mass loading of active S on each electrode was 0.8–1.2 mg cm^{-2}. The electrolyte used for the pre-cell is approximately 40 μL. Galvanostatic charging/discharging tests were performed between 1.7 and 3.0 V (vs. Li/Li^+) by using a Land CT-2001A (Wuhan, China) battery analyzer. Cyclic voltammograms (CV, 0.1 mV s^{-1}) and electrochemical impedance spectroscopy (EIS, 100 kHz-10 mHz,10 mV) measurements were performed on an electrochemical workstation(CHI760D). The cells were held at an open circuit at room temperature for 12 h before the electrochemical tests and the specific capacities were calculated based on the mass of active S.

3. Results and discussion

The synthetic procedures of S@MNSG composites are illustrated in Fig. 1a. As presented, MnS decorated N/S codoped graphene aerogels (MNSGA) is prepared via a one-pot hydrothermal treatment and then anneals at different temperatures to form MnS decorated N/S-codoped 3D graphenes (MNSG-T). The functional groups on the surface of GO, such as carboxyl, hydroxyl and epoxy groups, attribute to improved coordination on the surface with Mn ions to form well distribute MnS after reduction of $(NH_2)_2CS$. Some MnS nanoparticles are formed on N/S-GN nanosheets, which can block their self-aggregation. Sulfur is infiltrated into the MNSG composite host by a conventional melt-impregnation method. To better understand the synergetic effect of each component, various samples are synthesized through thermal treatment under different temperatures (600 °C of MNSG-600, 750 °C of MNSG-750 and 900 °C of MNSG-900). N/S codoped three-dimensional graphene (NSG-T) is also prepared by similar procedures without the addition of manganese salt.

X-ray diffraction (XRD) patterns of three MNSG composites are presented in Fig. 1b. All samples exhibit similar diffraction peaks, which indicates a well-developed crystal structure for MnS (Joint Committee on Powder Diffraction Standards (JCPDS) card no. 40-1289). With the increasing of temperature during thermal treatment, the diffraction peaks become steeper and narrow, which is attributed to the grown of aggregation of MnS nanoparticles. The XRD patterns of the S/MNSG-900 composite is also presented in Fig. S1a. The peaks can be assigned to orthorhombic sulfur (JCPDS no. 08-0247). The weak peaks of MnS in the MNSG compositeascribe to the relatively low amount of MnS after introduction of sulfur. To accurately calculate the content of sulfur in samples S/MNSG-900, the TGA date from environment temperature to 600 °C are tested in N_2 atmosphere with scan rate at 10 °C/min. As shown in Fig. S1b, the major mass loss occurs in the range of 180–260 °C, and the mass content of sulfur in the composite is 68.4 wt%.

Fig. 1(c–e) shows the typical scanning electron microscopy (SEM) images of MNSG annealed at different temperatures. All of them display a 3D interconnected network which is composed by wrinkled graphene sheets. The porous structure allows efficient ion diffusion and can also be considered as the buffering reservoir of polysulphides [33,34]. The porosity of the MNSG is further measured by N_2 adsorption. As shown in Fig. S1c, the sample exhibits a typical IV isotherm with a H3 hysteresis loop, which indicates that the pores is mainly composed of macropores and mesopores [35,36]. The as-prepared 3D MNSG-900, MNSG-750 and MNSG-600 have a Brunauer-Emmett-Teller (BET) specific surface area of 235.4 $m^2 g^{-1}$, 206.7 $m^2 g^{-1}$ and 186.3 $m^2 g^{-1}$. The larger surface area of high temperature treated sample would be due to deeper thermal cracking, which leads to more holes and defects. The transmission electron microscopy (TEM) images of MNSG-600 and 750 (Fig. 1f–h) show that MnS nanocrystals disperse uniformly