



## Short communication

## Long-term cycling stability of porous Sn anode for sodium-ion batteries



Changhyeon Kim<sup>a</sup>, Ki-Young Lee<sup>b</sup>, Icpyo Kim<sup>c</sup>, Jinsoo Park<sup>d</sup>, Gyubong Cho<sup>c</sup>,  
Ki-Won Kim<sup>a, c</sup>, Jou-Hyeon Ahn<sup>e</sup>, Hyo-Jun Ahn<sup>a, c, \*</sup>

<sup>a</sup> Department of Materials Engineering and Convergence Technology, Gyeongsang National University, 501 Jinju-daero, Jinju, Gyeongnam, 52828, Republic of Korea

<sup>b</sup> Jeonyoung ECP, 637-1, Sunggok-dong, Danwon-gu, Ansan, Kyunggi-do, 15410, Republic of Korea

<sup>c</sup> School of Materials Science and Engineering, RIGET, Gyeongsang National University, 501 Jinju-daero, Jinju, Gyeongnam, 52828, Republic of Korea

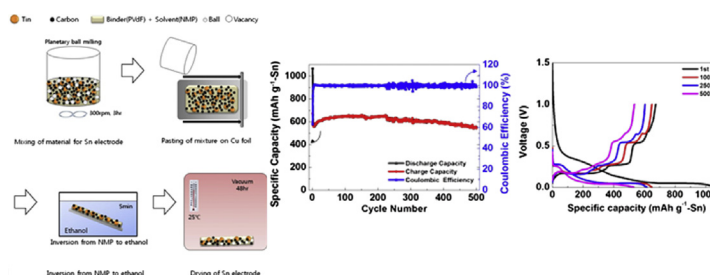
<sup>d</sup> Department of Materials and Energy Engineering, Kyungwoon University, 730 Gangdong-ro, Sandong-myeon, Gumi, Gyeongbuk, 39160, Republic of Korea

<sup>e</sup> Department of Chemical & Biological Engineering, Gyeongsang National University, 501 Jinju-daero, Jinju, Gyeongnam, 52828, Republic of Korea

## HIGHLIGHTS

- Porous Sn Anode (PSn) is prepared by phase-inversion technique.
- Pore volume of PSn is about eight times that of normal Sn anode (NSn).
- The first discharge and charge capacities of PSn are 1066 and 674 mAh g<sup>-1</sup>.
- The charge capacity of PSn is 519 mAh g<sup>-1</sup> after 500th cycles.
- PSn shows good long-term cycling stability with 0.046% per cycle for 500 cycles.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 15 December 2015

Received in revised form

23 February 2016

Accepted 17 March 2016

Available online 6 April 2016

## Keywords:

Tin anode

Phase inversion

Porous structure

Sodium ion battery

## ABSTRACT

A phase-inversion technique is introduced to produce a porous Sn anode for sodium batteries, which can accommodate volume changes during sodiation and desodiation. The Sn electrode shows two plateaus with a capacity of 1066 mAh g<sup>-1</sup> during the first sodiation and four flat plateaus with a charge capacity of 674 mAh g<sup>-1</sup> at the first desodiation process. During 500 cycles, the Sn electrode shows reversible capacity more than 519 mAh g<sup>-1</sup> with Coulombic efficiency of nearly 99%. The Sn electrode with a porous structure is a possible solution to the electrode degradation.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

The lithium-ion battery is a mature technology used as the power supply of portable electronic devices [1]. However, concerns over their cost have hindered their application to large-scale electrical-energy storage [2], in which the replacement of lithium with sodium is an alternative that offers benefits in terms of cost and the

\* Corresponding author. School of Materials Science and Engineering, RIGET, Gyeongsang National University, 501 Jinju-daero, Jinju, Gyeongnam, 52828, Republic of Korea.

E-mail address: [ahj@gnu.ac.kr](mailto:ahj@gnu.ac.kr) (H.-J. Ahn).

abundance of necessary resources [3].

In order to develop efficient sodium batteries, several cathode materials analogous to Li-metal oxides have been investigated [4–8]. In contrast, the choice of anode material is rather limited because the radius of a sodium ion is bigger than that of a lithium ion [9]. Graphite which is commercial anode material for lithium-ion battery cannot readily be used as an anode material because of its low capacity [10]. However, nano-porous hard carbon is a good candidate that offers a reasonable capacity of 220 mAh g<sup>-1</sup> during 100 cycles [11,12]. Amorphous TiO<sub>2</sub> nanotubes and Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> have also been investigated as alternatives to carbonaceous anode materials, but they achieved capacities of only 150 mAh g<sup>-1</sup> and 175 mAh g<sup>-1</sup>, respectively [13,14]. In order to meet the demand of high energy storage, Group IVA and VA elements such as Sn, Ge, Pb, Sb, and P have been suggested as potential candidates because sodium can be readily alloyed with these elements [15–18].

Sn has been regarded as one of the most promising anode materials owing to its high theoretical specific capacity of 847 mAh g<sup>-1</sup>, based on the full sodiation of Na<sub>15</sub>Sn<sub>4</sub>. However, the pure Sn anode has a severe problem of poor cycling properties, as it loses its initial capacity within the first 10 cycles [19,20]. It is believed that the rapid decay of capacity might be attributed to pulverization due to the volume change during sodiation/desodiation cycling [20]. The Sn anode material expands to 520% of its original volume during sodiation and contracts to its original volume during desodiation [21]. Several approaches have been investigated to overcome this problem. One approach involves embedding Sn into a soft matrix of carbon, which can physically accommodate the volume change [9,22–27]. Chen et al. achieved excellent cycling properties by embedding nanosized Sn in a carbon matrix and reported a capacity of 415 mAh g<sup>-1</sup> after 500 cycles [9]. Another approach involved decreasing the size of Sn to alleviate the strain from volume change. In this approach, Sn thin films had been used as the anode to solve the cycle life issue [20,28–35]. For example, a Sn-coated nanorod array was shown to achieve a reversible capacity of 405 mAh g<sup>-1</sup> after 150 cycles [20]. The adoption of cellulose from wood as a mechanical buffer for nanosized-Sn has resulted in long-term cycling over 400 cycles, but after the cycles, the capacity decreased to 145 mAh g<sup>-1</sup> [28]. Sn nanofilm adsorbed on Triton X-100 was very effective for improving the cycling property, showing a capacity of 776 mAh g<sup>-1</sup> after 100 cycles [35]. In the case of nanosized powder [19,21,36–39], a conventional electrode using Sn nanopowder, a conducting additive, and a binder showed poor cycling properties. Although the cycling properties of Sn anode could be improved using a conductive binder or polyacrylate binder in short-term cycling of 20 cycles [19,39], improved long-term cycle performance of a conventional electrode has not reported yet.

Previous studies indicate that the cycling properties of Sn electrode could be improved by the release or suppression of accumulated stress in a Sn sample due to volume change. In order to release stress of conventional electrode, the Sn electrode should have extra free space to accommodate volume expansion during sodiation and to prevent the detachment of Sn particles from the electrode to the electrolyte.

In this study, the phase-inversion technique was used to fabricate an electrode with a porous structure [40–44]. In particular, polyvinylidene fluoride (PVdF), which is a well-known binder material [45] as well as porous polymer electrolyte [41] prepared using the phase-inversion technique [43,44]. We prepared a porous Sn electrode with PVdF binder and investigated the electrochemical properties of the porous Sn anode for sodium batteries over 500 cycles.

## 2. Experimental

To prepare a Sn electrode, polyvinylidene fluoride (PVdF, average  $M_w \sim 534000$ , Sigma-Aldrich) was completely dissolved in 1-Methyl-2-pyrrolidinone solvent (NMP, anhydrous, 99.5%, Sigma-Aldrich). Subsequently, Sn nanopowder (<150 nm, Sigma-Aldrich) and acetylene black (AB, >99.9%, Alfa Aesar) were mixed in the PVdF solution with 70% Sn, 15% AB, and 15% PVdF by using a planetary ball mill for 3 h. The mixed slurry was pasted onto a copper current collector and dried in a vacuum oven to produce a normal Sn anode (hereafter referred to as NSn). A phase-inversed Sn anode was prepared by immersing the mixed slurry of NSn on copper foil into a nonsolvent binary mixture of 95% ethanol and 5% water before drying. This phase inversion process was performed for 5 min, causing the initial volatile solvent (NMP) to be replaced by the nonsolvent of ethanol and water, thereby producing a solid porous PVdF structure through precipitation because PVdF is insoluble in the nonsolvent. The phase-inversed Sn electrode (hereafter referred to as PSn) was then dried in a vacuum oven at room temperature over 2 days. The Sn electrodes were cut into a circle of diameter 1 cm. The final mass loading of Sn electrodes were 1–1.5 mg cm<sup>-2</sup>. The Na electrode was prepared by cutting out of bulk sodium metal into a circle of diameter 1 cm. The electrolyte was 1 M NaBF<sub>4</sub> salt (99.8%, Sigma-Aldrich) in tetra (ethylene glycol) dimethyl ether (TEGDME, 99%, Sigma-Aldrich).

The XRD patterns of the Sn electrodes were collected by X-ray diffractometry (XRD, D8 Advance, Bruker). The thermal stability of the Sn electrodes was evaluated with a differential scanning calorimeter (DSC, TA Instruments, Q20) at a heating rate of 5 °C min<sup>-1</sup> from 50 to 250 °C. The structure of the Sn electrode was characterized through field emission scanning electron microscopy (FESEM, Philips XL30S FEG) with cross-sectional images prepared using ion-beam polishing (JEOL IB-09020CP). The inner structures of the electrodes were observed by carefully cutting it and polishing its cross-section using a cross-section polisher. The density, pore volume, and porosity of electrodes were obtained by measuring the parameters of height, diameter, and weight. Details were explained in Supplementary Note 1.

The Sn anode (PSn or NSn), TEGDME electrolyte, a separator (Celgard 2400), and a Na counter electrode were assembled in a Swagelok-type cell. The electrochemical properties of Na/TEGDME/Sn cells were investigated using a galvanostatic test (WBSC, WonATech). The discharge–charge cycling was performed across a range of 0.001–1.0 V at 0.5 C-rate (1 C-rate = 847 mAh g<sup>-1</sup>). The rate capability was obtained by the galvanostatic test with sequential C-rate of 0.5 C–10 C.

## 3. Results and discussion

Based on the XRD and DSC results, it was confirmed that PSn and NSn were composed of raw materials without the formation of new compounds (Figs. S1–4). The shapes of PSn and NSn were compared by SEM. Fig. 1a shows the surface morphology and cross-sectional images of NSn and PSn. The surface of PSn shows small pores of a few micrometers in diameter without any cracking, while NSn has rather smooth and dense surface. The cross-sectional image of PSn showed more pores and a slightly rougher surface compared to that of NSn. NSn has a thickness of approximately 5.5 μm, and the thickness of PSn is nearly four times of this value. The PSn was circular electrode of 0.87 mg with 1 cm diameter, which is same shape as NSn. As the thickness of PSn increases, the density of the PSn decreases. PSn gained less density (0.55 g cm<sup>-3</sup>) than NSn (2.45 g cm<sup>-3</sup>). The pore volume of PSn was 1.35 × 10<sup>-3</sup> cm<sup>3</sup>, which was about eight times that of NSn. The physical properties of PSn and NSn were summarized in Table 1.

Download English Version:

<https://daneshyari.com/en/article/1286155>

Download Persian Version:

<https://daneshyari.com/article/1286155>

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