



Enhancing Ni–Sn nanowire lithium-ion anode performance by tailoring active/inactive material interfaces

Miao Tian¹, Wei Wang¹, Se-Hee Lee¹, Yung-Cheng Lee¹, Ronggui Yang^{*,1}

Department of Mechanical Engineering, University of Colorado, Boulder, CO 80309, USA

ARTICLE INFO

Article history:

Received 11 June 2011

Received in revised form 12 August 2011

Accepted 13 August 2011

Available online 22 August 2011

Keywords:

Lithium-ion battery

Anode material

Tin-based intermetallics

Nanowire arrays

ABSTRACT

Nanowire arrays have attracted great attention due to their great potential to improve the performance of Li-ion batteries. In this work, we studied anode performance of lithium-ion batteries using Ni–Sn nanowire arrays. A versatile method through a porous anodic alumina (PAA) template-assisted electrochemical deposition process was developed to directly synthesize Ni–Sn nanowire arrays on copper current collectors. This method presents significant advantage that the as-prepared Ni–Sn nanowire arrays can be directly used as anode electrode without any binder or conductive materials. However, the formation of a continuous Ni–Sn film at the base of the nanowires result in quick loss of electrical contact between the active material and the current collector because of the large strain mismatch at the large continuous active/inactive material (A/I) interface. By growing short Cu nanoscrews as a buffer layer before Ni–Sn nanowire growth, the formation of Ni–Sn film was inhibited and the A/I interface was scaled down to nanoscale islands. The strain mismatch is thus significantly reduced, which results in enhanced structural stability and battery performance. The effect of the composition and the length of Ni–Sn nanowire arrays on the electrochemical performance of lithium ion batteries are also systematically studied.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Nanostructured electrodes have great potential in significantly improving the performance of rechargeable Li-ion batteries which have been widely used as power sources for cell phones [1], laptop computers [2], and electric vehicles [3–7]. Among various nanostructures, nanowire electrodes have recently attracted great interests [8–10]. Many features of nanowires lead to significant improvements in battery performance: (1) the free spaces between nanowires provide easy access of the electrolyte to all the surfaces of the electrode and accommodate volume changes during lithium ion insertion; (2) the small diameter of nanowires allows for fast Li-ion diffusion and high power delivery; (3) direct connection of nanowires to the current collector ensures direct transportation of electrons to the current collector, which eliminates the necessity of any binder materials or conducting additives [11,12]. Electrodes with nanowires of various materials such as Si, TiO₂, Fe₃O₄, SnO₂,

Co₃O₄, and V₂O₅ [11,13–17] have been studied and show improved performance compared to bulk electrodes.

The interface between the active material and the inactive current collector has also been found important for electrodes. It has been shown that failure of Si film anode is due to delaminating of Si film from the Cu substrate, isolating the electronic pathways from Si to the underlying Cu [18]. Similar phenomenon was observed for Sn alloy films [19]. Annealing and modification of current collector surfaces could improve the adhesion between the active material and the current collector and thus make the reversible capacity high and stable [20–22]. On the other hand, battery stability can also be improved by scaling down the heterogeneous interface of Si and carbon nanotubes [23]. The critical role of the active/inactive material interfaces (A/I interfaces) in electrodes can be systematically studied using nanowires since their unique structure offers a way to tailor the A/I interfaces.

In this study, we used a facile method with the assistance of free-standing porous anodic alumina (PAA) templates to fabricate high-aspect ratio Ni–Sn nanowire arrays directly on current collectors. PAA template, produced by electrochemical oxidation of aluminum, is widely used to fabricate nanowire arrays due to the tunability and the compatibility with various materials [24,25]. Ni–Sn nanowire arrays with different A/I interface areas were realized to study the effect of A/I interface scaling on the electrochemical performance. The effect of the composition and the

* Corresponding author. Tel.: +1 303 735 1003; fax: +1 303 492 3498.

E-mail addresses: mmtian@colorado.edu (M. Tian), wei.wang-1@colorado.edu (W. Wang), Sehee.Lee@colorado.edu (S.-H. Lee), leeyc@colorado.edu (Y.-C. Lee), ronggui.yang@colorado.edu (R. Yang).

¹ DARPA Center for Integrated Micro/Nano-Electromechanical Transducers (iMINT), USA.

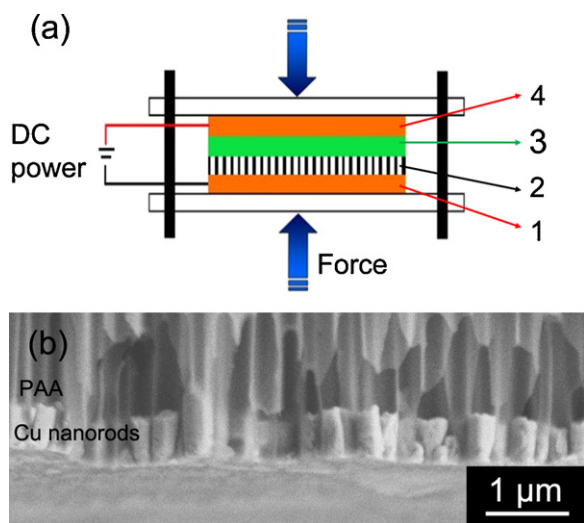


Fig. 1. (a) Schematics of the sandwich structure used for electroplating short nanorods to bond the PAA template on the Cu substrate: 1 – copper foil which serves as current collector and as the substrate of nanowire arrays, 2 – PAA template, 3 – filter paper saturated with electrolyte solution, and 4 – copper plate which serves as counter electrode. (b) Short Cu nanorods deposited in the PAA template which bonds PAA template on Cu substrate for the second electroplating step.

length of Ni–Sn nanowires on the electrode performance were also systematically studied.

2. Experimental

Commercial and homemade PAA templates were used for the synthesis of Ni–Sn nanowire arrays. The commercial PAA templates (Anodisc 47, Whatman 6809-5522) have an average pore diameter of 200 nm. The homemade PAA templates with an average pore diameter of 80 nm were obtained by anodizing high-purity (5N) aluminum foil at 40 V in 0.3 M oxalic acid for 24 h at 5 °C.

A two-step electrochemical deposition process was developed to directly grow nanowire arrays on Cu current collector.

The first step is to electrochemically deposit short nanorods to bond the PAA template onto the Cu substrate. Fig. 1 shows a typical sandwich-structure setup for this step. A constant voltage was applied between the Cu substrate and the counter-electrode for a certain time to grow short nanorods, which serve as “nanoscrews” to bond the PAA template onto the Cu substrate for the second step three-electrode electrochemical deposition. Two kinds of materials, intermetallic Ni–Sn or Cu, were electroplated as the bonding materials for different Ni–Sn nanowire on Cu current collector samples. For Ni–Sn bonding, the deposition was conducted at voltage of -1 V for 10 min and the electrolyte consisted of 17.82 g L^{-1} $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 39.4 g L^{-1} $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 165.15 g L^{-1} $\text{K}_4\text{P}_2\text{O}_7$, and 9.38 g L^{-1} glycine, with an addition of NH_4OH 5 mL L^{-1} for pH value control [26]. For Cu bonding, the deposition was conducted at voltage of -0.8 V for 10 min and the electrolyte consisted of 6 g L^{-1} cupric pyrophosphate ($\text{Cu}_2\text{P}_2\text{O}_7 \cdot x\text{H}_2\text{O}$; Sigma–Aldrich 344699), 25 g L^{-1} potassium pyrophosphate ($\text{K}_4\text{P}_2\text{O}_7$, Sigma–Aldrich 322431), and 2 g L^{-1} ammonium citrate ($\text{C}_6\text{H}_{17}\text{N}_3\text{O}_7$, Fluka 09831) [27]. Fig. 1b shows the short Cu nanoscrews grown in this step with length of $\sim 0.6 \mu\text{m}$. Similar nanorods of Ni–Sn with a length of $\sim 1 \mu\text{m}$ were observed when intermetallic Ni–Sn is deposited as the bonding material.

In the second step, Ni–Sn nanowires were fabricated by co-depositing Sn and Ni in a three-electrode glass cell filled with the same Ni–Sn electrolyte as that in the first step. An Ag/AgCl electrode immersed in the saturated KCl solution was used as a

reference electrode, and a Pt coil was used as the counter-electrode for three-electrode electrochemical deposition. The potentiostatic deposition was performed on a CHI 760c electrochemical work station. After electrochemical deposition, the final Ni–Sn nanowire array samples were obtained after immersing in 1 M NaOH solution to dissolve the PAA templates and cleaning with DI water.

The field emission scanning electron microscope (FE-SEM, JEOL's JSM-7401F) with energy-dispersive X-ray spectroscopy (EDS) option was employed to study the morphology and composition of the nanowires. X-ray diffraction spectrometer (Scintag PAD5) with Cu K α radiation ($1.54056 \text{ \AA}$) was used to record the XRD patterns. The as-prepared Ni–Sn nanowire arrays on Cu current collector were tested in the electrolyte containing 1 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 volume ratio, Aldrich), with Li foil (Alfa Aesar) as counter-electrode. The CR2032 coin-type cells were assembled in an argon-filled glove box system (Vacuum Atmosphere Nexus model) and tested with a computer controlled potentiostats/galvanostats system (Arbin BT-2000). The discharge–charge experiments were performed galvanostatically within the voltage window of 0.02–1.5 V (vs. Li/Li+).

3. Results and discussion

Fig. 2 shows the difference between the Ni–Sn nanowire arrays with two kinds of PAA template bonding materials. When Ni–Sn nanorods were used for bonding in the first step (Fig. 2(a)), a thin film of intermetallic Ni–Sn was formed in the gap between the PAA template and the Cu substrate due to the roughness on copper surface, which resulted in a large continuous A/I interface. The FE-SEM image of Ni–Sn nanowires on Cu current collector confirms the formation of continuous Ni–Sn film. In the other structure, Cu nanoscrews were used to bond the PAA template onto Cu substrate (Fig. 2(b)). Cu film was formed in the gap between the PAA template and the Cu substrate, followed by Cu nanoscrews in nanopores of the PAA (Fig. 1(b)), which reduces the A/I interface (Ni–Sn/Cu interface) to nanoscale islands on top of Cu nanoscrews. The FE-SEM image in Fig. 2(b) shows that the A/I interface is confined to the cross-section of each nanowire.

Fig. 3(a) and (b) shows the FE-SEM images of Ni–Sn nanowire arrays with a characteristic nanowire diameter of ~ 200 nm and ~ 80 nm, respectively. The length of the nanowires is controlled by adjusting the electrochemical deposition time, and the diameter is determined by the pore size of PAA templates, as shown in the inset figures. The nanowires are agglomerated, and micro-scale gaps are formed between nanowire clusters due to the high aspect ratio. In the XRD spectrum of the as-prepared Ni–Sn nanowires in Fig. 3(c), peaks of Ni_3Sn_4 alloy can be clearly identified, indicating that Ni_3Sn_4 is the predominant phase in the intermetallic Ni–Sn, consistent with reported results of electrodeposited Ni–Sn [28,29]. The peak of Cu comes from the Cu current collector. The EDS spectrum in Fig. 3(d) shows that the as-prepared Ni–Sn nanowire arrays contain about 82 wt% Sn.

Fig. 4(a) shows the discharge capacity over cycle number for Ni–Sn nanowire array anodes with different bonding materials at the base. The capacities of the electrodes using both Ni–Sn nanowire arrays drop substantially after the first cycle. Similar observation has been reported for most Sn based materials [30], due to the formation of solid-electrolyte interphase (SEI) and the irreversible decomposition of intermetallic Ni–Sn during the activation step. Much higher capacity is observed for Ni–Sn nanowire arrays with Cu nanoscrews at the base than that of Ni–Sn nanowire arrays with Ni–Sn film bonding, especially after the second cycle. FE-SEM image (Fig. 4(b)) shows that the Ni–Sn nanowires with Cu nanoscrews at the base maintain intact on the Cu current collector after 30 cycles. However, a large number of nanowires fell off from the Cu

Download English Version:

<https://daneshyari.com/en/article/1288688>

Download Persian Version:

<https://daneshyari.com/article/1288688>

[Daneshyari.com](https://daneshyari.com)