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Microwave Synthesis and Electrochemical Properties of Ultrafine SnO_2 Nanoparticles

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Ultrafine SnO_2 nanoparticles were successfully synthesized by microwave heating. Transmission electron microscopy images revealed that the size of primary particles of the synthesized SnO_2 was around 5 nm. The SnO_2 nanoparticles worked as a rechargeable electrode material, and the initial lithium insertion capacity of the SnO_2 nanoparticles was 1670 mA h g^{-1} which is significantly larger than that of a specimen synthesized by conventional method.

Nanoparticles have the potential to deliver a step change in the performance of lithium-ion batteries (LIB).[1] SnO_2 is expected to be a substitute material for conventional graphite anodes because of high theoretical lithium storage capacity (1493 mA h g^{-1}). A number of studies regarding SnO_2 as well as Sn-based anode materials have been done over the past several years.[2–8] However, SnO_2 electrodes show poor cyclability because of disruption of the electric path because the reaction is accompanied by a drastic volume change.[2]

Generally, smaller particles and a more uniform distribution of the particles tend to show more moderate volume changes and a stable microstructure and thereby give improved performance, as shown in Figure 1.

Microwave chemistry has received great attention in recent years.[9,10] The greatest advantage of microwave irradiation is that it can heat a substance uniformly, leading to a more homogeneous nucleation and a shorter crystallization time compared with those for conventional heating. This is beneficial to the formation of uniform colloidal materials.

Microwave syntheses of SnO_2 have been reported since 2001.[11–15] Although microwave-synthesized SnO_2 has been applied as an active material for LIB, the capacity retention is still in problem.[15] The particle size is still too large for stable cycling.

Recently, we have succeeded in synthesis of ultrafine α-Fe_2O_3 nanoparticles by microwave heating.[16,17] The α-Fe_2O_3 nanoparticles with a narrow distribution were rapidly synthesized and showed significantly high electrochemical performance because of uniformity and size. In this study, ultrafine SnO_2 nanoparticles were synthesized in shorter times by microwave heating, and LIB performance was investigated.

A household microwave oven, modified by Shikoku Instrumentation Co., Ltd., was used to prepare the SnO_2 nanoparticles. One hundred cm^3 of 0.1 mol dm^{-3} $SnCl_4 \cdot 5H_2O$ solution was prepared and added to a round-bottom glass flask in the microwave cavity. The solution was heated by microwave irradiation (2.45 GHz, 1200W) for 5 min with stirring. The temperature of the solution was increased rapidly to 100 °C within 100 s, and the color of the solution changed from clear and colorless to white, as shown in Figure 2. The resulting suspension was washed with deionized water and then freeze-dried.

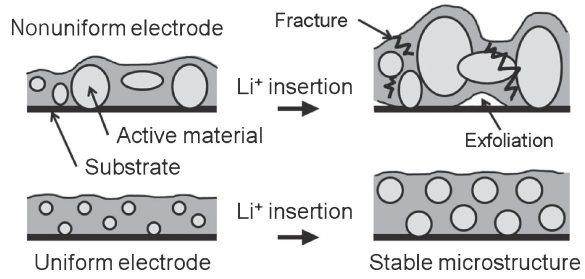

Figure 1. Conceptual diagram of lithium insertion of uniform or nonuniform electrodes.

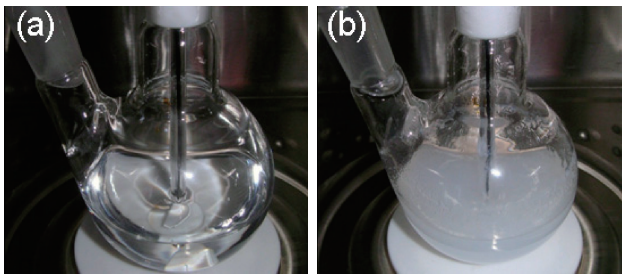

Figure 2. The color of the solution (a) before and (b) after microwave irradiation for 5 min.

Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2010 microscope at an accelerating voltage of 200 kV. Specimen for TEM analysis was prepared by placing a small drop of the sonicated solutions onto a microgrid supported on a Cu mesh. X-ray powder diffraction (XRD) data were collected on a Rigaku RINT-2550VHF diffractometer with Cu Kα radiation. Nitrogen adsorption–desorption isotherms were obtained on a BEL Japan BELSORP-mini II apparatus. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method.

Charge–discharge measurements were performed using charge–discharge equipment (Nagano Co., Ltd., BTS-2004W) at 25 ± 1 °C in a thermostatic chamber. The electrolyte was a 1 mol dm^{-3} solution of $LiPF_6$ in blended ethylene carbonate and diethyl carbonate at a volumetric ratio of 1:1. The counter electrode was Li foil. The working electrode consisted of active material, acetylene black, and poly(vinylidene fluoride) in a weight ratio of 6:3:1. The working electrode slurry-coated on Cu foil was dried at 80 °C in an argon-filled glove box (−95 °C dew point) before the fabrication of a test cell.

Figure 3 depicts TEM images of the synthesized SnO_2 particles. The TEM observations revealed that nanosized SnO_2 particles were successfully synthesized by the microwave heating. Most of the primary particles had ellipsoid shapes,

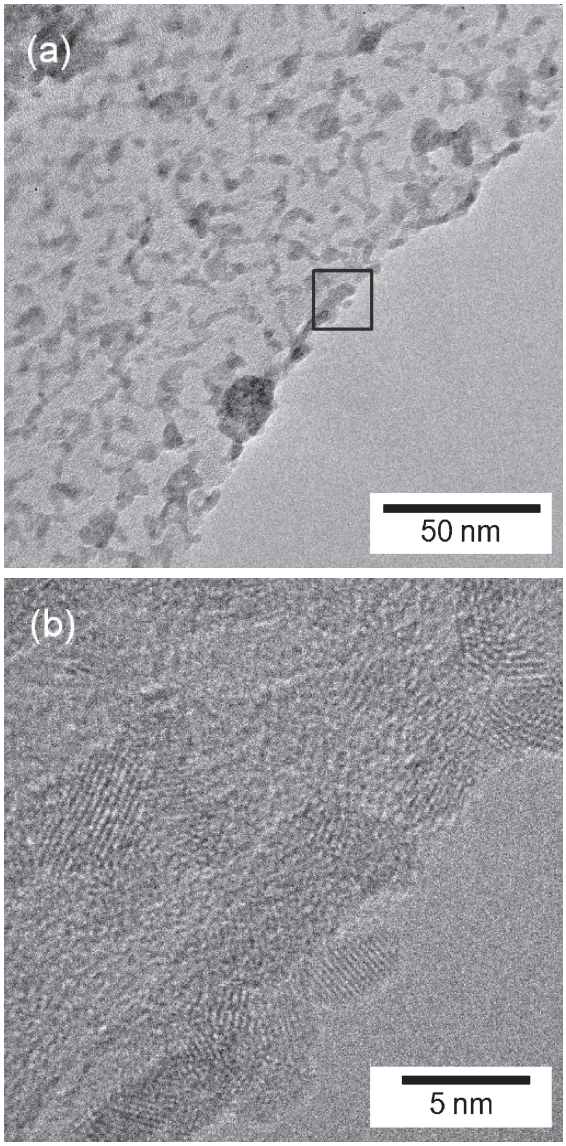

Figure 3. (a) TEM image of the microwave-synthesized SnO_2 nanoparticles on the edge of porous microgrid and (b) a magnified TEM image of the square-marked area in (a).

and their sizes were around 5 nm. Although these primary particles partly agglomerated, most particles were dispersive due to the freeze-drying. The nanoparticles were highly crystalline because the lattice images were clearly observed.

Figure 4a shows an XRD pattern of the SnO_2 nanoparticles synthesized by the microwave heating. The diffraction peaks for the nanoparticles were significantly broadened because of the small crystallite size. The XRD pattern was consistent with that of the rutile-type SnO_2.[18] SnO_2 nanoparticles could be obtained directly by the microwave heating without calcination, whereas the reaction process is not elucidated. The crystallite size of the nanoparticles was estimated to be about 3 nm from Scherrer's formula, which is in reasonable agreement with the TEM observations.

For comparison, a SnO_2 specimen was synthesized by the conventional method.[19] A hydroxide precursor was precipitated

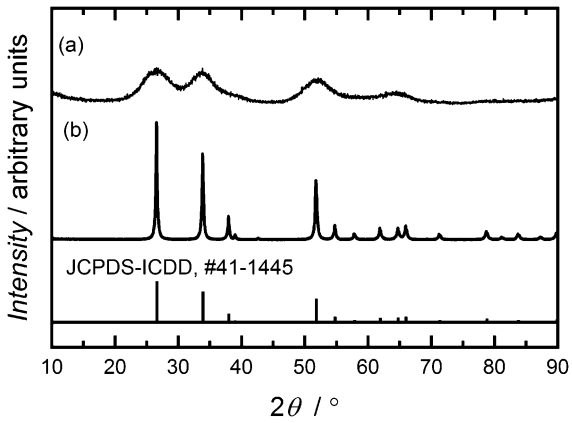

Figure 4. XRD patterns of the SnO_2 nanoparticles synthesized (a) by microwave heating and (b) by conventional method.

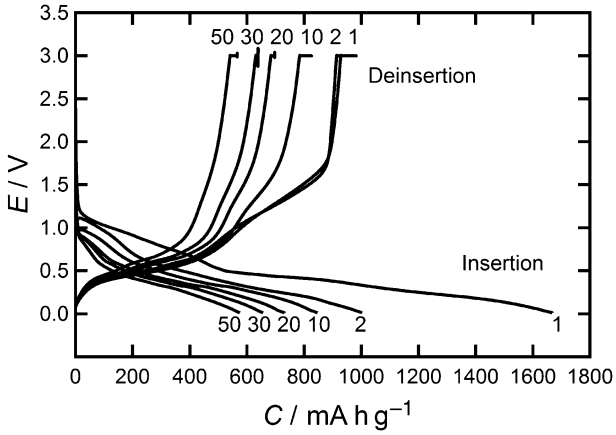

Figure 5. Lithium insertion–deinsertion curves of the SnO_2 nanoparticles synthesized by microwave heating.

by conventional heating using a magnetic hot-stirrer and then heated by an electric furnace at 600 °C for 3 h. As Figure 4b shows, the XRD pattern confirmed that a single-phase specimen of SnO_2 was obtained. The crystallite size was calculated to be about 40 nm by Scherrer's formula, which was about 10 times larger than that of the nanoparticles synthesized by microwave heating.

The BET surface areas, S_{BET}, were 175 $m^2 g^{-1}$ for the microwave-synthesized SnO_2 nanoparticles and 18 $m^2 g^{-1}$ for the SnO_2 specimen synthesized by the conventional method. Assuming spherical particles, the particle diameter, $d_{surface}$, was evaluated using the formula,

$$d_{surface} = 6000/(\rho \times S_{BET}) \quad (1)$$

where ρ is the theoretical density (7.0 g cm^{-3}).[18] The $d_{surface}$ were calculated to be about 5 nm for the microwave-synthesized nanoparticles and 48 nm for the specimen synthesized by the conventional method, which is consistent with those estimated from the XRD analyses.

Figure 5 presents lithium insertion–deinsertion curves of the SnO_2 nanoparticles over 50 cycles. The nanoparticles worked as a rechargeable electrode material. The initial capacity of 1670 mA h g^{-1} (cut-off voltage: 10 mV) was achieved. The

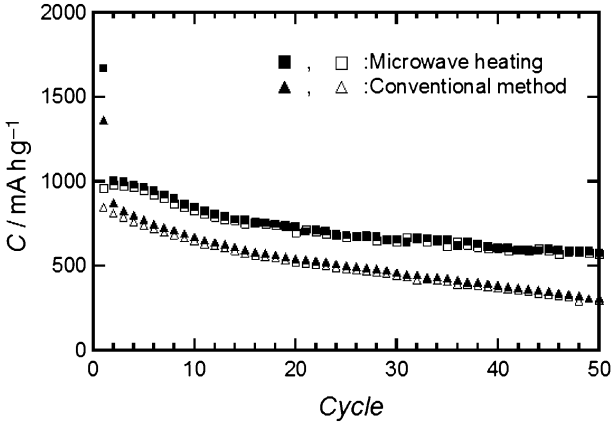

Figure 6. Cycling performance of the SnO_2 nanoparticles synthesized by microwave heating and by conventional method. The closed symbols show lithium insertion capacities, and the open symbols present lithium deinsertion capacities.

insertion capacity on the 2nd cycle was 1000 mA h g^{-1}, and thereafter the capacity gradually decreased with increasing of cycle numbers.

The SnO_2 specimen synthesized by the conventional method showed similar lithium insertion–deinsertion curves, whereas the capacities at each cycle were smaller than those of nanoparticles synthesized by microwave heating. The surface area of the SnO_2 nanoparticles is about 10 times larger than that of the SnO_2 specimen. The increment of initial capacity was not proportional to the surface area.

The initial insertion curve of SnO_2 electrodes can be characterized by two reactions:[2]

$$SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O \quad (2)$$

$$Sn + 4.4Li^+ + 4.4e^- \rightarrow Li_{4.4}Sn \quad (3)$$

SnO_2 is initially reduced to Sn metal, which is known as conversion reaction. Subsequently, alloying occurs up to the limit of lithium insertion. Thus, the total reaction can be described as

$$SnO_2 + 8.4Li^+ + 8.4e^- \rightarrow 2Li_2O + Li_{4.4}Sn \quad (4)$$

Our initial insertion curve is essentially characterized by the two reactions. The slope in the curve from 1 to 0.5 V associates with the conversion reaction, and the gently sloping curve below 0.5 V corresponds to the alloying reaction.

The theoretical capacity of eq 4 is calculated to be 1493 mA h g^{-1}.[2] The initial capacity of both SnO_2 specimens exceeded the theoretical capacity. This extra capacity has also been reported in other literature.[15] The extra capacity would be ascribed to the low-voltage decomposition of electrolyte and/or interfacial reaction due to charge separation at the metal/Li_2O phase boundary.[20,21]

Figure 6 shows cycling performance of the SnO_2 specimens synthesized by microwave heating and by the conventional method. The capacity retention of the microwave-heated specimen was about 60% from the 2nd to the 50th cycle, which is higher than the 35% of the conventionally heated specimen. The cycle performance of SnO_2 was clearly improved by the new technique.

Compared with other nanosized SnO_2,[6,7,15] our ultrafine SnO_2 nanoparticles showed significantly high electrochemical performance because of uniformity and smallness. This enhancement demonstrates the advantage of microwave heating.

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