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Buffer layer enhanced stability of sodium-ion storage

Xusheng Wang [a, b], Zhanhai Yang [b], Chao Wang [a], Dong Chen [b], Rui Li [c], Xinxiang Zhang [a], Jitao Chen [a, *], Mianqi Xue [b, **]

[a] *Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*
[b] *Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100190, China*
[c] *School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen 518055, China*

HIGHLIGHTS

- Layered $SnSe_2$ single crystal with integrated Se—Se buffer layers is prepared.
- Se—Se buffer layers could accommodate the intercalation process.
- Autogenous Na_2Se layers could confine the structural damage of tin sequences.
- $SnSe_2$ single crystal realizes efficient, fast and long-term sodium-ion storage.
- Sodiation/desodiation processes of the $SnSe_2$ single crystal are investigated.

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ABSTRACT

Se—Se buffer layers are introduced into tin sequences as $SnSe_2$ single crystal to enhance the cycling stability for long-term sodium-ion storage by blazing a trail of self-defence strategy to structural pulverization especially at high current density. Specifically, under half-cell test, the $SnSe_2$ electrodes could yield a high discharge capacity of 345 mAh g^{-1} after 300 cycles at 1 A g^{-1} and a high discharge capacity of 300 mAh g^{-1} after 2100 cycles at 5 A g^{-1} with stable coulombic efficiency and no capacity fading. Even with the ultrafast sodium-ion storage at 10 A g^{-1}, the cycling stability still makes a positive response and a high discharge capacity of 221 mAh g^{-1} is demonstrated after 2700 cycles without capacity fading. The full-cell test for the $SnSe_2$ electrodes also demonstrates the superior cycling stability. The flexible and tough Se—Se buffer layers are favourable to accommodate the sodium-ion intercalation process, and the autogenous Na_2Se layers could confine the structural pulverization of further sodiated tin sequences by the slip along the $Na_2Se—Na_xSn$ interfaces.

1. Introduction

Lithium-ion batteries (LIBs) technology has driven the storage of electrical energy on the path to the indispensable regulation for everyday life in the past decades [1–3], now that sodium-ion batteries (SIBs) technology is bouncing back to resurge the vitality of next-generation batteries by addressing to the sustainable sodium reserves [4–7]. Similar to the operational mechanism of LIBs, the SIBs could balance the energy storage and release through the extraction and insertion of sodium ions along with the circuit of electrons [8]. However, direct extrapolation from LIBs technology is insufficient to build the SIBs system. For instance, the commercialized graphite anode in the LIBs field cannot provide enough sodium-ion storage in the specific electrolytes for its relatively narrow interlayer spacing [9–11], thus causing very poor stability. And the prosperous studies of silicon material for LIBs (typically via Cui's group [12,13]) are relatively deserted for the inactive Na-Si alloys [14,15]. Hence, developing feasible SIB anodes with long-term cycling stability is looming ahead.

At present, strategies to improve the cycling stability of the electrode materials have focused on the structure and space designs which mainly based on the nanocomposite technology with the strengths of reducing the path length of inward ion diffusion and enhancing the resistance to the structural pulverization [16–25]. Take the tin-enriched materials as example, Jahel et al. [26] confined crystalline SnO_2 nanoparticles in mesoporous carbon

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[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: chenjitao@pku.edu.cn (J. Chen), xuemq@iphy.ac.cn (M. Xue).

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as SIB anode with a capacity retention of 417 mAh g^{-1} at 1.8 A g^{-1} even after 4000 cycles. A SnS_2 NC/EDA-RGO (NC, nanocrystal; EDA, ethylenediamine; RGO, reduced graphene oxide) nanocomposite prepared by Jiang et al. [27] exhibited a high capacity of 480 mAh g^{-1} at 1 A g^{-1} after 1000 cycles. Zhou et al. [28] reported a SnS@graphene hybrid SIB anode with an excellent sodium-ion storage of 308 mAh g^{-1} at 7.29 A g^{-1} after 250 cycles. Although these achievements have shown remarkable progresses in the cycling stability, the simple production processes, satisfactory compacted density, and long-term operation at high current density are still the eternal goals of battery materials [4,29–33]. In this view, blazing a trail of self-defence strategy to structural damage could be feasible to implement the long-term cycling stability.

Inspired by the Se-doping induced improvement in the cycling stability of tin microparticles [34], the exfoliation characteristic of $SnS_{2-x}Se_x$ ($0 \le x \le 2$) single crystal materials [35], and the incomplete ionization in the Li-FeSe system [36], here we introduce the Se–Se layers as the buffer device in fabricating the $SnSe_2$ single crystal to solve the stubborn nature of poor cycling stability for SIBs. In the study of the $SnSe_2$/RGO nanocomposites [37], due to the enhancement in electrical conductivity and structural stability derived from graphene, the $SnSe_2$/RGO nanocomposites demonstrated excellent capacity delivery and cycling stability at 0.1 A g^{-1}, which is much better than that of the pure $SnSe_2$ nanosheets, despite the high-rate and long-term performances are unavailable to us. Further study on the two-dimentional $SnSe_2$ with confined nanostructures and patterns [38] may indeed help us recognize the characteristics of $SnSe_2$. For this matter, owing to the high integrity and regularity of single crystal, the encoded Se–Se buffer layers should possess admirable flexibility and toughness, which is favourable to accommodate the sodium-ion intercalation process, and the Na_2Se layers generated from the conversion reaction could confine the structural pulverization of further sodiated tin sequences by the slip along the Na_2Se–Na_xSn interfaces during the alloying process [21], thus leading to the superior long-term cyclability at high current density. Under half-cell test, the $SnSe_2$ electrodes, prepared by simple ball mill mixing technology, are able to yield a high discharge capacity of 345 mAh g^{-1} after 300 cycles at 1 A g^{-1} and a high discharge capacity of 300 mAh g^{-1} after 2100 cycles at 5 A g^{-1} without capacity fading. Even with the ultrafast sodium-ion storage at 10 A g^{-1}, a high discharge capacity of 221 mAh g^{-1} is still delivered after 2700 cycles with no capacity fading. The full-cell test for the $SnSe_2$ electrodes also demonstrates the superior cycling stability. The encoded Se–Se buffer layers could work along with the published nanocomposite technology for the tin-enriched materials or even go beyond them in long-term cycling stability at high current density. The concept of encoding integrated and regular Se–Se buffer layers into tin sequences should be applied to other SIB anodes [21,22], or even other battery systems. Furthermore, the repertoire of the highly ordered and extended layers with superior resistance to the structural pulverization could be amplified to build the graphene- and even polymer/protein-mimetic materials [39,40].

2. Experimental

2.1. Synthesis of $SnSe_2$, SnS_2, and $Na_3V_2(PO_4)_3$ material

The $SnSe_2$ material was synthesized by solid-state reaction of tin (Alfa Aesar, 99.9%) and selenium (Alfa Aesar, 99.999%) at 400 °C for 20 h and then 900 °C for another 20 h in an evacuated quartz tube. The SnS_2 material was synthesized by the same procedure as comparison. The $Na_3V_2(PO_4)_3$ material was synthesized by using a sol-gel method with NaOH, NH_4VO_3, $NH_4H_2PO_4$, and citric acid as raw materials.

2.2. Material characterizations

The crystal structures of $SnSe_2$ and other intermediate products were measured by X-ray diffraction (XRD, PANalytical diffractometer) with Cu Kα radiation ($\lambda = 1.5416$ Å). The morphologies and microstructures of $SnSe_2$ and other intermediate products were visualized by scanning electron microscopy (SEM, S4800, Hitachi), transmission electron microscopy (TEM, JEM-2100F, JEOL), and energy dispersive spectroscopy (EDS, JEM-2100F, JEOL). The surface elemental analyses were performed by X-ray photoelectron spectroscopy (XPS, Axis Ultra, Kratos Analytical Ltd.).

2.3. Preparation of the $SnSe_2$, SnS_2, and $Na_3V_2(PO_4)_3$ electrodes

The $SnSe_2$ electrodes were prepared by mixing the $SnSe_2$ powders, carbon black, and sodium carboxymethylcellulose (CMC) at a weight ratio of 75: 15: 10. The slurry was spread on a copper foil and then dried in an electric thermostatic drying oven at 90 °C. The dried copper foil was cut into disks with the diameter of 11 mm (the average loading of $SnSe_2$ is 1.8 mg cm^{-2}) as the $SnSe_2$ electrodes and then dried in an oven at 80 °C for 12 h under vacuum. The SnS_2 electrodes were prepared by the same procedure as comparison. The $Na_3V_2(PO_4)_3$ electrodes were prepared by mixing the $Na_3V_2(PO_4)_3$ powders (90 wt% of pure $Na_3V_2(PO_4)_3$ and 10 wt% of carbon), carbon black, and polyvinylidene fluoride (PVDF) at a weight ratio of 75: 15: 10. The slurry was spread on the aluminum foils and then dried in an electric thermostatic drying oven at 90 °C. The dried aluminum foils were cut into disks (11 mm) as the $Na_3V_2(PO_4)_3$ electrodes and then dried in an oven at 120 °C for 12 h under vacuum.

2.4. Electrochemical performances of the $SnSe_2$ and SnS_2 electrodes

The half-cell performances of the $SnSe_2$ and SnS_2 electrodes were characterized with sodium metal foils as the counter electrodes, glass fibers as the separators, and 1 mol L^{-1} sodium trifluomethanesulfonate ($NaCF_3SO_3$) in diethylene glycol dimethyl ether (DEGDME) as the electrolyte, and then assembled into LIR2032-type coin cells in an argon-filled glove box in which the moisture and oxygen contents were below 0.1 ppm. The half-cell performances of $Na_3V_2(PO_4)_3$ material were characterized by 1 mol L^{-1} sodium perchlorate ($NaClO_4$) in propylene carbonate (PC) with 5 vol% fluoroethylene carbonate (FEC) as the electrolyte. The full-cell performances of the $SnSe_2$ electrodes were characterized by the similar procedure only with the differences of the $Na_3V_2(PO_4)_3$ as the cathode and 1 mol L^{-1} sodium perchlorate ($NaClO_4$) in DEGDME as the electrolyte. The cycling tests of the assembled cells were performed on a Land CT2001A battery testing system within the voltage range of 0.1–3.0 V *versus* Na^+/Na (Moreover, the voltage range of 2.2–4.0 V was used for the $Na_3V_2(PO_4)_3$ half-cell test and the voltage range of 0.3–2.9 V was used for the full-cell test). Cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS) were measured on an Autolab electrochemical workstation. The cycle number of the cycling performances for the $SnSe_2$ half cells in the text starts after several discharge-charge processes, in which a small current density (0.1–0.5 A g^{-1}) was used to activate the electrodes to achieve the stable cycling state.

3. Results and discussion

Fig. 1a presents the X-ray diffraction (XRD) pattern of the $SnSe_2$ crystal. All the peaks located at 14.5°, 29.1°, 44.3°, 60.4°, and 77.8° could be severally indexed to the (001), (002), (003), (004), and (005) crystal planes of the hexagonal $SnSe_2$ P-3m1 crystal system