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 SnO₂ 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 submicrometer size. MSCS have high pore volume (0.8-1.9 mL/g), high specific surface area (1000-2000 m²/g) and nanospaces (1-4 nm) between carbon nanorods. Therefore, nanoparticles of metal oxides such as Tin oxide (SnO₂) can be uniformly confined in the nanospaces of MSCS in the MSCS/metal oxide composites [4]. Herein, we present the synthesis of MSCS/SnO₂ composite and their electrochemical properties, which overcome the above mentioned disadvantages of SnO₂ 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 SnCl₄. This solution was stirred for 4 h at room temperature, followed by filtration and rinse with distilled water twice, and the MSCS/SnO₂ composite was obtained. Very broad peaks corresponding to SnO₂ were observed in the XRD pattern for the composite (Fig. 1(a)). Nano crystals of SnO₂ dispersed into nanospaces of carbon were observed by TEM (Fig.1(b)). The SnO₂ content of the composite was estimated to be 63 wt% by a TG analysis. Pure SnO₂ with particle size of 22-43 nm, which was purchased from Wako Pure Chemical industries, was also used as an active material.

A slurry containing MSCS/SnO₂ composite (or pure SnO₂), Ketjen Black, and PVDF binder in a mass ratio of 95:5:20 dispersed in N-methylpyrrolidione was pasted on Cu foil, and dried overnight at 393 K in vacuo to prepare a working electrode. 1M LiPF₆ 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 SnO₂ and carbon.

Galvanostatic discharge/charge profiles and cycle performances of MSCS/SnO₂ composite and pure SnO₂ were shown in Fig. 2 and 3, respectively. MSCS/SnO₂ shows a high reversible capacity of 863 mAh/g after 40 cycles, while the capacity of pure SnO₂ decreases rapidly. The confinement in the nanospace of MSCS would prevent SnO₂ from pulverization. A practical capacity of SnO₂ 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).

\[
\text{Sn} + x \text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Sn} \quad (\text{x}=4.4) \quad (1)
\]

The conversion reaction (2) would also contribute to the high capacity of MSCS/SnO₂ composite.

\[
\text{SnO}_2 + 4\text{Li}^+ + 4e^- \rightarrow \text{Sn} + 2\text{Li}_2\text{O} \quad (2)
\]

Furthermore, the effect of some factors such as particle size of the composite, SnO₂ content, crystallization of SnO₂ will be investigated.

References