Surface & Coatings Technology 288 (2016) 62–68

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Electrolytic coating of Sn nano-rods on nickel foam support for high performance lithium ion battery anodes

M. Tokur *, H. Algul, M. Uysal, T. Cetinkaya, A. Alp, H. Akbulut

Sakarya University Engineering Faculty, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54187, Sakarya, Turkey

ARTICLE INFO

Article history:
Received 30 November 2015
Revised 5 January 2016
Accepted in revised form 11 January 2016
Available online 13 January 2016

Keywords:
Lithium batteries
Nickel foam
Pulse electrodeposition
Electrochemical behavior
Stress bearing
Nano-rods

ABSTRACT

In this study, Sn was electrodeposited onto the porous nickel foam substrate under pulse electrodeposition conditions. Pulse electrodeposition was carried out at three different peak current densities of 10, 20 and 40 mA/cm^2 for 5 min in a pyrophosphate bath containing 40 g/L $SnCl_2.2H_2O$, 164 g/L $K_4P_2O_7$ and 19 g/L Glycin. Surface morphology of Sn–Ni foam electrodes were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) to understand the elemental surface composition of composites. X-ray diffraction (XRD) analysis was carried out to investigate the crystal structure of Sn–Ni foam electrode. The electrochemical performances of electrodes were investigated by charge/discharge tests, cyclic voltammetry experiments and the ac impedance technique. The results yielded encouraging discharge capacities since Ni foam behaves as a stress buffering layer as well as an electronic conductivity component.

1. Introduction

Due to their high energy density, long cycle life, high safety and low cost, lithium ion batteries have been a wise choice for portable electronic devices such as laptops, mobile phones and hybrid electric vehicles. Carbon materials such as graphite have been extensively used as anode material in lithium ion battery applications. However, the low theoretical specific capacity of carbon based materials has been a bottle neck for their usage as an anode material in portable devices. In recent years, many studies have been focused on developing new materials suitable for high-energy capacity and reasonable rate capability in order to replace a new anode material with the conventional graphite. Because of their high capacity of about 991 mAh/g, Sn-based anode materials are considered as a promising candidate as an anode material in lithium ion batteries [1]. Maghrabi et al. [2] studied Sn–Si–C composites as an anode material to improve the electrochemical performance of lithium ion batteries. Nevertheless, the main drawback of this material is the volume expansion/shrinkage of up to about 260% during the process of lithiation/delithiation, which causes crumbling and cracking of the electrode, inducing a poor electrochemical performance [3]. There are two different approaches to alleviate these problems. The first is to modify the morphology and prepare specific structures of Sn, such as nano powders, hollow structures, nanotubes, nanowires, nano-rods and mesoporous structures [4]. As described by Kim et al. [5] the morphologies of nano-rods or nanowires not only ensure a large surface area, but also provide facile strain relaxation and efficient three-dimensional electron transport pathways during electrochemical tests. The second approach is to disperse Sn nanostructures into a 'buffering' matrix such as nickel foam [6], copper foam [7] and cobalt foam [8]. Thus, it could cushion the mechanical effects of the volumetric changes. Nam et al. [9] prepared a 3D porous anode by coating a thin layer of Sn on copper foam of which provided a higher electrode/electrolyte interfacial contact area and better accommodation of structural strain during the charge/discharge process. Xu et al. [10] reported that the porous structure of nickel foam can promote penetration of electrolyte and maximize the utilization of active material.

The aim of this study is to synthesize metallic Sn-nanorods (Sn-NRs) on the porous nickel foam substrate and to characterize for the production of high capacity lithium ion batteries. The synthesis of Sn-NRs was obtained by pulse electrodeposition with three different peak current densities in a bath containing pyrophosphate and the morphology of produced Sn-NRs were confirmed by scanning electron microscopy (SEM). The charge/discharge cycles of the synthesized Sn-NRs revealed that the electrochemical properties of Sn-NRs have greatly improved by the obtained 3D structure of Sn-NRs.

2. Experimental procedure

A chloride bath was used for the electrodeposition of Sn coatings onto the nickel foam, under pulsed current conditions. For all of the experiments, the reagents were in analytical grade and used without further purification for the preparation of the plating bath. Pulsed

---

* Corresponding author.
E-mail address: mtokur@sakarya.edu.tr (M. Tokur).

http://dx.doi.org/10.1016/j.surfcoat.2016.01.015

electrodeposition parameters and components for the optimized Sn coatings are given in Table 1.

250 ml of the solution in a plating cell was immersed in a large volume water bath which was thermostatically controlled to be kept constant at room temperature. The schematic presentation of electrodeposition system is shown in Fig. 1. A high-purity (99.99%) electrolytic tin sheet was used as the soluble anode. The nickel foam substrates (with 99.99% purity, 80 μm thickness, and 70–80% porosity), (MTI Corporation) were cleaned with deionized water, acetone and ethanol for the electrodeposition process. After the preparation of the substrate surface, nickel foams were activated in a 25% H_2SO_4 solution for about 30 s. The activated nickel foams were then replaced parallel to the vertically oriented tin plate in the plating bath with a distance of 5 cm. All the electrodeposition processes were carried out at room temperature and, a magnetic stirring bar was used to continuously stir the electrolyte. Different peak current densities of 10 mA/cm^2 (Sn-I), 20 mA/cm^2 (Sn-II) and 40 mA/cm^2 (Sn-III) were applied in the bath for 3.0 min deposition time at room temperature. Bath composition and electrodeposition parameters are given in Table 1.

The specific structure and surface morphologies of the composite anodes were analyzed using X-ray diffraction (XRD) (Rigaku D/MAX 2000 with thin film attachment and Cu Kα radiation) and scanning electron microscopy (SEM) (JSM-6060 LV system). For the electrochemical tests, the coin type cells were assembled in a glove box in an Argon atmosphere (MBRAUN LABstar). Sn coated composites of different structures were then cut into cylindrical coupons of about 2.54 cm^2 in area and used as working electrode along with a Li foil as a counter electrode (2.01 mm^2) in Li-ion cell. The anode and cathode were separated with a polypropylene (PP) membrane. 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (1:1:1 in volume) was used as the commercial electrolyte. The electrochemical performances of produced electrodes were obtained on MTI Model BST8-MA electrochemical analyzer by using charge/discharge tests and cyclic voltammetry technique with an electrochemical workstation (Gamry Instruments Reference 3000) with a voltage range of 0.02 V and 1.5 V and a constant current density of 0.2 mA/cm^{-2} in CR2016 test cells at room temperature. The resistances of the all cells were then investigated using the ac impedance technique.

3. Results and discussion

Table 1
Overview of pulse electrodeposition parameters for the preparation of Sn coatings.

Bath composition	
$SnCl_2 \cdot 2H_2O$	25 g/L
$K_4P_2O_7$	170 g/L
Gelatin	0.5 g/L
Pulse electrodeposition parameters	
Peak current density	10–20-40 mA/cm^2
pH	8.0–9.0
Duty cycle %	50%
Frequency	100 Hz
Plating time	3 min
Temperature	25–30 °C
Sample codes	
10 mA/cm^2	Sn I
20 mA/cm^2	Sn II
40 mA/cm^2	Sn III

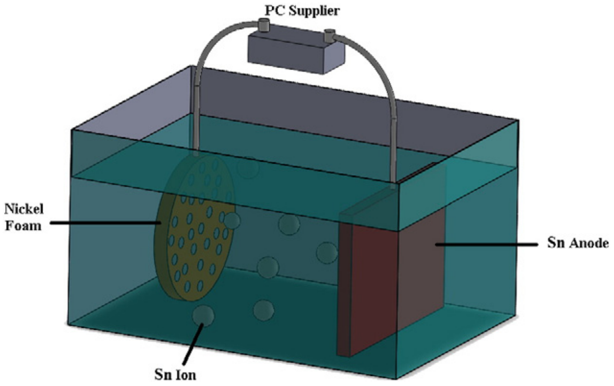

Fig. 1. The schematic illustration of plating cell system.

X-ray diffraction patterns of the Sn film coated electrodes with different current densities are shown in Fig. 2. XRD was performed on Sn films both before and after the formation of nano-rods. It can be concluded that the amount of deposited Sn element depend on different peak current densities. The investigated patterns of the electrodes show that the Sn content of coatings were increased by increasing the current density as expected [8]. XRD results of the nanocomposites indicate the presence of two different active material phases. It can be clearly seen from the patterns that the typical patterns of nickel are observed at 2θ values of 44.5°, 51.8° and 76.4°, whereas the peaks of 2θ at 30.7°, 32°, 55.4°, 62.5°, 64.6°, 72.4° and 79.5° correspond for Sn. The intensity of Sn peak at 32° (101) plane is stronger in the depositions at high current densities compared to those obtained at low current densities. The figure endorses the growth orientations of Sn thin films with emission peaks at $2\theta = 32°$, corresponding to (101) orientation. This indicates that the Sn nano-rods were grown with a preferred (101) orientation [11] which was also confirmed by SEM images, showing the nanostructured Sn thin film as seeding layer which is nucleated by Ni-mesh.

In Fig. 3 the SEM images distinctly show the Sn nanostructures which are produced with different current densities of 10 mA/cm^2, 20 mA/cm^2, 40 mA/cm^2, respectively. As may be seen from the figure, the surface morphologies of Sn film coatings were clearly distinguishable from each other by applying different current densities. The microstructure and surface morphology of the electrodeposits show that Sn-NRs were perfectly grown using higher current density process directly on nickel foam substrates. This is due to the higher cathodic overpotential on the electrodeposit and the accompanying increase in nucleation rate at instantaneously high current density [12]. In the Sn-NRs structure it is therefore considered that each nano-rod electrically connects to the metallic current collector. In addition, formation of the nano-rods is expected to allow large volume changes without pulverization of the Sn electrode and act as mechanical bumpers and enhance

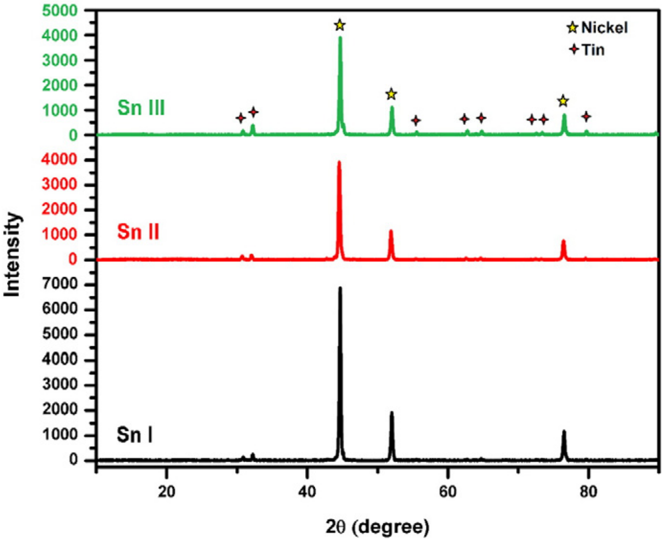

Fig. 2. XRD pattern of the pulse electrodeposited Sn nanocomposite electrodes.