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FeS nanosheets as positive electrodes for all-solid-state lithium batteries

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ABSTRACT

Transition metal sulfides have attracted particular interests owing to their extremely higher specific capacity and more compatible with sulfide electrolyte than lithium transition-metal oxide for all-solid-state lithium batteries. FeS nanosheets with thickness of 10 nm are synthesized by a poly (vinyl alcohol)-assisted precipitation method and further successfully employed in Li/70%Li_2S-29%P_2S_5–1%P_2O_5/$Li_{10}GeP_2S_{12}$/FeS all-solid-state lithium batteries. The obtained all-solid-state lithium batteries show reversible discharge capacity of 550 mAh g^{-1} after 50 cycles at current density of 0.1 A g^{-1} and exhibit superior rate performances.

1. Introduction

One of the major challenges for traditional lithium ion batteries is the safety issue. All-solid-state lithium batteries employing inorganic solid electrolytes instead of organic liquid electrolytes may completely solve combustion and thermal runaway problems [1,2]. Among various inorganic solid electrolytes, sulfide solid electrolytes, such as $Li_{10}GeP_2S_{12}$ [3] or $Li_7P_3S_{11}$ [4], show very high ionic conductivities in the order of 10^{-2} S cm^{-1}, which are close to conductivities of organic liquid electrolytes, making them suitable in determining the performance of all-solid-state lithium batteries. Moreover, the softness of sulfide solid electrolytes makes it possible to get compact contacts with active materials only by cold-pressing. Another limitation for traditional lithium ion batteries is relatively low energy density. Owing to their higher specific capacity and moderate voltage plateau as well as good interfacial compatibility with sulfide solid electrolytes, transition metal sulfides based on conversion or alloying reaction mechanism have been considered as promising alternatives to conventional oxide positive materials [5]. However, structural damage caused by large volume expansion will lead to poor cycling stability and low capacity retention during repeated lithium intercalation and deintercalation process [6].

Up to now, there have been many methods reported to synthesize transitional metal sulfide materials for various applications. Taking iron sulfides as examples, different stoichiometries and crystal structures of iron sulfides have been prepared [7,8]. Among them, nanocrystalline FeS could be synthesized by a solvothermal decomposition of a ferrous precursor complex in the presence of thiourea [9]. Pure hexagonal FeS nanotubes were prepared *via* sulfurization of α-Fe_2O_3 nanowires with H_2S gas at relatively low temperatures [10]. Besides, iron sulfide/carbonaceous materials composites have been synthesized to improve their electrical conductivities and structural stabilities [11]. FeS nanoparticles wrapped in reduced graphene oxide were produced *via* a direct-precipitation approach [12]. Moreover, FeS nanodots accommodated in porous graphitic carbon nanowires was constructed *via* a combination of electrospining technique and biomolecular-assisted hydrothermal method [13]. However, most of these synthesis methods are either complicated or time-consuming, even some of them are environmentally harmful.

Recently, two-dimensional nanostructured materials have received widely attention in lithium ion batteries owing to their high specific surface area and providing short pathways and high kinetics for lithium ion insertion/extraction. The high specific area can provide abundant electrochemical reaction sites and large interfacial contact area with electrolytes. Meanwhile, due to their loosely stacked structures, they can further accommodate volume expansion and alleviate inner strain during conversion or alloying reaction [6]. Hence, it is anticipated that all-solid-state lithium batteries employing two dimension sulfide electrode could exhibit excellent cycling stability and rate performances. Moreover, ultrathin nanosheets can shorten Li-ion diffusion path length and improve charge transfer and kinetics of electrode reaction according to the law of diffusion. FeS is an attractive electrode material because of its various advantages such as affordable cost, environmentally benign, abundant resources and its high theoretical specific capacity of 609 mAh g^{-1}. To the best of our knowledge, there is no prior publication reporting FeS nanosheets in all-solid-state

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lithium batteries. Moreover, there are still strong demands for simple and scalable procedures for the preparation of two dimensional FeS.

Herein, we present a simple and high-yield poly(vinyl alcohol)-assisted precipitation method to synthesize homogeneous FeS nanosheets. The all-solid-state lithium batteries employing FeS nanosheets exhibit stable reversible capacity of 550 mAh g^{-1} after 50 cycles at a current density of 0.1 A g^{-1} and superior rate performances.

2. Experimental

2.1. Synthesis of FeS nanosheets

FeS nanosheets were synthesized by a poly(vinyl alcohol)-assisted precipitation method. Typically, 15 g of 33.3 wt% $FeSO_4{\cdot}7H_2O$ (99%, Sinopharm Chemical Reagent. Co., Ltd.) aqueous solution was mixed with 30 g of 1.0 wt% polyvinyl alcohol (99%, Sinopharm Chemical Reagent. Co., Ltd.) aqueous solution under argon atmosphere at room temperature. Then, equivalent amount of $Na_2S{\cdot}9H_2O$ (99%, Aladdin Chemistry. Co., Ltd.) solution was added into the above mixture, yielding black precipitates immediately. After being stirred for 30 min, the obtained precipitates of FeS were collected and washed with deionized water and finally freeze dried. The synthesis procedure of $Li_{10}GeP_2S_{12}$ and 70%Li_2S-29%P_2S_5–1%P_2O_5 electrolyte can be found elsewhere [14,15]. The ambient temperature ionic conductivities of $Li_{10}GeP_2S_{12}$ and 70%Li_2S-29%P_2S_5–1%P_2O_5 are 8.27×10^{-3} S cm^{-1} and 2.0×10^{-3} S cm^{-1}, respectively [16].

2.2. Characterization

The phase composition and valence states of as-prepared samples were characterized by X-ray diffraction (XRD, D8 Advance, Bruker) and X-ray photoelectron spectrometry (XPS, AXIS ULTRA^{DLD}, Kratos). The morphologies and microstructures were observed with field emission scanning electron microscope (FESEM, S-4800, Hitachi) and high-resolution transmission electron microscope (HRTEM, Tecnai G^2 F20, FEI). The Brunauer-Emmett-Teller (BET) test was determined *via* a nitrogen adsorption apparatus (ASAP 2020M, Micromeritics) and pore size distribution plot was obtained by the Barrett-Joyner-Halenda (BJH) method.

2.3. Electrochemical performance measurements

All-solid-state lithium batteries were fabricated to investigate the electrochemical performances of FeS nanosheets. For the cathode, FeS nanosheets were mixed manually with $Li_{10}GeP_2S_{12}$ solid electrolytes and conductive additive super P in weight ratio of 45:50:5 using mortar and pestle. The mass loading of composite cathode is around 2.5–3.0 mg cm^{-2}. Firstly, 100 mg of $Li_{10}GeP_2S_{12}$ powders and 50 mg of 70%Li_2S-29%P_2S_5–1%P_2O_5 powders were pressed into bilayer pellet under 240 MPa successively [17]. Then the obtained composite cathodes were uniformly spread on $Li_{10}GeP_2S_{12}$ side and pressed under 240 MPa. Finally, lithium foil (99%, 0.1 mm thickness) was attached to 70%Li_2S-29%P_2S_5–1%P_2O_5 side by pressing under 360 MPa. All the pressing was carried out in polytetrafluoroethylene mold with stainless steel as current collectors. All the processes were operated in a dry argon-filled glove box. Galvanostatic charge/discharge and cycle performance testing were performed on a multichannel battery test system (LAND CT-2001A, Wuhan Rambo Testing Equipment CO., Ltd.) between 0.5 and 3.0 V (*vs.* Li/Li^+) at room temperature. Cyclic voltammetry (CV) measurements were carried out on multi-channel potentiostat electrochemical workstation (Solartron 1470E) and recorded between 0.5 V and 3.0 V under a scan rate of 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were conducted in the frequency range from 10^6 HZ to10 HZ with the amplitude of 15 mV.

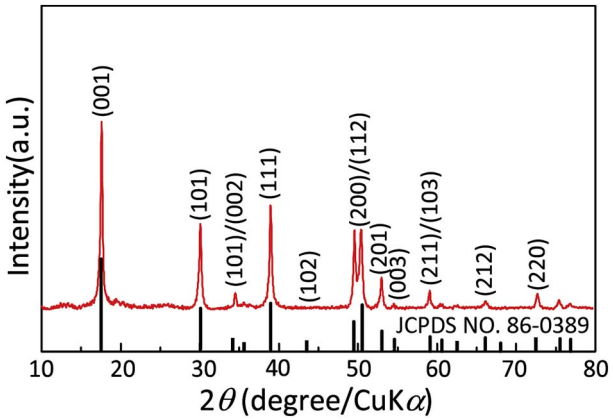

Fig. 1. XRD pattern of as-synthesized FeS nanosheets.

3. Results and discussion

Fig. 1 shows the XRD patterns of FeS nanosheets obtained by the poly(vinyl alcohol)-assisted precipitation method. The main characteristic diffraction peaks at 2θ = 17.61, 30.09, 34.50, 36.65, 38.99, 43.56,49.59 and 50.45, corresponding to diffraction from the (001), (101), (110), (002), (111), (102), (200),and (112) crystal planes, respectively, can well be indexed to the tetragonal mackinawite (FeS) phase with a space group of P4/nmm (129) (JCPDS No. 86–0389). The sharp and narrow diffraction peaks indicate the high crystallization nature of the products. Meanwhile, no diffraction peaks resulting from other iron-sulfur related phases like troilite (FeS), greigite (Fe_3S_4), marcasite (FeS_2), or pyrrhotite ($Fe_{1-x}S$), were detected, indicating the high purity of the as-obtained samples. Fig. 2a and b show the XPS spectra of Fe 2p and S 2p. The peaks at 711 eV and 725 eV can be

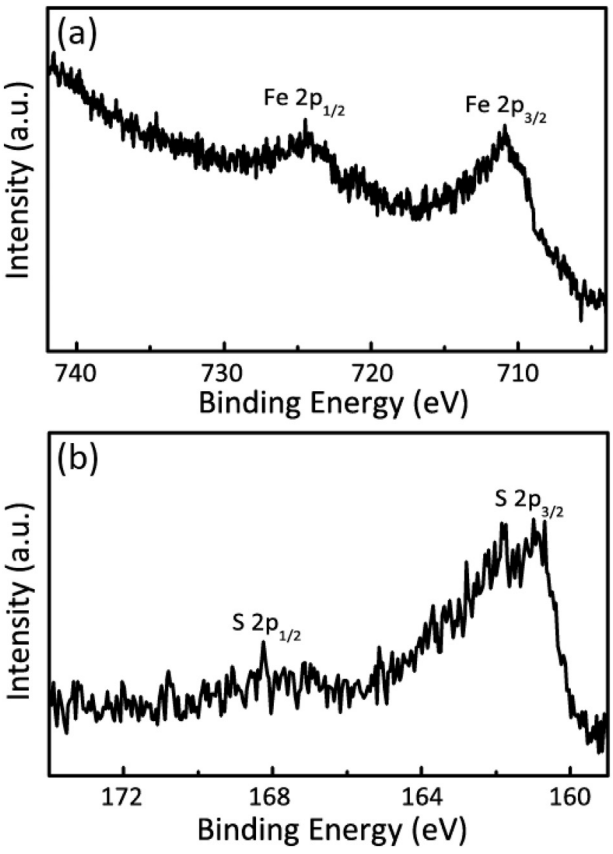

Fig. 2. XPS spectra of (a) Fe 2p and (b) S 2p for the FeS nanosheets.