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Synthesis and Electrochemical Properties of $SnCo_{1-x}Fe_x/C$ Composite

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The $SnCo_{1-x}Fe_x/C$ (x=0.1, 0.2, 0.3, 0.4) composites as novel anode materials for lithium-ion batteries with large capacity were prepared by ball milling first and then solid-state sintering. The influences of the partial substitution of inert metal Fe for Co on material structures and the electrochemical properties were investigated. Structure analyses show that the uniform solid dissolution of Fe into CoSn phase promotes the formation of $CoSn_2$ impurity phase. With the growth of x, the cell volumes of CoSn phase is enlarged, the grain size decreases and the content of $CoSn_2$ increases. Carbon black is mainly physically mixed with other phases on the surface of particles. Electrochemical analyses reveal that the reversible capacity and cycle performance are both improved through the introduction of Fe. When x is 0.2, the cycle performance is up to the maximum, 85.1% of the reversible capacity after 50 cycles. During cycling, among SnCo/C, $SnCo_{0.8}Fe_{0.2}/C$ and $SnCo_{0.6}Fe_{0.4}/C$ samples, the grain size of CoSn phase for $SnCo_{0.8}Fe_{0.2}/C$ sample increases leastly. It is usually believed that the comprehensive effects of grain size, structure stability and impurity-phase content lead to the maximum of the cycle performance at appropriate content of Fe (x=0.2).

KEY WORDS: Lithium-ion batteries; SnCo/C; Fe; Cycle performance; Grain refinement

1. Introduction

Lithium-ion batteries, with high energy density and perfect cycle performance, have become one of the most important research areas in the new resources development. At present, the actual storage capacity of the commercial graphite anode materials is approaching the theoretical capacity (372 mAh/g). So, there is little room to upgrade and it is difficult to meet the extensive requirement for the miniaturization development of the modern portable electronic devices and electric vehicles with high capacity and high power. Therefore, more attention is increasingly paid to the development of the new generation of non-carbon anode materials. Silicon and tin, which can be alloyed with lithium, have high capacities. However, their structures are suffered from pulverization which is resulted from the large volume expansion during the charge-discharge, leading to the deterioration of the cycle performance and thus lose its practical value. Since the theoretical capacity of tin (992 mAh/g) is much higher than that of graphite and the volume expansion is lower than that of silicon during the charge-discharge, the improvement of the cycle performance has become a highlighted topic in the study of tin-based materials.

At present, four routes have been proposed to improve the electrochemical properties of tin-based materials. One method is refining grains or particles. Whitehead *et al.*[1] found that nano-tin particles which were prepared by templating could improve the capacity and cycle performance, but nano-particles tend to agglomerate[2]. Another method is alloying. It was found that the cycle performance could be improved by introducing Cu into Sn to form an active/inactive structure[3]. Moreover, introducing Sb into Sn to form active/active structure could also im-

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prove the cycle performance[4]. The third method is preparing composite. The introduction of C into Sn improved the cycle performance significantly[5,6].

Based on the above three methods, Sn-Co-C composite was prepared and applied in "Nexelion" battery by Sony Corporation in 2005, which marked the beginning of commercialization of tin-based composites. At the same time, fabricating an amorphous material was suggested as the fourth method to improve electrochemical properties. Hereafter, extensive attention has been paid to the Sn-Co-C composite. Todd *et al.*[7] produced $Sn_{1-x}M_x$ (M=Ti, V, Cr, Mn, Fe, Co, Ni, Cu) alloys by co-sputtered method and found that only $Sn_{1-x}M_x$ (M= Ti, V, Cr, Co) alloys had high amorphous-forming ability. Among them, Sn-Co alloy had high capacity and Sn-V alloys had a good cycling performance.

It was also suggested by Sony[8] that the introduction of the fourth element into Sn-Co-C ternary composite could further improve the reversible capacity and cycle performance. However, there is little report about the mechanism that the fourth element improves electrochemical properties. Furthermore, the expensive Co, as a rare resource, limits the further application of the Sn-Co-C system. In this paper, the influences of the partial substitution of inert metal Fe for Co in Sn-Co-C composites on structures and electrochemical properties were investigated.

2. Experimental

Element powders and carbon black with purity better than 99.9 wt pct were used as starting materials in stoichiometric proportion of $SnCo_{1-x}Fe_x$ (x=0.1, 0.2, 0.3, 0.4), which were mixed with carbon black at the weight percentage of 5%. The mixture was milled for 10 h by planetary ball miller under vacuum condition, and then sintered at 600°C for 10 h in nitrogen atmosphere. When it was cooled down to the room temperature in the furnace, the $SnCo_{1-x}Fe_x$/C powder sample was obtained through the standard screen with 320 mesh. For comparison, the SnCo/C sample without Fe was prepared by the same way.

The working electrodes were prepared first by dispersing 87% active materials, 3% carbon black, and 10% poly (vinylidene fluoride) (PVDF) as the binder in N-methyl-pyrrolidinone (NMP) solvent to form a homogeneous slurry, then spreading onto copper foil and pressing, lastly drying at 120°C for 12 h. Porous polypropylene (Celgard 2400) was used as a separator. The electrolyte was 1 mol/L $LiPF_6$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (1:1:1 by volume). The cells were assembled in argon filled glove-box.

The phase constitutions of $SnCo_{1-x}Fe_x$/C powders and working electrodes were analyzed by X-ray diffraction spectroscopy (XRD, D/max 2500 vpc apparatus with Cu$K\alpha$ radiation). Scanning electron microscopy (SEM) observation of $SnCo_{1-x}Fe_x$/C samples was carried out in JSM-630F SEM. The local compositions were determined by an energy dispersive X-ray spectrometer (EDS, Link ISIS) attached to the SEM. The specific surface areas of powders were measured by means of the nitrogen adsorption Brunauer-Emmett-Teller (BET) on a high-speed automated BET analysis instrument (NOVA 4000). The particle sizes of the powders were determined by a laser granulometer (Mastersizer 2000).

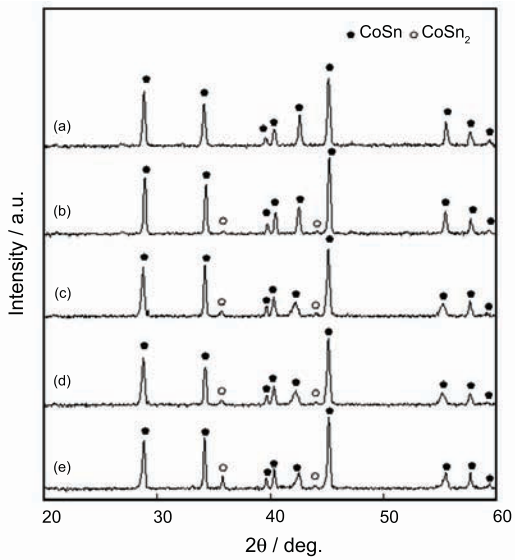

Fig. 1 XRD patterns of $SnCo_{1-x}Fe_x$/C samples with (a) x=0, (b) 0.1, (c) 0.2, (d) 0.3 and (e) 0.4 sintered at 600°C for 10 h

The charge-discharge measurements was carried out at the current density of 0.05 mA/cm^2 over the voltage range of 0.02∼1.5 V (*vs.* Li^+/Li) by a cell program-controlled test system (BTS).

3. Results

3.1 Structure and Morphology

Figure 1 shows XRD patterns (normalized) of SnCo/C and $SnCo_{1-x}Fe_x$/C samples. It is obvious that the SnCo/C sample is mainly composed of hexagonal CoSn phase, and the introduction of Fe causes the appearance of a small amount of tetragonal $CoSn_2$ impurity phase. Furthermore, the diffraction peaks intensity of $CoSn_2$ increase with x growing, indicating that the relative content of $CoSn_2$ increases. In addition, there is no obviously detectable diffraction peak of Fe (or Fe alloy) being found, revealing that Fe mainly dissolves into the CoSn or $CoSn_2$ phase. Since the CoSn phase coexists with a little amount of Sn-rich phase ($CoSn_2$) in $SnCo_{1-x}Fe_x$/C samples, according to the lever rule and mass conservation law, there must be Co-rich phases such as Co or Co_3Sn_2.

Figure 2 shows functional curves of the lattice parameters a and c, unit cell volume V and grain size d of CoSn phase *vs.* x. The values of a, c and V for the SnCo/C sample are 0.5248, 0.4238 nm and