Nano Energy (2014) 9, 61–70

Available online at www.sciencedirect.com

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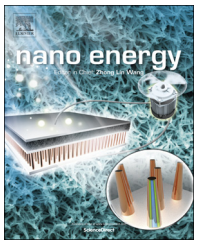

RAPID COMMUNICATION

Tin quantum dots embedded in nitrogen-doped carbon nanofibers as excellent anode for lithium-ion batteries

Guanhua Zhang[a], Jian Zhu[a], Wei Zeng[a], Sucheng Hou[a], Feilong Gong[b], Feng Li[b], Cheng Chao LI[a,*], Huigao Duan[a,*]

[a]College of Physics and Microelectronics, State Key Laboratory for Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, China
[b]State Laboratory of Surface and Interface Science and Technology, Zhengzhou University of Light Industry, Zhengzhou 450002, China

Received 17 May 2014; received in revised form 18 June 2014; accepted 26 June 2014
Available online 5 July 2014

KEYWORDS
Sn quantum dots;
N-doped carbon nanofibers;
Electrospinning;
Anode;
Li-ion battery

Abstract
Sn/C composites with sub-10-nm-scale tin nanoparticles uniformly dispersed in a carbon matrices are believed to be excellent anode materials for high energy and power density lithium-ion batteries. However, it is difficult to incorporate high-capacity, active Sn into the carbon structures due to the hydrophobic nature of the carbon surface. Surfactants and/or templates are always required for uniform dispersion of active Sn, inevitably increasing the production cost and degrading the electronic conductivity. In this work, we reported a facile and scalable electrospinning technology to synthesize Sn quantum dots finely embedded in N-doped carbon nanofibers. The composite electrode exhibited a high reversible capacity of 887 mAh g^{-1} at a current density of 0.1 A g^{-1} after 200 cycles, about 75% retention of the initial capacity. Moreover, it showed good rate capability even when cycled at 0.2 A g^{-1} about 685 mAh g^{-1} after 500 cycles and 508 mAh g^{-1} at 0.4 A g^{-1} after 200 cycles. The exceptional performance is supposed to benefit from the high electric conductivity of N-doped porous carbon nanofiber structures, which not only provides fast and versatile transport pathways for the electrolyte ions and electrons, but also simultaneously solves the major problems of pulverization, loss of electrical contact, and particle aggregation of Sn anode. Moreover, the short diffusion path for both electrons and ions provided by the ultrasmall Sn particles further improved the rate performance.
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*Corresponding authors.
E-mail addresses: ghzhang2012@126.com (G. Zhang), licc@hnu.edu.cn (C.C. LI), duanhg@hnu.edu.cn (H. Duan).

http://dx.doi.org/10.1016/j.nanoen.2014.06.030
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Introduction

Development in automobile market is presently aimed at producing low emission cars, such as zero emission electric vehicles (EVs) and hybrid electric vehicles (HEV). Suitable energy storage devices are the key parts of electric vehicles (EVs) and high-energy storage lithium ion batteries (LIBs) are considered as ideal candidates [1-3]. To make these batteries appropriate for EVs applications, more improvements are necessary in terms of energy density, cycle life and capacity retention. Pure metallic Sn has attracted considerable attention as an anode material for LIBs owing to its high theoretical specific capacity (992 mA h g^{-1} or 7262 mA h cm^{-3} for $Li_{4.4}Sn$), which is almost 3 times higher than that of commercialized graphite (372 mA h g^{-1} for LiC_6) [1,4], and its high operating voltage along with the absence of solvent intercalation [2,5,6]. Unfortunately, the huge volumetric expansion and aggregation of Sn nanoparticles (NPs) during lithium alloying and dealloying processes lead to severe degradation of the electrodes upon cycling and dramatically shorten the cycle life of the Sn electrode [1-6]. Therefore, it is still a huge challenge to further improve or optimize the electrochemical performance of the Sn electrode.

To overcome these issues, considerable efforts have been made to improve the structural stability and integrity of Sn anodes [7-9]. It is believed that two strategies are feasible. The first is the fabrication of uniformly dispersed nano-Sn in a conductive matrix (such as carbon) to accommodate volume change and maintain the mechanical integrity of the composite electrode [3,5,8-11]. The second strategy to enhance the electrochemical performance is to reduce the particle size of Sn to sub-10-nm scale to form quantum dots (QDs), which may efficiently mitigate the absolute strain induced by the large volume change during lithiation/delithiation, and retard particle pulverization. Definitely, a Sn/C composite with uniform sub-10-nm-scale tin NPs dispersed in a carbon matrix would be a promising anode for LIBs. For instance, Scrosati and co-workers synthesized a nanostructured Sn/C composite which could provide a stable capacity of 500 mAh g^{-1} over more than 200 cycles [12]. The carbon matrices not only acted as a buffer to accommodate the volume expansion, but also prevented the aggregation of Sn NPs. Moreover, Xu's group demonstrated that Sn nanograin uniformly dispersed in spherical conductive carbon matrices still contained a reversible capacity of 710 mA h g^{-1} after 130 cycles at 0.2 A g^{-1} [9]. The remarkable performance is attributed to the small particle size (~10 nm) and continuous path for Li ions and electrons inside the nano-Sn/C composite spheres. More recently, ultrasmall Sn NPs (~5 nm) embedded in nitrogen-doped porous carbon network has been synthesized from the organic framework, delivering a capacity of 722 mA h g^{-1} after 200 cycles at the current density of 0.2 A g^{-1} [8]. Although various synthetic routes have been successfully developed for nano-Sn/C composite, it should be noted most of these products are irregular particles with relatively large size.

One-dimensional (1D) carbon nanoarchitectures such as nanotubes (NTs) [13,14], nanowires (NWs) [1,15], nanorods (NRs) [16-18] and nanofibers (NFs) [19-21] are proven to have much better kinetic properties than reported carbon matrixes with particle morphology. Their uniform structure, orientated electronic and ionic transport path and strong tolerance to stress change can enable efficient transport of both Li-ions and electrons [19]. However, it is difficult to incorporate high-capacity, active Sn into these 1D carbon structures due to the hydrophobic nature of the carbon surface. Surfactants and/or templates are always required for uniform dispersion, inevitably increasing the production cost and degrading the electronic conductivity [19,22]. Hence, it is desirable to synthesize uniform dispersion Sn QDs within conductive CNFs supports that not only retains the high capacity of the nanosized material but also shows excellent cycling performance by avoiding excessive subreactions and aggregation of Sn.

Herein, we reported a facile, straightforward method to synthesize of Sn QDs finely embedded in N-doped CNFs by the electrospinning technique followed by annealing under nitrogen. Compared to other reported Sn/C nanocomposites [1,11,12,14,20,23-25], our sub-5-nm Sn QDs can further enhance Li ion insertion by reducing diffusion/migration barrier and allow easy penetration of the electrolyte between neighboring NPs and hence reduce internal resistance, which is particularly helpful for high energy/power applications. Moreover, the N-doped carbon matrices with high electric conductivity could provide extra "cushion" for the structure to accommodate large volume change induced by Li-Sn alloying/dealloying reactions. This newly designed Sn QDs@CNFs displayed extraordinary LIBs performance with outstanding reversible capacity, excellent capacity retention, high Coulombic efficiency, good rate capability and superior cyclic performance, highlighting the importance of the unique combination of ultrasmall Sn QDs and CNFs matrices to overcome the aforementioned problems and achieve the maximum electrochemical performance. We demonstrated the discharge capacity up to 200 cycles with 887 mAh g^{-1} at a current density of 0.1 A g^{-1}, and 508 mAh g^{-1} at 0.4 A g^{-1}.

Experimental

Synthesis

All the chemicals were of analytical grade and used as received without further purification. Typically, 0.8 g of polyacrylonitrile (PAN, Mw=150,000, Sigma) was dissolved in 10 mL of N, N-dimethylformamide (DMF, Tianjin Chemicals, 99.0%), and then 0.28 g of Tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$, 98.5% purity, National Medicine Co., Ltd., Shanghai, China) was added to form a mixed solution. After vigorous stirring for 4 h at 60 °C, buff and sticky polymer solution was obtained for the subsequent electrospinning process. As for a typical electrospinning process (shown in Scheme 1), the spinneret had an inner diameter of 0.6 mm. Grounded aluminum strips (20 cm in width) with parallel gaps of about 1 cm were used as collectors. A distance of 15 cm and a direct current voltage of 18 kV were maintained between the tip of the spinneret and the collector. The as-electrospinning $SnCl_2$/PAN nanofibers (denoted as $SnCl_2$-PAN) were dried for 24 h in vacuum at 60 °C. The dried $SnCl_2$-PAN were further annealed in an air-circulated oven at 280 °C for 2 h at a heating rate of 2 °C min^{-1}, and then

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