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A novel oxygen vacancy introduced microstructural reconstruction of SnO_2-graphene nanocomposite: Demonstration of enhanced electrochemical performance for sodium storage

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ABSTRACT

This paper reported an oxygen vacancy contained SnO_2-graphene nanocomposite (OVs-SnO_2-Gr), which was prepared by annealing SnO_2-graphene nanocomposite in 3 vol% H_2/Ar atmospheres. It demonstrated with a high reversible capacity of around 510 mAh g^{-1} after 300 cycles at a current density of 40 mA g^{-1}, and an impressive reversible rate performance of 391 mAh g^{-1} can be obtained even at a high current density of 1200 mA g^{-1} when applied as anode for sodium storage. Evidenced by a new phase of Na_2SnO_3 during sodium storage reactions, it is found that sodium can insert into crystal lattice of oxygen vacancy contained SnO_2. Moreover, sodium insertion could arouse a novel structural reconstruction and introduce amorphous phase SnO_2, which promotes the surface-controlled reaction process and Na^+ diffusion rates, and enables a good rate performance. Additionally, the H_2/Ar annealing process increases overall conductivity of electrodes, which further reduces the barrier of Na^+ diffusion. It is believe that the as-prepared OVs-SnO_2-Gr is a promising anodes for Na-ion batteries with outstanding electrochemical performance.

1. Introduction

Due to properties of low costs and nature abundance of sodium, Na-ion batteries are highly promising power sources in large-scale stationary energy storage as compared to Li-ion batteries [1–3]. Graphite is known as the standard anode material for commercial Li-ion batteries, which has reasonable reversible capacity, low lithium insertion potential and flat discharge plateaus, and can provide a high battery voltage, superior cycling behavior and high Coulombic efficiency [4,5]. However, conventional graphite is not suitable for sodium storage application, due to sodium has a larger ionic radii of 0.102 nm, makes it difficult to insert into lattice planes of graphite [2,3]. Although, the expanded graphite has been demonstrated as anodes for Na-ion batteries [2,5], but electrochemical performance of specific capacities, operation voltages and Coulombic efficiency are still far away from practice requirements. Therefore, a major challenge in developing Na-ion batteries could be lie in finding suitable anode materials [3,5,6]. Currently, researches are moved to active materials of $NiSe_2$ [7], TiO_2 [8], Fe_2O_3 [5,9], SnO_2 [10,11], Co_3O_4 [12], NiO [13] and $Na_3V_2(PO_4)_3$ [14]. Among them, SnO_2 is a particularly attractive material due to its high theoretical sodium storage capacity (1378 mAh g^{-1}) [9]. However, SnO_2 anodes suffer with low rate performance and pulverization problems during sodium storage processes. The former problem should be caused by the limitation of reaction kinetics, and the later one is aroused by volume expansion stress when sodium ions insert into the electrode [6,11,15]. In order to alleviate these problems and improve electrochemical performance, microstructures of SnO_2 should be modified. Nanocompositing is a commonly used method to improve the electrochemical performance of SnO_2 anodes. Benefit from nanocrystalline features and enhanced overall conductivity, electrochemical performance and cyclability of SnO_2 anodes can be significantly improved [10,16,17]. Following this concept, Wang et al. [18] reported a SnO_2-carbon nanotube nanocomposite which revealed a high specific capacity of 839 mAh g^{-1}

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in the first cycle, and maintained a reversible capacity of 400 mAh g^{-1} after 50 cycles at a current density of 50 mA g^{-1}. Zhang et al. [19] prepared an ultrafine SnO_2 on graphene sheets, it delivered a high reversible capacity of 369 mAh g^{-1} after 100 cycles at a current density of 100 mA g^{-1} as anode for sodium ion batteries. Then, defect modification is another method to improve electrochemical performance of transition metal oxide in sodium storage application [20–22]. Defects such as doping elements [23,24] and oxygen vacancies [22,24,25] can trigger changes in the chemical and structural characteristics of crystal materials to affect the energetics for electron and ion transport, facilitate the phase transition in electrochemical reactions, and modify surface thermodynamics, and electrochemical performances can be benefit from these changes. For example, Zhang et al. [8] prepared an oxygen vacancies evoked blue TiO_2 nanobelts and obtained a higher capacity 210.5 mAh g^{-1} and remarkable long-term cyclability (capacity retention of 94.4% at a high rate of 10 C after 5000 times). Xu et al. [22] reported an oxygen vacancies contained amorphous SnO_2, which exhibits high reversible capacity and good cycle life by retaining the capacities of 376 mAh g^{-1} after 100 cycles at 50 mA g^{-1} and 220 mAh g^{-1} after 800 cycles at 1000 mA g^{-1}.

In this work, an oxygen vacancies contained SnO_2-graphene nanocomposite (OVs-SnO_2-Gr) has been prepared by annealing SnO_2-graphene nanocomposite (SnO_2-Gr) under 3 vol% H_2/Ar atmosphere. By incorporating merits of nanocompositing and defect modification, the OVs-SnO_2-Gr was demonstrated with an impressive rate capacity and good cyclability when used as anodes for Na-ion batteries.

2. Experimental

2.1. Preparation of the OVs contained SnO_2-graphene

Graphene oxide (Aldrich, 2 mg ml^{-1}, water suspension) and $SnCl_4 \cdot 5H_2O$ (Aldrich, 98%) were used as precursors for SnO_2-graphene nanocomposite (SnO_2-Gr) preparation. Firstly, 200 mg $SnCl_4 \cdot 5H_2O$ was added into 15 ml deionized water under continuous stirring to make a $SnCl_4$ solution. Then, 10 ml graphene oxide suspension was quickly added into the $SnCl_4$ solution. After treated by ultrasonication for 0.5 h, the mixture was transferred to 25 ml Teflon lined autoclaves, heated to 160 °C for 16 h. After the autoclave was cooling down, the slurry-like SnO_2-Gr was separated by centrifugation and washed several times with de-ionized water, followed by drying the product at 60 °C under the vacuum. Then, the as-prepared SnO_2-Gr was annealed in a low oxygen atmosphere to introduce oxygen vacancies in the SnO_2 nanocrystals [22,26,27]. Due to SnO_2 is an oxygen-deficient n-type semiconductor, the concentration of oxygen vacancies in the SnO_2 is determined by the partial pressure of oxygen at a certain temperature [28]. Comparing with pure Ar atmosphere, the H_2/Ar mixture gas can provide a lower partial pressure of oxygen, and high temperature annealing provide enough energies for oxygen ions to move toward to the outside of SnO_2 nanocrystals [27]. So that, the oxygen vacancies (OVs) contained SnO_2-Gr (OVs-SnO_2-Gr) can be prepared by annealing the as-prepared SnO_2-Gr in 3 vol% H_2/Ar mixture gas at 500 °C for 3 h with a flow rate of 500 ml min^{-1}. For comparison, the as-prepared SnO_2-Gr was annealed in pure Ar atmosphere at same experimental conditions. In order to study the sodium storage performance which is contributed from reduced graphene oxide (RGO) components, RGO was individually prepared for comparison by annealing graphene oxide at same experimental conditions.

2.2. Sample characterization

Crystal structures were characterized by X-ray diffraction (XRD, Philips, X'pert PW1830) using a Cu Kα radiation at a scan rate of 1° min^{-1}. For ex-situ XRD tests, each scan was collected between 5° and 35° at a scanning speed of 0.5° min^{-1}, and samples at the different discharging states were attached to Kapton tapes and measured in thin film diffraction mode. The carbon component were examined by Raman spectra, and performed on a Renishaw Raman microscope 1000 system using HeNe laser (a wavelength of 633 nm). Chemical state analysis was performed by X-ray photoelectron spectroscopy (XPS, Phi 5702, Physical Electronics). Room temperature electron spin resonance (ESR) spectra were obtained using an ESR spectrometer (300 K, ADANI SPINSCAN X). Thermal stabilities were determined by thermal gravimetric analysis (TGA), which carried out on a Setaram S60 TGA by measuring the weight loss over a temperature range of 100–800 °C in an air atmosphere with a ramp rate of 5 °C min^{-1}. Morphologies of as-prepared samples were observed by scanning electron microscopy (SEM, XL30, FEI) and transmission electron microscopy (TEM, Tecnai G2, 200 KV, FEI). For ex-situ TEM analysis, samples were soaked in diethyl carbonate for 48 h and washed several times with methanol to remove the remaining electrolyte, then dropped on a copper grid (Agar, S166-3H) for TEM analysis.

2.3. Electrochemical measurement

The active material contained the as-prepared sample and polyvinylidene fluoride (PVDF) binders with a weight ratio of 9:1 (without conductive agent), and dispersed in NMP solvent to form a uniform slurry. Then, working electrodes were prepared by coating the above slurry on a carbon sheet (MTI Corp. USA, EQ-P11440), drying on a vacuum oven at 130 °C over 12 h and cutting to disks with a diameter of 16 mm. The loading weight of the OVs-SnO_2-Gr and the SnO_2-Gr on this electrode was measured as 1.5 mg. The electrochemical performance was assessed on a traditional coin type cells (RC2032). Cells were assembled in an Ar-filled glove box, using the as-prepared electrode and a metallic sodium tablet as working and counter electrodes. A solution of 1 M $NaPF_6$ in a mixture of ethylene carbonate/dimethyl carbonate (EC: DMC = 1:1 in volume) was used as electrolyte, and a glass microfiber filter (Whatman, Cat No. 1825–090) was used as separators. The cycling performance was evaluated at a constant current density of 40 mA g^{-1} in a potential range of 0.05–3 V (*vs.* Na^+/Na) on a battery tester (Neware CT–3008w, China). The rate performance was inspected in a potential range of 0.05–3 V (*vs.* Na^+/Na) at rates of 40, 100, 240, 600 and 1200 mA g^{-1}. Cyclic voltammograms (CV) were performed on a Princeton Applied Research VersaSTAT 3 electrochemistry workstation in a potential range of 0.05–3 V (*vs.* Na^+/Na) at a scanning rate of 0.1 mV s^{-1}. To evaluate the Na^+ diffusion coefficient, series of CV experiments have been carried out at various scanning rates of 0.1, 0.3, 0.5, 0.7 and 1.5 mV s^{-1} in a potential range of 0.05–3 V (*vs.* Na^+/Na). Electrochemical impedance spectroscopy (EIS) were carried out in a frequency range between 100 kHz and 0.01 Hz with an AC amplitude of 5 mV, and the bias voltage mode was set as open circuit potential (OCP). For ex-situ XRD tests, cells were galvanostatically discharged to target potentials at a current density of 40 mA g^{-1} and terminated at 5 target potentials in the first cycle.

3. Results

3.1. Structures and morphologies

Thermal properties of samples were characterized by the thermal gravimetric analysis (TGA) in air atmosphere. As shown in Fig. 1(a), weight loss mainly occurs between 350 and 500 °C, which could be attributed to the oxidation of graphitic materials. When