

## Aggregation behavior of tin in tin oxides reacted with lithium

Goojin Jeong<sup>a</sup>, Chorong Shin<sup>a</sup>, Young-Jun Kim<sup>a,\*</sup>, Hyukjae Lee<sup>b</sup>, Hun-Joon Sohn<sup>c,\*\*</sup>

<sup>a</sup> Advanced Battery Research Center, Korea Electronics Technology Institute, Seongnam, Gyeonggi 463-816, South Korea

<sup>b</sup> Materials Research Center for Energy and Green Technology, Andong National University, Andong, Gyeongbuk 760-745, South Korea

<sup>c</sup> School of Materials Science and Engineering, Seoul National University, Seoul 151-744, South Korea

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### ABSTRACT

Tin aggregation behavior during charge/discharge of tin oxide electrodes is investigated using Li/Sn<sub>2</sub>BPO<sub>6</sub> and Li/SnO cells. Sn aggregation is identified by the peaks in the derivative capacity vs. voltage plot. Scanning electron microscope, transmission electron microscope, and Auger electron spectroscopy are used to investigate the formation and growth of Sn aggregates. Sn aggregation is more prominent when the upper cutoff voltage is higher than 1.0 V, and Sn aggregates continue to grow with cycling. The upper cutoff voltage is the most critical factor for Sn aggregation as it governs the size and growth rate of aggregates, whereas the effect of the lower cutoff voltage on Sn aggregation behavior seems relatively insignificant. Sn aggregation shows limited effect on cycling behavior of tin oxide electrode.

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### 1. Introduction

Graphitic carbon has been used for the negative electrode since the first commercial lithium-ion batteries from SONY in 1991. Recently, investigation on new electrode materials is conducting extensively as lithium-ion batteries have found new applications, and tin based material becomes one of the prominent candidates for negative electrode material [1–5]. Tin reacts with lithium to yield several Li–Sn alloys and theoretically 4.25 atoms of Li can be accommodated into a tin atom, giving the theoretical gravimetric capacity of 960 mAh g<sup>−1</sup> (volumetric capacity of ca. 2000 mAh cm<sup>−3</sup>), which is much higher than that of graphite. Nevertheless, the co-existence of Li–Sn intermetallic alloy phases during charge/discharge results in severe volume changes accompanying large mechanical strains, that lead to cracking as well as pulverization of electrode and quick capacity fade upon cycling [6].

Several tin based oxide materials have drawn interest as well since they have large theoretical capacity, e.g., SnO: 875 mAh g<sup>−1</sup>, and their lithia (Li<sub>2</sub>O) matrix, which is formed in the first discharge, can suppress the drastic volume changes during alloying/de-alloying reactions [7]. The basic reaction mechanism of SnO with Li is a two-step reaction [7–9]:



In the early stage of the first discharge, Li bonds to the oxygen from SnO irreversibly to produce Li<sub>2</sub>O and metallic Sn, and then, by further discharge, the metallic Sn reacts reversibly with Li to form Li–Sn alloys up to Li<sub>4.4</sub>Sn [8]. Sn based oxide electrodes have shown better cycling performance than metallic Sn electrode, although the capacity fade upon repeated cycles is still observed in Sn oxide electrodes. In their pioneering work on the lithium electrochemistry of Sn based oxides, Courtney and Dahn [10,11] claimed that Sn atoms aggregated in certain voltage range during cycling, and the co-existence between the Sn aggregates and Li–Sn alloy phases caused fracturing and eventual capacity fade upon cycling. These Sn aggregates were directly observed by transmission electron microscopes later [12–16]. As a part of the work toward a comprehensive understanding of lithium electrochemistry of tin based oxides, the Sn aggregation behavior in oxides has been revisited and the results from the investigation on SnO and Sn<sub>2</sub>BPO<sub>6</sub> are presented here. Since the overall Sn aggregation process was well documented in many previous studies [10,11,17,18], the present study focuses on the new findings which were not addressed in the past works.

### 2. Experimental

For SnO electrode, commercially available SnO powders (Junsei Chemical), which had thin plate-like morphology, were used without any further treatment. Sn<sub>2</sub>BPO<sub>6</sub> powders were prepared by the solid state reaction of SnO, B<sub>2</sub>O<sub>3</sub>, and P<sub>2</sub>O<sub>5</sub> (all from Sigma–Aldrich). After stoichiometric amounts of the starting powders were mixed, they were heat-treated at 1000 °C for 12 h on an alumina boat in an

\* Corresponding author. Tel.: +82 31 789 7490; fax: +82 31 789 7499.

\*\* Corresponding author.

E-mail address: [yjkim@keti.re.kr](mailto:yjkim@keti.re.kr) (Y.-J. Kim).

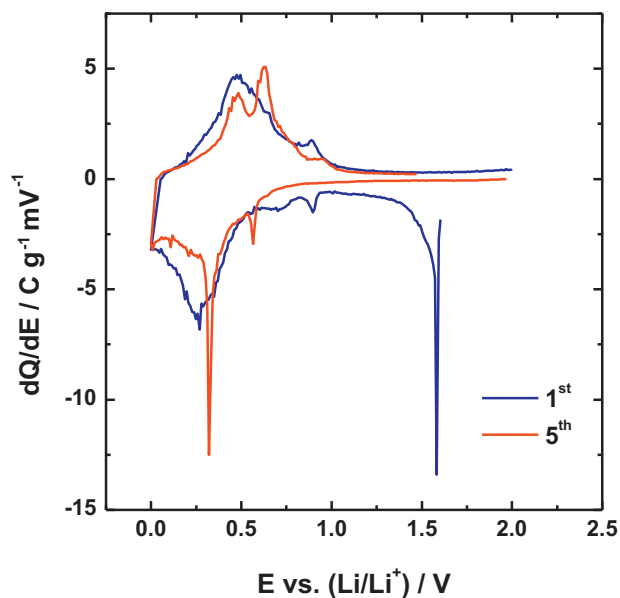


Fig. 1. Derivative capacity plots of Li/Sn<sub>2</sub>BPO<sub>6</sub> cell at the first and fifth cycles.

Ar-flowing tube furnace, and then cooled in air. Final product was yellowish semi-transparent glass.

For electrochemical tests, a working electrode was prepared by the following procedure. Firstly, an active material (85 wt.%) was mixed with 10 wt.% carbon black as conducting agent and 5 wt.% polyvinylidene fluoride (PVDF) as binder in *n*-methyl-2-pyrrolidinone (NMP) solvent. The slurry was coated on copper foil.

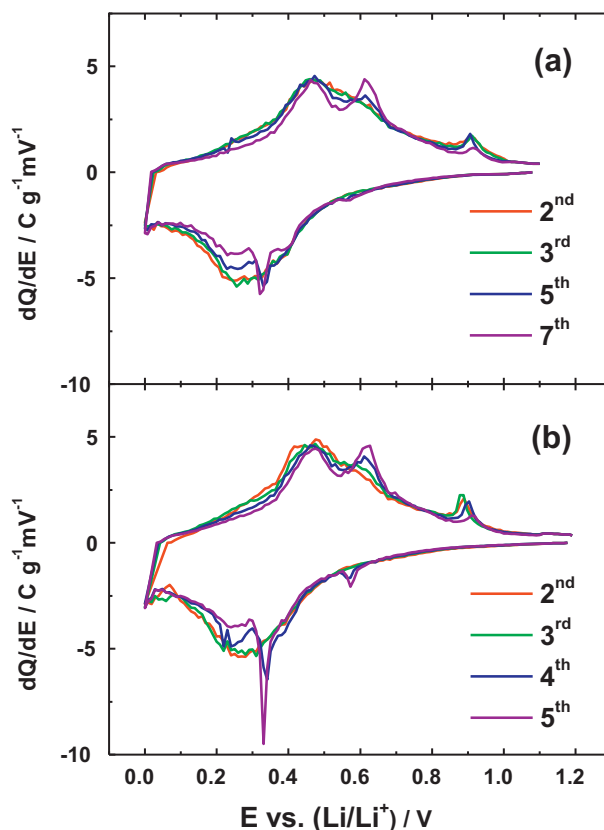


Fig. 3. Derivative capacity plots of Li/Sn<sub>2</sub>BPO<sub>6</sub> cell cycled between (a) 0.0 and 1.1 V, and (b) 0.0 and 1.2 V.

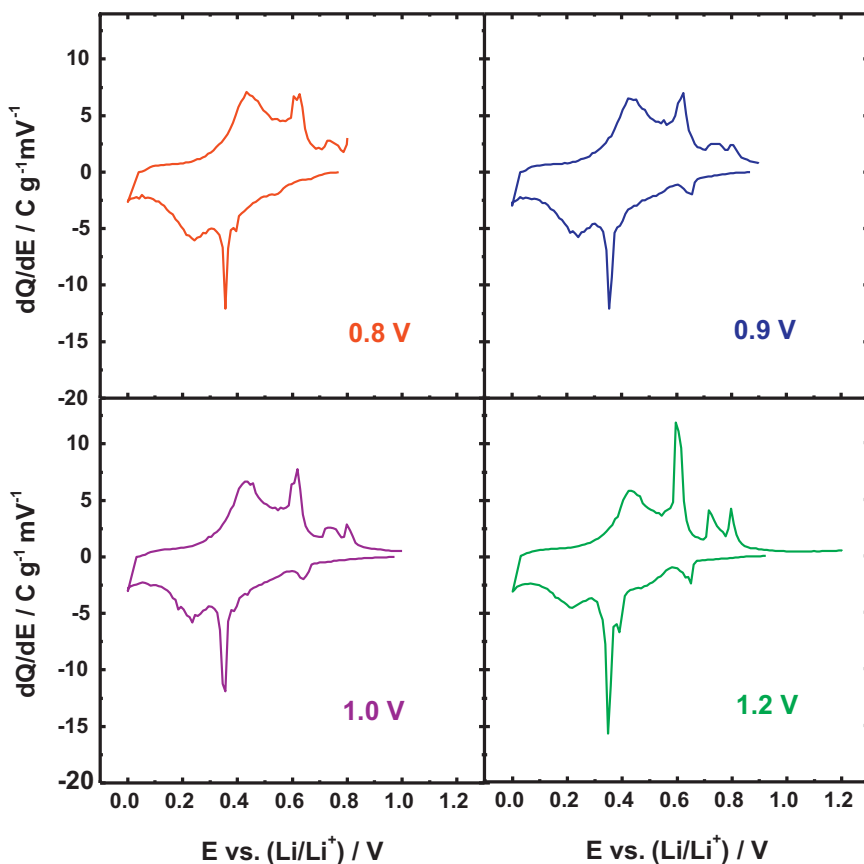


Fig. 2. Derivative capacity plots of Li/SnO cells with various upper cutoff voltages.

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