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Nickel Sulfide Nanocrystals Decorated Graphene Sheetsas Anode Materials for Lithium Ion Batteries

Xianggang Guan, Xuehua Liu, Hongliang Li*, XiuSong Zhao*

Institute of Materials for Energy and Environment, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, China

Abstract: **Ni_3S_2 nanocrystals decorated reduce graphene oxide (RGO) sheets (Ni_3S_2/RGO) has been obtained through a Reaction under Autogenic Pressure at Elevated Temperature (RAPET). In comparison with pristine Ni_3S_2 material, his Ni_3S_2/RGO composite showed a high reversible capacities and excellent rate performance due to the integration of Ni_3S_2 nanocrystals with the high-conductivity graphene sheets and the synergistic effect between them.**

Keywords: Ni3S2; Reduced graphene oxide; RAPET; Lithium ion battery

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*Corresponding Author: Hongliang Li, XiuSong Zhao

1. Introduction

As a promising energy storage device, lithium ion batteries (LIBs) have attracted intense attentions due to their high energy density and environmentally friendly. [1,2] The major problem which hinders its application in electric vehicle is the poor reversible capacity of the anode material such as carbon materials. Therefore, alternative anode materials with high electrochemical performance are desirable. In recent years, transition metal sulfide (TMS) has been explored widely as anode materials for LIBs. [3] Several nickel sulfides with different stoichiometric ratios of nickel and sulfur elements such as NiS, Ni_3S_2, NiS_2, Ni_3S_4, Ni_7S_6, and Ni9S8 have been reported. [4, 5] Hereina kind of composite composing ofNi3S2nanoparticle deposited onreduce graphene oxide (RGO) has been prepared (named as NiS_2/RGO). The structures and electrochemical properties of the composites have been investigated and been discussed. The resulted composite showedboth good cycling performance and excellent rate capability.

2. Experimental Section

2.1. Materials

Anhydrous ethanol, nickel nitrate hexahydrate ($Ni(NO_3)_2$ $6H_2O$), sodium sulphide (Na_2S $9H_2O$), cetyltrimethyl ammonium bromide (CTAB). All these chemicals were of AR grade and purchased from Sinopharm and used without further purification. Graphene oxide (GO) powder, kindly provided by the Sixth Element (Changzhou) Ltd, was sonicated for 3h before use. Deionized water was used in all experiments.

2.2. Sample preparation

In a typical preparation, 3.4g of Ni(NO3)2 6H2O and 0.1g of GO were dispersed in 50ml of distilled water, meanwhile 4.6g Na_2S 9H2O and 0.2g CTABwere dissolved into another 50ml of distilled water, and then these two solutions were mixed under stirring for 4h. Thereafter, the mixture was freeze-dried for two days and black solid was obtained. This black solid was dispersed in N-menthyl-2-pyrrolidinone (NMP) and transferred into a 12ml corundum-lined stainless autoclave. The autoclave was sealed and maintained at 700 ℃ for 2h.Areaction under autogenic pressure at elevated temperature (RAPET) took place. The product derived from the RAPET was washed with ethanol and water three times. After a two-day freezedrying process, solid designated as Ni3S2/RGOwas obtained (scheme. 1).

2.3. Characterization

X-ray power diffraction (XRD) patterns were recorded on a Rigaku Ultima IV X-ray diffractometer with Cu-Kα radiation (λ = 0.15418nm). Raman spectra were collected using a Renishaw inVia Plus Micro-Raman spectroscopy system equipped with a 50mW DPSS laser at 532nm. The morphologies and the microstructures of the samples were examined by using a JEOL JSM-7800F scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) and a JEOL JEM-2100Plus transmission electron microscope (TEM).

2.4 Electrochemical Measurements

For preparing the working electrodes, a mixture of 80wt% active materials, 10wt% carbon black and 10 wt% polyvinylidene fluorides (PVDF) were mixed into NMP. Afterwards, the obtained slurry was cast onto a copper foil and dried in vacuum at 110 ℃ for 10h. The active materials loaded on the electrode were approximately 0.6-1.0mg per piece.CR2016 type coin cells were assembled in a high-purity Argon filled glove box, by using pure lithium as anode, 1mol L-1 LiPF6 (Shenzhen Capchem TechnologyCo., Ltd, China) as the electrolyte and Celgard 2400 membrane as the separator. The cycle stability of the cells was tested at the potential range of 0.01-3V on a Land testing system. Cyclic voltammetry (CV) measurements were performed at a scan rate of 0.2mV s-1 between 0.01 and 3V. Electrochemical impedance spectra (EIS)

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wascarried out at a frequency range from 100KHz to 1 Hz with a signal amplitude of 5mV.

3. Results and discussion

3.1. Structure and Morphology

The XRD pattern of Ni3S2/RGO is displayed in Figure 1. The 6 sharp peaks can be indexed to the (101), (110), (003), (202), (113) and (122) planes of Ni3S2crystal (PDF # 44-1418), indicatingthat the Ni_3S_2/RGO is of high purity and well crystallized.

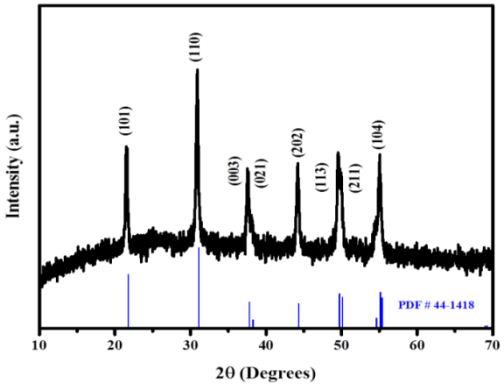

Figure 1. XRD pattern of Ni_3S_2/RGO composite material.

The SEM images of Ni_3S_2/RGO composite are shown in Figure 2. From images a and b, it can be seen thatNi3S2 nanoparticles have been deposited uniformly on the RGO layers.Interestingly, uniform and regular carbon spheres have been collected outside of the corundum crucible (see images c and d of Figure 2). The presence of carbon spheres can be due to the evaporation of NMP and then carbonization under high temperature and high pressure outside of the crucible.

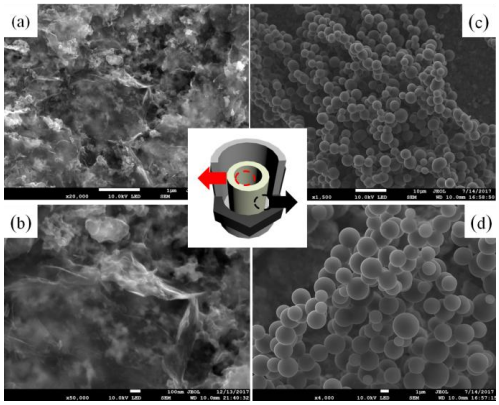

Figure 2. SEM images of Ni_3S_2/RGOcomposite obtained inside the crucible (a,b) and the carbon sphere collected outside of the crucible (c,d). The inset at the center of these images indicates the place where the samples were collected.

The Ni_3S_2/RGO composites are further characterized by TEM technique. Ni3S2 nanoparticles and graphene sheets can be clearly seen in Figure 3a, which matches well with the SEM images (Figure 2a and 2b). The high-resolution TEM (HRTEM) image is shown in Figure 3b,which indicates that Ni3S2 nanoparticles were depositedongraphene layers. Such a structure can deliver a high cycling performance by effectively reducing volumechange of Ni3S2 by the graphene substrates. From the image one can also see clearly the lattice fringe of a Ni3S2 crystal. A spacing of about 0.41nm has been calculated, indexing to the (101) plane of the Ni3S2 crystal.

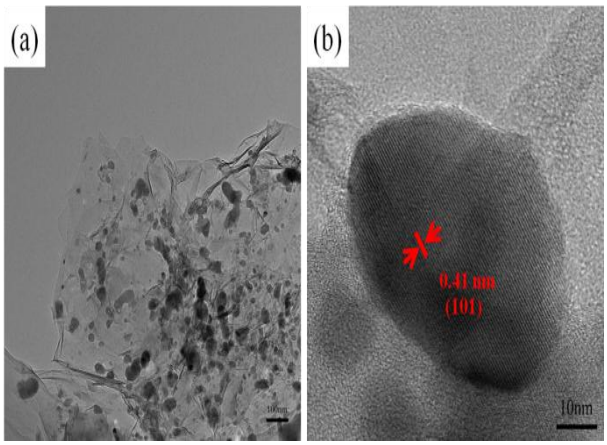

Figure 3. TEM image of Ni_3S_2/RGO (a), and HRTEM of Ni_3S_2 nanocrystal (b)

3.2. Electrochemical Performance

Electrochemical performance of the composites is characterized by cyclic voltammety (CV) at a scan rate of 0.2mV s-1 (Figure 4a). During the first negative scan, there is a reduction peak appeared at 0.73V which then disappeared at the next scan, corresponding to the formation of the solid electrolyte interface (SEI) film. [6, 7] While for the anodic sweep, two small peaks originated from the formation of Ni3S2 are found at 1.98 and 2.45V. During the subsequent cycle, the cathodic peak shifts to 1.28V and anodic peak appears at 2.0V. As is shown in Fig. 4b, the discharge and charge plateaus match well with the corresponding reactions in the CV analysis. To test the cycling stability of Ni3S2/RGO charge-discharge cycling is examined at a current density of 100mA g-1 between 0.01 and 3.0V (Fig. 4c). The irreversible capacity in the first discharge cycle is common for carbon materials such as graphene and porous carbon, which can be ascribed to the formation of a SEI. The reversible capacity of 682.3mAh g-1 is attained in the 5th cycle and then gradually increased to 831.8mAh g-1 after 100th cycle, which is due to the destruction of the graphite lattice during the cycling process. [8] Fig. 4d shows the rate capacity of the compositewith current density from 0.1 to 10A g-1. Theelectrode delivers stable charge capacity of 930.2mAh g-1 at 0.1A g-1. With the current density increase to 10A g-1, the charge capacity still remains at 445.0mAh g-1. After the current density switches back to 0.1A g-1, the capacity of electrode material recovers to 960.0mAh g-1 and then increase to 1592.8 mAh g-1 in the 120th, revealing the high stable cycling properties and good rate capability.

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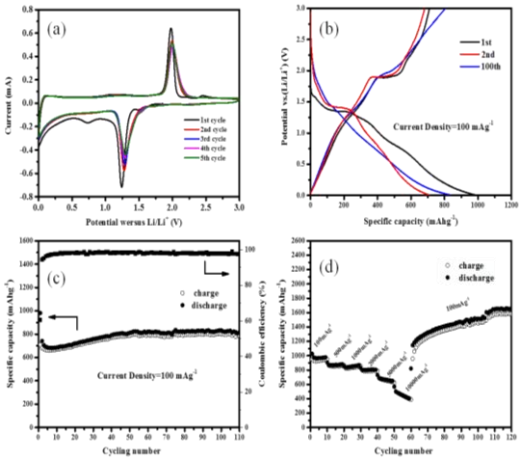

Figure 4. Electrochemical performance of the Ni_3S_2/RGO composite. (a) CV curves, (b) charge and discharge curves of the Ni_3S_2/RGO electrode at a current density of 100mA g-1 for the first five cycles, (c) cycling performance of the electrode at a current density of 100mA g-1, (d) Rate properties.

4. 4. Conclusion

In summary, Ni3S2/RGOcomposites have been synthesized by a reaction under Autogenic Pressure at Elevated Temperature (RAPET).The Ni_3S_2 nanoparticleswere anchored tightly on the surface graphene sheets. The prepared Ni3S2/RGOcomposites showed a high reversible capacity of over 800mAh g-1 and an excellent rate performance of about 450mAh g-1 at the current density of 10A g-1. The high stable cycling performance and superior rate capability demonstrate that the Ni_3S_2/RGOcomposite can be considered as a potential anode candidate for high-performance lithium ion batteries.

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