



Sn-C binary nanocomposites for lithium ion batteries: Core-shell vs. multilayer structure



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ABSTRACT

Rational design of carbon based binary composites is of critical importance to improve the performance of alloy type anode materials in lithium ion batteries. In this work, two thin film Sn-C electrodes with similar Sn/C ratio but distinct nanostructures, namely carbon coated core-shell structure and alternating Sn/C multilayers, are prepared by direct plasma deposition in a tandem plasma reactor and are compared for their performance as anode materials for lithium ion batteries. Lithiation/delithiation behaviors of the two samples are comprehensively studied by cyclic voltammetry, galvanostatic intermittent titration technique and electrochemical impedance spectroscopy. The results suggest that the core-shell Sn@C electrode is more favorable for Li⁺ transport and the interface charge transfer, which leads to higher cyclic stability and rate performance than the alternating Sn/C multilayer electrode, featuring for a high capacity of 849 mAh g⁻¹ (0.083 mAh cm⁻²) after more than 600 cycles at a current density of 100 mA g⁻¹ (0.01 mA cm⁻²) and a high capacity of 500 mAh g⁻¹ (0.049 mAh cm⁻²) at high current density of 2000 mA g⁻¹ (0.2 mA cm⁻²).

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1. Introduction

Rechargeable lithium-ion batteries (LIBs) with higher energy density are highly desired to meet the increasing demand for more efficient energy storage systems. The prevailing commercial graphite anode material is insufficient to fulfil the requirement due to its low specific capacity [1–3]. Therefore, materials with higher lithium storage performance are receiving wide research interest from both academia and industry [4–10]. Tin is one the most extensively studied anode materials due to its high volumetric (7313 Ah L⁻¹) and gravimetric capacity (993 mAh g⁻¹ for Li_{4.4}Sn) [11–13]. However, the rapid capacity fading that results from the huge volume change during alloying-dealloying reactions between Sn and Li has greatly hindered the practical application of Sn based anode materials. Tremendous efforts have been devoted to solve the above issue [14–17]. Carbon introduction is a widely used strategy to improve the electrical conductivity and structural

stability of the electrodes in LIBs. Various carbon materials, including amorphous carbon [18–21], graphene [22–24], and carbon nanotubes [25–27] with well tailored structures have been successfully applied to Sn based anode materials.

Understanding the correlation between electrode structure and the corresponding electrochemical performance is of critical importance for rational design of electrode. Unfortunately, Sn-C composites prepared by different methods are difficult to compare directly, due to the diversity in active material/carbon ratio and carbon structure. To carry out such comparison experimentally, it is essential to prepare two electrodes with different electrode structures while keeping the same Sn/C ratio. Achieving such accurate control in fabrication is very challenging for conventional processing approaches. Recently we have developed a general tandem plasma reaction (TPR) approach for accurately controlled preparation of carbon based thin film binary composites. The TPR integrates two plasma sources into one reactor: a magnetron sputtering (MS) source for metal cluster generation and an inductively coupled plasma (ICP) source for carbon generation. This configuration allows independently generating two components in the two separate plasma zones, which offers the accuracy

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for component regulation and versatility for electrode structure control.

In this work, two representative electrodes with distinct structures, i.e., core-shell Sn@C structure and multilayer Sn/C structure with alternating Sn and carbon layers, are compared for their electrochemical performance. The two electrodes are fabricated by operating the TPR in two different modes. Operating the two plasma sources simultaneously and alternatively leads to core-shell Sn@C electrode and multilayer Sn/C electrode, respectively. Sn/C ratio is kept the same for the two electrodes. Electrochemical performance of the two electrodes is compared and the difference is understood based on comprehensive electrochemical studies. To the best of our knowledge, such accurate comparison has not been carried out experimentally. Therefore, the results will provide insights into rational design of the Sn-C composites with optimized performance as anode materials for LIBs.

2. Experimental

2.1. Setup and experimental details

The Sn-C electrodes are prepared in a home-designed tandem plasma reactor (TPR), which is composed of a radio frequency magnetron sputtering (MS) source to produce Sn nanoclusters and an inductively coupled plasma (ICP) coil between the target and the substrate to generate carbon by decomposition of CH₄.

To prepare carbon coated core-shell Sn@C electrode, the MS source and ICP source need to work simultaneously. Pure Ar is injected with a constant flow rate of 10 standard cubic centimeter per second (sccm) to the MS zone for sputtering. CH₄ is injected with a constant flow of 1.0 sccm into the ICP zone. The power for MS and ICP is 80 and 100 W, respectively.

To prepare multilayer Sn/C electrode, the MS source and ICP source need to be operated alternatively. The Sn layer is deposited by sputtering in pure Ar with MS power of 100 W and ICP off. The carbon layer is deposited in the mixture of Ar-CH₄ (Ar:CH₄ = 10:1) through decomposition of CH₄ using ICP power of 120 W with the MS off. The thickness of each Sn and C layer is 35 nm, controlled by deposition time.

Before deposition, the chamber is first evacuated to 5×10^{-4} Pa. The pressure during deposition is 2 Pa. Sn-C composites directly deposit onto copper foils, which are directly used as electrode in the electrochemical measurements. The substrate is not intentionally heated but the temperature rises to 50 °C caused by the effect of plasma under the deposition conditions. In this work, Sn weight percentage is kept at around 76% in both electrodes. Composition of the electrode can be accurately controlled by adjusting the power of the two plasma sources. Total thickness of the Sn-C composite layer is ~220 nm for both samples. Mass loading of the two thin film electrodes is identical according to the weighing results of the 1/1000000 balance (0.110 mg). Diameter of the electrode is 1.2 cm, corresponding to ~1.13 cm² in area.

2.2. Structure characterization

Structures of the electrodes are characterized by scanning electron microscopy (SEM, Hitachi S4800, 10 kV) with an energy dispersive X-ray spectroscopy (EDS) analyzer, atomic force microscopy (AFM, Seiko SPA-400), transmission electron microscopy (TEM, JEOL JEM-2100F, 200 kV) and X-ray photoelectron spectroscopy (XPS, Kratos Analytical, Ultra Axis). For TEM characterization of the core-shell Sn@C electrode, the sample is directly deposited on a TEM grid, while the thickness is limited to 50 nm to achieve better resolution.

2.3. Electrochemical measurement

Coin-type test cells are assembled in an argon filled glove box using polypropylene films (Celgard 2400) as the separator. The sample deposits on copper foil is directly used as working electrode. 1 M LiPF₆ in polycarbonate (PC)/ethylene carbonate (EC)/diethyl carbonate (DEC) (Volume ratio = 1:1:1) is used as electrolyte, and Li foil as counter electrode. The charge (Li⁺ removal) and discharge (Li⁺ insertion) experiments are performed galvanostatically on the LAND CT20001A system, voltage limits are set at 5 mV versus Li/Li⁺ (reduction) and 3 V versus Li/Li⁺ (oxidation) for discharge and charge processes, respectively.

3. Results and discussion

3.1. Structure and morphology analysis

The preparation of Sn-C electrodes is illustrated in Fig. 1. After alternating operation of the magnetron sputtering (MS) source and inductively coupled plasma (ICP) source, the multilayer Sn/C composite is obtained, which is further confirmed by cross section SEM image (Fig. 2a). The core-shell Sn@C electrode is successfully prepared simply through simultaneously operating both of the two plasma sources (MS and ICP), as identified by cross section SEM image and TEM image (Fig. 2b and l). Both electrodes have very close thickness of 220 nm according to Fig. 2a and b. The Sn/C multilayer sample exhibits clear alternating layers, with three ~35 nm layers for each component. On the other hand, Sn and C in the core-shell Sn@C electrode are homogeneously distributed on current collector. Such structures are well expected from the corresponding operation modes of the TPR.

Fig. 2c shows XRD patterns of the two Sn/C electrodes. Only diffraction peaks corresponding to tetragonal metallic Sn (JCPDS NO. 04-0673) are observed, indicating that both electrodes are composed of crystalline Sn and amorphous carbon. It is in agreement with our previous results that carbon formed from low temperature plasma dissociation of CH₄ is amorphous [28,29]. Clear peak broadening is observed, which is attributed to the small crystallite size. Moreover, the amorphous nature of carbon is further confirmed by Raman spectrum in Fig. 2d. Typical D band at 1360 cm⁻¹ and typical G band at 1590 cm⁻¹ are clearly identified in both electrodes. Presence of the D band and their overlapping in both electrodes demonstrates the amorphous structure of carbon [30]. Atomic force microscopy (AFM) is employed to further understand the surface state of both electrodes (Fig. 2e–h). Root mean square (RMS) roughness of the Sn@C electrode is 17.0 nm, which is smaller than that of the multilayer Sn/C electrode (RMS roughness = 28.2 nm). This is consistent with the cross-section SEM image (Fig. 2a and b). In addition, small surface roughness is considered to be helpful for avoiding segregation of lithium during the reaction process. Elemental analysis suggests that the Sn weight percentage in both samples is around 76% (Fig. S1), two dimensional elemental mapping of the core-shell Sn@C electrode suggests that the two elements of Sn and C are uniformly distributed on the surface of copper current collector (Fig. 2i–k).

The core-shell Sn@C sample is further characterized by TEM. As shown in Fig. 2l, the sample is composed of homogeneously distributed nanoparticles with narrow size distribution. The average particle size is around 10 nm. Owing to the incorporation of amorphous carbon, these particles are well separated with each other. Clear diffraction rings are observed (Fig. 2m), which matches well to that of tetragonal Sn. Lattice image of a single Sn nanocrystal in Fig. 2n exhibits well defined four fold symmetry, Lattice fringes separated by 0.29 nm are clearly resolved in two perpendicular orientations, which agrees well with the two perpendicular (200)

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