



Preparation and electrochemical properties of core-shell carbon coated Mn–Sn complex metal oxide as anode materials for lithium-ion batteries



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ABSTRACT

In this study, we synthesized a carbon coated Mn–Sn metal oxide composite with core-shell structure (MTO@C) via a simple glucose hydrothermal reaction and subsequent carbonization approach. When the MTO@C composite was applied as an anode material for lithium-ion batteries, it maintained a reversible capacity of 409 mA h g⁻¹ after 200 cycles at a current density of 100 mA g⁻¹. The uniformed and continuous carbon layer formed on the MTO nanoparticles, effectively buffered the volumetric change of the active material and increased electronic conductivity, which thus prolonged the cycling performance of the MTO@C electrode.

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1. Introduction

Lithium-ion batteries are currently the dominant power source and have been considered as a candidate for power sources of electric vehicles (EVs) and hybrid electric vehicles (HEVs), due to their advantages of high energy density, high efficiency, and long life-span [1,2]. Graphite is the current choice of anode materials for commercial Li-ion batteries, thanks to its long cycle life, abundant material supply and relatively low cost [3]. However, the graphite anode materials have disadvantages of low theoretical capacity (372 mA h g⁻¹) and safety issues related to lithium-ion deposition which causes short-circuit inside battery [4,5]. To meet the increasing demand for high energy and performance along with safety, a raising interest is focused on developing new alternative anode materials that could replace the current graphite material [6–8]. Among the possible candidate anode materials of Li-ion battery, Sn-based metal oxides, and composites have been intensively studied as negative electrode materials due to their high theoretical capacity at low potentials, as well as their availability and safety [9,10]. Nevertheless, tin-based anode materials also suffer from

large volume change during Li⁺ insertion and extraction, which inevitably lead to cracking of the electrode and consequently a large irreversible capacity loss and poor cycling characteristics [11,12]. Several strategies have been proposed to overcome this problem.

Recently, ternary tin-based complex metal oxides, such as MSnO₃ (M=Co [13–15], Mn [16], Zn [17], Ca [18,19], Li [20]), M₂SnO₄ (M=Co [21], Zn [22,23], Mn [24], Mg [9]), have received special attention as prospective anode materials for Li-ion batteries because of their ability to relieve the internal stress of the electrode from the isotropic volume change upon cycling, thus minimizing the capacity fading [15]. For example, Zhou et al. prepared a cobalt-tin nanocomposite oxide (CoSnO₃) by means of the pyrolysis of CoSn(OH)₆ precursor at 400 °C in argon atmosphere. Their results revealed that the electrochemical performances of CoSnO₃ was relatively better than that of the mixture of CoO and SnO₂ [14]. Furthermore, Sun et al. synthesized amorphous nano-sized MnSnO₃ by the pyrolysis of precursor MnSn(OH)₆ and studied its electrochemical properties. It delivered an initial charge capacity of 982 mA h g⁻¹ which faded to 422 mA h g⁻¹ after 20 cycles [16]. Therefore, ternary tin-based metal composites can alleviate capacity fading to some extent, but there are still spaces for further improvement in their reversible capacities and cycling stabilities. On the other hand, carbon coating has commonly been addressed to be an effective strategy for improving the electrochemical properties of ternary tin-based oxides anode materials, such as, Co₂SnO₄@C [21], carbon-coated CaSnO₃ [19], and Zn₂SnO₄/C [25]

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etc. The core-shell structure can efficiently accommodate the volume change during lithium insertion and extraction, leading to substantial enhancement of the cycling performance. Thus, carbon coated Mn–Sn complex metal oxide with core-shell structure (named as MTO@C, hereafter) is expected to show the improved electrochemical performance. Meanwhile, to the best of our knowledge, the synthesis of MTO@C composite for anode material has been rarely reported.

Herein, we report the synthesis of MTO@C material through a simple glucose hydrothermal and subsequent carbonization approach. When evaluated as an anode material for LIBs, MTO@C composite exhibits higher reversible capacity and better cycling performance compared to pure MnSnO₃ or Mn–Sn complex metal oxide (MTO).

2. Experimental

2.1. Synthesis of amorphous nanosized MnSnO₃

All reagents and solvents were purchased or obtained from Sinopharm Chemical Reagent Co. Ltd unless described otherwise. All the chemicals were analytical grade without further purification. Amorphous nanosized MnSnO₃ was synthesized through a decomposition reaction according to the equation:



The MnSn(OH)₆ precursor was obtained by mixing stoichiometric Na₂SnO₃ and MnSO₄ solution. In a typical synthesis, 0.1 M Na₂SnO₃ was dropped into an equal volume aqueous solution of 0.1 M MnSO₄ drop by drop at room temperature under vigorous mechanical stirring. After the reaction was finished, the precipitation was centrifuged and washed thoroughly with distilled water to remove Na⁺ and SO₄²⁻ ions and finally dried in an oven at 80 °C for 12 h. The resulting product was then heated at 400 °C for 4 h in nitrogen atmosphere to form amorphous nanosized MnSnO₃.

2.2. Synthesis of core-shell MTO@C composite

MTO@C composite was prepared by a glucose hydrothermal process and subsequent carbonization approach. In a typical synthesis, 0.4 g nanosized MnSnO₃ were dispersed in 40 mL and 0.25 M aqueous glucose solution. After agitation for 30 min and sonication for 20 min, the solution was transferred into an 80 mL Teflon-lined stainless steel autoclave, sealed, and maintained at 180 °C for 12 h. After the reaction was finished, the resulting solid products were filtered, rinsed with distilled water and ethanol several times to remove possibly remaining in the final products, and then dried at 80 °C for 12 h in an oven under air. Finally, the as-synthesized sample was further annealed at 500 °C for 3 h under N₂ flow at a ramp rate of 5 °C min⁻¹ in a tube furnace to obtain the final product MTO@C. For comparison, the sample obtained by the calcination of MnSnO₃ under the same condition was named as MTO.

2.3. Characterization and electrochemical measurement

The phase composition and structure of the as-prepared materials was examined using X-ray diffractometer equipped with Cu K α radiation (XRD, Rint1000, Rigaku, Japan). The morphologies and sizes of the samples were evaluated by transmission electron microscopy (TEM, G220, Tecnai, Nederland). Raman spectroscopy was performed with a confocal Raman microscope (Lab-Ram, Jobin Yvon, France) using an excited laser of 514.5 nm. Carbon content in the sample was determined from the weight change detected in a temperature region from 50 to 800 °C operated with a ramp rate of 10 °C min⁻¹ by using a thermal gravity analyzer (TGA4000,

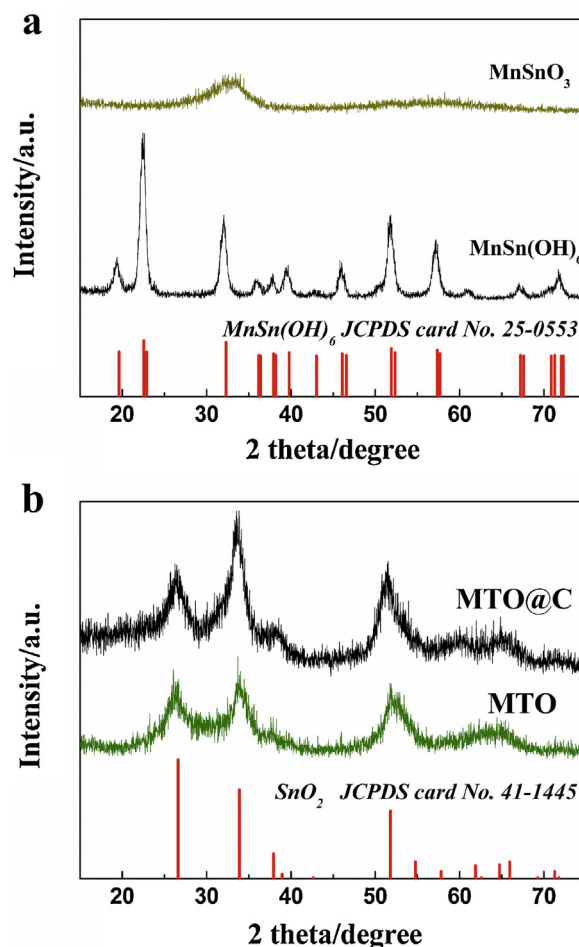


Fig. 1. XRD patterns of (a) the MnSn(OH)₆ precursor and MnSnO₃, (b) the MTO, and MTO@C composite.

PerkinElmer, USA) under a continuous air gas flow with a flow rate of 100 mL min⁻¹.

Electrochemical performances of the as-synthesized materials were investigated using CR2032 coin-type cell. The active materials were mixed with acetylene black (10 wt.%) and polyvinylidene fluoride (PVDF, 10 wt.%) as conductive agent and binder, respectively, and then dissolved in N-methyl-2-pyrrolidone (NMP) to form slurries. The slurries of the mixture were spread out on the copper foil to make electrode laminates. The electrode laminates were dried at 110 °C under vacuum for 12 h. The test cells were assembled in a dried argon filled glove box. A lithium metal was served as counter and a Celgard 2400 porous polypropylene film as separator. The electrolyte was 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 by volume). Cycling tests were carried out at a current density of 100 mA g⁻¹ between 0.01 and 3.0 V (vs. Li/Li⁺) using a battery evaluation system (LAND CT2001, Wuhan, China). Ac impedance measurements and cyclic voltammograms test were conducted using a three-electrode cell consisting of the laminate as a working electrode, and two lithium foils as counter and reference electrodes in a EC/DEC solution containing 1 M LiPF₆. The electrochemical tests were carried out at room temperature.

3. Results and discussion

The composition of the as-synthesized products was characterized by X-ray diffraction (XRD). Fig. 1a shows the XRD patterns of the as-prepared samples before and after calcination in N₂ at 400 °C for 4 h, respectively. It is clear that for the MnSn(OH)₆

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