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Synthesis and electrochemical performance of a novel nano sized Sn₂SbNi composite

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Abstract: Chemical reduction method was employed to prepare nano-sized Sn_2SbNi alloy composites used as anode material for rechargeable lithium ion batteries. This strategy was adopted to combine the virtues of both active/inactive and active/active alloys to fabricate a Sn_2SbNi alloy powder with two active components and one inactive component. The two active components can realize the high capacity feature of electrode and can make the volume change of electrode take place in a stepwise manner due to the different lithiation potentials of two active components, leading to a stable cycling performance. Sn_2SbNi alloy provides a reversible specific capacity over 640 mA·h/g with an excellent cyclic ability. The Sn-Sb-Ni alloy composite material shows to be a good candidate anode material for the lithium ion batteries.

Key words: Li-ion batteries; Sn₂SbNi composite; anode materials; chemical reduction method

1 Introduction

Rechargeable lithium-ion batteries with their light weight and high energy density have become an important source for powering in many applications. Although the widely current used Li-ion battery is a successful technology in conquering the battery market, the new challenges to achieve higher energy density, higher rate, higher stability, longer cycle life, and improved safety stimulate the research for grand new breakthroughs in electrode materials [1-2]. Among the varieties of anode materials, Sn-based materials with high theoretical specific capacity (994 mA·h/g) have been projected as one of the most promising candidates in substitute of the already-commercialized graphite, due to their high capacity, high packing density and safe thermodynamic potentials compared with carbonaceous materials for lithium secondary batteries. However, they usually undergo severe structural and volume changes during the process of Li uptake and removal, which results in mechanical disintegration of the electrode and consequent capacity fade, and greatly limits the commercialization. Many efforts, therefore, have been devoted to improve the cycling duration of Sn-based system[3–5], which includes using nano sized intermetallics or composite host material instead of pure metal. Related reports have revealed that reducing the size of active particles is an effective method to improve the cycleability of the alloy materials for the case of Sn, such as active/active SnSb, and active/inactive SnCu and SnNi[6–9].

In the present work, a strategy was adopted to combine the virtues of both active/inactive and active/active alloys to fabricate a Sn₂SbNi alloy powder with two active components and one inactive component. The nano-sized grains can homogenize the expansion/contraction strains, and thus relieve the mechanical stress and buffer the volume change of the particles caused by the lithiation and delithiation processes. The two active components can realize the high capacity feature of electrode and can make the volume change of electrode take place in a stepwise manner due to the different lithiation potentials of two active components, leading to a stable cycling performance. Though Ni shows to be inert with Li, its excellent flexibility and electric conductive character will contribute greatly to the cycling stability of electrode. Therefore, Sn₂SbNi alloy is expected to have high specific capacity and good cycling stability. The

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effect of chemical composition on the electrochemical properties of Sn₂SbNi electrode was investigated in terms of cyclic performance and cyclic voltammetry (CV) features.

2 Experimental

Aqueous solutions were used for the synthesis of Sn_rSbNi powder, namely, solution A formed by SnCl₂·2H₂O (99.9%, STREM Chemicals), SbCl·H₂O (99.9%, STREM Chemicals), and complexant citrates; and solution B formed by NaOH and NaBH₄(99.9%, STREM Chemicals). The procedure follows basically the procedure recommended in Refs.[10-11]. The precipitate was filtrated and subsequently washed with distilled water, 0.35 mol/L HCl and acetone, followed by drying in vacuum. X-ray diffraction (XRD) was at 120 carried out to identify the phase composition of synthesized powders over the 2θ range from 10° to 90° using a Rigaku D/max-A diffractometer with Cu K_a radiation. The particle morphologies and phase compositions of the synthesized Sn_xSbNi powders were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM, JEM-100CX); and the corresponding lattice structure was identified by selected area electron diffraction (SAED) technique. For electrochemical performance evaluation, half-cell studies were performed. In the experimental Sn_xSbNi electrode, C (acetylene black) powder and polyvinylidene fluoride (PVDF) were used as conductive additive and binder, respectively. The synthesized Sn_xSbNi powders were mixed with acetylene black and PVDF dissolved in N-methyl-pyrrolidinone in the mass ratio of 85:10:5 to form slurry, which was painted on a copper foil used as current collector. After solvent evaporation, the electrode was pressed and dried at 120 under vacuum for 48 h.

The cells were assembled in argon filled glove-box. Metallic lithium foil was used as counter electrode. The electrolyte was 1 mol/L LiPF₆ (Merck, battery grade) in a mixture of ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume ratio). Celgard 2400 polyethylene was used as the separator. Cycling tests were carried out at the charge and discharge conditions of 100 mA/g in the voltage range of 0.01–1.5 V versus Li/Li⁺ by LAND BT–10 tester (Wuhan, China). Cyclic voltammetry was performed between 0.01 and 1.5 V with scan rate of 0.05 mV/s.

3 Results and discussion

XRD pattern of the synthesized Sn₂SbNi alloy composite powder is shown in Fig.1. It reveals that all the products are multiphase compounds, which mainly consist of SnSb, and Sn, Ni metals. No peaks assignable



Fig.1 XRD pattern of Sn₂SbNi alloy composite powders

to raw materials were identified, indicating that all oxides have been reduced completely. No obvious peaks corresponding to metal Sb were found in XRD pattern, implying that most of the Sb component has combined with Sn to form SnSb intermetallic, and some other Sb may exist in amorphous state, as evidenced by the relatively high background of XRD pattern.

The SEM image of synthesized alloy composite powders is presented in Fig.2. The synthesized powder showed mainly spherical conglomeration from 40 to 100 nm. EDS analysis of the synthesized Sn₂SbNi alloy composite powders, shown in Fig.3, gave a Sn to Sb to Ni molar ratio of 52.77:24.51:22.72, showing seemingly that tin-rich composite is obtained. The chemical composition of synthesized material is closed to the starting molar ratio of Sn to Sb to Ni, i.e. 2:1:1 before reaction.



Fig.2 SEM image of Sn₂SbNi composite powders

Fig.4 shows TEM image of a Sn₂SbNi alloy powder prepared by chemical reduction. It shows clear grain shapes, and the crystal edges can be observed. The granularity of particles is 10–30 nm, illumining that the relatively large particles observed in SEM are configuration from little particles. A multi-crystal structure



Fig.3 EDS spectrum of Sn₂SbNi powder



Fig.4 TEM image of Sn_2SbNi alloy powders(The inset is the selected area electron diffraction of a area of Sn_2SbNi alloy particle, showing multi-crystalline characteristic of SnSb)

with clear crystal loops of diffraction structure can be detected by SAED, as illustrated in Fig.4. This also indicates again that the single spherical particles observed in SEM are practically aggregates of nano-sized grains.

Lithium ions inserting into and extracting from Sn_xSbNi alloy composite electrode are defined as discharge and charge processes, respectively. The cyclic performance profiles of Sn_xSbNi alloy composite electrode (x=1, 2 and 3) at 100 mA/g are shown in Fig.5. The first discharge capacity of SnSbNi, Sn_2SbNi , and Sn_3SbNi electrode are 894, 961 and 1 020 mA·h/g, respectively. The increase in initial discharge capacity with the increase of Sn content is mainly attributable to the high lithium storage capacity of Sn. In the following 20 cycles, except Sn_3SbNi , the synthesized SnSbNi and Sn_2SbNi alloy electrodes exhibit good stability with discharge capacities of about 500 mA·h/g and about 710 mA·h/g, and the columbic efficiencies of 97.8% and



Fig.5 Cyclic performance of Sn_xSbNi alloy composite electrodes at 100 mA/g (x=1, 2 and 3)

97.5%, respectively. The results are understandable because of the nano-structural and the multi-element characteristics. The former can accommodate the volume change caused by the lithiation/delithiation of electrode, while the latter allows the lithiation/delithiation of Sn_xSbNi electrode to take place at different potentials, i.e. in a stepwise behavior, thus makes the volume change of electrode occur more smoothly. These will eventually result in a good structural and cyclic stability of electrode. The inactive matrix Ni can buffer the volume change of Sn and Sb in the electrochemical cycling process, and can also prevent the aggregation of the alloy particles in a certain extent, thus will also contribute to the good cycleability of electrode. In addition, the good electronic conductivity of component nickel should also be responsible for the better electrochemistry performance of electrode. However, when the molar ratio of Sn to Sb to Ni arrived at 3:1:1, the capacity of Sn₃SbNi electrode faded drastically from 1 020 to 383 mA·h/g after 20 cycles. The relatively excessive amount of Sn in Sn_xSbNi alloy electrode will result in large volume expansion upon lithiation of electrode, which is considered to be the main reason of the poor cycling behavior of electrode. The maximal volume expansion of tin can reach as high as 300% according to Ref.[12]. Another reason is that more Sn content in Sn_xSbNi composite alloy may easily congregate together upon electrochemical cycling to form large Sn particles, which will readily result in mechanical pulverization of the electrode and consequent capacity drop of electrode. The increased kinetic polarization of tin-rich electrode is another reason for the unstable cyclic ability.

The initial capacity loss is about 200 mA·h/g for synthesized Sn_2SbNi , which is similar to that of most reported alloy anode electrodes fabricated by liquid coprecipitation reduction[10, 13–14]. The possible oxide existing on the surface of nano particles should be

responsible for the unconventionality. Due to the large specific surface area of Sn_xSbNi , it is readily to be contaminated by oxygen during the preparation process. In the first lithiation phase, the oxides will be reduced to yield Li₂O, resulting in the irreversible capacity, as Li cannot be extracted from Li₂O during the electrochemistry reaction[13]. Moreover, the formation of SEI film on the electrode surface may also make contribution to the high initial capacity of Si film[15].

Cyclic voltammetry(CV) plots of Sn₂SbNi alloy electrode for the first and the following 2 cycles are shown in Fig.6. In the initial discharge, the potential drops rapidly to 0.8 V, then decreases to 0.01 V gradually. The difference between the 1st and 2nd cycle is considered to result from the inactive features of alloy composite against the electrochemical reactions, and the decomposition of oxides on the particle surface during the first discharge process. From the second cycle, the CV profiles of batteries become almost overlapping in the following cycles evidently, illuminating the excellent durability of Sn₂SbNi alloy composite electrode. The CV plots show four pairs of peaks, corresponding to the four potential plateaus in charge/discharge curves. For lithiation process, SEI film will form firstly on the particle surface before A during the first cycle, and always starts at about 1.0 V. Peak A at around 0.8 V corresponds to the formation of Li₃Sb, while the peaks B, C and D represents the potential dependent formation of various Li-Sn alloys, because Sn can form different Li-Sn phases with Li. For delithiation process, these insertion processes are reversible. Li will first be extracted from the Li-Sn alloy (D', C' and B'), then from Li-Sb alloy (A'). The Sn₂SbNi alloy composite electrode will be resumed when it is recharged to 1.2 V. However, the formation of the SEI film is irreversible.



Fig.6 Plots of cyclic voltammetry of Sn_2SbNi composite electrode for the first 3 cycles(Cut-off voltage of 0.1–1.5 V)

4 Conclusions

1) Nanosized Sn_xSbNi alloy composite anode powder

was fabricated by reduction precipitation reduction. The nano structure can accommodate the volume change caused by the lithiation/delithiation of electrode. The multi-element characteristics of active material allow the volume change to take place in a stepwise manner. The ductile component Ni will play as a buffer to relieve the volume change stress of electrode. All these factors contribute greatly to the excellent cycling stability of Sn_xSbNi alloy electrode.

2) Increasing the Sn content in Sn_xSbNi composite powder can increase the capacity of alloy electrode; however, excessive Sn may cause the fast electrode fading. Sn_2SbNi electrode shows a high reversible specific capacity and an excellent cyclic ability.

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