

RAPID COMMUNICATION

Unveiling origin of additional capacity of SnO₂ anode in lithium-ion batteries by realistic *ex situ* TEM analysis



Seung-Yong Lee, Kyu-Young Park, Won-Sik Kim, Sangmoon Yoon, Seong-Hyeon Hong, Kisuk Kang, Miyoung Kim*

Department of Materials Science and Engineering and Research Institute of Advanced Materials, Seoul National University, Seoul 151-744, Republic of Korea

Received 23 March 2015; received in revised form 14 October 2015; accepted 26 October 2015
Available online 5 November 2015

KEYWORDS

Lithium ion battery;
Anode material;
Tin oxide;
Transmission electron microscopy;
Electrochemical reaction mechanism

Abstract

The SnO₂ material has been considered as a promising lithium-ion battery anode candidate, and recently, the importance has been increased due to its high performance in sodium-ion batteries. Remarkably, the SnO₂ lithium-ion battery anode usually shows extra specific capacity that greatly exceeds the theoretical value. Partial reversibility of conversion reaction has been commonly considered to contribute the extra capacity, however, this has not clearly solved due to the indirect experimental evidences. Here, a realistic *ex situ* transmission electron microscopy (TEM) analysis technique was developed to reveal the origin of the extra capacity. We demonstrate that reactions of Li₂O phase contribute to the extra capacity and the reverse conversion reaction of SnO₂ hardly occurs in the real battery system. This work provides significant implications for establishing an accurate electrochemical reaction mechanism of SnO₂ lithium-ion battery anode, which may lead to inspiration on enhancing performance of the SnO₂ anode in lithium- and sodium-ion batteries as well. Furthermore, the robust *ex situ* TEM experimental approach we have introduced is extensively applicable to analyses of various battery electrode materials.

© 2015 Elsevier Ltd. All rights reserved.

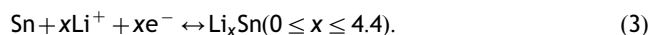
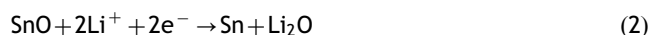
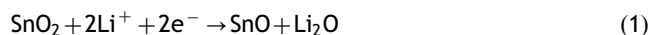
Introduction

Lithium ion rechargeable batteries having high energy densities are widely used for portable electronic devices, and they are still the subject of intensive investigation

*Corresponding author.

E-mail address: mkim@snu.ac.kr (M. Kim).

because of the possibility on a wide range of future applications. Tin oxide (SnO₂) has been studied as a promising alternative to the commercially used graphite anode material because of its much higher theoretical specific capacity, which arises from different electrochemical reactions [1-5]. Recently, it has attracted increasing interest again due to its high performance in sodium-ion batteries [6,7]. The reaction mechanism includes conversion and subsequent alloying reactions as follows:



This mechanism was first proposed in 1997 based on *in situ* X-ray diffraction (XRD) studies [8-10]. The SnO₂ material is first transformed into tin metal (Sn) and lithium oxide (Li₂O) (Eqs. (1) and (2)), and then the rechargeable battery operates by a reversible alloying reaction (Eq. (3)). The conversion reactions (Eqs. (1) and (2)) usually occur as a single step under experimental conditions. Although reactions 1 and 2 are believed to be irreversible and consume considerable amounts of lithium ions, this could be an advantageous situation; the resulting Li₂O could act as a mechanical buffer against significant volume changes during de/lithiation [11,12].

However, a few unresolved but important questions concerning the reaction mechanisms of SnO₂ anodes in the lithium-ion battery system remain. First, the issue of extra specific capacity that exceeds the theoretical value, commonly reported for metal oxide/lithium (MO/Li) batteries, also occurs in the SnO₂/Li battery [13-17]. Many studies have tried to explain this phenomenon in MO/Li batteries using various analytical techniques such as infrared spectroscopy [18], nuclear magnetic resonance (NMR) [19,20], X-ray photoelectron spectroscopy [18], mass spectroscopy [21], and theoretical calculations [22-24]. These experiments commonly ascribed the origin of extra capacity to electrolyte decomposition [19,24,25] and interfacial storage [22,23,26,27], however, it is still under debate. Recently, Hu et al. elucidated the origin of the additional capacity of the RuO₂/Li battery by *in situ* X-ray and NMR studies [19]. They showed that the additional capacities of transition metal oxide/lithium (TMO/Li) batteries derive from the reversible reaction between lithium hydroxide (LiOH) and Li₂O phases, which are initially formed by electrolyte decomposition and conversion reactions, respectively. However, TMO/Li batteries such as the RuO₂/Li cell operate by the reversible conversion reaction [13], whereas the SnO₂/Li battery operates by the reversible alloying reaction of (Eq. (3)).

Second, the partial reversibility of the conversion reactions (Eqs. ((1) and 2)) has long been a subject of interest. Previous studies mostly provided indirect evidences such as interpretations of cyclic voltammogram [28-31], Mössbauer spectroscopy [32-34], energy-dispersive X-ray spectroscopy (EDS) [2,35] and conductivity studies [36] to assert partial reversibility. Since it is known that Li-Sn alloys de-alloy below 1 V, reaction curve shown above 1 V is attributed to the additional reverse conversion reaction [28-31]. Furthermore, increased Sn-O bonding was observed by Mössbauer

spectroscopy [32-34], oxygen atoms were observed by EDS [2,35] and conductivity of the lithiated SnO₂ electrode was drastically decreased [36] during the delithiation process. Accordingly, the partially reversible reaction may primarily contribute to the extra capacity of the SnO₂/Li battery [3,15,17,37], provided that it is correct, but more direct and convincing evidence is required.

In this work, we studied the electrochemical reactions within the SnO₂ anode material to elucidate the origin of the extra capacity and the possibility of the reverse conversion reaction. Each major electrochemical reaction of the SnO₂/Li battery system was investigated by *ex situ* transmission electron microscopy (TEM). Using TEM for the structural and chemical analyses allowed the examination of distinctive features in each nano-area, which facilitated the detection of partial or localized reactions. The strategy applied for this work was to trace the same particles during the complete reaction cycle and to observe the phase evolution of the SnO₂ material during each electrochemical reaction stage. For the precise investigation, we developed an *ex situ* TEM characterization process to ensure that each electrochemical stage was the same as that occurring in a real battery cell. This approach is more realistic than conventional *in situ* TEM analysis in that it reflects the actual battery-operating environment. For instance, it uses the usual ethylene carbonate/dimethyl carbonate (EC/DMC) electrolyte instead of an ionic liquid electrolyte. Moreover, it analyzes the electrode materials dis/charged in the all-around-electrolyte-covering environment of the real system rather than one-side-electrolyte-contacting condition for the traditional *in situ* TEM analysis method. The phase evolution of the SnO₂ electrode was further compared with that of the Sn electrode in which only reversible alloying reaction (Eq. (3)) takes place, using the same experimental procedure to reach an accurate conclusion. In this way, we concluded that the reactions associated with the Li₂O phase generated the extra capacity of the SnO₂/Li battery. Additionally, there was no trace of the reversed SnO₂ phase at all. Few re-oxidized SnO phases were observed, however, which turned out to have negligible effect on the capacity.

Material and methods

Directly (dis)chargeable TEM grid electrode preparation

For *ex situ* TEM analysis of the various (dis)charged states of SnO₂ particles, commercial SnO₂ particles (Sigma-Aldrich) and a carbon-support-film-coated copper mesh TEM grid (Ted Pella) were used as an active material and a current collector. SnO₂ particles ground by a mortar and pestle were dispersed in methanol, sonicated, and dropped onto the TEM grid. The grid was air dried overnight before being studied by TEM. For *ex situ* TEM investigation of Sn electrode as a comparison group, commercial Sn particles (Sigma-Aldrich) were used as an active material. The preparation method was identical to that of the SnO₂ sample, except that the Sn particles were dispersed in anhydrous DMC, the entire process of which was performed in an argon-filled glove box to avoid oxidation of the material.

Download English Version:

<https://daneshyari.com/en/article/1557323>

Download Persian Version:

<https://daneshyari.com/article/1557323>

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