Electrochimica Acta 245 (2017) 587–596

Contents lists available at ScienceDirect

Electrochimica Acta

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

A novel microstructural reconstruction phenomenon and electrochemical performance of cactus-like SnO_2/carbon composites as anode materials for Na-ion batteries

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ARTICLE INFO

Article history:
Received 29 November 2016
Received in revised form 15 May 2017
Accepted 27 May 2017
Available online 30 May 2017

Keywords:
Na-ion battery
Tin dioxide
Amorphous carbon
SEI

ABSTRACT

A hydrothermal synthesis and a subsequent carbon coating process have been used to prepare a cactus-like SnO_2/carbon composite as anodes for Na-ion batteries. This composite was demonstrated with enhanced cyclability and outstanding electrochemical performance when used as anode for Na-ion batteries. It delivered an initial discharge capacity of 1259 $mAh\,g^{-1}$, and then retained a high reversible capacity of around 500 $mAh\,g^{-1}$ after 50 cycles at a current density of 20 $mA\,g^{-1}$. When the current density increased to 1200 $mA\,g^{-1}$, a reversible capacity of 120 $mAh\,g^{-1}$ can be obtained. Comparing the difference of microstructures before and after cycling, it is found that the cactus-like SnO_2/carbon composite presents a novel carbon coating introduced microstructural reconstruction phenomenon. Moreover, the carbon coating was proven to stabilize a spatial cactus structure and induce a high quality solid electrolyte interface (SEI) layer, which effectively enhanced the cyclablity of the cactus-like SnO_2/carbon composite. It is believed that carbon coating is an effective way to improve the electrochemical performance of the cactus-like SnO_2.

1. Introduction

Rechargeable Li-ion batteries have been considered as the most important electrochemical power sources and overwhelmingly dominated among the energy storage market in the last decade [1–4]. Li-ion batteries show high power, high energy density, high cell potential, long cycling life and light weight, can be widely used in portable devices, electrical vehicles, and even play an important role in electrical energy storage [5–7]. However, as the focus shifts from vehicles to large-scale stationary energy storage systems and large vehicles, costs are the paramount consideration [8,9]. Stationary batteries need to be cheaper and more environmentally friendly, but costs of lithium sources have increased at an astonishing rate in the last decade, while the sodium counterpart are much cheaper and more abundant [10–12]. It is considered that, replacing Li-ion batteries by Na-ion batteries in specific applications can significantly reduce costs of energy storage.

It is well known that some important performance characteristics, such as specific capacities and operation voltages are mainly determined by electrochemical properties of electrode materials [8,13]. Therefore, the major challenge in developing Na-ion batteries lies in finding suitable materials. Commonly, a crystal structure which allows lithium intercalation is also allowed sodium intercalation, but the intercalation process should suffer with more barriers [8,13]. For example, transition metal oxides, such as Fe_2O_3 [14–16], SnO_2 [17,18], Co_3O_4 [19] and NiO [20] revealed excellent electrochemical performance in Li-ion batteries, but they became low performance materials in sodium storage [8,13]. Even so, SnO_2 is a particularly attractive anode material, due to its high theoretical sodium storage capacity (1378 $mAh\,g^{-1}$) and natural abundance [5]. But SnO_2 anodes suffer with serious pulverization and microstructural reconstruction problems, because a volume expansion stress is generated when sodium intercalates into the electrode [5,21]. The smashed SnO_2 particles gradually agglomerate into large clusters in several discharging-charging cycles, which could barrier the process of Na^+ diffusion

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http://dx.doi.org/10.1016/j.electacta.2017.05.181
0013-4686/

[22]. Moreover, electrochemical deconstruction processes always associate with continual consumption of the electrolyte, which further aggravate capacity fading [25].

In order to overcome above problems, nanostructured materials has been developed as anodes for Li-ion and Na-ion batteries [23–25]. Nanostructured SnO_2 commonly has unique 1D, 2D and 3D textures, which provide large contact area with electrolyte [7]. Moreover, nanostructured SnO_2 contains both microporous and nanocrystalline SnO_2, which buffer volume changes during discharging-charging cycles and shorten the Na^+ diffusion length respectively [15,24,26]. Based on above aspects, electrochemical performance can be effectively improved. Compositing SnO_2 with conductive buffer materials is another method to improve the electrochemical performance. By increasing the overall conductivity of the electrode and buffering volume changes during discharging-charging cycles, cyclability and rate performances can be significantly enhanced. Following this concept, Wang *et al.* [21] reported a SnO_2–carbon nanotube nanocomposite which exhibited a high specific capacity of 839 mAh g^{-1} at a current density of 50 mA g^{-1} in the first cycle, and it maintained a reversible capacity of 400 mAh g^{-1} after 50 cycles. Also, a SnO_2–graphene nanocomposite was prepared as anode for sodium ion batteries, which delivered a stable reversible capacity of 330 mAh g^{-1} after 150 cycles at a current density of 50 mA g^{-1} [10]. Xie et al. [27] reported a nitrogen-doped SnO_2/graphene electrode and demonstrated with high capacities of 305 and 283 mA h g^{-1} after the 50th and 100th cycles.

In this paper, a cactus-like SnO_2/carbon composite has been prepared via a hydrothermal synthesis and subsequent carbon coating processes. When used as anodes for Na-ion batteries, it was demonstrated with enhanced cyclability and good rate performance. It is found that the amorphous carbon component introduced a novel structural reconstruction phenomenon and significantly increased the battery performances by means of stabilizing the spatial structure of anode materials and introducing a high quality solid electrolyte interface (SEI) layer.

2. Experimental

2.1. Preparation and characterization

The cactus-like SnO_2 was prepared by a self-assembling synthesis method, then a layer of amorphous carbon coating was applied on the cactus-like SnO_2 via a hydrothermal method. A typical procedure of sample preparing can be described as below: 250 mg $SnSO_4$ (Aldrich, 98%) and 56 mg 1,4-diazabicyclo[2.2.2] octane (DABCO, Aldrich, 98%) were dissolved in 40 ml distilled water with continuous stirring to form a homogeneous solution. Then, this solution was transferred to a 50 ml Teflon lined autoclave, keeping at 180 °C for 3 hours. After the autoclave cooling down to room temperature, the obtained precipitate was separated by centrifugation and washed several times with distilled water. By drying the product at room temperature under vacuum, the cactus-like SnO_2 was prepared. In order to apply amorphous carbon coatings on the as-prepared cactus-like SnO_2, the un-dried sample was dispersed into 40 ml distilled water, and then 200 mg glucose (carbon sources) was added into the suspension as carbon sources. Followed by 10 minutes ultrasonication, the suspension was sealed in a 50 ml Teflon lined autoclave and heated at 180 °C for 3 hours. Under the hydrothermal condition, the glucose slowly converts to burnt glucose (the thermal degradation products of glucose). After cooling down to room temperature, the as-prepared sample was separated by centrifugation. Followed by washing and drying processes, the cactus-like SnO_2 and the cactus-like SnO_2/C were heat treated in an Ar-shield tube furnace at 500 °C for 3 hours to increase crystallinity of SnO_2 and carbonize the burnt glucose to obtain the carbon coating. In order to study the sodium storage capacity which is contributed from the carbon coating, amorphous carbon was individually prepared as the comparison by carbonizing of glucose by using same hydrothermal procedures above and subsequent heat treatment in furnaces.

Crystal structures of samples were characterized by X-ray diffraction (XRD, X'pert PW1830, Philips) using a Cu Kα radiation at a scan rate of 1° $minute^{-1}$. 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). The thermal stability was determined by thermal gravimetric analysis (TGA), which carried out on 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 $minute^{-1}$. Morphologies of as-prepared samples were observed by scanning electron microscopy (Magellan 400L, FEI) and transmission electron microscopy (TEM, Tecnai G2, 200 KV, FEI). To prepare samples for *ex-situ* TEM and *ex-situ* XRD analysis, cycled batteries were disassembled in a glove box, followed by soaking electrode materials in diethyl carbonate for 48 hours and washing several times with methanol to remove the remaining electrolyte. The cycled electrodes were dispersed in methanol by an ultrasonic treatment, and the resulting solutions were dropped on copper grids (S166-3H, Agar, UK) for TEM analysis. Additionally, the cycled active materials were peeled off from the substrate of electrodes, pasted on a single crystal silicon wafer and dried in an oven for XRD analysis.

2.2. Electrochemical measurement

The electrochemical performance was assessed in swagelok cells (EQ-STC and EQ-3ESTC, MTI Corporation, USA). The working electrode contained the cactus-like SnO_2/carbon nanocomposite (70 wt.%), the super P carbon black (20 wt.%) and polyvinylidene fluoride (PVDF) (10 wt.%), which dispersed in 1-methyl-2-pyrrolidinone (NMP) solution to form a uniform slurry. The homogenous slurry was painted on copper foil and followed by drying on a vacuum oven at 130 °C over 12 h. Then, the foil was cut to disks with a diameter of 16 mm as the working electrode, which had a mass loading of 0.75 mg/cm^2. For comparison, the bare cactus-like SnO_2 and the amorphous carbon electrodes were prepared by the same method. A solution of 1 M $NaClO_4$ in a mixture of ethylene carbonate and propylene carbonate (EC:PC = 1:1) was used as electrolyte, and a glass microfiber filter (Whatman, Cat No. 1825–090) was used as separators. Swagelok cells were assembled in an Ar-filled glove box, using the as-prepared electrode and a metallic sodium foil (Aldrich, 99.9%) as counter and reference electrodes. Cycling performance were evaluated at a constant current density of 20 mA g^{-1} in a potential range of 0.05–3 V (*vs.* Na^+/Na) on a battery testing system (Neware CT–3008w, China). The rate performance was inspected in a potential range of 0.05–3 V (*vs.* Na^+/Na) at current densities of 20, 60, 180, 540 and 1200 mA g^{-1} after previous 50 cycles. Electrochemical properties were examined on a Princeton Applied Research VersaSTAT 3 electrochemistry workstation at room temperature. Cyclic voltammograms (CV) were performed on the as-prepared swagelok two-electrode cell in a potential range of 0.05–3 V (*vs.* Na^+/Na) at a scanning rate of 0.1 mV s^{-1}, by using the sodium counter electrode as counter and reference electrodes. To evaluate the Na^+ diffusion coefficient, a series of CV experiments were carried out at various scanning rates of 0.1, 0.3, 0.5 and 0.7 mV s^{-1} in a potential range of 0.05–3 V (*vs.* Na^+/Na). After cells were cycled 50 times and terminated at 3.0 V, 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