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Three-dimensional porous Sn–Cu alloy anode for lithium-ion batteries

Leigang Xue, Zhenghao Fu, Yu Yao, Tao Huang, Aishui Yu*

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Institute of New Energy, Fudan University, Shanghai 200438, China

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ABSTRACT

A binder-free three-dimensional (3D) porous Cu_6Sn_5 anode was prepared for lithium-ion batteries. In this novel approach, tin was deposited by electroless-plating on copper foam which was served as anode current collector as well as the source of copper for Cu_6Sn_5 alloy formation. With optimized post-treatment condition, Cu_6Sn_5 alloy with thickness of 1.2 μm was formed on the surface of copper foam network. 3D porous Sn–Cu_6Sn_5 and Cu_3Sn–$Cu_{10}Sn_3$–Cu_6Sn_5 composite anodes were also prepared for comparison. Electrochemical tests showed that 3D porous Cu_6Sn_5 anode exhibits the best electrochemical performance in terms of specific capacitance and cycleability, which delivers a rechargeable capacity of 404 mAh g^{-1} over 100 cycles.

1. Introduction

Lithium-ion batteries have a variety of applications ranging from portable electronic devices to electric vehicles [1–3]. The most common used anode materials in lithium-ion batteries are still carbonaceous materials, however, alternative anode materials with higher specific capacities are in great demand to increase the energy density of batteries. Meanwhile, safety concerns of carbonaceous materials due to their low lithiated potentials close to lithium also require searching for new anode materials [4,5]. Among them, tin provides much higher theoretical capacity (991 mAh g^{-1}, 7200 mAh cc^{-1}) than graphite (372 mAh g^{-1}, 837 mAh cc^{-1}), and behaves a slightly higher discharge voltage (0–400 mV) than metallic lithium which could reduce safety concerns during cycling, however, pure tin presents a limited cycle life due to pulverization and delamination from copper foil current collector caused by volume expansion and contraction associated with the lithiation and delithiation [6]. Recently, there has been considerable interest in exploiting intermetallic compounds Sn_xM_y (M = Fe, Co, Cu, Ni, etc.) as anode materials for rechargeable lithium-ion batteries, where M is an inactive element [7–11]. It is believed that the inactive element can provide an electronically conducting and ductile matrix to contain the lithiated tin particles to accommodate at least some of the damaging expansion/contraction of the Li_xSn particles during discharge and charge. One of the materials that has been found to be a possible alternative for graphite in lithium-ion batteries is Cu_6Sn_5 [12]. Liu et al. electrodeposited 3D porous Cu_6Sn_5 material on copper foil using a hydrogen bubble template method [13], which is an electrochemical deposition process accompanying hydrogen evolution at high current densities. Sun et al. prepared 3D porous Cu_6Sn_5 anode by electrodepositing Cu_6Sn_5 alloy onto a porous Cu substrate, which was firstly prepared by electrodepositing porous Cu on copper foil also using the hydrogen bubble template method [14,15]. Tamura et al. reported that it was feasible to prepare Cu_6Sn_5 film anode by annealing electrodeposited tin on copper foil and cycling performance was greatly improved due to the enhanced bonding force between Cu_6Sn_5 and copper foil [16].

Compared with electrodepositing method, electroless tin plating which is widely used in printed circuit boards (PCBs) is a much simpler immersion technique to deposit tin onto copper, especially for copper substrates with pores and complex shapes due to its excellent pore-filling capability. In a recent paper, Wang et al. prepared a 3D porous tin anode by electroless-plating tin on copper foam without heat treatment [17], however, heat treatment is a key factor to improve cycling stability, not only because Cu_6Sn_5 phase can be formed during the heat treatment but also the bonding force between active material and current collector can be greatly enhanced by this post-treatment. In this work, a 3D porous Cu_6Sn_5 anode was prepared by electroless-plating of tin onto commercial copper foam associated with heat treatment. In this approach, copper foam was not only used as current collector, but also participated in the formation of the Cu_6Sn_5 phase as the source of copper. The Cu_6Sn_5 material obtained by alloying process between the deposited tin and the copper foam could have an excellent bonding force with the current collector, and the 3D porous structure could further enhance the bonding force due to its larger surface area than copper foil, thus improving the cycling stability. In addition,

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* Corresponding author. Tel.: +86 21 51630320; fax: +86 21 51630320.
E-mail address: asyu@fudan.edu.cn (A. Yu).

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at the same mass loading, using the 3D porous current collector, the thickness of active material will be much thinner, which has better elasticity to effectively accommodate the strain of volume change during Li^+ insertion/extraction. Moreover, the 3D porous structure results in maximization of the contact area between the anode and the electrolyte, which is conducive to the improvement of specific capacity.

2. Experimental

2.1. Preparation of 3D porous Sn–Cu alloy anode

Copper foam was purchased from Changsha Lyrun New Material Co., Ltd. Electroless tin plating solution and polishing solution were purchased from Weihai Yunqing Chemical Industry Research Institute. Acetone was purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further treatment. Deionized water was used in all experiments.

Copper foam was successively cleaned with acetone and polishing solution to remove oil and oxides on the surface in an ultrasonic cleaner. Then, the copper foam was immersed in the electroless tin plating solution for 3 min at room temperature. In order to plate tin film onto the 3D porous substrate more uniformly and completely, the electroless tin plating process was conducted in an ultrasonic device. Finally, the as-deposited electrodes were calcined in vacuum. The as-prepared Sn–Cu alloy electrodes were directly used in lithium-ion batteries after being compressed under pressure of 3 Mpa.

2.2. Characterization and electrochemical measurements

The top and cross-section micrographs of the deposited tin films without and with heat treatment were obtained using a scanning electron microscope (SEM, JSM-6390 JEOL). The phase compositions of the tin-based compounds were characterized by X-ray diffraction with Cu Kα radiation (XRD, Bruker D8 X-ray diffractometer). The weight of tin was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid, Thermo Elemental). The typical mass loading of tin was about $0.8\,\mathrm{mg\,cm^{-2}}$, according to which specific capacities of tin-based anodes were computed.

Electrochemical tests were performed using a CR2016-type coincell. The as-prepared tin-based electrodes were cut into sheets of $1\,\mathrm{cm^2}$ before being used as working electrodes. Cell assembly was operated in a glove box (Superstar 1220/750, Mikrouna) filled with pure argon. The electrolyte solution was 1 M $LiPF_6$/ethylene carbonate (EC)/diethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1 by volume). The cell was assembled with as-prepared tin-based electrode, lithium metal anode, and a Celgard 2300 separator. Charge/discharge experiments were performed on a battery test system (LAND CT2001A, Wuhan) with a constant current density of $100\,\mathrm{mA\,g^{-1}}$ between 0 V and 2.0 V.

3. Results and discussion

Fig. 1 is the SEM image of copper foam current collector, it is a cellular structure composed of interconnected macropores with diameter of 100–200 μm. After electroless-plating process, a thin layer of tin is coated on the surface of copper foam (inset in Fig. 1). Fig. 2 shows the typical photographs of copper foam and tin-coated copper foam without/with heat treatments. The fresh deposited tin film is gray and darkens a little after calcination at 150 °C for 2 h, further increasing calcination temperature to 200 °C for 24 h, the color of the layer changes from gray to grayish-black, which should be attributed to the increase of Cu content in the tin layer caused by atom diffusion during heat treatment.

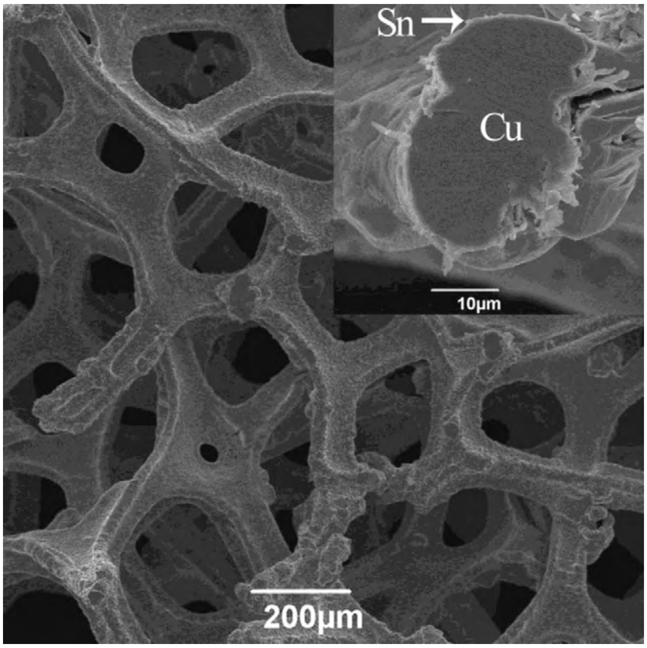

Fig. 1. SEM image of copper foam, the inset shows a cross-section micrograph after electroless-plating of tin.

Shown in Fig. 3a is the surface morphology of the tin coating without heat treatment, it is a uniform film with line-like texture features. There is no significant change on the surface after heat treatment (Fig. 3b and c), however, the interface between tin coating and current collector has undergone great changes. In the as-prepared sample without heat treatment, two layers can be clearly seen (Fig. 3d), which could be attributed to deposited tin layer and copper foam underneath. The thickness of the coated layer is about 0.7 μm. After the sample was calcined at 150 °C for 2 h, there are still two layers (Fig. 3e). The colors of the layers change stepwise from light to dark from the surface to bulk copper foam and the boundary between these two layers becomes unclear due to atom diffusion during heat treatment. The thickness of the outer layer increases to about 1.2 μm which clearly indicates the Sn–Cu

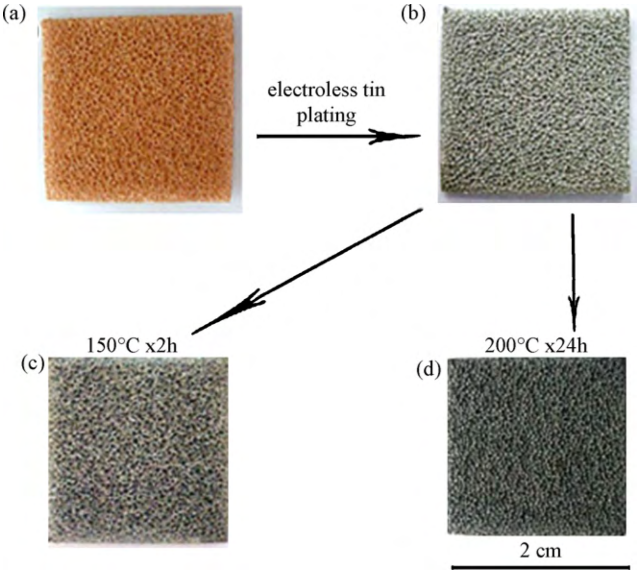

Fig. 2. Representative photographs of (a) copper foam, (b) tin-coated copper foam and after calcination under different conditions: (c) 150 °C for 2 h and (d) 200 °C for 24 h.