



Short communication

Bismuth sulfide: A high-capacity anode for sodium-ion batteries



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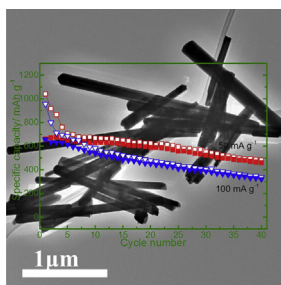
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HIGHLIGHTS

- Bi₂S₃ was demonstrated to exhibit high-capacity sodium storage for the first time.
- Bi₂S₃ nanorods were synthesized by a facile refluxing process.
- Sodium storage in Bi₂S₃ is achieved by a conversion-intercalation mechanism.

GRAPHICAL ABSTRACT



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ABSTRACT

Exploring high-performance anode materials is currently one of the most urgent issues towards practical sodium-ion batteries (SIBs). In this work, Bi₂S₃ is demonstrated to be a high-capacity anode for SIBs for the first time. The specific capacity of Bi₂S₃ nanorods achieves up to 658 and 264 mAh g⁻¹ at a current density of 100 and 2000 mA g⁻¹, respectively. A full cell with Na₃V₂(PO₄)₃-based cathode is also assembled as a proof of concept and delivers 340 mAh g⁻¹ at 100 mA g⁻¹. The sodium storage mechanism of Bi₂S₃ is investigated by ex-situ XRD coupled with high-resolution TEM (HRTEM), and it is found that sodium storage is achieved by a combined conversion-intercalation mechanism.

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1. Introduction

Sodium-ion batteries (SIBs) recently have been attracting ever-growing research attention. Compared with the widely used

lithium-ion batteries (LIBs), SIBs show a greater potential for large-scale grid energy storage systems due to the abundance of sodium [1–3]. However, the electrode materials cannot meet the demands for high-capacity and durable sodium storage at present, which is one of the major obstacles in realizing practical SIBs.

To date, research on cathode materials for SIBs is very progressive [4–10]. Some reported extraordinary performances in terms of specific capacity and energy density are even comparable

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to those of typical cathode materials for LIBs. In the case of anode materials, although sodium is hard to intercalate into graphitic carbons, some disordered carbons (e.g., hard carbons) and carbonaceous nanostructures show improved sodium storage performance [11–14]. Some intercalation-type compounds (e.g., $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, etc.) are also an important category of anode materials [15–17]. Meanwhile, metal oxides and sulfides were extensively investigated for sodium storage [18–23], which generally store sodium by a similar conversion-reaction mechanism to the lithium counterpart. However, most of the reported metal oxides deliver much lower reversible capacities than the theoretical values, which are possibly induced by the sluggish electrochemical reaction kinetics. Some research attention was also focused on alloying-type materials that were extensively investigated for lithium storage. Such kind of materials usually have high gravimetric and volumetric capacities, e.g., Sn (847 mAh g^{-1} and 1210 mAh cm^{-3} , respectively), Sb (660 mAh g^{-1} and 1120 mAh cm^{-3} , respectively), and Bi (385 mAh g^{-1} and 1075 mAh cm^{-3} , respectively) [24–29]. However, it was found that the sodium storage mechanism of such materials may be different from lithium storage that is already well recognized as alloying reaction. The reported sodium storage mechanisms in Bi are contradictory. Ellis et al. [24] reported that the sodiation of Bi follows the Na–Bi equilibrium phase diagram, with the formation of NaBi and Na_3Bi . Su et al. [25] found that Bi could provide facile sites for Na ion diffusion and accommodation and proposed the intercalation reaction mechanism instead of the alloying process. It should also be noted that, as compared with the bare metals, the corresponding metal oxides and sulfides possess higher theoretical capacities due to the combined conversion-alloying reaction mechanism, e.g., 1378 mAh g^{-1} for SnO_2 , 1136 mAh g^{-1} for SnS_2 , 946 mAh g^{-1} for Sb_2S_3 , and 1102 mAh g^{-1} for Sb_2O_3 [30–35]. Thus, such metal oxides and sulfides appear to be more promising for high-capacity sodium storage.

Herein, for the first time, we report Bi_2S_3 as an anode material for SIBs. Bi_2S_3 nanorods were synthesized via a facile refluxing process and delivered high specific capacity and promising rate performance for sodium storage. A full cell with $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ -based cathode was assembled and showed encouraging performance. Besides, the corresponding sodium storage mechanism was also investigated by ex-situ XRD coupled with HRTEM techniques.

2. Experimental

2.1. Synthesis

The synthesis process was carried out in a three-neck flask (100 mL) by a refluxing process. In a typical synthesis of Bi_2S_3 , 1.6 mmol BiCl_3 (Alfa Aesar, 99.9%) and 3.2 mmol 1,3,4-Thiadiazole-2,5-dithiol (DMCT) (Sigma-Aldrich, 98%) were added to the flask containing 30 mL ethylene glycol (EG) (Alfa Aesar, 99%) and 10 mL 1-octadecene (ODE) (Sigma-Aldrich, 90%). Then, argon gas was introduced to purge the suspension for about 30 min. The suspension was quickly heated up to 180 °C. During heating, BiCl_3 and DMCT were completely dissolved. The solution was maintained at 180 °C for 2 h under stirring, and black product was gradually formed with time. After reaction, the reaction mixture was naturally cooled down to room temperature. The black product was collected by centrifugation followed by repeated washing with ethanol for several times, and then dried at 60 °C overnight in a vacuum oven.

2.2. Materials characterization

Phase structure of the samples was investigated by a Bruker AXS D8 advance X-ray diffractometer (XRD) using Cu K α radiation. The

morphology was performed by a field-emission scanning electron microscopy (FESEM) (JEOL, Model JSM-7600F), and the nanostructure was characterized by a transmission electron microscopy (TEM) (JEOL, Model JEM-2100) operating at 200 kV.

2.3. Electrochemical measurements

The working electrode slurry was prepared by mixing Bi_2S_3 , carbon nanotubes (CNT) and poly(vinylidene fluoride) (PVDF) at a weight ratio of 70:20:10 thoroughly in *N*-methylpyrrolidone (NMP) solvent. The slurry was pasted on copper foils followed by vacuum-drying at 60 °C overnight to obtain the working electrodes. The mass loading of the active material is around 0.6 mg cm^{-2} . The coin-type half and full cells were assembled in an argon-filled glove-box, where both moisture and oxygen levels were less than 1 ppm. The sodium foils were used as counter/reference electrodes for half cells, Whatman GF/D microfiber filter paper was used as the separator, and 1 M NaClO_4 dissolved in propylene carbonate (PC) with 5% fluoroethylene carbonate (FEC) was used as electrolyte. All the cells were tested by a NEWARE multi-channel battery test system with galvanostatic charge and discharge in the voltage range of 0.005–3.0 V. The cyclic voltammetry (CV) curves of the cells were carried out with an electrochemical workstation (Solartron, 1470E). For coin-type full cell testing, the Bi_2S_3 anode was operated for one discharge/charge cycle (0.005–3.0 V) in half cell before assembling the full cell. The full cell was tested in the voltage range of 0.8–3.0 V, and the specific capacity was calculated based on the mass of Bi_2S_3 anode.

3. Results and discussion

Fig. 1a shows the XRD pattern of the as-prepared Bi_2S_3 powders. All the diffraction peaks can be indexed as orthorhombic phase Bi_2S_3 (space group Pbnm), which are in good agreement with the information given in the standard card (JCPDS card No. 17-0320). Fig. 1b–c shows typical SEM images of the Bi_2S_3 powders. The product shows rod-like morphology with average diameters and lengths ranging between 50–100 nm and 1–2 μm , respectively. Energy-dispersive X-ray analysis reveals that the Bi:S molar ratio is about 2:3 (Fig. S1, Supporting Information). The detailed morphology and crystal structure of Bi_2S_3 nanorods were analyzed by TEM and HRTEM. The TEM image of Bi_2S_3 (Fig. 1d) confirms the nanorod morphology. Fig. 1e–f shows a typical Bi_2S_3 nanorod with clear lattice fringe pattern. The calculated fringe width of 0.56 nm and 0.35 nm corresponds to the d-spacing of the (020) and (310) planes of orthorhombic phase Bi_2S_3 , respectively, suggesting that the Bi_2S_3 nanorods grow along the preferential [100] direction and the nanorod has high crystallinity [36]. Furthermore, the selected area electron diffraction (SAED) shows a spotted pattern, indicating the single-crystalline nature of the Bi_2S_3 nanorod.

Coin-type half cells with sodium foils as counter/reference electrodes were assembled and tested in order to evaluate the sodium storage capability of the Bi_2S_3 nanorods. The cyclic voltammetric (CV) curve of the cell at a scan rate of 0.1 mV s^{-1} is shown in Fig. 2a. During the first cathodic scan, four cathodic peaks can be observed. The cathodic peak located at around 1.15 V can be assigned to the intercalation of sodium ion into Bi_2S_3 , forming $\text{Na}_x\text{Bi}_2\text{S}_3$. The cathodic peak at 0.94 V can be ascribed to the conversion reaction with the formation of metallic Bi and Na_2S . The following peaks at 0.48 and 0.24 V correspond to the reaction between sodium and metallic Bi. However, these two cathodic peaks shift to lower potential compared with those of Bi@graphene anode [25]. In the anodic scan, the two oxidation peaks located at 0.7 and 0.8 V correspond to the reversible desodiation reaction of Na-Bi phases [25], and the peak at 1.75 V can be assigned to the

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