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Electrochemically Synthesized Sn-O-C Composite with Nano Core/Shell Structure for Anode of Lithium Secondary Batteries

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Introduction

A Sn-based material shows much higher theoretical capacity ($Li_{4.4}Sn$, 994 mAh g^{-1}) than that of graphite anode. Nevertheless, commercial use of Sn-based anode material is restricted by severe capacity fading during electrochemical cycling. The massive volume change of Sn, which is caused by Li-Sn intermetallic phase, undergone during cycling leads to cracks and pulverization of active material from current collector; consequently, the poor capacity retention results. To overcome the severe problems, nanostructured active materials with Sn-based composite which show improved capacity retention compared to metallic Sn anode have been investigated.[1,2]

In our previous work, we reported electrochemical synthesis of Sn-O-C composite and the analysis of its electrodeposition mechanism. The Sn-O-C composite anode was successfully prepared via consecutive potential step deposition including different stages for reduction of Sn^{2+} ion, decomposition of organic carbonate electrolyte and co-deposition of Sn^{2+} and Li^+ ions.[3]

Herein, we prepared Sn-O-C composite by electrodeposition in organic carbonate solution. In order to control the structure of the deposited particle in the composite, agitation conndition during the electrodeposition was controlled.

Experimental

The electrolytic bath was prepared as reported at the previous work. In briefly, 2.5 mM $SnCl_2$ was dissolved in mixture of EC : PC (1:1 v/v) containing 1 M $LiClO_4$, used as a supporting electrolyte. The three different potential steps including 2.2, 1.5 and 0.3 V vs Li/Li^+ were consecutively applied under agitation condition for electrodeposition of Sn-O-C composite. The crystalline phases of the deposits were investigated by GIXRD and HR-TEM. Galvanostatical charge/discharge test was performed by means of three-electrode system. A lithium foil was used as counter and reference electrode. 1.0 mol L^{-1} $LiClO_4$ in EC : PC (1 : 1 v/v) mixture was used electrolyte. The charge/discharge test was performed between 0.01 and 1.5 V vs Li/Li^+ with current density of 20 µA cm^{-1}.

Results and discussion

As shown in Fig. 1, GIXRD pattern, SAED patterns and HR-TEM image were investigated showing that the core structure consists of crystalline β-Sn. From STEM images and XPS results, it is assumed that the shell structure is the decomposition product of organic carbonate electrolyte. It is assumed that the preparation of core/shell structure is related to influence of agitation condition causing increase in diffusion controlled growth rate. Consequently, the smaller size of particles are deposited which makes the decomposition products of the organic carbonate electrolyte homogeneously coated on the surface of Sn deposit. The charge/discharge test obtained discharge capacity of 612.3 mAh g^{-1} at 40th cycles. The stable coulombic efficiency, *i.e.*, higher than 95 %, was also achieved except for several initial cycles (Fig. 2). There was no decrease in discharge capacity of 0.1 C to 1 C; meanwhile, decrease in 17 % at 5 C was obtained. The core/shell structure of Sn-O-C composite anode presumably influences on the enhanced cycle performances by acting as a buffer layer to endure volume expansion.

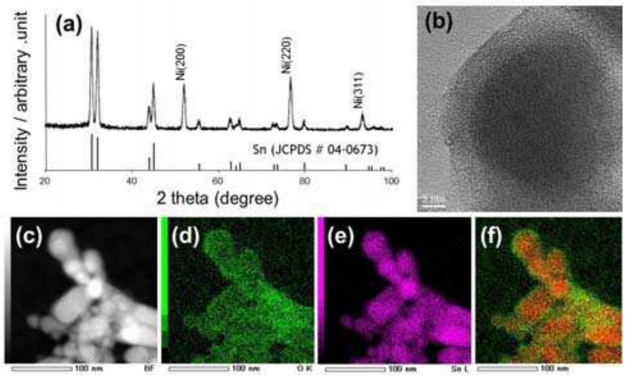

Figure 1. GIXRD pattern (a), HR-TEM image (b), STEM images (c), element mapping of O (d), Sn (e), composite of O and Sn (f) of electrochemically synthesized Sn-O-C composite.

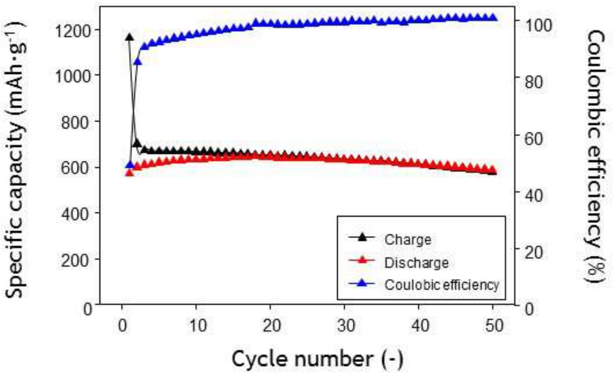

Figure 2. Specific capacity and coulombic efficiency of Sn-O-C composite anode with nano core/shell structure.

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