



ELSEVIER

Contents lists available at ScienceDirect

Journal of Power Sources

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

Solvothermal preparation of tin phosphide as a long-life anode for advanced lithium and sodium ion batteries



Shuling Liu ^{a,*}, Hongzhe Zhang ^a, Liqiang Xu ^{b,**}, Lanbing Ma ^a, Xiaoxia Chen ^b

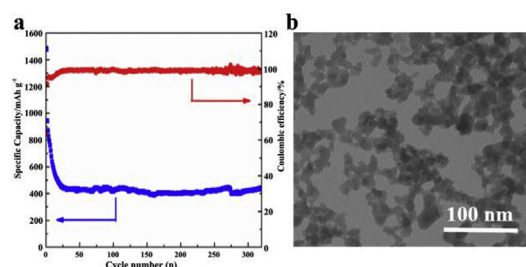
^a College of Chemistry & Chemical Engineering, Shaanxi University of Science & Technology, Xi'an, Shaanxi 710021, PR China

^b School of Chemistry and Chemical Engineering, Shandong University, Ji'nan, Shandong 250100, PR China

HIGHLIGHTS

- Sn₄P₃ nanoparticles were synthesized via a simple solvothermal route at 180 °C for 10 h.
- The solvent ratio play crucial roles on the size modulation of Sn₄P₃ nanoparticles.
- The long cycle stability of Sn₄P₃ nanoparticles is firstly reported in this study.
- It is the first time to report the rate performance of Sn₄P₃ nanoparticles.
- The Sn₄P₃ nanoparticles have also been applied as an anode material for Na-ion batteries.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 September 2015

Received in revised form 10 November 2015

Accepted 16 November 2015

Available online 6 December 2015

Keywords:

Sn₄P₃

Solvothermal

Anode material

Lithium ion batteries

Sodium ion batteries

ABSTRACT

Tin phosphide (Sn₄P₃) nanoparticles with different sizes are synthesized via a facile solvothermal method at 180 °C for 10 h. The as-prepared Sn₄P₃ nanoparticles have an average size of about 15 nm. Meanwhile, their size could be easily controlled by the solvent ratio. The long cycle stability and rate performance of the as-obtained Sn₄P₃ nanoparticles have been tested as an anode material for lithium ion batteries for the first time. Electrochemical measurements show that the Sn₄P₃ nanoparticles with a smallest size give the best cycling and rate performances. They deliver a discharge capacity of 612 mAh g⁻¹ after 10 cycles and could still maintain 442 mAh g⁻¹ after 320 cycles at the current density of 100 mA g⁻¹ within voltage limit of 0.01–3.0 V. Even after 200 cycles at a current density of 200 mA g⁻¹, the specific capacity still could be remained at 315 mAh g⁻¹. The improved electrochemical performances of Sn₄P₃ electrode might be largely attributed to their small-size. Furthermore, the as-prepared Sn₄P₃ nanoparticles have also been tested as an anode material for Na-ion batteries, this Sn₄P₃ anode can deliver a reversible capacity of 305 mAh g⁻¹ after 10 cycles at the current density of 50 mA g⁻¹.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Transition metal phosphides possess particular physical and chemical properties which make them attractive and promising for future applications in the fields of electronics, electrode materials, catalysis, and magnetic systems [1–4]. Thus, they have obtained

* Corresponding author.

** Corresponding author.

E-mail addresses: shulingliu@aliyun.com (S. Liu), xulq@sdu.edu.cn (L. Xu).

more and more public's attention, especially as a promising candidate for traditional anode material [5], and have been widely investigated due to their higher specific capacity, better cycling behavior and lower cost, such as CoP_3 [6], MnP_4 [7], Zn_3P_2 [8], Cu_3P [9] and FeP [10]. In addition, the major potential voltage of metal phosphide is much higher compared to the voltage of lithium deposition, which reduces the risk of lithium dendrite and improves the intrinsic safety when overcharge. Moreover, phosphorus and lithium can form a compound and Li/P molar ratio can be up to 3. Its theoretical capacity can reach to 2600 mAh g^{-1} [11], which is 7 times than carbon material. Although their own values are very favorable when compared to the graphite, they cannot be retained without obvious capacity fade over prolonged cycles. The decrease of specific capacity is commonly attributed to the structure change and serious volume expansion, which usually leads to the irreversible collapse and mechanical damage during lithiation and delithiation processes. In order to solve the issues, some strategies have been realized to improve their performances, including the fabrication of one-dimensional nanomaterials [12,13], the surface-modified of conductive polymer or graphite [14,15], hollow/porous structures [16,17], and the formation of hierarchical surfaces [18–20]. These controls could effectively shorten the Li/Li⁺ diffusion pathway, enhance the electronic conductivity, accommodate the volume change during the discharge/charge processes, and improve the contact between electrolyte and electrode to a large extent.

Among the phosphides, tin phosphide (Sn_4P_3) possesses a layered structure with alternating phosphorus and tin layers being grouped into seven-layer blocks (all phosphorus atoms are octahedrally coordinated by tin atoms, while half of tin atoms are octahedrally coordinated by phosphorus atoms), which propagate along the *c*-axis. One can expect the possibility of intercalation of cations in between two weakly bound tin layers [21]. The Sn_4P_3 material has been firstly synthesized at 400°C through the silica tubes in 1967 [22], but its electrochemical property was firstly reported in 2004, which has a specific capacity of 370 mAh g^{-1} up to 50 cycles at 100 mA g^{-1} within 0–0.72 V. Sn_4P_3 with a theoretical capacity of 1230 mAh g^{-1} has become a promising anode material and hot spot today owing to their reversibility and large lithium ingestion at relatively low potential [23–26]. For example, Sn_4P_3 film was announced to have a discharge capacity of 550 mAh g^{-1} after 10 cycles at the current density of 100 mA g^{-1} using a Pulsed Laser Deposition (PLD) method in 2009 [27]. Recently, the Sn_4P_3 microstructures were firstly prepared as a negative electrode for all-solid-state lithium ion batteries, which displayed the first discharge capacity of 1080 mAh g^{-1} and the initial coulombic efficiency of 88% [28]. Up to date, the Sn_4P_3 materials are mainly fabricated through high energy consumption or expensive devices, and it is difficult to achieve the controls for material on the shape, size, surface and structure synchronously. In order to further facilitate the fabrication process, new progresses and strategies are required for this material. It is well known that solvothermal method [29] is considered to be a convenient and competitive method due to its facility and well-controlling, which is benefited to control shape and size of nanomaterials. However, to the best of our knowledge, there are few reports on the synthesis of Sn_4P_3 via a mixed solvent method and applications as a relative high performance negative electrode for lithium batteries and Na-ion batteries.

In our experiment, Sn_4P_3 nanoparticles have been successfully fabricated by a facile mixed solvents solvothermal method. It is found that the solvent ratio is an important factor in controlling the size of the as-prepared Sn_4P_3 sample. The Sn_4P_3 nanoparticles with different grain diameters are applied as anode materials for lithium ion rechargeable batteries. It is found that the Sn_4P_3 nanoparticles with the smallest diameter show the best cycle performance. The long cycle stability and rate performance of the

as-prepared Sn_4P_3 nanoparticles have been tested for the first time. It delivers a specific capacity of 442 mAh g^{-1} after 320 cycles at a current density of 100 mA g^{-1} . Even after 200 cycles at a current density of 200 mA g^{-1} , the specific capacity still could be maintained at 315 mAh g^{-1} . Furthermore, the Sn_4P_3 nanoparticles have also been tested as an anode material for Na-ion batteries, this Sn_4P_3 anode can deliver a reversible capacity of 305 mAh g^{-1} after 10 cycles at the current density of 50 mA g^{-1} . These results demonstrate the potential application of the Sn_4P_3 electrode in rechargeable batteries.

2. Experimental

2.1. Sample preparation

All the raw materials used here were of analytic grade without further purification. In a typical experimental procedure, an appropriate amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.226 g, 1 mmol) was dissolved in the solvent ($V_{\text{Ethanol}}/V_{\text{DMF}}$ is 3:1) to form a uniform solution. After vigorously stirring at room temperature for 20 min, proper amount of NaBH_4 (0.037 g, 1 mmol) was added into the above solution under stirring, which was then stirred vigorously at room temperature for 10 min, the resultant solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. Then, an appropriate amount of white phosphorus (0.248 g, 2 mmol) was added into the above system. The autoclave was sealed and maintained at 180°C for 10 h. Afterwards, it was cooled at air to room temperature. The black precipitate was filtered and washed continuously using benzene, absolute ethanol, distilled water and absolute ethanol several times to remove the impurities. Finally, the as-obtained samples were dried at 60°C for 12 h in a vacuum and collected for characterization. The as-prepared product was denoted as "Sample II".

The preparation of the Sn_4P_3 nanoparticles with different solvents ratios was similar to that of Sample II. The products obtained with the solvents ratios of 1:1 ($V_{\text{Ethanol}}/V_{\text{DMF}}$) and 4:1 ($V_{\text{Ethanol}}/V_{\text{DMF}}$) were denoted as "Sample I" and "Sample III".

2.2. Characterization

The X-ray diffraction (XRD) patterns of the Sn_4P_3 sample were measured by a Bruker D8 advanced X-ray diffractometer provided with graphite monochromatized $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. The Field emission scanning electron microscope (FESEM; JEOL JSM-6700F) and the transmission electron microscopy (TEM, JEM-2011) were used to characterize the size and morphology of the Sn_4P_3 samples.

2.3. Electrochemical measurements

The electrochemical discharge-charge performances of the samples were tested on a Land battery test system (CT2001A) at 25°C . The working electrodes were consisted of 70 wt % active materials (Sn_4P_3 nanoparticles), 20 wt % carbon black, and 10 wt % polyvinylidene fluoride (PVDF). N-Methylpyrrolidone (NMP) was used as the solvent. The mixed slurry was spreaded onto a slice of Cu foil and dried in vacuum oven at 60°C for 12 h, then the obtaining foil was roll-pressed and cut into discs with diameter of 12 mm. The weight of the active material is estimated about 1.5 mg for each half-cell. Celgard 2300 membrane was used as the separator. The electrolyte of lithium ion batteries was composed of 1 mol L^{-1} LiPF_6 dissolved ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC, volume ratio was 1:1:1). Lithium foils with the diameter of 14 mm were used as the counter electrodes. The electrolyte used in Na-ion batteries was 1.0 mol L^{-1} NaClO_4 in ethylene carbonate(EC)/diethyl carbonate(DEC) solution with addition of 5%

Download English Version:

<https://daneshyari.com/en/article/1285660>

Download Persian Version:

<https://daneshyari.com/article/1285660>

[Daneshyari.com](https://daneshyari.com)