Solid State Ionics 325 (2018) 120–127

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Electrochemical performance and morphological evolution of hollow Sn microspheres

Meiqing Guo[a,b,c,d], Xiaogang Zhang[a,b], Weijia Meng[a,b], Xiao Liu[a,b], Genwei Wang[a,b,c], Zhongchao Bai[e], Zhihua Wang[a,b,c,*], Fuqian Yang[d,**]

[a] Institute of Applied Mechanics and Biomedical Engineering, Taiyuan University of Technology, Taiyuan 030024, China
[b] Shanxi Key Laboratory of Material Strength & Structural Impact, College of Mechanics, Taiyuan University of Technology, Taiyuan 030024, China
[c] National Demonstration Center for Experimental Mechanics Education, Taiyuan University of Technology, Taiyuan 030024, China
[d] Department of Chemical and Materials Engineering, University of Kentucky, Lexington 40504, USA
[e] College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China

ARTICLE INFO

Keywords:
Sn
Hollow microspheres
Anode
Lithium-ion batteries

ABSTRACT

Using shell-like structures in lithium-ion battery (LIB) can limit the structural degradation/damage induced by the volumetric change during electrochemical cycling. In this work, we synthesize hollow Sn microspheres (Sn-HMSs) via a galvanic replacement reaction, and study the electrochemical performance of the lithium-ion cells with Sn-HMSs as the working electrode. The lithium-ion cells have a charge capacity of 205.9 mA h g^{-1} after 100 cycles at a current density of 100 mA g^{-1}. In comparison with the charge capacities of 148 mA h g^{-1} of solid Sn nanospheres and 516.1 mA h g^{-1} of hollow Sn nanospheres, the results reported in this work reveal the importance of shell-like structures in the retention of the energy storage for LIBs and the size effect on the energy storage. The smaller the hollow Sn spheres, the better is the cycle performance. There are two modes of structural degradation/damage contributing to the capacity loss during electrochemical cycling; one is the disintegration of the Sn-HMSs, and the other is the fracturing of the electrode layer.

1. Introduction

Sn has potential as an anode material for lithium-ion batteries (LIBs) because of high theoretical capacity (993 mA h g^{-1}), nontoxicity and low cost [1,2]. One of the challenges for the applications of Sn-based anode in LIBs is the specific volumetric strain of ~300% associated with alloying/dealloying of Sn during electrochemical cycling, which can lead to significant loss in the energy storage through surface cracking and the formation of a layer of solid electrolyte interphase (SEI) [3,4]. Continuous formation and growth of SEI layer can cause the loss of electric contact between active materials and current collector [5–9] and the degradation of LIBs.

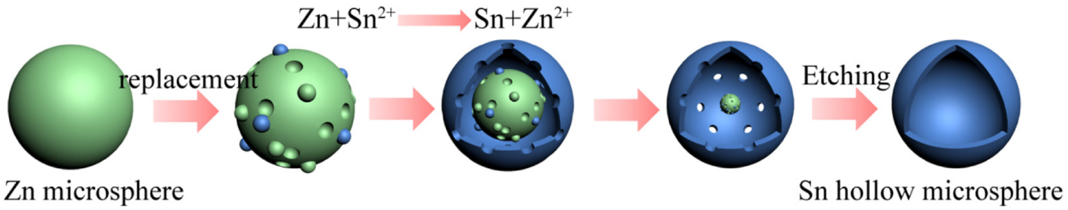
To limit the capacity loss of LIBs due to the volumetric change of Sn during lithiation and delithiation process, various strategies have been proposed, including the use of nanostructured Sn [10,11] and buffering matrixes, such as hollow Sn [11], Sn/M (M = Sb, Zn, Cu and Ni) [4,12], and Sn@C composites [1,13]. In the heart of these strategies is the restraint to the volumetric change during the alloying/dealloying of Sn since Sn of submicron sizes can facilitate the migration of Li and limit the lithiation-induced stress/strain. Currently, most studies have been focused on the use of Sn nanostructures to confine the lithiation-induced volumetric change of Sn [1,3,4,13,14]. However, Sn nanostructures often undergo aggregation to form large particles during electrochemical cycling, resulting in the pulverization of the large particles during subsequent cycles [1,15]. Also, electrodes made from nanoparticles have relatively low packing densities and low volumetric energy densities [16]. Thus, it is of practical importance to explore the possibility of using microparticles in the electrode of LIBs.

There are reports that using microspheres can form close-pack structures with relatively high packing densities [17,18]. However, electrodes made from solid microspheres generally exhibit poor cycle stability, which is attributed to the serious pulverization caused by lithiation-induced surface cracks [8]. It has been reported that hollow structures, such as hollow Sn-nanospheres, can effectively improve the cycling performance since hollow nanospheres can reduce the mechanical stress induced by lithiation and/or delithiation [11,19]. This trend has stimulated interest in studying electrochemical stability of hollow structures of micron scales.

---

* Correspondence to: Z.H. Wang, Institute of Applied Mechanics and Biomedical Engineering, Taiyuan University of Technology, Taiyuan 030024, China.
** Corresponding author.
E-mail addresses: wangzh@tyut.edu.cn (Z. Wang), fyang2@uky.edu (F. Yang).

https://doi.org/10.1016/j.ssi.2018.08.004
Received 23 April 2018; Received in revised form 18 July 2018; Accepted 14 August 2018
0167-2738/



Scheme 1. Schematic of the synthesis of Sn-HMSs.

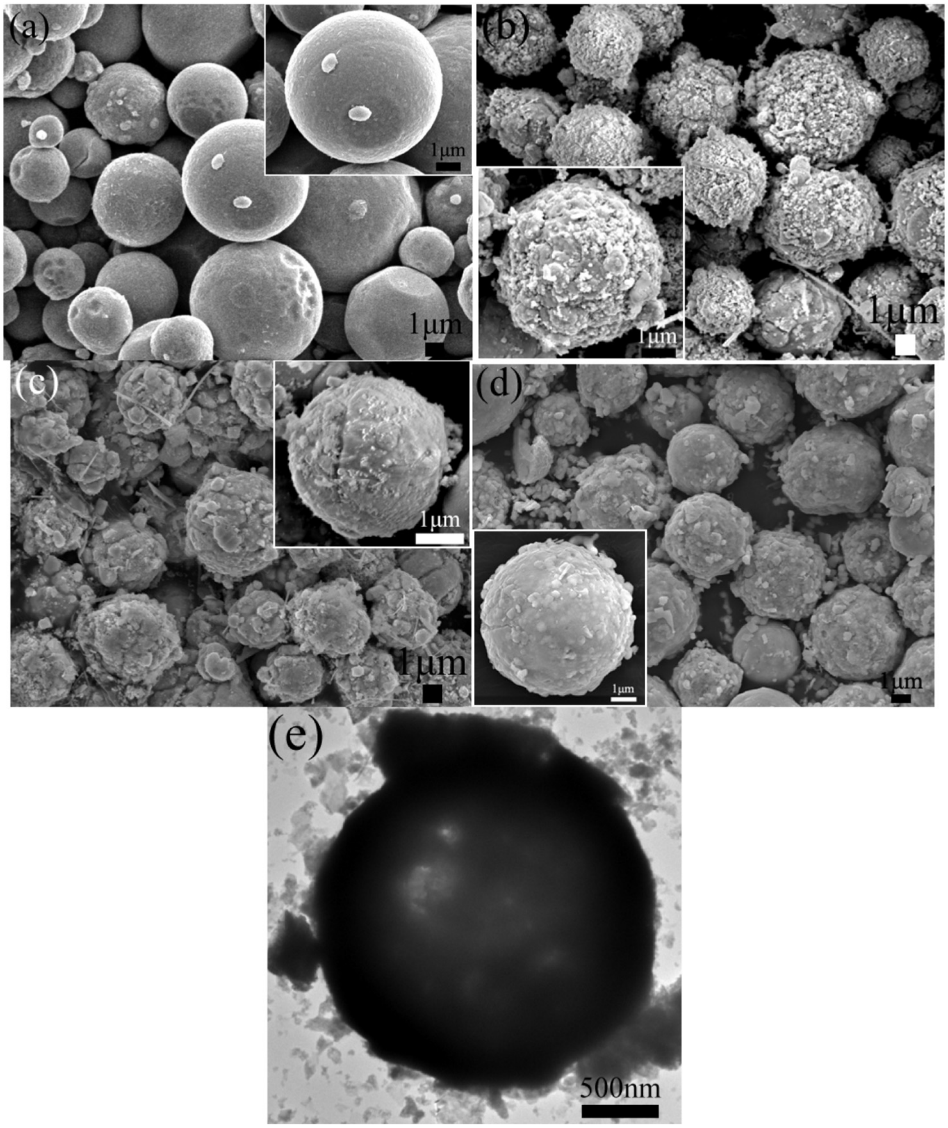


Fig. 1. SEM images of the microspheres at different instants during the synthesis of Sn-HMSs: (a) 0 h, (b) 2 h, (c) 4 h, and (d) 5 h; (e) TEM image of Sn-HMSs (5 h).

In this work, we synthesize hollow Sn microspheres (Sn-HMSs) via a galvanic replacement reaction. The synthesized Sn-HMSs are used as electric anode of LIBs, and the electrochemical performance of the LIBs is investigated. The morphological evolution of the Sn-HMSs during electrochemical cycling is also analyzed.

2. Experimental details

2.1. Synthesis of Sn-HMSs

Zn powders of 0.14 g and $SnCl_2$ of 0.45 g were ultrasonically dispersed in ethanol of 30 ml, respectively, to form two suspensions. These two suspensions were then mixed together, and maintained at room temperature for 2 h in a nitrogen atmosphere. HCl aqueous solution (0.01 M) of 2 ml was added to the mixture to remove superfluous Zn, and centrifugation was used to collect hollow Sn-microspheres. The hollow Sn-microspheres were washed with ultrapure water and ethanol five times, and dried in vacuum at 60 °C for 5 h. Hollow Sn nanospheres (Sn-HNSs) and solid Sn nanospheres (Sn-SNSs) were synthesized, following the approach reported by the literature [11,19].

Scheme 1 shows schematically the process for the synthesis of Sn-HMSs in a galvanic replacement reaction, in which the Zn in Zn microspheres is replaced by Sn due to that Zn has a higher activity than Sn. During the replacement reaction, Zn atoms on the surfaces of Zn