



Ternary tin-based chalcogenide nanoplates as a promising anode material for lithium-ion batteries



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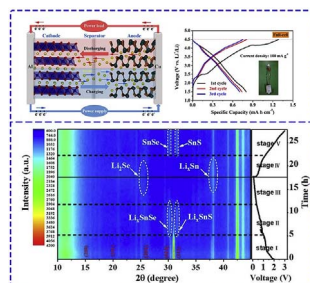
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HIGHLIGHTS

- A new anode material, SnSe_{0.5}S_{0.5} nanoplate, is synthesized.
- As an anode for LIB, it exhibits 1144 mA h g⁻¹ after 100 cycles.
- Mechanism analysis was completed by *in-situ* XRD.
- For full cell, it delivers 535 mA h g⁻¹ after 50 cycles.

GRAPHICAL ABSTRACT

A unique SnSe_{0.5}S_{0.5} nanoplate is synthesized as an anode for lithium-ion batteries. Also, it is the first that *in-situ* XRD analysis of SnSe_{0.5}S_{0.5} demonstrates that the stable conversion to SnSe and SnS is favorable to the electrochemical reaction process. This nanoplate anode achieves a capacity of 681 mA h g⁻¹ after 200 cycles at 0.5 A g⁻¹.



ARTICLE INFO

Keywords:

Anode
Lithium-ion batteries
Tin chalcogenide
High electrochemical performance
In-situ XRD

ABSTRACT

As an advanced anode material for lithium-ion batteries, tin-chalcogenides receive substantial attention due to their high lithium-ion storage capacity. Here, tin chalcogenide (SnSe_{0.5}S_{0.5}) nanoplates are synthesized using a facile and quick polyol-method, followed by heating at different temperatures. Results show that the as-prepared of SnSe_{0.5}S_{0.5} heated at temperature of 180 °C exhibits the best electrochemical performance with an outstanding discharge specific capacity of 1144 mA h g⁻¹ at 0.1 A g⁻¹ after 100 cycles and 682 mA h g⁻¹ at 0.5 A g⁻¹ after 200 cycles with a high coulombic efficiency (CE) of 98.7%. Even at a high current density of 5 A g⁻¹, this anode material delivers a specific capacity of 473 mA h g⁻¹. The high electrochemical performance of SnSe_{0.5}S_{0.5} is shown by *in-situ* XRD analysis to originate from an enhanced Li⁺ intercalation and an alloy conversion process.

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1. Introduction

In the recent decades, electrical energy storage (EES) has witnessed unprecedented boom among which lithium-ion batteries (LIBs) are the most popular energy storage devices, powering portable electronics and electronic vehicles due to their high energy density [1–3]. In order to further improve the energy density for LIBs, massive efforts have been made to find new high-performance electrode materials. A great variety of cathode materials have been synthesized and these materials can meet the needs of high capacity demand in many fields [4]. However, research on high-performance anode materials still remains a big challenge. Graphite, a widely used anode material for LIBs, is not suitable for the requirement of high capacity due to a low theoretical capacity of 372 mA h g^{-1} [5]. Thus, it is extremely important to develop new anode materials for batteries with high energy density. Silicon is one of the numerous alternative anode materials but, despite a high theoretical capacity, shows serious volume expansion ($> 300\%$) and low electric conductivity which impedes its success in extensive application [6,7]. Tin, as a result of an alloying reaction with Li, delivers a high theoretical gravimetric capacity of 994 mA h g^{-1} with the additional merits of low cost and toxicologically and consequently is considered one of the most promising anode materials for lithium ion batteries. However, the principal remaining challenge is to reduce the volume change (260%) during cycle process, as this is believed to cause large internal stress and destroy the integrity of electrode structure during cycling [8,9].

In order to overcome this disadvantage, many strategies have been proposed in recent years including surface modification, novel design structure and morphology, nano-sized particles and nano-porous materials to improve the structural stability [10–14]. Various types of tin-based compounds have also been investigated to improve the performance as anode materials for LIBs. Zhang et al. designed a novel multi-shelled SnO_2 hollow microsphere anode material, through a sequential hard template method, which gave excellent rate capacity and good cycling performance [15]. However, layered tin-based chalcogenides with similar layered structures to graphite exhibited better electrochemical performance than tin-based oxides, such as tin sulfide (SnS_2 , SnS), and tin selenide (SnSe , SnSe_2), which have received tremendous attention [16–20]. Jiang et al. reported that a tin sulphide (SnS_2) and nitrogen doped graphene sheet (NGS) composite, obtained by a low-temperature solve-thermal method, exhibits a high discharge capacity of 1407 mA h g^{-1} at 0.2 A g^{-1} after 120 cycles and good rate performance with 200 mA h g^{-1} at the current density of 10 A g^{-1} [21]. Tin selenide (SnSe_2) is a 2D transition metal chalcogenide material with a sandwich layered structure, which is considered to benefit the process of Li^+ insertion and extraction processes, and recently Choi et al. and Zhang et al. prepared SnSe_2 nanoplate-graphene composites as the anode material for lithium-ion batteries that gave excellent electrochemical performance [22,23]. Many reports suggested Se could improve the electrochemical performance of SnS anodes in LIBs because it belongs to the same chemical group as S but has a higher electronic conductivity [24]. For example, Lu et al. demonstrated that cycling performance could be enhanced by Se doping on SnS which results in a Se-containing phase that acts as a cushion to buffer the volume change and limit Sn agglomeration upon cycling [25]. However, the majority of previous reports focus on tin-based compounds prepared using relatively complex processes while the pure Sn based anodes with S and Se have rarely been reported.

In this study, we successfully designed and synthesized a Sn-based chalcogenide ($\text{SnSe}_{0.5}\text{S}_{0.5}$) through a facile and fast polyol-method followed by low temperature heating to obtain a high-performance anode material for LIBs. An additional set of experiments with different low temperature heating (e.g. 160°C , 180°C and 200°C) was done to determine the best reaction condition to produce phase pure $\text{SnSe}_{0.5}\text{S}_{0.5}$. The anode material synthesized at 180°C exhibits the best electrochemical performance, e.g. a high reversible capacity with the

first discharge capacity of 1316 mA h g^{-1} at a current density of 0.1 A g^{-1} , enhanced rate capability and excellent cyclic stability. As a proof-of-concept for practical LIB applications, full cells with Li ($\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}$) O_2 (LNCM) as cathode and $\text{SnSe}_{0.5}\text{S}_{0.5}$ -180 as an anode were fabricated. The LNCM// $\text{SnSe}_{0.5}\text{S}_{0.5}$ -180 full cell is operated between 1.5 and 4.5 V delivers a discharge capacity of 1111 mA h g^{-1} under a current density of 0.5 A g^{-1} . Moreover, *in-situ* X-ray diffraction (*in-situ* XRD) has been employed to give a better understanding of electrochemical reaction mechanism that occurs for this anode material.

2. Experimental section

2.1. Chemicals

All chemicals and solvents were purchased from commercial sources and used as-received without any further purifications. Sulphur powders (S, $> 99.5\%$), selenium powders (Se, $> 99.9\%$), diethylene glycol (DEG, $> 99.0\%$), ethanol (AR), tin chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $> 99.0\%$), carboxymethylcellulose sodium (CMC, $\text{C}_8\text{H}_{16}\text{NaO}_8$), polyvinylidene Fluoride (PVDF), n-methyl-2-pyrrolidone (NMP) and carbon black (super P) were purchased from Aladdin; ethylene-diamine (EN, $> 99.0\%$, AR) was purchased from Guangzhou Panyu Liqiang Chemical Technology Co., Ltd. Lithium hexafluorophosphate (LiPF_6), fluoroethylene carbonate (FEC, $\text{C}_3\text{H}_3\text{FO}_3$), ethylene carbonate (EC, $\text{C}_3\text{H}_4\text{O}_3$), ethyl methyl carbonate (EMC, $\text{C}_4\text{H}_8\text{O}_3$), and Diethyl carbonate (DEC, $\text{C}_5\text{H}_{10}\text{O}_3$) were from Shenzhen CAPCHEM Technology Co., Ltd. The $\text{Li}(\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2})\text{O}_2$ cathode material (LNCM) was obtained from Beijing Easpring Materials Technology Co., Ltd.

2.2. Synthesis of $\text{SnSe}_{0.5}\text{S}_{0.5}$ nanoplates

Synthesis of the $\text{SnSe}_{0.5}\text{S}_{0.5}$ nanoplates was based on a previous report [26]. The schematic illustration of fabrication $\text{SnSe}_{0.5}\text{S}_{0.5}$ nanoplates was shown in Fig. S1 (Supporting Information). In a typical synthesis, 45 mL of DEG was added to a 250 mL three-necked round-bottom flask and heated under magnetic stirring in an oil bath set to 100°C for 20 min. Then 0.01 mol S powders and 0.01 mol Se powders mixed by grinding in an agate mortar and then added into the flask. After stirring this mixture for 10 min, 2 mL EN was introduced into the flask using a pipet, followed by vigorously stirring and refluxed at 140°C for 30 min. After 10 min, 0.01 mol $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was added into the mixture and refluxed at 180°C for 2 h with a constant stirring. After cooling down to room temperature, the resulting products were centrifuged and washed with ethanol and deionized water in a high-speed centrifugation (8600 r min^{-1}) several times to remove any remaining precursor, DEG, EN, followed by drying at 80°C under vacuum for 12 h. Finally, the brown powder was annealed at 400°C under Ar flow for 20 h, resulting in the $\text{SnSe}_{0.5}\text{S}_{0.5}$ nanoplates (referred to as $\text{SnSe}_{0.5}\text{S}_{0.5}$ -180). For comparison, polyol reactions were performed at temperatures of 160°C and 200°C , and the corresponding products were marked as $\text{SnSe}_{0.5}\text{S}_{0.5}$ -160 and $\text{SnSe}_{0.5}\text{S}_{0.5}$ -200, respectively.

2.3. Characterizations

XRD patterns were collected on SHIMADZU/XRD-6100 instrument with a scanning rate of 2° min^{-1} and a range of 10 – 80° . The morphology was observed using a field-emission scanning electron microscopy (FE-SEM, HITACHI, SU8010) with an energy-dispersive X-ray spectrometer for chemical analysis. A field-emission transmission electron microscopy (FE-TEM, JEOL, JEM-2011) was used to obtain high-resolution TEM images and selected area electron diffraction (SAED) patterns. The valence state of elements in the tin-dichalcogenide nanoplates was studied by XPS (Kratos AXIS-Ultra DLD). *In-situ* XRD experiments were conducted on the Bruker D8 Advance

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