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Nanostructured $Sn/TiO_2/C$ composite as a high-performance anode for Li-ion batteries

Cheol-Min Park [a], Won-Seok Chang [a], Heechul Jung [a], Jae-Hun Kim [b], Hun-Joon Sohn [a,*]

[a] Department of Materials Science and Engineering, Research Center for Energy Conversion and Storage, Seoul National University, Seoul 151-742, Republic of Korea
[b] Chemical and Biosciences Center, National Renewable Energy Laboratory, Golden, Colorado 80401, USA

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ABSTRACT

A nanostructured $Sn/TiO_2/C$ composite was prepared from SnO, Ti, and carbon powders using a mechanochemical reduction method and evaluated as an anode material in rechargeable Li-ion batteries. The $Sn/TiO_2/C$ nanocomposite was composed of uniformly dispersed nanocrystalline Sn and rutile TiO_2 in amorphous carbon matrix. In addition, electrochemical Li insertion/extraction in rutile TiO_2 was examined by *ex situ* XRD and extended X-ray absorption fine structure. The $Sn/TiO_2/C$ nanocomposite exhibited excellent electrochemical performance, which highlights its potential as a new alternative anode material in Li-ion batteries.

1. Introduction

Currently, graphite (LiC_6: 372 mAh g^{-1}) is used as an anode material in lithium secondary batteries. However, higher-capacity alternatives are being actively pursued, particularly for anode materials. Among the many possible alternatives [1,2], a large number of studies have focused on nanostructured Sn-based composites because Sn has a high gravimetric ($Li_{4.4}Sn$: 990 mAh g^{-1}) and volumetric capacity (ca. 7000 mAh cm^{-3}) [3–8]. Although Sn-based systems have a higher energy density, they suffer from poor cycling behavior because a large volume change occurs during discharge/charge. Nanocomposite materials containing carbon have been considered as candidates for the anode material in lithium secondary batteries [7–12]. Among the many methods for preparing nanocomposite materials, mechanochemical reduction is quite interesting because the method provides well dispersed active and inactive nanocrystallites [13,14].

Nanostructured TiO_2 materials, such as anatase, rutile and brookite, have been studied widely as an anode material in Li-ion batteries [15–22]. Although, anatase TiO_2 is generally considered to be the most favorable TiO_2 material to react reversibly with Li, recent studies have shown that nanostructured rutile TiO_2 also reacts reversibly with Li [17–22].

In this study, a new nanostructured $Sn/TiO_2/C$ composite was prepared by mechanochemical reduction using SnO, Ti, and carbon via the following reaction Eq. (1):

$$2SnO + Ti \rightarrow 2Sn + TiO_2 \ (\Delta G^\circ = -385.593 \text{ kJ mol}^{-1},\ 298\ K) \quad (1)$$

where, ΔG° is the standard free energy.

Based on a concept of an active material (Sn)/active ceramic (TiO_2) along with an active and buffer matrix (Carbon) against volume expansion during cycling, the nanostructured $Sn/TiO_2/C$ composite material was tested as an anode material to enhance the electrochemical performance of alloy-based anode materials in Li rechargeable batteries.

2. Experimental

The $Sn/TiO_2/C$ nanocomposite was prepared as follows. SnO (Aldrich, >99%, 10 μm), Ti (Aldrich, 99.98%, −325 mesh), carbon (Timcal, Super P, −100 nm), and stainless steel balls (diameter: 3/8″ and 3/16″) were placed into a hardened steel vial with a capacity of 80 cm^3, and a ball-to-powder ratio of 20:1. The high energy mechanical milling (HEMM) process (Spex-8000) was carried out under an Ar atmosphere for 10 h. Preliminary studies showed that the optimum amounts of SnO + Ti and C were 60% and 40% by weight, respectively. In addition, the amount of amorphous TiO_2 in the $Sn/TiO_2/C$ nanocomposite estimated was ca. 15.1% by

* Corresponding author. Address: Department of Materials Science and Engineering, Research Center for Energy Conversion and Storage, Seoul National University, San 56-1, Sillim-Dong, Kwanak-Gu, Seoul 151-742, Republic of Korea. Tel.: +82 2 880 7226; fax: +82 2 885 9671.
E-mail address: hjsohn@snu.ac.kr (H.-J. Sohn).

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weight, and the wt.% of Sn:TiO_2:C were 44.9:15.1:40, respectively. Rutile TiO_2 was prepared from anatase TiO_2 (Aldrich, >99%, −325 mesh) using the same method reported above.

The Sn/TiO_2/C nanocomposite sample was characterized by X-ray diffraction (XRD, Rigaku, D-MAX2500-PC), X-ray photoelectron spectroscopy (XPS, Kratos, AXIS), and high-resolution transmission electron microscopy (HRTEM, JEOL 3000F operating at 300 kV). The Ti K-edge extended X-ray absorption fine structure (EXAFS) spectra of the TiO_2 powder was recorded at the BL3C1 (Electrochemistry) beamline in a storage ring of 2.5 GeV with a ring current of 120–170 mA, at the Pohang Light Source (PLS), Korea.

For the electrochemical evaluation, test electrodes consisting of the active powder material (70 wt.%), carbon black (Denka black, 15 wt.%) as the conductor, and polyvinylidene fluoride (PVDF) dissolved in *N*-methyl pyrrolidinone (NMP) as the binder (15 wt.%). Each component was mixed well to form a slurry, which was then coated on a copper foil substrate followed by pressing and drying at 120 °C for 4 h under a vacuum (electrode; thickness: ca. 0.045 mm, area: 0.79 cm^2, weight of active material: ca. 2.5 mg). Laboratory-made coin-type electrochemical cells were assembled in an Ar-filled glove box using Celgard 2400 as the separator, Li foil as the counter and reference electrodes, and 1 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume, Samsung) as the electrolyte. All the cells were tested galvanostatically between 0.0 V and 2.5 V (vs. Li/Li^+) at a current density of 10 mA g^{-1} or 100 mA g^{-1} using a Maccor automated tester. Li was inserted into the electrode during the discharge step, and Li was extracted from the working electrode during the charge step.

3. Results and discussion

Fig. 1a shows the XRD pattern of a Sn/TiO_2/C nanocomposite. In Fig. 1a, all the peaks of the Sn/TiO_2/C nanocomposite correspond to Sn with no other phases detected. Although the TiO_2 phase was not detected by XRD, XPS clearly showed the presence of TiO_2 (Ti; $2p_{1/2}$: 464.2 eV, $2p_{3/2}$: 458.4 eV), as shown in Fig. 1b.

TEM bright-field and HRTEM images combined with the Fourier transformed (FT) patterns show a dispersion of approximately 5 nm-sized Sn nanocrystallites and ~3 nm-sized rutile TiO_2 in the amorphous carbon matrix as presented in Fig. 1c and d, respectively. In addition, the STEM and EDS mapping images show that nanocrystalline Sn, and TiO_2 are dispersed uniformly within the amorphous carbon matrix, as shown in Fig. 1e.

Among the many polymorphs of TiO_2, rutile TiO_2 is thermodynamically the most stable phase, even though anatase be more stable at the nanometer size, as suggested by Hu et al. [18]. In a previous report, red phosphorus was transformed to its allotropic form of black phosphorus by HEMM [23]. The temperature during HEMM can increase to more than 200 °C and the pressure gener-

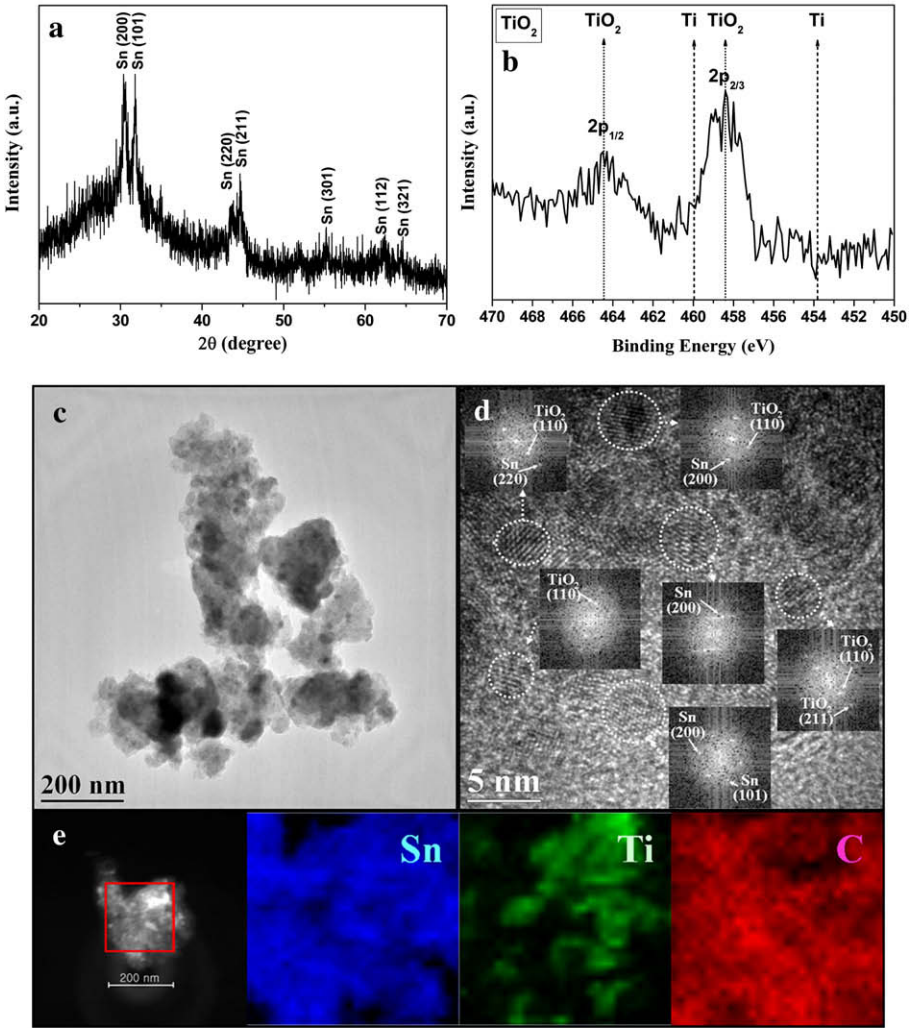

Fig. 1. Characterization of the Sn/TiO_2/C nanocomposite: (a) XRD patterns, (b) XPS result, (c) TEM bright field image, (d) HRTEM image with FT patterns, and (e) STEM and EDS mapping images.