



Three-dimensional ordered macroporous Cu/Sn anode for high rate and long cycle life lithium-ion batteries

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ABSTRACT

To overcome the shortcomings of poor conductivity and large volume change, we proposed a novel three-dimensional ordered macroporous Cu/Sn (3DOM Cu/Sn) composite material as the anode of lithium-ion batteries (LIB). Electron microscopies and X-ray diffraction revealed that this new 3DOM Cu/Sn composite has the surface of the 3DOM Cu framework covered with a uniform layer of Sn nanoparticles. As a binder-free anode of LIB without conductive additives, this 3DOM Cu/Sn composite demonstrated an extremely high rate capability of about 707 mAh/g at 5C, which is 4 times higher than that of bare Cu/Sn anode, and excellent durability of 851 mAh/g up to 250 cycles. The post-test analysis showed that extraordinarily electrochemical performances of this composite anode are ascribed to the unique 3DOM microstructure.

1. Introduction

It has been well known that the metallic Sn is a promising anode with the advantages of high capacity of 994 mAh/g, low potential of lithium-ion intercalation and low cost [1–4]. However, the practical application of metallic Sn as anode of lithium-ion batteries (LIBs) is limited by its fast capacity decay. The root cause of capacity fading is the low electronic conductivity of Sn [5,6], combined with dramatic volume expansion (nearly 300%) along the lithium insertion/extraction, leading to the pulverization of Sn particles, depletion of electrolyte and degrading electrical connectivity between Sn and current collector [7–10].

To overcome these barriers, a lot of approaches have been developed to improve the performance of LIBs with Sn anodes. For instance, LIBs with SnO₂ based materials, rather than pure Sn, showed improved cycle life. The electrochemically irreversible Li₂O generated in the initial cycle could effectively buffer the volume change of Sn, but always results in anodes with high initial irreversible capacity loss (ICL) [11–13]. Similarly, LIBs adopting metallic alloys of Sn_xM_y (M = inactive metal) such as Cu₆Sn₅ [14], Cu₃Sn [15] as anodes also demonstrated promising cycling stability, but at the price of the reduced capacity [16–19]. Reducing the size of Sn particles, synthesizing Sn with special structures and fabricating hybrids of Sn with other porous

materials could also improve the durability of Sn anodes [20–23]. However, the improved durability of Sn anodes through these approaches is a trade-off with the low capacity of final electrodes.

Most recently, 3D ordered microporous (3DOM) Cu current collectors coated with a secondary component such as Li₂O and Sn-Co alloys have been utilized as anodes of LIBs [24–26]. LIBs with these composites have demonstrated promising performances with high capacity, high rate capability and long cycle life [27–29]. It has been recognized that the high performance of LIBs is associated with the 3DOM Cu current collector, which provides the good electrical connectivity, accommodates stress, and supports the fast ionic and electronic conductivity [30–32]. Inspired by this, we proposed to develop a novel anode comprising of metallic Sn supported by the 3DOM Cu current collector for LIBs with high performance.

Here, the preparation of a novel 3DOM Cu/Sn composite will be shown first. Used as conductive additive- and binder-free anode, the electrochemical performances of obtained 3DOM Cu/Sn anode are also demonstrated and discussed.

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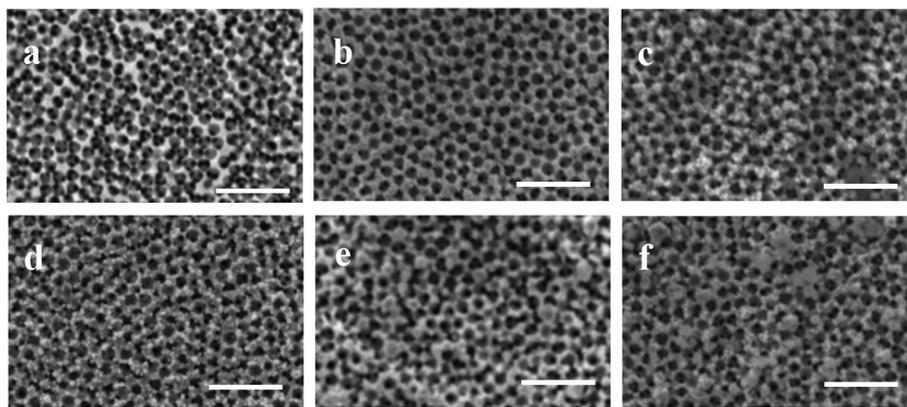


Fig. 1. SEM images of 3DOM Cu/Sn composite with the depositing time of 0 (a), 10 (b), 30 (c), 60 (d), 120 (e), and 200 (f) seconds. Scale bars for all images are 2 μm .

2. Experimental section

2.1. Materials

Tin (II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, Macklin Inc.), Methyl methacrylate (MMA, Aladdin Chemicals), 2, 2-azobisisobutyronitrile (AIBN, Aladdin Chemicals), Choline chloride ($\text{C}_5\text{H}_{14}\text{ClNO}$, Aladdin Chemicals), Polyethylene glycol 200 (PEG-200, Sinopharm Group Chemical Reagent Co., Ltd), Copper pyrophosphate ($\text{Cu}_2\text{P}_2\text{O}_7$, Sinopharm Group Chemical Reagent Co., Ltd), Potassium pyrophosphate ($\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$, Sinopharm Group Chemical Reagent Co., Ltd), Ammonium citrate dibasic ($(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$, Sinopharm Group Chemical Reagent Co., Ltd) and ethylene glycol ($(\text{CH}_2\text{OH})_2$, Sinopharm Group Chemical Reagent Co., Ltd) were analytically pure and used without further purification.

2.2. Synthesis of 3DOM Cu/Sn composites

The process of preparing 3DOM Cu/Sn composite is shown in Figure S1. At first, 3DOM Cu current collector was prepared through a process involving four steps: (1) synthesis of Poly (methyl methacrylate) (PMMA) microsphere; (2) PMMA template formation on Cu substrate; (3) Cu deposition on PMMA template substrate; (4) removal of PMMA template. Details about fabricating 3DOM Cu current collector could be found in our previous report [33].

3DOM Cu/Sn composite was synthesized through an electrochemical deposition process using a double-electrode system. 3DOM Cu current collector and a pure tin plate was used as working and counter electrodes respectively. A solution containing 0.1 M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in the mixture of 1 $\text{C}_5\text{H}_{14}\text{ClNO}$: 2 $(\text{CH}_2\text{OH})_2$ (mol: mol), a homogeneous colorless solution formed by stirring the two components at 80 $^\circ\text{C}$ for about 30 min, was used the electrolyte. The deposition of metallic Sn was conducted at 0.5 V for various time at 25 $^\circ\text{C}$. For comparison, the same depositing approach was used to prepare the Cu/Sn composite but with a bare Cu as the substrate. The active materials mass was measured carefully by calculating the weight difference of the sample before and after deposition.

2.3. Materials characterization

To obtain the phase information of samples, X-ray diffraction (XRD) patterns were collected on a Combined Multifunctional X-ray Diffractometer (UltimaIV, Japanese, $\lambda = 1.54 \text{ \AA}$). The morphology of samples was characterized by using a field emission scanning electron microscopy (FEI NanoSEM 450, America) with energy-dispersive X-ray spectrometer (EDX). The microstructure of the obtained materials was characterized by using a transmission electron microscope (TEM, Tecnai G2 F30 S-Twin, Holland) with the accelerating voltage of

300 kV.

The obtained 3DOM Cu/Sn and bare Cu/Sn were used as binder- and conductive-free electrodes and were directly assembled into coin cells with lithium metal as counter electrode. The electrolyte used here was composed of 1 M LiPF_6 in the mixture of 1 ethylene carbonate (EC): 1 diethyl carbonate (DEC) (v: v). The cell assembly was conducted in an argon-filled glove box filled with both moisture and oxygen level controlled below 1 ppm. Galvanostatic cycling tests of the half cells were conducted on battery test system within the voltage range of 5 mV to 3 V at room temperature. A constant current density of 0.5 C was initially applied to all cells (formation cycle) to obtain the practical specific capacity of electrodes. The rate capability of cells was tested following the protocol: charge cells to 3 V with a constant current density of 0.5 C, and discharged to 5 mV with various current densities of 0.5, 1, 2, 3 and 5 C (1 C = 500 mA/g). At every current density, cells underwent ten cycles. After rate capability test, the cycling test was conducted with constant current density of 0.5/0.5 C for charge/discharge process.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were collected on an electrochemical workstation CHI760D (shanghai chenhua). CV was tested between 5 mV and 3 V at a scan rate of 0.1 mV/s. For EIS, the amplitude of 5 mV was applied to all cells with the frequency ranged from 0.01 Hz to 100 kHz. Before the EIS measurement, the cells underwent 100 cycles were discharged to 2.0 V and kept until the open circuit voltages were stabilized.

3. Result and discussion

Initially, the effect of electrochemical deposition time varied from 0 s to 200 s on the porous structure of composite was investigated, as shown in Fig. 1. Regardless the deposition time, all samples demonstrate porous architecture after the deposition of Sn. When the deposition time was less than 60 s, the well-ordered 3D architecture, which is the same as that of original 3D Cu framework, is found to be well preserved (Fig. 1a–d), indicating that the uniform Sn layer coated on the wall of 3D porous Cu framework other than aggregated inside pores. However, when the deposition time was increased to 120 s, partial pores are found to be blocked, which are discretely distributed at the surface of the obtained product (Fig. 1e). Further increasing time to 200 s leads to regions with blocked pores connected laterally (Fig. 1f). As the proceeding of deposition, the average wall thickness increased gradually, it was 37.2, 79.5, 93.1, 120.3, 156.9 and 210.6 nm at the deposition time of 0, 10, 30, 60, 120 and 200 s, respectively. Given the requirements for both high capacity and durability of anodes in LIBs, the product obtained with the depositing time of 60 s is considered as the optimal sample with well-preserved 3D porous architecture and high content Sn and was used for further characterizations below.

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