



Short communication

## Electrochemical performance of a tin electrodeposit with a multi-layered structure for Li-ion batteries

RyoungHee Kim, DoHwan Nam, HyukSang Kwon\*

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 335 Gwahangno, Yuseong-gu, Daejeon, Republic of Korea

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## ABSTRACT

The electrochemical performance of a tin electrode synthesized on copper foil by electrodeposition in a pyrophosphate-based bath is examined by modifying its morphology via controlling the cathodic current density. As this current density increases, the morphology of the tin electrodeposit changes from a smooth and compact structure to a microscopically multi-layered structure with open spaces between adjacent layers. The porosity of the multi-layered tin electrode is more than 60% of its volume. The cycle performance and coulombic efficiency of the multi-layered tin electrode are higher than those of the smooth tin electrode, primarily due to the buffering effects of the open spaces between the layers against the volume expansion of the tin anode during cycling.

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### 1. Introduction

The demand for lithium-ion batteries is expected to increase markedly due to the expanding market for electric vehicles, hybrid electric vehicles and electronic mobile devices. The graphite currently used as the negative electrode (anode) material has a limited Li capacity of 372 mAh g<sup>-1</sup>. Many researchers have made efforts to develop alternative electrode materials to replace the conventionally used graphite. Tin has received much attention as a substitute for graphite in lithium-ion batteries given its high theoretical capacity (991 mAh g<sup>-1</sup>) [1,2]. On the other hand, pure tin anodes have exhibited poor cyclability due to crumbling under severe volume expansion (up to about 260%) during Li ion insertion [1]. The volume change causes cracking of the active tin material, such that each pulverized fragment subsequently becomes electrically isolated from the Cu current-collector, and therefore results in fading in the charge/discharge capacity. To overcome the problem, Sn–M alloys (M = Ni, Cu, Co, and so forth) [3–5] and tin-based composites [6,7] have been designed to provide a matrix phase buffering against the volume expansion of tin.

Synthesis of tin electrodes by electrodeposition is simpler than that by the conventional slurry process. For the tin-based electrodes prepared by electrodeposition, the effects of substrate morphology

[8] and buffering phase in Sn–Ni [3] or Sn–Cu [9] on the cycle performance have been studied. There are few studies on fabricating a porous tin anode for Li-ion batteries via a simple electrodeposition process.

The research objective of the present work is to develop a porous tin electrode with a multi-layered structure by electrodeposition, with emphasis on the effects of the porous structure on its cycling characteristics.

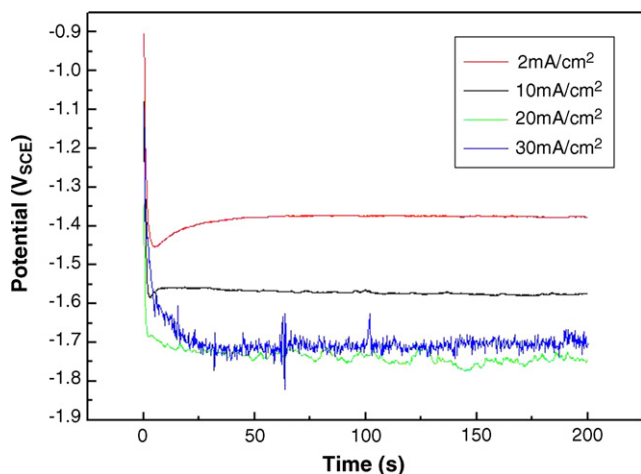
### 2. Experimental

#### 2.1. Preparation of tin electrodes

tin electrodes with a thickness of ~1 μm were synthesized on the shiny side of a Cu foil (18 μm thick) by electrodeposition in a pyrophosphate bath containing 30 g L<sup>-1</sup> Sn<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, 120 g L<sup>-1</sup> K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and 0.3 g L<sup>-1</sup> gelatin (pH 9.3). The Cu foil was cut into a 1 cm<sup>2</sup> disc, dipped in a 10 wt% H<sub>2</sub>SO<sub>4</sub> solution for 1 min to remove the air-formed oxide film on the surface of the Cu foil, and then used as a cathode. Galvanostatic electrodeposition was conducted in a standard three-electrode cell that consisted of a Cu foil cathode, a pure tin anode of 3 cm diameter as a counter electrode, and a saturated calomel electrode (SCE, 0.241 V vs. SHE) as a reference electrode. The cathodic current density was varied from –10 to –30 mA cm<sup>-2</sup> to modify the morphology of the tin electrodeposit. The applied net charge was fixed at 2.0 C cm<sup>-2</sup> to maintain an almost constant mass of the tin electrode in spite of the changing cathode current density.

\* Corresponding author. Tel.: +82 423503326; fax: +82 423503310.

E-mail address: [hskwon@kaist.ac.kr](mailto:hskwon@kaist.ac.kr) (H. Kwon).



**Fig. 1.** Effects of cathodic current density on galvanostatic potential-transient curve for electrodeposition of tin in pyrophosphate bath at room temperature.

The bath solution was stirred magnetically at about 500 rpm, and the solution temperature was kept at 25 °C throughout the deposition. The prepared electrodes were dried in a vacuum chamber for more than 10 h.

## 2.2. Charge–discharge test and structural analysis

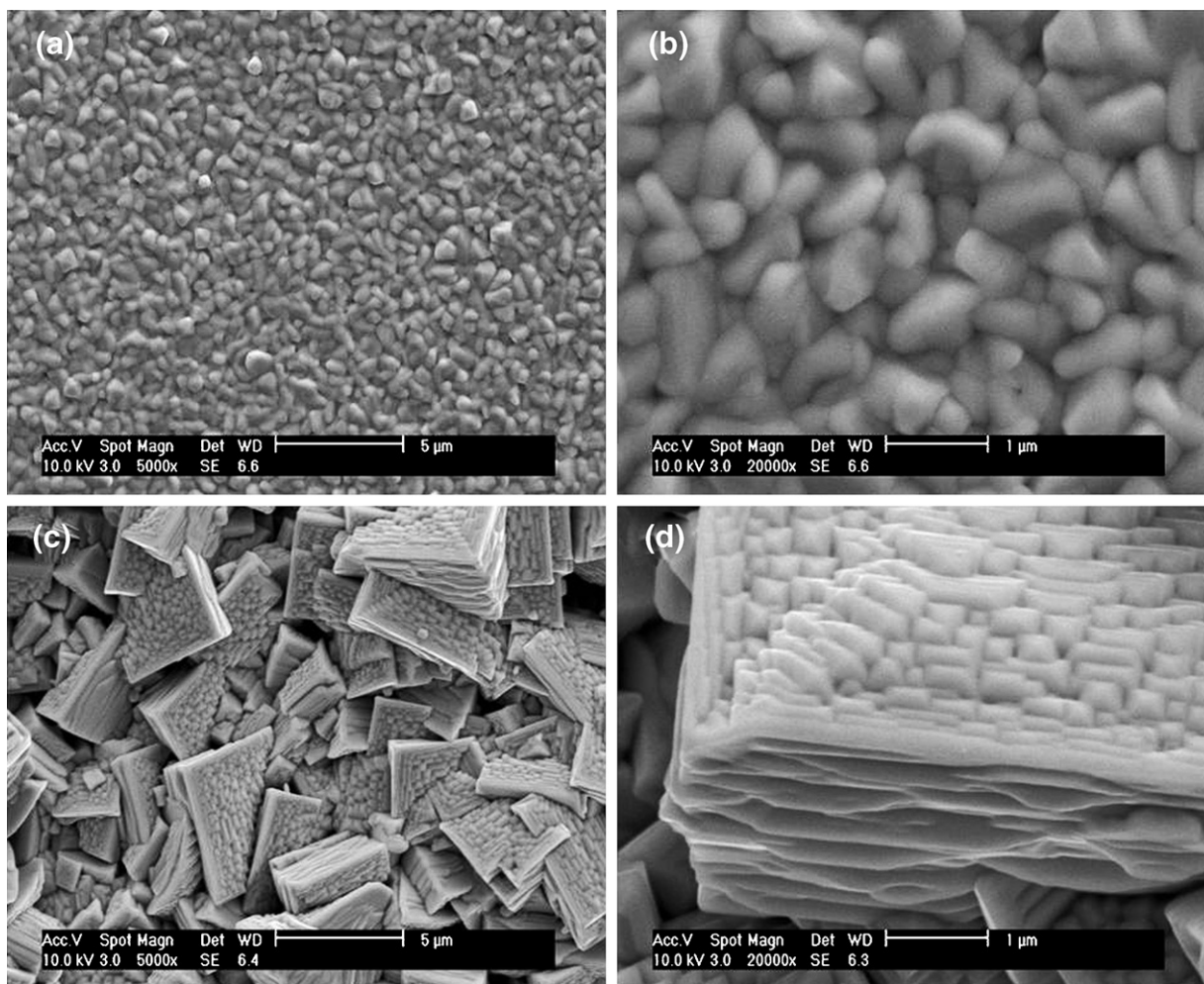
The Li/tin cells were assembled in the form of 2016 coin-type cells in an argon-filled glove-box. A 1 M LiPF<sub>6</sub> solution dissolved in EC:DMC (1:1 volume ratio) was used as the electrolyte. Lithium metal was used as the counter electrode, and a polypropylene separator was placed between the Li metal and the tin electrode. The charge–discharge characteristics of the tin electrodes were measured at a constant current density of 100 mA g<sup>-1</sup> between 0.02 and 1.0 V (vs. Li/Li<sup>+</sup>).

The crystal structure, surface morphology and porosity of the tin electrode were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and mercury porosimetry (Micromeritics, Autopore IV 9500), respectively.

## 3. Results and discussion

### 3.1. Effect of hydrogen evolution on morphology of tin electrodeposit

The effect of cathodic current density on the galvanostatic potential-transient curve measured during the electrodeposition of tin on the Cu foil is shown in Fig. 1. The electrode potential shifts in the active direction on the application of the cathodic current density, and then remains almost constant after 20–30 s, specifically in the range of –2 to –10 mA cm<sup>-2</sup>. This observation



**Fig. 2.** SEM images of tin electrodes electrodeposited at cathodic current densities of (a) and (b) –10 mA cm<sup>-2</sup> and (c) and (d) –30 mA cm<sup>-2</sup> in pyrophosphate bath at room temperature.

**Table 1**

Effects of cathodic current density on apparent density, skeletal density and calculated porosity of tin electrodeposit measured by mercury porosimeter.

	Smooth-type tin electrode	Multi-layered tin electrode
Bulk density ( $\text{g ml}^{-1}$ ) (=apparent density)	1.81323	2.56872
Skeletal density ( $\text{g ml}^{-1}$ ) (=sample weight/(sample volume – pore volume))	2.35793	6.51166
Porosity (%) (= $(1 - \text{bulk density/skeletal density}) \times 100$ )	23.1006	60.5519

suggests that tin electrodeposits with an almost uniform grain size are continuously formed on the substrate, and hence the surfaces of the electrodeposits are expected to be smooth. When the cathodic current density increases to  $-20 \text{ mA cm}^{-2}$ , the electrode potential fluctuates during the electrodeposition. The potential fluctuation or electrochemical noise at relatively high cathodic current density appears to be caused by the generation of gas bubbles on the cathode surface [10]. The gradual potential increase in the potential fluctuation is associated with bubble growth when the growth is controlled by gas molecule diffusion, whereas a steep potential decrease in the potential fluctuation is related to the detachment of bubbles from the surface of the electrode. It is evident from the  $E$ -pH diagram for water that hydrogen gas is generated vigorously at about  $-1.73 \text{ mV}_{\text{SCE}}$  in pH 9.3 solution [11]. On increasing the cathodic current density up to  $-30 \text{ mA cm}^{-2}$ , the frequency of the potential fluctuation increases. This implies that the electrodeposit formed at  $-30 \text{ mA cm}^{-2}$  is highly porous primarily due to the severe formation of hydrogen bubbles accompanying the electrodeposition of tin.

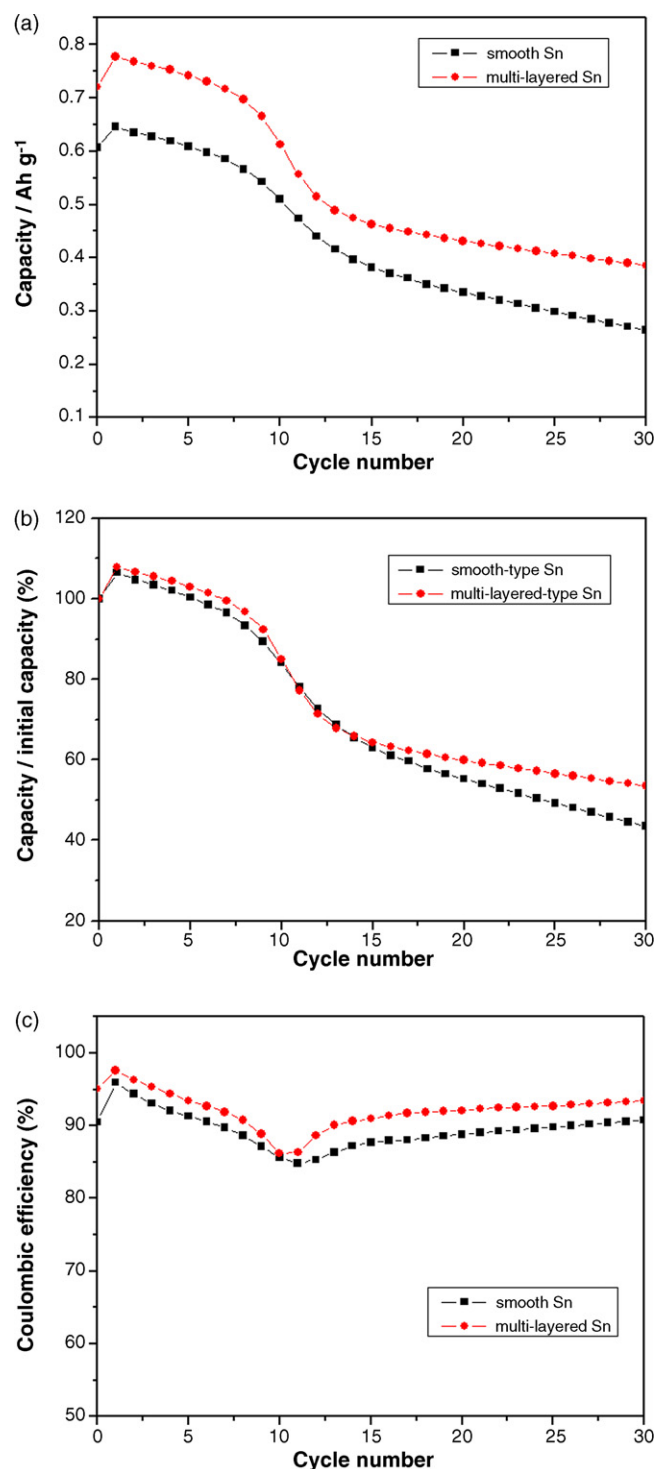
The surface morphology of tin electrodeposits formed at different cathodic current densities is given in Fig. 2. The morphology changes drastically from smooth grains at a low cathodic current density of  $-10 \text{ mA cm}^{-2}$ , as presented in Fig. 2(a), to a multi-layered structure with vacant spaces between layers at a high cathode current density of  $-30 \text{ mA cm}^{-2}$ , as presented in Fig. 2(c). Fig. 2(b) and (d) is the magnified SEM image given in Fig. 2(a) and (c), respectively. The hydrogen gas bubbles formed at a high cathodic current density act as dynamic templates and hence contribute to the formation of the multi-layered structure of the tin electrodeposit.

Although the electroplating of tin was performed under a constant charge of  $2.0 \text{ C cm}^{-2}$ , the thickness of the smooth-type tin electrode ( $\sim 1.3 \mu\text{m}$ ) is much thinner than that of the multi-layered-counterpart ( $\sim 2.2 \mu\text{m}$ ). On the other hand, the mass of the smooth-type tin electrodeposit ( $0.95 \text{ mg cm}^{-2}$  averaged over 10 electrodes) was greater than that of the multi-layered-form ( $0.72 \text{ mg cm}^{-2}$  averaged over 10 electrodes). The difference in the mass of the electrodeposit between the two electrodes is primarily due to the large difference in the cathodic efficiency between the two types of electrodes; the cathodic efficiency of the smooth-type tin is 77.24% and that of the multi-layered one is 55.71%. The poor cathodic efficiency of the multi-layered tin deposit results from the severe hydrogen evolution reaction that occurs during the electrodeposition of tin at  $-30 \text{ mA cm}^{-2}$ .

### 3.2. Porosity of tin electrode and its effect on buffering volume expansion

The porosity of the tin electrodes was measured by means of a mercury porosimeter. Since mercury is non-wetting for almost all materials, pores or vacant narrow spaces cannot be filled with

mercury without an adequate pressure. The bulk density of the tin electrode defined here was measured without applying pressure, and is therefore the density of the tin electrodeposit that contains empty spaces. By contrast, the skeletal density (measured under a sufficient pressure) is that of the tin electrodeposit excluding pores or narrow empty spaces. The bulk density, the skeletal density and the calculated porosity for the tin electrodes are listed in Table 1. It is significant that the porosity of the multi-layered tin electrode is three times greater than that of the smooth-type electrode.



**Fig. 3.** Effects of surface morphology on: (a) cycle performance, (b) percent of capacity vs. initial capacity, and (c) coulombic efficiency of tin electrode.

It is well known that the volume of the tin electrode expands by up to ~260% during charging with Li when tin fully reacts with Li to form the  $\text{Li}_{22}\text{Sn}_5$  phase [1]. It was reported recently, however, that the stable final phase at room temperature when tin particles discharge to 0.01 V is typically not  $\text{Li}_{22}\text{Sn}_5$ , but  $\text{Li}_7\text{Sn}_2$  [12]. When the tin electrode is fully charged with  $\text{Li}^+$  by transformation into  $\text{Li}_7\text{Sn}_2$ , its volume expands by about 200%. Assuming that the tin anode is in the form of a sphere, its diameter increases by a factor of 1.44 when the tin anode is fully charged with  $\text{Li}^+$ . This suggests that a tin anode with open spaces greater than 66% of its volume is able to buffer the volume change that may occur during charging with  $\text{Li}^+$ . Accordingly, it is expected that a multi-layered tin anode should buffer the volume expansion sufficiently during charging with Li and consequently exhibit better cycle performance than a smooth tin electrode.

### 3.3. Effect of open space on cycle performances

Fig. 3(a) compares the cycle performance of a tin electrode with smooth morphology with that of a multi-layered counterpart. It has been reported [13] that a thicker tin electrode is more easily pulverized during charge–discharge cycling. Although the multi-layered tin electrode is thicker than the smooth electrode, the initial charge capacity (in a half-cell) of the former electrode is much higher than that of the latter i.e.,  $757 \text{ mAh g}^{-1}$  vs.  $606 \text{ mAh g}^{-1}$ . At the 30th cycle, the charge capacity of the multi-layered electrode is  $412 \text{ mAh g}^{-1}$ , whereas that of the smooth electrode has decreased to  $264 \text{ mAh g}^{-1}$ . In addition, as presented in Fig. 3(b), the percent of capacity vs. initial capacity of the multi-layered tin electrode is higher than that of the smooth electrode after 30 cycles. It is evident in Fig. 3(c) that the coulombic efficiency of the multi-layered tin electrode is slightly higher than that of the smooth electrode over 30 cycles. The difference in the coulombic efficiency between the two electrodes increases after 11 cycles and thereby demonstrates that the degradation in the cycle performance of the multi-layered electrode with cycling is much less than that of the smooth electrode.

It appears that the improvement in the  $\text{Li}^+$  capacity and cycle performance of the multi-layered tin electrode is primarily due to the buffering effects of the open or narrow empty spaces against the volume expansion of the tin anode. Based on the above results, it is concluded that a free volume of more than 60% in the tin electrode acts as a buffering space during the charge–discharge reaction. In the smooth tin electrode, the initial tin grains expand during lithiation, and the initial structures are destroyed. By contrast, in the multi-layered tin electrode, the open spaces suppress the crum-

bling. After delithiation, some tin particles are electrically isolated in the smooth tin electrode; however, few tin particles are segregated in the multi-layered electrode. It is noteworthy that the two electrodes exhibit an abrupt decrease in capacity at about the 10th cycle. The abnormal phenomena appear to originate from the brittleness of the electrodeposited tin.

## 4. Conclusions

The charge–discharge performance of a tin electrode synthesized on Cu foil by electrodeposition in a pyrophosphate-based bath is examined by modifying its morphology through controlling the cathodic current density. A tin electrode with a relatively condensed structure and a smooth surface has been fabricated at a low current density of  $-10 \text{ mA cm}^{-2}$ . By contrast, the tin electrode formed at a high current density of  $-30 \text{ mA cm}^{-2}$  shows a multi-layered morphology that contains more than 60% open space between adjacent tin layers. The charge capacity and coulombic efficiency of the multi-layered tin electrode are both higher than those of a smooth tin electrode over 100 cycles. This is primarily due to the fact that the open or narrow empty spaces in the multi-layered tin electrode buffer the volume expansion of tin while it is being charged with  $\text{Li}^+$ .

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