



Toward cyclic durable core/shell nanostructure of Sn-C composite anodes for stable lithium storage by simulating its lithiation-induced internal strain



Hui Liu ^{a, b}, Renzong Hu ^{a, *}, Cunke Huang ^c, Wei Sun ^a, Hanyin Zhang ^a, Min Zhu ^a

^a School of Materials Science and Engineering, South China University of Technology, Guangdong Provincial Key Laboratory of Advanced Energy Storage Materials, Guangzhou, 510640, PR China

^b College of Science, Hunan Agriculture University, Changsha, 410128, PR China

^c Guangxi Colleges and Universities Key Laboratory of Novel Energy Materials and Related Technology, College of Physics Science and Technology, Guangxi University, Nanning 530004, PR China

ARTICLE INFO

Article history:

Received 4 December 2016

Received in revised form

15 January 2017

Accepted 5 February 2017

Available online 8 February 2017

Keywords:

Lithium ion batteries

Tin anode

Deformation

Whisker growth

Structural design

ABSTRACT

To explore the capacity fading mechanism during long-term cycling of the milled Sn-C lithium storage anodes, the structural stability of the cycled Sn-C electrodes has been investigated using internal strain distribution as indicator by simulation with different two-dimensional core/shell nanostructure models solved by Lagrangian description, combining with experimental results. It is revealed that the Sn-C composite of a double-coating structure with the smaller Sn coated by a stiff layer Li₂O and embedding in graphite sustains less deformation, and has higher structural stability than the single-coating one. Due to the lithiation-induced stress and strain effect, Sn particles aggregate and the Sn whiskers grow in the cycled Sn-C electrodes that observed by SEM and TEM, which is closely related to the Sn transportation. This strain induced structural damage causes the capacity fading of Sn anodes. Based on the simulation of strain distribution induced by lithiation, the nanostructure has been designed for Sn-C electrodes of smaller Sn particles embedded in matrix with large elastic modulus and proper thickness to obtain optimized combination of capacity and cycleability. It would provide a guideline for designing material and microstructure of anodes for lithium ion batteries.

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1. Introduction

Tin (Sn) is a promising alternative anode material for new generation high-energy lithium ion battery, because it possesses a moderate average voltage of ~0.5 V (vs. Li/Li⁺), and can host more Li ions to form Li_xSn (0 ≤ x ≤ 4.4), reaching a maximum theoretical volumetric capacity of 2111 mAh/cm³ [1–3]. However, the pure Sn anode experiences significant volumetric change during alloying/de-alloying of lithium, which creates very large internal stress and serious deformation [4–6]. This results in disintegration of electrode structure, in which Sn particles loss lithiation activity due to the loss of electrical contact with the surrounding Sn phase, Cu current collector or conductive matrix. In addition, the volume expansion would also induce breaking of solid-electrolyte-

interphase (SEI) film, and then SEI film would continuously grow on the fresh surface of cracks during cycling, following with continuous irreversible consumption of electrolyte and leading to electrolyte-degradation. Thus, the Sn based anodes suffer structural fracture and fast capacity degradation.

In order to improve the cycling performance of Sn based anodes, the most effective approach is to embed nanostructured Sn-based materials in various carbon materials [7,8] or elastic alloy matrix [9–13]. Thus, the volume change of Sn can be homogenized and diluted, and become reversible. In addition, the carbon matrix provides conductive networks for the whole electrodes [14,15], and prevents Sn from aggregation. Therefore, nanostructured Sn-C composites have better structure stability, yielding much enhanced capacity retention compared with pure Sn micro-sized particles [16–18]. Recently, we have developed a high-efficiency method of dielectric barrier discharge plasma assisted milling (P-milling), and used it to synthesize Sn-C and Sn@SnO_x/C hybrid anode materials [19,20]. Those hybrids have a nanocomposite

* Corresponding author.

E-mail address: msrenzonghu@scut.edu.cn (R. Hu).

structure of nanosized Sn particles embedded in graphite matrix, which show higher capacity and better capacity retention than those Sn-C composites prepared by conventional milling (C-milling) without the assistance of plasma, demonstrating the positive effective of plasma on the fast refining of Sn. However, there is no clear guidance suggesting that which Sn particle size and distribution would have better electrochemical performance, leading to a great blindness on microstructure tuning of the Sn based carbonaceous composite anodes.

Recently, it has been observed by *in-situ* TEM that Sn aggregates and then Sn whiskers grow presumably due to large internal stress in Sn thin film and SnO₂ nanowire during lithiation/delithiation [21,22], but the Sn precipitation can be suppressed by carbon coating on SnO₂ nanowires [21]. With respect to the P-milled Sn-C composites, we noted that the capacity degradation of Sn becomes more serious at a certain cycling stage. This might be related to a sudden activity loss of aggregated Sn, which is probably due to the formation of Sn whisker owing to the stress effect in case that graphite matrix is broken down and could not suppress Sn aggregation after a certain period of cycling. Obviously, the Sn particle size and distribution determine the stress and strain distribution during the lithiation/delithiation, and thus the stability of carbon matrix, as well as the aggregation and growth tendency of Sn. In addition, the practical capacity of the anode is also dependent on the size and distribution of the Sn phase. Thus, it is of great significance to explore the quantitative relationship between the particle size and distribution of Sn and structural structure stability of the Sn-C composite anodes, which could give a design guidance for Sn-C and other metal-carbon composite anodes for Li-ion battery.

In this work, two-dimension geometric models are designed to predict the structural stability of active Sn particles in our previous reported Sn-C composites. ANSYS Workbench interface is used to solve these models. The growth mechanism of Sn whiskers in cycled Sn-C is revealed. Combining the simulated strain distribution and experimental results of the electrochemical performance, the criterion of structural stability of Sn and carbon matrix upon lithiation/de-lithiation cycling is proposed for Sn-C based nanocomposites with core-shell configurations.

2. Experimental methods

Two kinds of Sn-C nanocomposites, as prepared by milling a Sn/C mixture (1:1 of mass ratio) using a discharge plasma assisted milling method (Plasma-BM-L) for 10 h in Ar and O₂ atmosphere respectively, are denoted as P-milled Sn-C and O-P-milled Sn@SnO_x-C, respectively. The details of P-milling have been reported in our previous works [19,20]. A Sn-C composite, denoted as C-milled Sn-C, is fabricated by a conventional milling for 10 h with the same milling parameters but without the assistance of discharge plasma. The distributions of Sn particle size were evaluated from powder X-ray diffraction (XRD), and small-angle X-ray scattering (SAXS) data. The microstructures of samples were characterized by field-emission scanning electron microscopy (FE-SEM, Carl Zeiss Supra 40), and transmission electron microscopy (TEM, JEOL-2100) at 200 kV. Cycled electrodes were washed in diethyl carbonate and absolute ethanol to remove the electrolyte before microstructure analysis.

The electrochemical properties of the as-prepared composites were evaluated using coin-type half-cells (CR2016) constructed in an argon-filled glove box with lithium ribbon serving as the counter and reference electrodes. The electrode slurries were prepared by mixing 80 wt% active powder, 10 wt% Super-P, and 10 wt% PVdF. The slurries were coated on Cu foil and dried at 120 °C for 10 h. The loading of active materials on working electrode was 1–1.5 mg/cm².

The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate/diethyl carbonate/ethyl methyl carbonate (1:1:1, v:v:v, Shanshan Tech Co., Ltd.). Galvanostatic charge–discharge measurements were performed with battery testers (CT2001A, Land, China) at a current density of 100 mA/g in the range of 0.01–1.5 V vs. Li/Li⁺. All the electrochemical tests were carried out at ambient temperature.

The internal strain and its variation in the above three Sn based anodes during lithium inserting was simulated by using ANSYS Workbench interface. Table 1 lists the parameters of materials used for simulation. The elastic constant of Li₂O are performed with the Vienna *ab initio* simulation package (VASP) within the projector-augmented plane wave (PAW) method of density functional theory (DFT), and the details of the calculation is given in the Supplement Information. The tangent modulus (*G*) is calculated by the formulation of $G = E/(1 + 2\mu)$. The designed geometry models are solved by Lagrangian description using ANSYS WORKBENCH from the following boundary conditions: assumed the deformation of origin as zero, and expanding freely of the graphite outer edge.

3. Results and discussions

3.1. Microstructure and geometry models of the Sn-C composites

Fig. 1 shows the microstructures of C-milled Sn-C, P-milled Sn-C and O-P-milled Sn@SnO_x-C observed by TEM. As discussed previously [19,20], a single-coating structure of Sn particles dispersing in graphite is obtained for C-milled and P-milled Sn-C composites. However, as shown in Fig. 1 (a) and (b), the particle size of Sn (dark zones) in the P-milled Sn-C composite is much smaller than that of the C-milled Sn-C hybrid. In contrast, as the Sn-C mixture was milled with the assistance of O₂ plasma, there are 6–10 nm SnO_x layers coated on the surfaces of the ultrafine Sn particles, to form a Sn@SnO_x/C with a unique double-coating nanostructure. As shown in Fig. 1(c), the corresponding ring-like selected-area electron diffraction (SAED) patterns demonstrate the amorphous/nanocrystalline nature of the *in-situ* formed SnO_x during O-P milling of the Sn-C mixture. The dark field TEM image shown in Fig. 1(d), taken from the (101) diffraction spot of Sn, reveals that most of the Sn nanoparticles are less than 20 nm in size.

XRD patterns shown in Fig. 2(a) reveal the dramatically refinement of the Sn (JSCD: 00-001-0926) particles during P-milling, as well as the existence of the *in-situ* formed SnO (JSCD: 00-001-0891) and SnO₂ (JSCD: 00-001-0625) phase after P-milling in O₂ atmosphere. In order to evaluate the distributions of Sn particle size, SAXS was performed on the three Sn-C composite powders. Fig. 2(b), (c), and (d) show the relative frequency, cumulative distribution and mean particle size (*D_m*) of Sn particle for C-milled Sn-C, P-milled Sn-C, and O-P-milled Sn@SnO_x/C composites, respectively. Consistent with the statistics results of Sn size from TEM images [19], the majority of Sn particles have sizes between 40 and 200 nm, with a *D_m* of 70 nm in the C-milled Sn-C, while most Sn particles are less than 100 nm and the *D_m* is only 40 nm in the P-milled Sn-C. Not surprisingly, the Sn@SnO_x/C shows the smallest *D_m* of 21 nm, and the size of most Sn particles is less than 40 nm. Accordingly, as illustrated in Fig. 3, even with the same milling duration (10 h), the P-milled/C-milled Sn-C composites (Fig. 3(a)) and the O-P-milled Sn@SnO_x/C (Fig. 3(b)) have quite different particle size and distribution of Sn phase in the carbon matrix, forming two different kinds of core/shell structures both with dispersive Sn cores and continuous carbon shells.

According to those, as shown in Fig. 3(c), a simple 2D core-shell geometric model with Sn nanoparticles coating by graphite matrix is established for C-milled and P-milled Sn-C compositions by ANSYS Workbench interface. But for the Sn@SnO_x/C, actually after discharging in the first cycle, all the SnO_x (Fig. 3(b)) would be

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