Synthesis of monodispersed starburst carbon spheres / Tin oxide composite and their electrochemical properties

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Tin oxide has been investigated as a novel anode material for Li-ion batteries (LIBs), owing to its high theoretical reversible capacity (782 mAh/g), and moderate operating voltage. However, it is not so easy to apply SnO_2 anode to LIBs because of its low initial coulombic efficiency due to the irreversible reaction in the first cycle and poor material cycle stability arising from the large specific volume expansion (250 vol%) during the discharge/ charge processes.

We previously reported on the synthesis of highly monodispersed starburst carbon spheres (MSCS) [1], which can being synthesized by nanocasting method using mesoporous silica spheres (MMSS) [2, 3] as templates. MSCS are composed of carbon nanorods aligned radially with branching, because MMSS have radially aligned mesopores and particle size in submicronmeter size. MSCS have high pore volume (0.8-1.9 mL/g), high specific surface area (1000-2000 m^2/g) and nanospaces (1-4 nm) between carbon nanorods. Therefore, nanoparticles of metal oxides such as Tin oxide (SnO_2) can be uniformly confined in the nanospaces of MSCS in the MSCS/metal oxide composites [4]. Herein, we present the synthesis of MSCS/SnO_2 composite and their electrochemical properties, which overcome the above mentioned disadvantages of SnO_2 anode.

A 100 mg portion of MSCS, the pore size of which was 2 nm, was dispersed into the solution containing 250 mL of distilled water, 4 mL of conc. HCl, and 5.0 g of $SnCl_2$. This solution was stirred for 4 h at room temperature, followed by filtration and rinse with distilled water twice, and the MSCS/SnO_2 composite was obtained. Very broad peaks corresponding to SnO_2 were observed in the XRD pattern for the composite (Fig.1(a)). Nano crystals of SnO_2 dispersed into nanospaces of carbon were observed by TEM (Fig.1(b)). The SnO_2 content of the composite was estimated to be 63 wt% by a TG analysis. Pure SnO_2 with particle size of 22-41 nm, which was purchased from Wako Pure Chemical industries, was also used as an active material.

A slurry containing MSCS/SnO_2 composite (or pure SnO_2), Ketjen Black, and PVDF binder in a mass ratio of 95:5:20 dispersed in N-methylpyrrolidone was pasted on Cu foil, and dried overnight at 393 K in vacuo to prepare a working electrode. 1M $LiPF_6$ in ethylene carbonate, and dimethyl carbonate (1:1 v/v) and Li metal were used as electrolyte and counter electrode, respectively. The discharge/charge measurements were carried out at a current density of 100 mA/g. The specific capacity of the composite was calculated by using the total mass of SnO_2 and carbon.

Galvanostatic discharge/charge profiles and cycle performances of MSCS/SnO_2 composite and pure SnO_2 were shown in Fig. 2 and 3, respectively. MSCS/SnO_2 shows a high reversible capacity of 863 mAh/g after 40 cycles, while the capacity of pure SnO_2 decreases rapidly. The confinement in the nanospace of MSCS would prevent SnO_2 from pulverization. A practical capacity of SnO_2 in the composite was estimated to be 1000 mAh/g with consideration of the mass of MSCS and Ketjen Black. The value is higher than the theoretical capacity of 782 mAh/g, which is calculated with the following reaction (1).

$$Sn + x\,Li^+ + xe^- \leftrightarrow Li_xSn \quad (x \leq 4.4) \qquad (1)$$

The conversion reaction (2) would also contribute to the high capacity of MSCS/SnO_2 composite.

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

Furthermore, the effect of some factors such as particle size of the composite, SnO_2 content, crystallization of SnO_2 will be investigated.

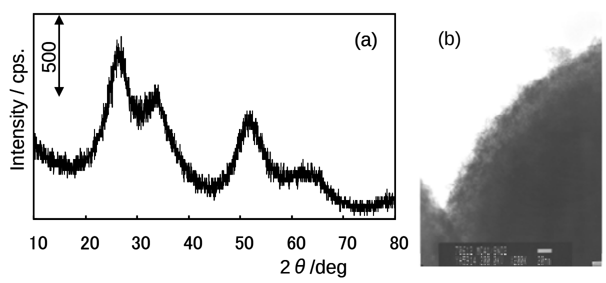

Figure 1. (a) XRD pattern for MSCS/SnO_2 composite. (b) TEM image for the composite.

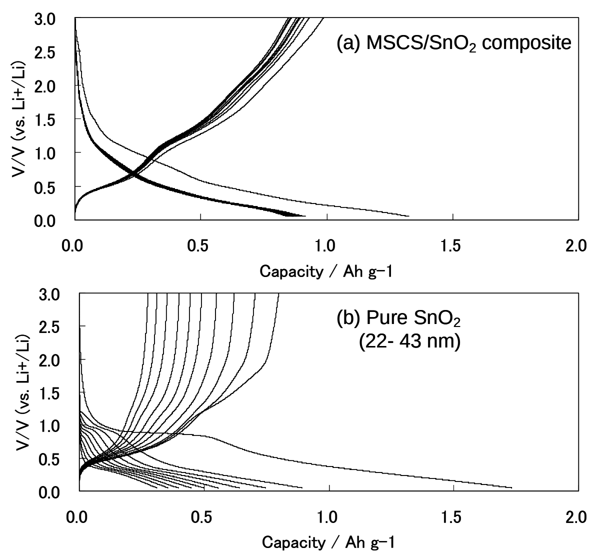

Figure 2. Galvanostatic discharge/charge profiles.

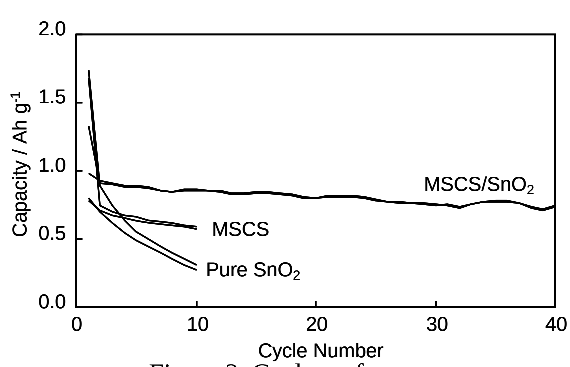

Figure 3. Cycle performances.

Reference

1. K.Yano, Y.Fukushima, *J. Mater. Chem.* **2004**, 14, 1579.
2. T.Nakamura, Y.Yamada, K.Yano, *Chem. Lett.* **2006**, 35, 1436.
3. N.Tatsuda, K.Yano, *Carbon* **2013**, 51, 27.
4. N.Tatsuda, T.Nakamura, K.Yano, *Chem. Mater.* **2009**, 21, 5252.