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ZnS_xSe_{1-x}/N-C ($x = 0.24$) hierarchical nanosphere with improved energy storage capability as sodium-ion battery anode

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Anode materials are demonstrated to essentially affect the electrochemical performance of sodium-ion batteries (SIBs), which are considered as a promising large-scale energy storage device. In this work, alloying ZnS_xSe_{1-x} ($x = 0.24$) and N doped carbon composite (ZnS_xSe_{1-x}/N-C ($x = 0.24$)) hierarchical nanospheres are prepared by selenizing the ZnS precursor. The corresponding X-ray diffraction and high-resolution transmission electron microscopy results prove the formation of an alloyed phase, resulting in a wider lattice compared with ZnS. Benefitting from the coexistence of S^{2-} and Se^{2-} in the ZnS_xSe_{1-x} lattice, the weaker Zn-Se bonds and wider lattice spacing facilitate ultrafast pseudocapacitive sodium storage capability and enhanced cycling stability, when ZnS_xSe_{1-x}/N-C is used as anode material for SIBs. At current of 1.0 A g^{-1}, it delivers a capacity of 378 mAh g^{-1} after 130 cycles with capacity retention of 87.9%, which is much higher than 34.3% for the ZnS/N-C electrode. In addition, for the rate performance, it can maintain an impressive capacity of 233 mAh g^{-1} at 10.0 A g^{-1} with a capacity retention of 55.9% in comparison with the capacity at 0.2 A g^{-1}. This work provides us common thoughts to enhance the electrochemical performance of transition metal chalcogenide anode through anion substitution.

1. Introduction

In order to guarantee the large-scale and sustainable utilization of renewable clean energy, sodium-ion batteries (SIBs) have attracted our increasing attention as one of the most promising energy storage devices, owing to the most principal advantage of the high abundant and widespread sodium resource [1,2]. On the other hand, SIBs possess a similar structure characteristics and energy storage mechanism to lithium ion batteries (LIBs), making it easier developed through drawing on the success of marketization for LIBs [3]. However, the unsatisfactory electrochemical performance resulted from the poor kinetics and the unstable solid electrolyte interphase (SEI) layer caused by the larger ion size of Na^+ ion (~1.09 Å, 55% larger than Li^+ ion) has greatly impeded the development and application of SIBs [4,5]. It is known that anode materials play a key role on the electrochemical performance improvement. As a result, it is urgent to exploit anode materials with rational structures to enhance Na^+ ion insertion/extraction kinetics and alleviate the strain and stress from the volume changes during charge/discharge process.

In the past decade, many efforts have been devoted to explore potential anode candidates for SIBs [6–14]. Among them, metal chalcogenides (MCs) are considered as one type of the most promising anodes because of their higher theoretical capacities (500–1000 mAh g^{-1}) based on reversible conversion and/or Na-metal alloying mechanism, which is 2–3 times that of commercial graphite electrode materials (372 mAh g^{-1}) [15,16]. Nonlayered MCs (such as FeS_2, CoS_2, NiS_2, CuS, ZnS, and MnS, etc.) are very popular due to their low price [17–22], compared with layered MCs (such as MoS_2, WS_2, and $MoSe_2$, etc.) [23–25]. Particularly, nontoxic Zn-based MC anodes (ZnS or ZnSe) exhibit high initial Coulombic efficiencies (CEs) and high theoretical capacities based on sodiation/desodiation mechanism ($ZnS/ZnSe + 2Na + 2e^- \leftrightarrow Na_2S/Na_2Se + Zn$) combined with alloying/dealloying reaction ($13Zn + Na+ + e^- \leftrightarrow NaZn_{13}$), which is drawing our more and more attention for SIB anodes [18,26–31]. However, pure ZnS always suffers from poor rate capability and cycling stability based on the fact of its poor electrical conductivity and serious volume change.

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Generally, in order to improve the electrochemical performance of MC anodes, many strategies have been developed, generally including nanostructure engineering and carbon materials modification [15]. In addition, doping or alloying through partially substituting cation or anion in the crystal cells, has also been employed to improve the electrical conductivity of MC anodes due to the increasing diffusion defects and synergetic effects among the various cations or anions. Kang' group reported a yolk–shell structured $(Fe_{0.5}Ni_{0.5})_9S_8$ solid solution, which delivered a high and stable capacity of 527 mAh g^{-1} in the 100th cycle with a high capacity retention of 99% compared with that for 2nd cycle [32]. They also prepared $Ni_3Co_6S_8$ plate-shape nanocrystals combined with the rGO ($Ni_3Co_6S_8$–rGO) composite with both excellent cycling performance and rate capability [33]. Although doping cations into the crystal cells to prepare MC anodes has been widely studied, anion doping to fabricate binary anion-based MC anodes, such as MS_xSe_{1-x}, is seldom reported. However, the incorporation of Se into sulfide forming an alloying phase, can benefit from both the conductivity of selenide and the interlayer-spacing of sulfide, thus enhancing the corresponding electrochemical performance of the alloying anodes remarkably. Recently, $Mo(Se_{0.85}S_{0.15})_2$:C hierarchical nanotubes were obtained by selenizing the MoS_2 nanotube precursor, which exhibited outstanding cycling stability and fast reaction kinetics [34]. The $SnSe_{0.5}S_{0.5}$/C nanocomposite has also been synthesized and demonstrated a high specific capacity and a long-term cycling stability for SIBs (430 mAh g^{-1} in a SIB at current of 200 mA g^{-1} after 100 cycles) [35]. These results demonstrated that the alloyed nanostructured anodes especially novel binary selenium-sulfide material could potentially be an excellent anode material for Na-ion storage.

In this work, alloying ZnS_xSe_{1-x} and N doped carbon composite (ZnS_xSe_{1-x}/N-C ($x = 0.24$)) hierarchical nanospheres were prepared by selenizing the ZnS precursor at 700 °C through a gas-solid reaction. The X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) results confirm the Se^{2-} ions are successfully incorporated into ZnS precursor forming the ZnS_xSe_{1-x} solid solution. And the *in-situ* N-C is achieved by carbonization of adsorbed polyvinyl pyrrolidone (PVP) molecules, which originated from the ZnS preparation process. The carbon content and the x value in ZnS_xSe_{1-x}/N-C can be estimated to be 2.14% and 0.24, respectively, from the thermogravimetric analysis (TGA) results. Compared with the ZnS precursor, the lattice spacings of ZnS_xSe_{1-x} are increased, which may be in favor of the Na^+ ion insertion/desertion, when ZnS_xSe_{1-x} nanospheres are used as anode material for SIBs. As expected, ZnS_xSe_{1-x}/N-C ($x = 0.24$) exhibits superior sodium storage capability compared to the ZnS/N-C nanosphere anodes. Our work provides a facile method to enhance the electrochemical performance of MC anodes for SIBs.

2. Experimental

2.1. Synthesis of ZnS/N-C and ZnS_xSe_{1-x}/N-C ($x = 0.24$)

ZnS precursor was obtained using a modified method according to previous report [36]. Typically, $Zn(COOH)_2 \cdot 2H_2O$ (0.878 g) and PVP with average molecular weight of 40000 (2.0 g) were added into 400 mL deionized (DI) water and stirred for 15 min to form a transparent solution-1. Thioacetamide (TAA, 3.0 g) was dissolved into 200 mL DI water to form a solution-2. Subsequently, solution-2 was added into solution-1 in a round bottomed flask and then stirred for 2 h in an oil bath at 100 °C. After cooled down naturally to the room temperature, the white precipitate was collected by centrifugation, washed with ethanol three times and finally dried at 80 °C. The obtained powder was further thermal treated for 2 h at 700 °C with a heating rate of 2 °C min^{-1} in H_2/Ar atmosphere to prepare ZnS/N-C sample.

To obtain ZnS_xSe_{1-x}/N-C ($x = 0.24$), a ceramic boat containing 0.1 g of the as-prepared ZnS powder was located at tube furnace with another ceramic boat containing 0.2 g of Se powder placed at upstream. Then the tube furnace was heated to 700 °C with a heating rate of 2 °C min^{-1} and kept for 2 h in H_2/Ar atmosphere with a flow rate of 10 mL/min, producing the ZnS_xSe_{1-x}/N-C ($x = 0.24$) sample. And the x value can be controlled through changing the weight ratio of Se powder and ZnS precursor powder.

2.2. Material characterizations

The phases of the samples were carried out by X-ray diffraction (XRD) on a Rigaku Ultima IV X-ray diffractometer. To study the including elements and their corresponding oxidation states in the samples, X-ray photoelectron spectrometer (XPS) was carried out with a Thermo ESCALAB 250 surface analysis system. The morphology and structure characteristics of the samples were determined by scanning electron microscopy (SEM, GeminiSEM 500), transmission electron microscopy (TEM, FEI Tecnai G2 F30). Thermogravimetric analysis (TGA) was measured by PerkinElmer TGA 7 in an air atmosphere (10 °C min^{-1}). Fourier transform infrared (FTIR) spectra of the samples were collected on a PerkinElmer Frontier FTIR spectrometer in the range of 4000–400 cm^{-1} with 2 cm^{-1} resolution. Raman spectra were measured with via a HORIBA Evolution Raman spectroscope using 532 nm incident wavelength.

2.3. Electrochemical measurements

The electrochemical performances were evaluated through assembling half cells. Firstly, the as-prepared samples were made into working electrodes as follows. The as-prepared samples, carbon black (ECP600JD), and sodium carboxymethyl cellulose (CMC) (6:2:2 in a weight ratio) were mixed using DI water to form a slurry coating on Cu foils. The coated foils were dried at 80 °C and then cut into discs with diameters of 12 mm to obtain working electrodes. Secondly, the coin cells were assembled in a glovebox filled with Ar atmosphere with both H_2O and O_2 contents $<$ 0.01 ppm. The electrolyte was prepared by dissolving $NaSO_3CF_3$ into diethylene glycol dimethyl ether (DIGLYME, 1.0 mol L^{-1}). Sodium metal and glass microfiber (Whatman, GF/A) were used as the counter electrode and separator, respectively. Finally, galvanostatic discharge/charge cycling were measured using Neware-5 V10 mA system (Shenzhen Xinwei) in the voltage range of 0.01–3.0 V. On the Gamry 30115 electrochemical workstation, cyclic voltammetry (CV) curves were collected in the voltage range of 0.0–3.0 V at various scan rates, and electrochemical impedance spectroscopy (EIS) was carried out with frequency range of 0.1 MHz–10 mHz.

3. Results and discussion

Alloying ZnS_xSe_{1-x}/N-C ($x = 0.24$) hierarchical nanospheres were obtained through a gas-solid reaction using ZnS as reaction template as illustrated in Fig. 1. And ZnS nanosphere precursor can be firstly large-scale prepared under a mild condition using PVP as additive, which is in favor of the self-assembly of the hierarchical nanospheres [18]. After calcination at with Se powder in the upstream in H_2/Ar flow 700 °C, ZnS can be successfully transformed into alloying ZnS_xSe_{1-x}/N-C ($x = 0.24$) hierarchical nanosphere solid solution.

The phases of the samples are further analyzed by XRD. The corresponding patterns are shown in Fig. 2a. For the XRD pattern of ZnS/N-C, there are three strong peaks around 28.6°, 47.5° and 56.3°, which should index to (111), (220) and (311) planes of cubic 3C-ZnS,