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Research paper

Hydrothermal synthesis of antimony oxychlorides submicron rods as anode materials for lithium-ion batteries and sodium-ion batteries

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ABSTRACT

Antimony oxychlorides submicron rods have been successfully synthesized by a simple and facile hydrothermal reaction, as characterized by a series of physical tests. Antimony oxychlorides material shows outstanding lithium-storage performance, which has a high initial discharge capacity of 1355.6 mAh g^{-1} and maintaining a discharge capacity of 402 mAh g^{-1} after 100 cycles at a current density of 50 mA g^{-1} in the voltage range of 0.01-2.0 V (*vs.* Li/Li^+). Even up to 5000 mA g^{-1}, the discharge capacity of 485 mAh g^{-1} is obtained, indicating an excellent rate capability and a prominent cycle performance. What's more, antimony oxychlorides material also exhibits brilliant cycle property in NIBs at a current density of 50 mA g^{-1} in the voltage range of 0.01-2.0 V (*vs.* Na/Na^+). Antimony oxychlorides submicron rods have remarkable rate performance and distinguished cycle capability, indicating that antimony oxychlorides material is one of promising anode materials for both lithium-ion batteries and sodium-ion batteries.

1. Introduction

Because of exhausted energy and environment pollution issues, there has been an increasing dramatically demand in emerging renewable energy. In recently years, lithium-ion batteries (LIBs) have generally been used as an effective energy storage approach in the consumer electronics and electric vehicles (EVs) [1–3]. As a similar energy storage device, sodium-ion batteries (NIBs) also have attracted increasing attention as candidate power sources to LIBs, owing to the relatively low cost and infinity of sodium resources [4–6]. More importantly, LIBs and NIBs have a similar energy storage mechanism [7–10].

Among the various anode materials for both LIBs and NIBs, the antimony-based materials, such as antimony-based oxides, antimony-based sulfides, and antimony metals, have drawn much attention as potential substitutes for carbon (graphite) anode materials due to their high theoretical specific capacities. The theoretical specific capacities of Sb_2O_3 (1028 mAh g^{-1}) [11], Sb_2S_3 (946 mAh g^{-1}) [12], Sb (660 mAh g^{-1}) [13], and SbSn (824 mAh g^{-1}) [14], are much larger than that of carbon (graphite) [15]. These types of antimony-based materials have different compositions, structures and performance, but the lithium/sodium-storage mechanisms are mainly based on alloying/de-alloying reaction. They have a very flat electrochemical reaction platform and stable working voltage in the process of lithiation/de-lithiation, the corresponding voltage is about 0.8 V (vs. Li/Li^+), which can effectively obstruct the formation of lithium dendrite and enhance the safety of the battery [16]. Therefore, antimony-based materials have an unexceptionable development prospect in the field of LIBs and NIBs, and have become a hot topic of concern and research. However, very few researches of anode materials are focusing on antimony oxychlorides, for example $Sb_4O_5Cl_2$, which was previously reported as the flame retardant [17,18] and the photocatalysts for the degradation of methyl orange (MO) [19,20]. Nevertheless, its lithium/sodium-storage performance as the anode material for LIBs/NIBs has rarely been reported.

Herein, we have successfully used a facile and direct hydrothermal reaction to obtain antimony oxychlorides submicron rods, which possess the high capacity, superior rate performance,

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and excellent cycling capability as novel anode material for LIBs and NIBs.

2. Experimental Section

2.1. Materials preparation

All the solvents and reactants were analytical reagent grade and directly used without further purification. The antimony oxychlorides submicron rods were prepared using hydrothermal reaction. 2 mmol $SbCl_3$ was dissolved in 20 mL distilled water at room temperature to form a milky suspension liquid. Next, 20 mL distilled water and 3 mmol L-cysteine were orderly added into the above solution. Then the solution was stirred sostenuto for 50 min, and it was transferred into the 80 mL Teflon-lined stainless-steel autoclave, which was kept in the oven for 12 h at 120 °C. After the autoclave cooled naturally to room temperature, the brick-red precipitate was swilled into the centrifuge tube. Wash the precipitate with distilled water and absolute ethyl alcohol for six times and dry in vacuum at 60 °C for 5 h. The final sample was gained.

2.2. Structure and morphology characterization

The structure, crystallinity and phase composition of the as-prepared sample was performed by X-ray diffraction (XRD). The XRD pattern was getting by using a Rigaku D/MAX-2500 power diffractometer. The morphology and size of the sample were collected by a scanning electron microscope (SEM JEOL JSM-6610). The element composition of the sample was confirmed by using energy-dispersive X-ray spectrometry (EDS) with SEM. The internal microstructure and interplanar distance were recorded by using the transmission electron microscopy (TEM, JEOL JEM-2100F with an acceleration voltage of 200 kV).

2.3. Electrochemical measurements

The working electrodes for LIBs and NIBs were prepared by mingling the active material (as-synthesized), acetylene black (AB), and the carboxymethyl cellulose Na salt (CMC) with a weight ratio of 6:2:2 in distilled water, which were adhered to copper foil with a slicker and then dried under vacuum at 80 °C for 12 h, followed by drying under vacuum at 110 °C for 48 h. The weight of the electrode materials is about 0.0013 g (be exclusive of copper foil), and the loading mass of the active material is around 1 mg cm^{-2}. For LIBs, the testing batteries were fabricated with the working electrode already prepared, metallic lithium as the counter and reference electrode, Celgard 2300 film as the separator obstructs the electrode transport between positive and negative electrode, and 1 M $LiPF_6$ dissolved in a mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) with a volume ratio of 1:1 as the electrolyte. However, NIBs were fabricated with metallic sodium as the counter and reference electrode, glass fiber film (Whatman GF/D) as the separator, and 1 M $NaClO_4$ dissolved in a mixture of ethylene carbonate (EC) and propylene carbonate (PC) with a volume ratio of 1:1 as the electrolyte. All the batteries were assembled in an argon-filled glove box, where the water and oxygen content was maintained under 1 ppm. The charge/discharge measurements of antimony oxychlorides electrodes were executed at room temperature at various current densities on a Neware battery tester (CT-3008, Neware Co., Ltd.). Cyclic voltammetry (CV) measurements and EIS test were executed on a Zahner Zennium electrochemical workstation.

3. Results and discussion

3.1. Characterization of antimony oxychlorides submicron rods

The crystal structure of the as-prepared sample was analyzed by XRD pattern in **Fig. S1**. The diffraction pattern revealed a series of narrow diffraction peaks in the range of 10−80°. It is observed that most of the diffraction peaks are corresponding to the characteristic peaks of the antimony oxychlorides, including monoclinic $Sb_4O_5Cl_2$ (PDF 70-1102, space group: $P2_1/c$) and $Sb_8O_{11}Cl_2$ (PDF 77-1583, space group: $C2/m$). The residual peaks were indexed to the orthorhombic Sb_2S_3 (PDF 42-1393, space group: $Pbnm$). No other diffraction peaks were existed, indicating that the product is antimony oxychlorides. To further gain quantitative crystallographic information, Rietveld refinements of the XRD data for sample was conducted based on the mixture of

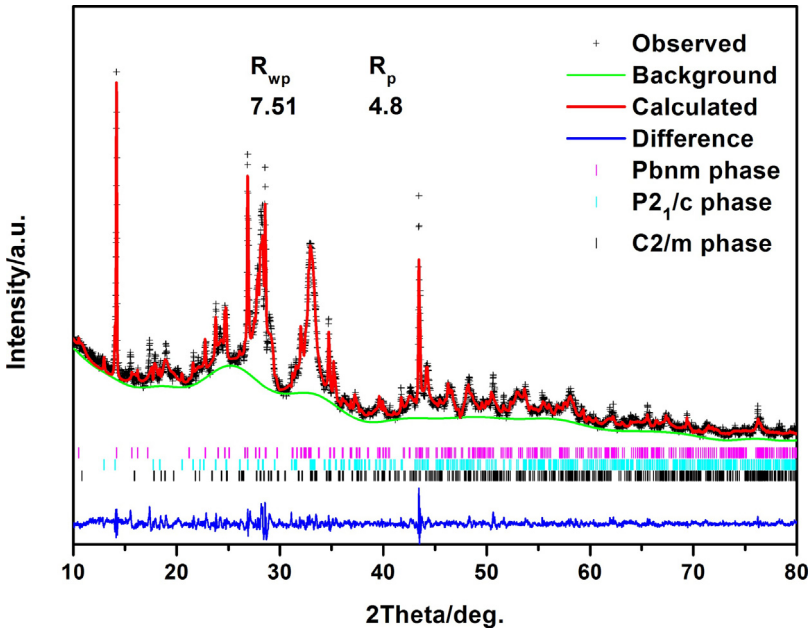

Fig. 1. Rietveld refined XRD profiles of antimony oxychlorides sample.