Electrochimica Acta 283 (2018) 683–690

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Hierarchical iron sulfide-graphene nanocubes consisting of multiple nanoparticles with superior sodium ion storage properties

Juan Xiang, Zhiming Liu, Taeseup Song*

Department of Energy Engineering, Hanyang University, Seoul 133-791, South Korea

ARTICLE INFO

Article history:
Received 20 April 2018
Received in revised form
26 June 2018
Accepted 3 July 2018
Available online 5 July 2018

Keywords:
Iron sulfide
Graphene
Nanocubes
Hierarchical
Sodium ion full battery

ABSTRACT

Hierarchical iron sulfide nanocubes consisting of multiple iron sulfide-carbon core-shell nanoparticles coated with few-layer graphene ($Fe_{1-x}S$@C/rGO) were prepared by a two-step *in-situ* transformation strategy employing Prussian blue (PB) as a starting material. The hierarchical nanocubes delivered an outstanding rate capability of 323 mAh g^{-1} at the current density of 10 A g^{-1} when used as the anode of sodium ion half cells. An iron-based sodium-ion full cell composed of a hierarchical $Fe_{1-x}S$@C/rGO anode and PB cathode had a capacity of 323 mAh g^{-1} for 150 cycles. We attributed the good sodium ion storage properties of the $Fe_{1-x}S$@C/rGO nanocubes to the stable hierarchical building structures and the high graphitization degree of carbon obtained during the transformation process. The graphene-coated nanocube structures inhibited the agglomeration of iron sulfide-carbon core-shell nanoparticles and accommodated the huge volume expansion that occurred during cycling. The high graphitization degree of carbon endowed $Fe_{1-x}S$@C/rGO nanocubes with high electronic conductivity, facilitated sodium ion accessibility, and increased mechanical durability.

1. Introduction

Sodium ion batteries have obvious cost advantages compared to commercialized lithium ion batteries [1–3]. Metal sulfides, especially iron sulfides, are regarded as promising candidates for sodium ion batteries based on their low cost, abundance, low toxicity, and large theoretical capacity [4–13]. Nevertheless, the significant volume changes associated with the charging/discharging process and the intrinsically low conductivity of metal sulfides has limited their application [8,9,14,15]. To address the issues of material fracture and low electron conductivity inside metal sulfide electrodes, various strategies have been devised, including reducing particle size [8,16], incorporating highly conductive carbon materials [5,6] and designing hybrid nanostructures [17]. One of the most efficient strategies to improve the electrochemical properties of metal sulfides is to synthesize carbon-coated core-shell nanostructures [18–20]. Carbon-film shells with high electrical conductivity can provide a more accessible surface area for charge transfer and decrease system resistance [21]. Huang and co-workers reported carbon-film-coated iron sulfide nanorods derived from an iron-based metal-organic framework as advanced conversion-type lithium ion storage materials. The hierarchically porous structure synthesized by these researchers had a high lithium-ion storage capacity of 1148 mAh g^{-1} at a current density of 500 mA g^{-1} [20]. Despite great advances in improving the electrochemical properties of metal sulfides, continuous charging/discharging results in the aggregation of metal sulfide nanoparticles and the loss of electrical contact between active materials and the current collector, which in return leads to rapid degradation of electrochemical properties [5,22]. Therefore, preventing the aggregation of core-shell nanoparticles may be of great help in enhancing the electrochemical performance of metal sulfide-based materials.

Another strategy that can improve the electrochemical properties of metal sulfides is to use hierarchical porous structures in energy storage systems to facilitate rapid ion/electron transport and electrolyte penetration [18,23–26]. For example, Choi and co-workers reported 3D graphene microspheres divided into several tens of uniform nanospheres coated with few-layer MoS_2. When these graphene microspheres were applied as the anode material for sodium-ion batteries, a reversible capacity of 323 mAh g^{-1} after 600 cycles was realized [27]. Based on the above observations, we hypothesized that the electrochemical performance of metal sulfides can be further improved by engineering core-shell nanoparticles and creating hierarchical three-dimensional structures.

---

* Corresponding author.
E-mail address: tssong@hanyang.ac.kr (T. Song).

https://doi.org/10.1016/j.electacta.2018.07.017

Herein, we reported the synthesis of hierarchical iron sulfide nanocubes consisting of multiple iron sulfide-carbon core-shell nanoparticles coated with few-layer graphene (denoted $Fe_{1-x}S$@C/rGO) by a two-step *in-situ* transformation process from Prussian blue (PB) nanocubes. We successfully synthesized $Fe_{1-x}S$ nanospheres coated with a highly graphitized carbon shell that facilitated faster electron and ion transport, displayed increase sodium ion accessibility, and had increased mechanical durability. Meanwhile, the graphene nanosheets on the nanocubes efficiently inhibited the agglomeration of $Fe_{1-x}S$@C core-shell nanoparticles and further maintained the integrity of the nanocube structure during the sodiation/desodiation process. During transformation of PB to $Fe_{1-x}S$, high temperature calcination promoted the graphitization of the carbon layer, in turn improving the electron/ion transportation ability of the final electrode material. The $Fe_{1-x}S$@C/rGO electrode exhibited a high reversible capacity of 378 mAh g^{-1} after 400 cycles at a current density of 0.5 A g^{-1} and an excellent rate capability of 323 mAh g^{-1} at the high current density of 10 A g^{-1}. An iron-based sodium ion full cell with a PB cathode and $Fe_{1-x}S$@C/rGO anode delivered a capacity of 323 mAh g^{-1} at a current density of 200 mA g^{-1}.

2. Experimental section

2.1. Material preparation

Preparation of PB: All purchased chemicals were used directly without further purification or treatment. In a typical synthesis procedure, 0.1375 g potassium hexacyanoferrate (II) trihydrate and 3.75 g polyvinylpyrrolidone (PVP, K30) were added to 65.0 mL of 0.1 N HCl solution. After stirring for 30 min, the solution was transferred into a 100-mL Teflon-lined stainless-steel autoclave and incubated at 80 °C for 24 h. The resulting blue solid was collected by centrifugation, washed with DI water several times, and vacuum-dried at 60 °C overnight [28].

Synthesis of $Fe_{1-x}S$@C/rGO: Graphene oxide (GO) was prepared according to a modification of Hummers' method [29]. As-prepared PB (100 mg) was dispersed in GO aqueous solution (0.5 g L^{-1}) by sonication for 10 min and then heated to complete dryness at 60 °C. The as-obtained PB/GO nanocubes were then thermally treated in an argon atmosphere at 800 °C for 3 h with a ramp rate of 2 °C min^{-1}. $Fe_{1-x}S$@C/rGO composite was prepared by mixing the as-obtained products with sulfur at the weight ratio of 1:2, followed by annealing at 600 °C for 2 h under 60 sccm argon flow. Bare $Fe_{1-x}S$/C composite without GO was also prepared using a similar procedure as the control sample. To study the influence of graphitization degree on electrochemical performance, PB/GO nanocubes were also annealed at 500, 600, and 700 °C for 3 h at a ramp rate of 2 °C min^{-1}. The as-obtained products were denoted Fe/Fe_3C@C/rGO-500, Fe/Fe_3C@C/rGO-600, and Fe/Fe_3C@C/rGO-700, respectively. $Fe_{1-x}S$@C/rGO-500, $Fe_{1-x}S$@C/rGO-600, and $Fe_{1-x}S$@C/rGO-700 were prepared as described for $Fe_{1-x}S$@C/rGO by mixing Fe/Fe_3C@C/rGO-500, Fe/Fe_3C@C/rGO-600, and Fe/Fe_3C@C/rGO-700 with sulfur at a weight ratio of 1:2 followed by annealing at 600 °C for 2 h under 60 sccm argon flows.

2.2. Material characterization

Field-emission scanning electron microscopy (FESEM; JEOLJSM07600F) and transmission electron microscopy (TEM; JEOL JEM-2100F) were used to characterize the microscopic features of the as-prepared samples. Element mapping was analyzed using an energy-dispersive X-ray (EDX) spectrophotometer attached to the TEM instrument. An X-ray photoelectron spectrometer (XPS, VG Microtech ESCA2000) was used to analyze the chemical composition and surface valance states. A Rigaku D/MAX RINT-2000 X-Ray diffractometer (XRD) was used to collect XRD patterns of the products with Cu Kα radiation at a voltage of 40 kV and a current of 40 mA. Raman spectra were recorded on an Invia Raman spectrometer. Thermogravimetric analysis (TGA) was performed using a ramp rate of 10 °C min^{-1} and N_2 flow.

2.3. Electrochemical measurements

$Fe_{1-x}S$@C/rGO and PB were firstly evaluated in R2032 type coin cell individually. To prepare $Fe_{1-x}S$@C/rGO working electrode, $Fe_{1-x}S$@C/rGO, conducting agent (super P), and binder (sodium carboxymethyl cellulose) were blended with the weight ratio of 8:1:1 and homogeneously dispersed in distilled water. The prepared slurry was then casted on the copper current collector and dried at 120 °C for 12 h in the vacuum oven. The mass loading of the $Fe_{1-x}S$@C/rGO electrode is around 0.9–1.2 mg. One molar $NaClO_4$ in ethylene carbonate/polycarbonate (EC/PC) with 5% fluoroethylene carbonate (FEC) additive was used as the electrolyte. Sodium metal was used as both the reference electrode and counter electrode. Cells were assembled in an argon filled glove box by stacking a Na metal disc and a Borosilicate Glass (WHATMAN) as separator. The electrochemical properties of the cells were then tested in a TOSCAT 3000 battery tester (Toyo Systems, Tokyo, Japan) within the voltage range of 0.01–2.3 V. Cyclic voltammetry measurements were carried out using Autolab potentiostat/galvanostat (Model PGSTAT-72637) electrochemical workstation. To prepare a PB cathode, PB, super P, and polyvinylidene fluoride (PVDF) were mixed with the mass ratio of 7: 2: 1 and blended homogeneously in N-methylpyrrolidone (NMP). The mixture was then casted on aluminum foil and dried at 120 °C for 12 h in the vacuum oven for the preparation of the working electrode. To match the specific capacity of anode and cathode, the mass ratio between cathode and anode is optimized to be around 5:1. The loading mass of PB is adjusted to be around 4.4–6 mg. The electrolyte was 1.0 M $NaPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1: 1) with 5% fluoroethylene carbonate (FEC) additive. Coin-type half cells were assembled using a Na metal as counter electrode and a polypropylene as separator and then tested using a TOSCAT 3000 battery tester (Toyo Systems, Tokyo, Japan) within the voltage range of 2.0–4.0 V.

To assemble sodium ion full cells, both the $Fe_{1-x}S$@C/rGO anode and the PB cathode were first assembled into a half coin cell and discharged to 0.01 V/charged to 4.0 V, respectively, to achieve the pre-sodiation/desodiation state. Then, the $Fe_{1-x}S$@C/rGO anode and PB cathode were taken out and paired together in a coin-type full cell. Sodium full cells were assembled in an argon-filled glove box and then tested in a TOSCAT 3000 battery tester (Toyo Systems, Tokyo, Japan) within the voltage range of 0.5–3.0 V.

3. Results and discussion

The process used to synthesize 3D $Fe_{1-x}S$@C/rGO composite from GO-wrapped PB is described in Scheme 1. Uniformly mixed PB/GO was prepared by sonication, followed by drying at 60 °C overnight. X-ray diffraction (XRD) analysis was performed to determine the phase composition of the product (Fig. S1a). All diffraction peaks were indexed by face-centered-cubic Prussian blue (JCPDS No. 52-1907). There were no significant differences in diffraction peaks between PB and PB/GO, suggesting that PB was homogenously coated with GO and that GO did not restack into graphite during the drying procedure. The PB/GO composite was then thermally treated at 800 °C to obtain an intermediate product, whose diffraction peaks were consistent with a mixture of Fe_3C, α-Fe, and newly-generated graphitic carbon (Fig. S1b). Reduction of