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Electrochemical properties of Sn-based nanopowders synthesized by a pulsed wire evaporation method and effect of binder coating

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ABSTRACT

Sn-based nanoparticles are prepared with the O_2 concentrations in chamber of Ar atmosphere (by v/v) by using the pulsed wire evaporation (PWE) method. The prepared electrodes are only Sn-based powder electrode, its binder coating electrode and Sn-based powder/graphene nanocomposite electrode. Morphology and structure of the synthesized powders and electrodes are investigated with a field emission scanning electron microscope (FE-SEM) and an X-ray diffraction (XRD) analysis. The electrochemical measurements were performed with galvanostatic cycling experiments using a coin type cell of CR2032 (Ø20, T3.2 mm). The binder coating electrode is superior to others and maintains delithiation capacity nearly of 501 mAh g^{-1} as 58.3% of first delithiation capacity at 0.2 C-rate up to 100 cycles.

1. Introduction

In Li-ion secondary batteries (LIBs), there have been many attempts to investigate high-capacity anode materials, such as metal oxides [1–3], Si-based [4,5] and Sn-based [6–9]. Among them Sn and Sn-based oxide are attractive materials as a potential substitute for the conventional graphite (372 mAh g^{-1}) anode due to theoretical, nontoxic, inexpensive and naturally abundant [10,11]. The theoretical capacities of Sn, SnO and SnO_2 are 992 mAh g^{-1}, which is 2.7 times higher than that of graphite, 875 mAh g^{-1} and 783 mAh g^{-1}, respectively [12–15]. Thus, many studies of experimental and theoretical efforts have been carried out in recent years. However, the large volume expansion, up to 300%, of Sn and Sn-based oxide during discharge/charge process causes the aggregation and pulverization of active material with quick capacity fading [16–19]. Meanwhile the electron conductivity is poor. Thus, it is focused on solving the problems caused by volume expansion for Sn-based material. Sn oxide material provides improved long-term cycle stability compared to metallic Sn due to a buffer matrix of Li_2O although aggregation of Sn may occur which can break down the Li_2O buffer matrix after only a few cycles [20]. Such a Sn-based material was frequently mixed with a material affiliated with carbon for cycle stability. Sn/graphene nanocomposites with various structures and morphologies have been explored in order to prevent the aggregation and pulverization of active material during the lithiation/delithiation, such as Sn/graphene, carbon coated Sn/graphene and Sn@CNT/graphene nanocomposites [21–25]. Although many methodologies for cycle performance of Sn-based electrode have been investigated, almost all of such researches have been applied with complicated methods.

In order to gain the Sn oxide nanopowders with various contents of oxygen, the pulsed wire evaporation (PWE) method, which is a physical process and has been introduced to produce metal nanopowders, was applied in this study. In this method, a high power pulsed dc current passing through a thin Sn wire leads to the wire explosion, and the large amount of heat energy causes the wire to melt, followed by subsequent evaporation and formation of plasma. The plasma formed during the process expands and cools when it interacts with a coolant such as an inert gas, and then nanoparticles are formed through the nucleation process. It was applied to various oxygen (O_2) concentrations in a chamber, in which the wire explosion takes place, of Ar atmosphere to synthesize the Sn-based nanopowders with various oxygen contents. Cycle stability was investigated with using the electrodes fabricated with three methodologies which were only

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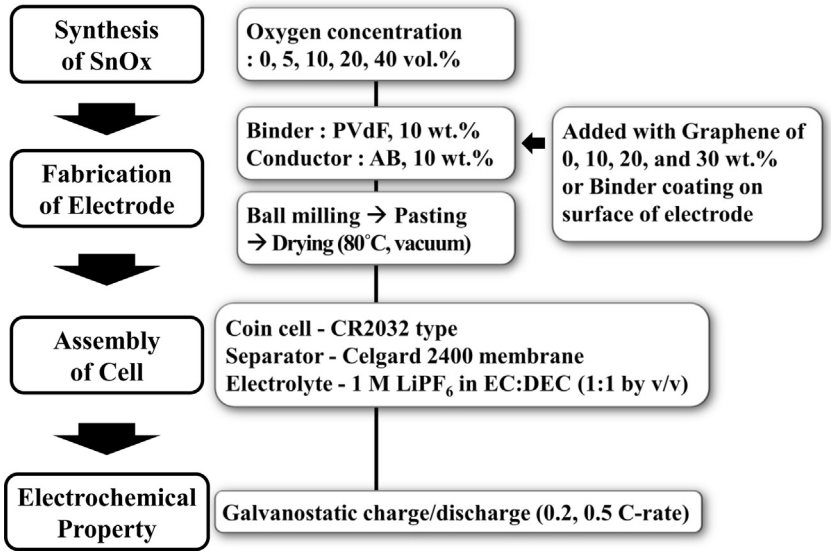

Fig. 1. Experimental flow chart of fabrication processes.

Sn-based powder electrode, its binder coating electrode and Sn-based powder/graphene nanocomposite electrode. Although binder coating layer causes increase of interfacial resistance, cycle stability can be greatly enhanced due to preventing the secession of Sn-based active material from electrode. Also, it is one of very simple and facial methods in many challenges for cycle stability of Sn-based materials. In this study, cycle stability with the effect on binder coating and graphene composite with synthesized Sn-based nanopowder was investigated.

2. Experimental

2.1. Preparation of Sn-based nanopowders

Experimental flow chart of fabrication processes consisting of synthesis of Sn-based nanopowder, fabrication of electrode, assembly of cell, and electrochemical property was shown in Fig. 1. First of all, the Sn-based nanopowders with contents of oxygen were synthesized with controlling the concentration of oxygen (O_2) in chamber of Ar atmosphere (by v/v) by a pulsed wire evaporation (PWE) method. The feed length of Sn wire per 1 explosion was set to 10 mm, and the voltage of power supply was fixed with 6.5 kV. The Sn-based nanopowders were synthesized at inner pressure of 2 bar in chamber of Ar atmosphere controlling the O_2 concentration, which were set to 0, 5, 10, 20 and 40%.

2.2. Fabrication process of Sn-based powder electrode

In this study, cycle stability was investigated with using the electrodes fabricated with three methodologies which were only Sn-based powder electrode, its binder coating electrode and Sn-based powder/graphene (Graphene Laboratories Inc.) nanocomposite electrode. The Sn-based powder electrodes were fabricated with using the as-prepared powder synthesized with O_2 concentrations in chamber of Ar atmosphere and the binder-coated electrode was fabricated with using the as-prepared powder of 5% O_2 concentration. And, the Sn-based powder/graphene composite electrodes were made with graphene of 10, 20 and 30% from active material (Sn-based powder + graphene) weight using the as-prepared powder of 5% O_2 concentration. The binder coating and graphene composite electrodes were prepared to improve the cycling performance. The active material that is Sn-based powder or Sn-based powder/graphene composite was mixed with conductor (acetylene-black, AB) of 10 wt.% and binder (poly (vinylidene fluoride), PVdF) of 10 wt.%, and then the mixtures were blended for 3 h. using the ball-milling method. Thereafter, the electrodes were dried in vacuum oven at 80 °C for 24 h, and the mean thickness of all electrodes was 7.2 μm excluding binder layer and Cu current collector. In binder coating process, the binder poly (vinylidene fluoride) (PVdF, Aldrich Co.) was mixed with 1-Methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%, Aldrich Co.) in the ratio of 1: 10 wt.% (PVdF: NMP). Thereafter, the binder was covered on the surface of Sn-based nanopowder electrode to restrain the secession of the powder from the electrode. This also helps in the electronic isolation during the cycling test. Finally, the binder-coated electrode was dried in vacuum oven at 100 °C for 24 h.

Morphology and structure of the synthesized powders and as-prepared powder/graphene composites were investigated with a field emission scanning electron microscope (FE-SEM, Philips Co., XL30 S FEG) and an X-ray diffraction (XRD, Bruker Co., DE/D2 PHASER) analysis.

2.3. Electrochemical measurements

The measurements for evaluation of electrochemical properties were performed at 25 °C using a half coin type cell of CR2032 (Ø20, T3.2 mm) as shown in Fig. 2. The Sn-based and graphene composite electrodes were used directly as the working electrode and lithium metal was used as the counter electrode. The Celgard 2400 membrane was used as the cell separator and the electrolyte (1 M $LiPF_6$) was dissolved in a mixed solvent comprising of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by vol.). All the cell assemblies were performed in a glove box (KK-021AS, Koreakiyon Co.) filled with pure Ar. Galvanostatic charge/discharge experiments was carried out using a battery test system (WBCS3000L, WonA Tech., Co.). The cycling behavior was studied at applied currents of 0.2 and 0.5 C-rate in a cut-off voltage range of 0.01–1.5 V.

3. Results and discussion

The Sn-based particles were synthesized with various O_2 concentrations by PWE method and the morphologies are shown in Fig. 3. The O_2 concentrations are 0, 5, 10, 20, and 40% in chamber of Ar atmosphere and those are (a)–(e) in the order named. And, those mean diameters are shown in Fig. 3(f). It was confirmed that the spherical particles were in Fig. 3(a), and the particles of