



Effective combination of FeS₂ microspheres and Fe₃S₄ microcubes with rGO as anode material for high-capacity and long-cycle lithium-ion batteries



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HIGHLIGHTS

- Iron sulfides@rGO obtained using a facile one-pot in-situ hydrothermal method.
- The mixed iron sulfides/rGO composite is firstly designed.
- The iron sulfides/rGO composite demonstrates excellent electrochemical performance.
- Minor FeS₂ inclusion can effectively enhance the electrochemical performance of Fe₃S₄.

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ABSTRACT

Iron sulfides receive special interests as anode materials for lithium or sodium ion batteries in view of their low-cost, environmental benign, and high conductivities. Here, a combination of FeS₂ microspheres and Fe₃S₄ microcubes with reduced graphene oxides (iron sulfides@rGO) is prepared by a facile in-situ hydrothermal method. As an anode material for lithium ion batteries, iron sulfides@rGO exhibits excellent lithium storage ability. It delivers a high initial discharge capacity of 1476.2 mA h/g at 100 mA/g, and 1189.6 mA h/g capacity can be maintained after 100 cycles. Most impressively, 800 mA h/g capacity can be remained after 1000 cycles even at 1 A/g.

1. Introduction

Nowadays, the huge energy demands and environmental pressure push scientists to explore green and clean energy sources to replace the present predominant fossil fuels, and to develop environmental benign and safe energy storage and conversion devices. Amongst the commercial energy storage devices, lithium ion batteries (LIBs) have received great success. However, to obtain LIBs with higher energy and power densities to meet the requirements of their applications in electric vehicles and smart grids, much more efforts should be made [1].

To date, Great progresses have been made to improve LIBs' electrochemical properties, which can be realized by employing various novel synthetic strategies, versatile hierarchical structures' design, and smart combination of LIBs' components [2–4]. Before the application of these techniques, the selection of suitable electrode materials is the first important matter. It is well-known that anode material is the main contributor of capacity for batteries, therefore, to develop anode materials possessing high theoretical capacities and stable cycling performance is necessary. As for the anode materials, the mostly investigated ones include the fourth group elements Si, Ge, Sn, transition metal

oxides, transition metal sulfides, transition metal fluorides, alloys, SnO₂, Li₄Ti₅O₁₂, Li_xV₃O₈, etc [5,6]. Amongst these promising candidates, iron-based materials are specifically studied in view of iron's abundance, low price, and non-toxicity. Sulfides usually have much higher conductivities and smaller volume expansions during cycling than those of oxides, which means that sulfides have better ion transport mobilities than oxides. The chemical bond between metal and sulfur is weaker than that of metal and oxygen, which can be advantageous to the conversion reactions. Moreover, metal sulfides usually have better mechanical and thermal stabilities than metal oxides [7].

Up to now, there are iron sulfides FeS [8–11], FeS₂ [12–15], Fe₃S₄ [16–19], and Fe₇S₈ [20,21], have been explored as anode materials for LIBs. The efforts are either focusing on nano-morphologies' design or inclusion of various carbon materials to overcome the bad cycling and rate performances of these iron sulfides' pristine samples. Here, some remarkable examples are simply overviewed. A pitaya-shape hierarchical structured FeS₂@porous carbon was designed and demonstrated a high energy density of ~1100 Wh/kg and ultrahigh rate capability [14]. Compared with pyrite FeS₂, marcasite FeS₂ has rarely

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investigated its electrochemical performance. Recently, a grape cluster-shape combination of marcasite-FeS₂ and carbon nanofibers (CNFs) was reported to show a capacity of 1399.5 mA h/g after 100 cycles at 0.1 A/g and a rate performance of 782.2 mA h/g at 10 A/g. It was supposed that CNFs aided decrystallization-recrystallization mechanism was the reason for the nice electrochemical properties [15]. For greigite Fe₃S₄, there are relatively few studies. One impressive example is that solvothermal method prepared Fe₃S₄ hollow spheres show a capacity of 750 mA h/g after 100 cycles at 0.2 A/g [19]. Another one is that octahedral-shape Fe₃S₄ microcrystals deliver a capacity of 1161 mA h/g at the 1st cycle and keep 563 mA h/g maintained after 100 cycles at 100 mA/g [22]. Very recently, Fe₃S₄ nanoparticles wrapped in rGO have been obtained by us and show outstanding cyclic and rate performance [18]. It is obviously that these iron sulfides are promising anode materials for LIBs.

Interested by the superior electrochemical properties of iron sulfides, we pay our attentions to improve their electrochemical performances via exploring novel synthetic methods—mainly one-step in-situ ones, and novel types of iron sulfide-based composites recently [18,23–25]. One-step in-situ method has more advantages than other methods to combine active materials and carbon matrix better with more distinctive structure and morphology for Li⁺ ions' transport [26–29]. The originality of this work is based on our ongoing efforts to study iron sulfide@carbon anode materials for LIBs [18,23–25], and the original intention is to employ several simple preparation methods to obtain such materials with simple morphologies but nice electrochemical performances, which is really meaningful for their scalable preparations and practical applications. In this work, a combination of FeS₂ microspheres and Fe₃S₄ microcubes with reduced graphene oxide (rGO), namely, (Fe₃S₄ + FeS₂)/rGO or Fe_xS_y/rGO, was designed to improve the previously successful Fe₃S₄/rGO composite's electrochemical performance [18]. This strategy is viable because the structure of Fe₃S₄ (*Fd3m*) can be considered as a superstructure of that of FeS₂, Fe₃S₄ and FeS₂ have the chance to be obtained meanwhile. Fe_xS_y/rGO was obtained via a one-step in-situ hydrothermal method, which shows a high initial discharge capacity of 1476.2 mA h/g and 1189.6 mA h/g remains after 100 cycles at 100 mA/g. Even at 1 A/g, it still has a capacity of around 800 mA h/g at the 1000th cycle, demonstrating much improved electrochemical behaviors for Fe₃S₄. To our best knowledge, there is no such a combination to improve the electrochemical performance for iron sulfides.

2. Experimental

2.1. Preparation of iron sulfides@rGO composite

All starting materials were used as received without any further purification. Graphene oxide (GO) was prepared using modified Hummer's method [30], which was dispersed in deionized water to form a certain concentration of homogeneous solution (6 mg/ml) under ultrasonic condition. The iron sulfides@rGO composite was synthesized by a facile in-situ hydrothermal approach. Firstly, 10 ml GO solution (60 mg GO) was added into 65 ml deionized water, stirring for 0.5 h. Secondly, 596.4 mg (3 mmol) FeCl₂·4H₂O and 612.1 mg (5 mmol) L-cysteine were carefully added into the solution and stirred for another 0.5 h to form a homogeneous solution. Thirdly, the above solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and maintained at 473 K for 24 h. Finally, the black products were collected by centrifugation (6000 rpm for 5 min) after naturally cooled to room temperature, washed for several times with deionized water and ethanol in turn, and then dried at 343 K for 12 h under vacuum to get the iron sulfides@rGO composite. Iron sulfides sample without rGO was obtained by using the same method.

2.2. Material characterizations

The structure information and phase purities of the as-prepared samples were characterized by powder X-ray diffraction (PXRD, Bruker D8 Advance) at 40 kV and 100 mA for Cu-Kα radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan speed of 5°/min at room temperature. The distributions of Fe, S and C on the surface of iron sulfides@rGO can be observed by employing EDS element mapping analysis. Scanning and transmission electron microscopies (SEM, Zeiss-Supra55, and TEM, Philips Tecnai12), and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F30 S-TWIN) were used to observe the surface morphologies and sizes of iron sulfides@rGO. X-ray photoelectron spectroscopy (XPS, ThermoFisher Scientific ESCALAB250Xi) and Raman spectrum (Renishaw inVia) were introduced to analyze the chemical structures and chemical composition of iron sulfides@rGO, respectively.

2.3. Electrochemical measurements

The electrode slurry of iron sulfides@rGO as active material for a half-cell was prepared by mixing 8: 1: 1 iron sulfides@rGO, carbon black, and polyvinylidene fluoride (PVDF) with a certain amount of N-methyl-2-pyrrolidinone (NMP) under the continuous stirring for 8 h. The uniform slurry was coated onto a copper foil, which was then cut into ϕ 1.6 cm disks after dried at 353 K for 8 h and 393 K for 12 h in a vacuum oven. The mass of the active material was around 1.3 mg. Iron sulfides sample without rGO was also employed as active material to prepare the electrode slurry using the same method.

The half-cells were assembled in a glovebox (VAC-Omni 102283). Li foil and Celgard 2325 film were used as the counter electrode and separator for the CR-2032 type coin cells, respectively. The glovebox filled with high purity argon where oxygen and water contents were less than 1 ppm. The used electrolyte was 1 M LiPF₆ in 1: 1 DEC/EC. Cyclic voltammetry (C-V) measurements from 0.005 to 3.0 V at a scan rate of 0.1 mV/s and the electrochemical impedance spectroscopies (EIS) at an open-circuit potential 2.9 V in the frequency range of 0.01 Hz–100 kHz were performed using the electrochemical workstation (CHI660D). The charge/discharge data was tested at 100 mA/g in the voltage range of 0.005–3.0 V by using a NEWARE CT-3008 battery charge–discharge system.

3. Results and discussion

3.1. Syntheses

Iron sulfides@rGO sample was prepared by a one-step in-situ hydrothermal method (Fig. 1). Graphene oxides (GO) have amounts of oxygen-containing functional groups such as carboxyl, hydroxyl, epoxy

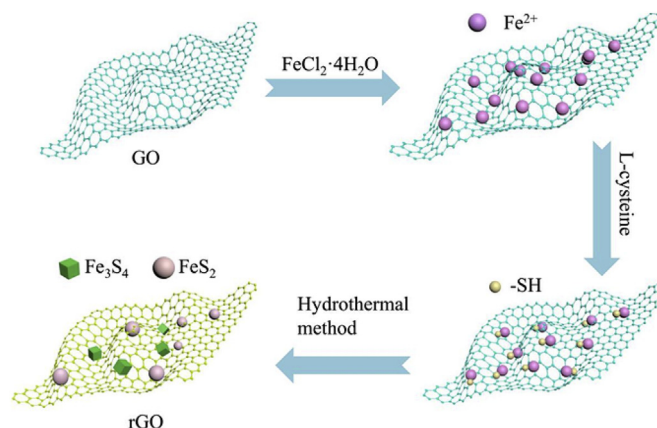


Fig. 1. Scheme illustration of the preparation of iron sulfides@rGO.

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