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Sn–O–C composite anode for Li secondary battery synthesized by an electrodeposition technique using organic carbonate electrolyte

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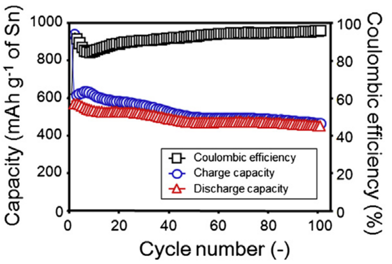
HIGHLIGHTS

- Sn–O–C composite material was electrochemically synthesized in organic electrolyte.
- Simultaneous reductions of $SnCl_2$ and electrolyte solution resulted in a Sn–O–C.
- Crystalline structure of Sn in Sn–O–C was characterized.
- Sn–O–C was revealed to have long cycling life as an anode of Li secondary battery.

GRAPHICAL ABSTRACT



Sn-O-C composite material was successfully synthesized by the electrochemical reductions of $SnCl_2$ and electrolyte solution in organic electrolyte. Crystalline structure of Sn in the deposit was characterized and the charge-discharge cycling performance as an anode of Li secondary battery was investigated.

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ABSTRACT

The Sn–O–C composite anode for the Li secondary battery was synthesized by electrodeposition using an organic carbonate solvent. The composite of Sn with organic/inorganic compounds was prepared by the simultaneous reaction of the reduction of Sn^{2+} ions and electrolysis of the mixture of ethylene carbonate and propylene carbonate. The galvanostatic potential transients for the electrodeposition of the Sn–O–C composite indicate that multiple steps of reactions corresponding to the electrochemical reduction of the tin precursor and the decomposition of organic solvents are involved. The morphology, crystalline structure and chemical composition of the as-deposited Sn–O–C composite anode were characterized to elucidate the mechanism of the synthesis of the buffering matrix enduring volume expansion.

The electrochemical behavior of the Sn–O–C composite anode was investigated by cyclic voltammetry and galvanostatical charge/discharged tests. The discharge capacity of 465 mAh (g of Sn)$^{-1}$ was obtained at the 100th cycle showing 80% of the capacity retention after the 100th cycle. The discharge capacity was stable after the 50th cycle, where the phase transformation of the Sn element from Sn to $Li_{0.4}Sn$ at the discharged state was found.

1. Introduction

Tin has been proposed as a promising element to be incorporated in the anode material ($Li_{4.4}Sn$, 994 mAh (g of Sn)$^{-1}$) for lithium secondary batteries instead of the commercial graphite anode (LiC_6, 372 mAh (g of C)$^{-1}$) to materialize an increased charge capacity of the lithium secondary battery. However, a pure tin anode suffers from a poor cycle life because of the occurrence of severe mechanical cracks and pulverization caused by significant volume expansion (~300%) during the lithiation/delithiation process [1–3]. To overcome this serious problem, various attempts, such as the use of nanostructured Sn active material [4–6], embedded matrix buffer [7–10], core–shell structure [11–13], and mesoporous structure [14–16] have been reported.

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Recently, many studies on Sn anodes prepared by electrodeposition techniques using aqueous solvents have been reported. The electrodeposition technique allows direct deposition of the active material onto conducting substrates; consequently, the electrodeposited anode can stand alone without employing a polymer binder. The co-deposition of Sn and nonactive inter-metallic compounds has been reported [17–22]. Furthermore, tin-based materials with carbon coating [23] or a 3D core–shell structure [24] have been prepared by an electrodeposition technique as well. Meanwhile, Sn-based anodes have been synthesized on porous Cu foam showing better cyclic performance and higher charge capacity than those deposited on a smooth Cu foil [25].

We previously investigated the electrodeposition of the Si–O–C composite anode by reducing $SiCl_4$ dissolved in polyethylene carbonate electrolyte [17,18]. The Si–O–C composite anode achieved remarkable cycling performance with outstanding durability and a high capacity of 1045 mA g^{-1} even at the 2000th charge–discharge cycle. The novel synthetic method by electrodeposition using an organic solvent makes it possible to take advantage of (i) the unnecessary nature of the polymer binder, (ii) the formation of a matrix whose chemical composition is similar to the solid electrolyte interphase (SEI) layer with permeability to Li^+ but not to electrons. The decomposition of the organic solution and the reduction of $SiCl_4$ simultaneously occurred. Consequently, the composite of Si with organic/inorganic compounds has been synthesized, which is assumed to effectively withstand the severe volume expansion.

In this study we electrodeposited an Sn–O–C composite anode using an organic solution to take advantage of the novel synthetic method examined in our previous work. It is expected that the Sn–O–C composite anode formed by the deposition of tin and the decomposition of organic solvents realizes the formation of organic/inorganic compounds, which reduces mechanical stress during the lithiation/delithiation process. In this work, we have thoroughly examined the characteristics of the electrodeposited Sn–O–C composite anode, the electrodeposition process using a new type electrolytic bath for Sn-based material, and its electrochemical performances as an anode for Li secondary batteries.

2. Experiment

The Sn–O–C composite was electrodeposited on a Ni plate substrate by a constant current deposition technique using an organic carbonate electrolytic bath. The electrolytic bath was prepared by dissolving 2.5 mmol dm^{-3} of $SnCl_2$ (Sigma–Aldrich) in an ethylene carbonate (EC): propylene carbonate (PC) (1:1 v/v) electrolyte solution (Kishida, H_2O content < 20 ppm) containing 1.0 mol dm^{-3} of $LiClO_4$ which serves as a supporting electrolyte. Ni plate substrates with dimensions of 10 $\times$ 10 mm used as the working electrodes were treated in trichloroethylene and ethanol followed by an acid treatment with 10% HCl before use. A tin plate and lithium metal in glass with a Vycor chip junction served as the counter and reference electrodes, respectively. The electrodeposition cell was prepared in a glove box filled with an Ar at the dew point of below -90 °C to avoid contact with air and moisture in the atmosphere. A constant cathodic current of 37.5 μA cm^{-2} was applied to pass a charge of 0.25 C cm^{-2} for the deposition. Field emission scanning electron microscopy (FE-SEM, Hitachi S-4500S) and scanning electron microscopy (SEM, Hitachi TM-3000) equipped with an energy dispersive X-ray spectroscopy (EDS) were performed to analyze morphologies and the chemical composition of the prepared Sn–O–C composite. X-ray diffraction (XRD) was carried out by Rigaku Rint-Ultima III equipped with Cu Kα ($\lambda = 0.1541$ nm) radiation operated at 50 kV and 300 mA. The scanning range (2θ) was from 25° to 80° and the scanning speed was 3° min^{-1} using a step width of 0.02°. The electrodeposited Sn–O–C composite anode was characterized by high-resolution transmission electron microscopy (HR-TEM, H-9000UHR, Hitachi) with an accelerating voltage of 300 kV. The TEM specimens were prepared by a focused ion beam (FIB, Hitachi, FB-2000A) technique. The element depth profile was analyzed by glow discharge optical emission spectrometry (GDOES, HORIBA, JY-5000RF) with Ar sputtering in an area of 2 mm diameter. The electrochemical measurements of the prepared Sn–O–C composite anodes have been evaluated with the charge/discharge unit (Hokuto Denko HJ-1010M) using lithium half-cells fabricated with Li foils, served as a counter and reference electrode, immersed in an EC:PC (1:1 v/v) electrolyte solution (Kishida, H_2O content < 20 ppm) containing 1.0 mol dm^{-3} of $LiClO_4$. The cyclic voltammetry (CV) measurement was carried out between 0.01 and 1.00 V at the scan rate of 10 mV s^{-1}. The cells were galvanostatically charged and discharged in the voltage range between 0.01 and 1.20 V vs. Li/Li^+ at the current density of 20 μA cm^{-2}.

3. Results and discussion

The electrodeposition of the Sn–O–C composite was carried out on a nickel substrate from an EC:PC electrolyte solvent containing 2.5 mmol dm^{-3} of $SnCl_2$ with 1.0 mol dm^{-3} of $LiClO_4$ used as the supporting electrolyte. Fig. 1 presents a galvanostatic potential transient during the electrodeposition of the Sn–O–C composite at 37.5 μA cm^{-2} applied with a passing charge of 0.25 C cm^{-2} for the deposition. The result reveals that the potential gradually reaches a value of 0.3 V as the deposition time is increased beyond 2500 s. The potential profile clearly shows two small and one large potential plateaus at ca. 2.2, 1.5 and 0.3 V, respectively. With the beginning of galvanostatic deposition, a rapid decrease in initial potential is followed by a small potential plateau at ca. 2.2 V. Afterward, the potential steeply reduces and reaches the stable value of ca. 1.5 V. Finally, the large plateau at ca. 0.3 V appeared after the gradual decrease in potential from 1.5 V to 0.3 V. The observed galvanostatic behavior consisting of multiple steps of potential transience may be derived from the reduction and the co-deposition of various components in the electrolytic bath, *i.e.*, Sn^{2+}, Li^+ ions and other species. Furthermore, several literature have reported that decomposition of the organic carbonate electrolyte, *i.e.*, herein EC and PC, is catalyzed by the pure tin surface, which causes SEI formation [25–27]. Therefore, it is assumed that the galvanostatic behavior indicating multiple steps of potential transients is preferable to produce the Sn–O–C composite with SEI formation by means of the co-deposition of Sn^{2+}, Li^+ ions and the decomposition of an organic carbonate electrolyte. The inset in

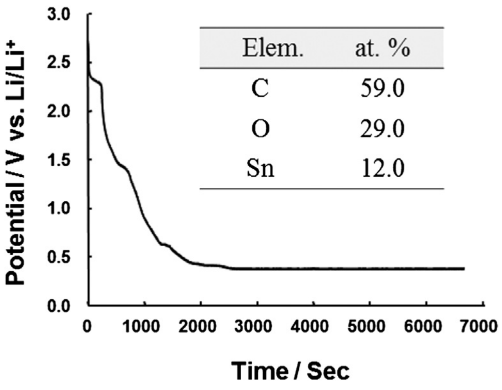

Fig. 1. The potential profile of the galvanostatic electrodeposition of Sn–O–C composite material, and the composition of the as-prepared Sn–O–C composite anode measured by EDS analysis (inset).