Journal of Power Sources 343 (2017) 513–519

Contents lists available at ScienceDirect

Journal of Power Sources

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

Origin of high Coulombic loss during sodiation in Na-Sn battery

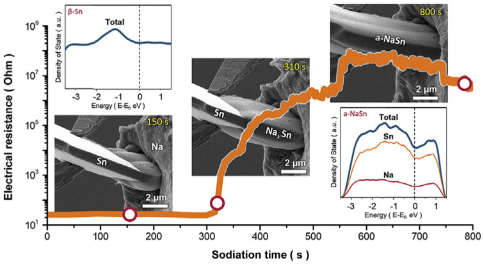
Young-Woon Byeon [a, b, 1], Yong-Seok Choi [a, 1], Jae-Pyoung Ahn [b, *], Jae-Chul Lee [a, *]

[a] Department of Materials Science and Engineering, Korea University, Seoul 02841, South Korea
[b] Advanced Analysis Center, Korea Institute of Science and Technology, Seoul 02792, South Korea

HIGHLIGHTS

- *In situ* sodiation experiment is performed to measure the resistivity of β-Sn.
- Sodiation increases the Sn anode resistivity by seven orders of magnitude.
- The increase in the resistivity is caused by the formation of the a-NaSn phase.
- Volume expansion during sodiation develops tensile residual stress.
- Tensile stress alters the band structure of a-NaSn, further increasing resistivity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 November 2016
Received in revised form
6 January 2017
Accepted 19 January 2017

Keywords:
Sodium-ion battery
Sodiation
Phase transition
Electrical resistivity
Ab initio calculation
Pseudogap

ABSTRACT

Electrochemical sodiation is performed in crystalline Sn foil using *in situ* scanning electron microscopy (SEM) to simultaneously measure the changes in the electrical resistivity and volume of the Sn anode in a Na-Sn battery. We observe that sodiation causes an increase in the Sn anode resistivity by six orders of magnitude. *Ab initio* molecular dynamics simulations of the Na-Sn alloy system demonstrate that the increased resistivity of the anode is caused by the formation of an electrically resistive amorphous NaSn phase (a-NaSn) with a pseudogap. It is also observed that the formation of a-NaSn is always accompanied by a large volume expansion of ~200%, causing the development of residual tensile stress. The residual stress in turn alters the electronic structure of the a-NaSn phase, further increasing the resistivity of a-NaSn and thus decreasing the energy efficiency of the Na-Sn battery.

1. Introduction

Sodium-ion batteries, with economic advantages and large energy storage capabilities [1–6], have recently attracted scientific attention as future alternatives to lithium-ion batteries. However, the larger Na^+ species, as compared to Li^+, requires anodic materials that can accommodate the volume expansion associated with sodiation, which is equivalent to electrical discharging. Among various group-14 elements, Sn is considered a potential candidate for the anode material because it shows a high theoretical capacity of 847 mA h/g [7,8]. However, the Na-Sn battery has two major drawbacks of poor cyclability and low Coulombic efficiency [8–10]. The poor cyclability of the Na-Sn battery is mainly caused by the pulverization of the Sn anode associated with the large volume

---

[*] Corresponding authors.
E-mail addresses: jpahn@kist.re.kr (J.-P. Ahn), jclee001@korea.ac.kr (J.-C. Lee).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jpowsour.2017.01.089
0378-7753/© 2017 Elsevier B.V. All rights reserved.

change during the repeated insertion–desertion of Na^+ [2,11]. Extensive studies to improve the cyclability of the Na-Sn battery are underway [12–14]. However, much remains uncertain regarding the low Coulombic efficiency of Na-Sn batteries, and thus, the problem requires analysis [5,15,16].

The Coulombic loss (also called the Faradaic loss) is a phenomenon that reduces the capacity of the battery during the repeated charge-discharge cycle. Any behaviors that impede charge transfer during the electrochemical reaction of a system cause increases in the Coulombic loss. Unlike the Li-Si battery system, the Na-Sn battery system experiences a series of phase transitions via electrochemical reactions [7,8,11]. Electrically resistive phases can form during this phase transition stage, thus increasing the electrical resistivity of the electrode [17]. Compared to the high Coulombic efficiency of 99% after 80 cycles in Li-Si batteries [18,19], the same property of the Na-Sn battery is only ~67% after the first cycle, probably because of the formation of electrically resistive Na_xSn phases and compounds during sodiation [15].

The first study on the measurement of the electrical resistivity of the Na_xSn phases was performed by Avci and Flynn [20]. They explored the electrical properties of amorphous Na_xSn phases prepared using the co-evaporation (or liquid quenching) technique on various compositions, observing a marked increase in the resistivity by two to three orders of magnitude as the amount of Na added to Sn was increased from 0 to 50% before a stress-free amorphous NaSn phase (a-NaSn phase) formed. This tendency was confirmed in the subsequent study [20,21]. These earlier studies indicate the high resistivity of the a-NaSn phase as a possible origin of the high Coulombic loss in Na-Sn batteries. However, these analyses were limited to the stress-free a-NaSn phase, and are not sufficient in explaining the origin of high Coulombic loss in the Na-Sn battery. This is because the measured resistivity of the a-NaSn phase during *in situ* sodiation experiments was much larger (by more than four orders of magnitude) than that of the stress-free a-NaSn phase prepared via quenching.

In the present study, we performed the *in situ* sodiation experiment inside a focused-ion beam (FIB) system to measure changes in both the electrical resistivity and volume of the sodiated Sn particles simultaneously. The result obtained from the *in situ* sodiation experiment was verified by measuring the current-voltage (I-V) characteristics for a pristine Sn crystal, the a-NaSn phase, and an a-NaSn/Sn bimetal. A series of experiments and simulation studies demonstrated that the electrically resistive a-NaSn phase, which caused the low Coulombic efficiency of Na-Sn batteries, was formed during sodiation. We also performed atomic simulations based on *ab initio* molecular dynamics (MD) to explain the high resistivity exhibited by a-NaSn formed during sodiation.

2. Experimental procedures

2.1. In situ sodiation experiments

In situ sodiation experiments on the electrochemically driven sodiation of Sn were performed using a solid-state half-cell battery assembled inside an airtight chamber equipped with FIB (Quanta 3D FEG, FEI) and a nano-manipulator (MM3A-EM, Kleindiek Nanotechnik). Lumps of pure Na (>99%) and a bulk β-Sn plate (>99%, ~125 μm in thickness) were used as the electrode materials. The β-Sn plate was machined to a ~1-μm-thin foil using a precision ion polishing system (PIPS Model 691, Gatan Inc.). The oxidation of all electrode materials was minimized by handling them inside a chamber filled with high-purity Ar (>99.999%) before placement in the FIB chamber using cryotransfer (ALTO 2500, Gatan Inc.). During the sodiation experiment, a lump of pure Na, used as the counter electrode, was transferred using the nano-manipulator with W tips (100 nm in diameter) and attached to the Sn foil anode to allow spontaneous sodiation.

2.2. Phase identification and electrical characterizations

The EDS line scanning was performed on the sodiated-Sn foil that has been oxidized intentionally prior to measurement. This oxidation was achieved by blowing a small amount of oxygen to the FIB chamber. The oxidation of the sodiated Sn foil not only interrupts the spontaneous Na diffusion (thus, phase evolution), but also prevents the sodiated Sn foil from desodiation under high current e-beam, which permits the phase identification using EDS. Energy dispersive X-ray spectroscopy analyses (EDS, SDD Sirius SD, EDAX Inc.) was then performed on the oxidized sodiated-Sn foil to measure the composition of all possible elements (Na, Sn, and O). The composition of the sodiated layer was identified by extracting the composition of O from the measurement. The lowest possible electric current and voltage were used to minimize charge accumulation and the associated electron-beam damage (i.e., desodiation) of the sodiated Sn during SEM observation and EDS analyses; they were ~26 pA at 5 keV and 3.9 nA at 5 keV for SEM and EDS, respectively.

Electrical characterizations of the Sn anode were conducted by measuring the change in the electrical resistance of the sodiated Sn during sodiation, while simultaneously observing the

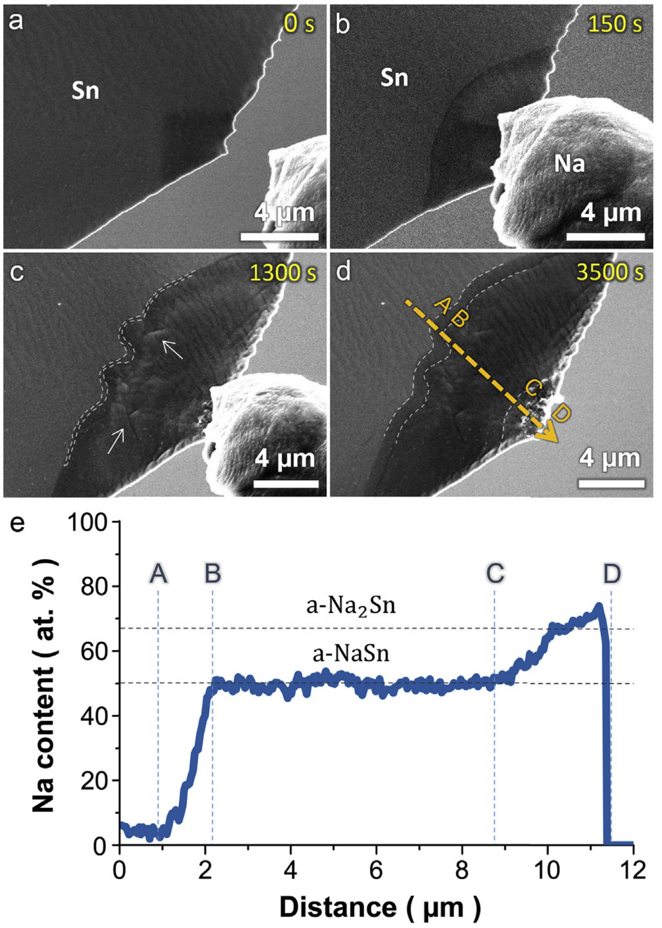


Fig. 1. A series of the snapshots captured from Supplementary Movie S1, showing the spontaneous and continuous insertion of Na in the pristine Sn foil at (a) 0, (b) 150, (c) 1300, and (d) 3500 s. (e) EDS line profile measured along the arrow denoted in (d), showing the changes in Na content with depth in the sodiated Sn foil.