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Morphology modification and irreversibility compensation for SnO anodes

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Abstract

SnO powders with different particle sizes have been examined as hosts for lithium insertion and extraction. The finer powder shows a better cycle performance. The high irreversible capacity of the SnO electrodes in the first cycle can be compensated by adding $Li_{2.6}Co_{0.4}N$ into the electrodes. The mixed-host electrode demonstrates a reversible capacity over 600 mAh/g and good cycling performance.

Keywords: SnO anode; Morphology modification; Irreversibility compensation; Lithium ion battery

1. Introduction

In recent years, tin oxides and related materials have been intensively investigated for anodes in lithium ion batteries [1–3]. These materials, especially amorphous Sn-based composite oxide, demonstrated much higher reversible capacities than graphite and much better cycling stability than lithium storage metals. Comparing with metallic tin, the tin-based oxides have a different reaction mechanism with lithium. Lithium reacts irreversibly with tin-bond oxygen to form amorphous Li_2O and metallic Sn first, followed by a reversible alloying reaction with Sn. By this way, the active Sn-domains can be finely dispersed in inert phases such as Li_2O. This greatly alleviates the volume change effect of the electrode and significantly improves the mechanical and cycle stability. However, the first step conversion from tin-bond oxygen to Li_2O brings a high irreversible capacity in the first cycle. In the case of SnO, the theoretical reversible capacity is 875 mAh/g for alloying, but the irreversible capacity is as high as 400 mAh/g. This high irreversibility limits the practical application of electrodes of this kind.

On the other hand, it is known that some lithium transition metal nitrides such as $Li_{2.6}Co_{0.4}N$ have high Li-extraction capacities but very low initial Li-insertion ones. They have demonstrated a good cycling stability [4,5]. Although these anode materials cannot directly combine with Li-rich cathode materials such as $LiCoO_2$ to form a cell, the high content of 'mobile' lithium insides is expected to be able to compensate the irreversible capacity of the tin-based oxides. In this work, the influence of the particle morphology of SnO powders on the electrode performance and the improvement in the first cycle efficiency by means of $Li_{2.6}Co_{0.4}N$ are investigated.

2. Experimental

Coarse SnO powder (square particles with an edge-length from 9 to 30 μm and the thickness of ca. 4 μm) was from Nacalai Tesque. Medium SnO powder (fiber- and irregular-shaped particles with the thickness below 4 μm) was synthesized by SnC_2O_4 decomposition. Fine SnO powder (typical particle size: <0.1 μm) was obtained by chemical precipitation: 200 ml, 0.08 M $SnCl_2{\cdot}2H_2O$ solution was mixed with 150 ml, 0.17 M LiOH solution under stirring to get suspend $SnO{\cdot}xH_2O$ solution. After filtering and washing, the precipitation was dried at 140°C for 1 h and further at 280°C under vacuum for 2 h. $Li_{2.6}Co_{0.4}N$ powder (particle size: <6 μm) was synthesized as described previously [6]. Ni powder (99.9%, ca. 0.03 μm) and polyethylene (PE) with ultra-high molecular weight (mp 144°C) were obtained, respectively, from Nilaco Corp. and Aldrich.

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The electrodes were fabricated by solvent-free method. A given weight of SnO powder was mixed with Ni powder and PE binder in mortar agate in glove box. The powder mixture was pressed onto a 280-mesh stainless steel grid which served as current collector. For a $SnO/Li_{2.6}Co_{0.4}N$ composite electrode, $Li_{2.6}Co_{0.4}N$ powder was finally added and mixed further. The geometric area of the composite electrodes was 0.5 cm^2 and the typical thickness was 50–60 μm.

Electrochemical measurements were performed in laboratory-type glass cells containing sufficient organic electrolyte of 1 M $LiClO_4$/EC + DEC (1:1). The electrodes were cycled at a current density of 0.4 mA/cm^2 and within a potential range of 0.1/1.3 V versus Li. The capacity was calculated according to the weight of SnO or SnO plus $Li_{2.6}Co_{0.4}N$.

3. Results and discussion

The three types of SnO powders with different particle morphology are used as hosts for lithium insertion and extraction. Fig. 1 exhibits the first discharge–charge profiles for these SnO hosts. The initial potential plateau in the lithium insertion process represents the conversion reaction of SnO into Li_2O and metallic tin. For coarse SnO powder, a long and distinct plateau from 0.85 to 1 V versus Li can be observed. With a decrease in the particle size, the plateau shifts upward and becomes shorter and more sloping. The calculated potential value based upon the thermodynamic date is 1.58 V versus Li for this conversion reaction [7]. A big deviation between theoretical value and the practical potential plateaus can be mainly attributed to slow reaction and diffusion kinetics. The finer SnO powder has a larger interface contact area and a shorter Li-diffusion length within the particles. Under the same current rate, the respective electrode has a smaller electrochemical and diffusion polarization. Therefore, its potential plateau is closer to the thermodynamic value. In addition, indistinct plateau character for fine SnO-based electrode can be linked to the poor crystallinity of the SnO powder.

On the other hand, the potential trends for lithium extraction are quite similar for all the three electrodes, implying that lithium extraction from Li_2O/Li_xSn composite is kinetically fast. The improved kinetics may be based on the formation of the Li-alloy and the Li_2O as well as penetration of the electrolyte into the electrodes. The first Li-extraction capacity is about 550 mAh/g with a potential upper-limit of 1.3 V versus Li, under which lithium is almost completely extracted from Li_xSn alloy. The first cycle efficiency turns to be lower with the decrease in SnO particle size. This could be, at least in part, attributed to the film formation on the surface of the SnO particles due to electrolyte decomposition [8]. A finer powder has a larger specific surface area and, thereby, contributes to a higher irreversible capacity.

Fig. 2 shows the cyclability of the three SnO electrodes. The use of the fine SnO powder improves the cycle stability. It seems that the host volume change extent mainly influences the cycle life of SnO electrodes under high Li-utilization. We observed that the electrode using the coarse SnO powder, which was vertically in the electrolyte, had a great deformation after the initial lithium insertion. But the deformation was not obvious for the electrode based on the fine SnO powder. The particle size effects have been revealed and discussed in several papers [9–11]. In addition, some studies revealed that the aggregation of Sn atoms occurred during cycling for tin oxide based anodes. The formation of large Sn regions will further result in microstructural instability of the host [2,12]. The use of the nano-SnO particles and the formation of the surface-passivating layer may limit the aggregation of Sn-domains within nanoscale regions. For these reasons, the electrode based on a finer SnO powder can display a better cycle performance. One point that should be mentioned here is that the electrode

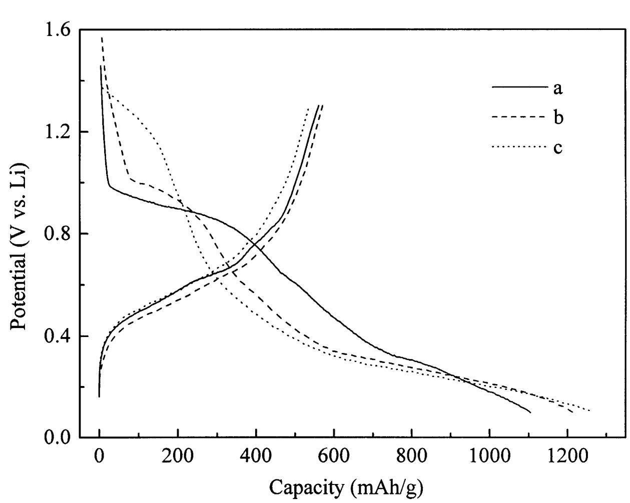

Fig. 1. The first cycle profiles for SnO-based electrodes: (a) 13% Ni, 10% PE and 77% coarse SnO; (b) 15% Ni, 10% PE and 75% medium SnO; (c) 20% Ni, 10% PE and 70% fine SnO.

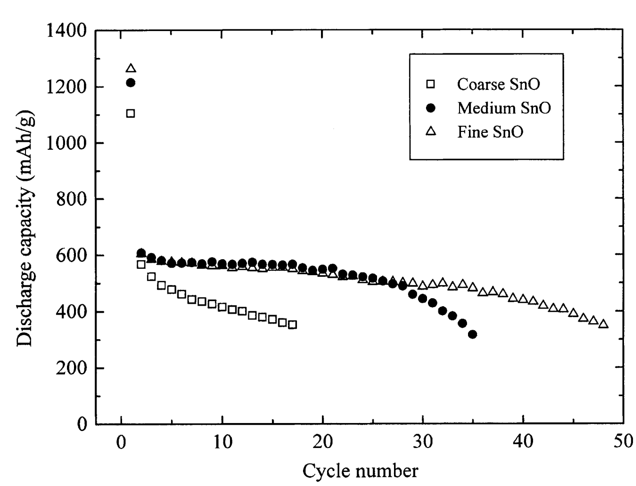

Fig. 2. Discharge capacity vs. cycle number for SnO-based electrodes with different particle size. Electrode compositions are the same as in Fig. 1.

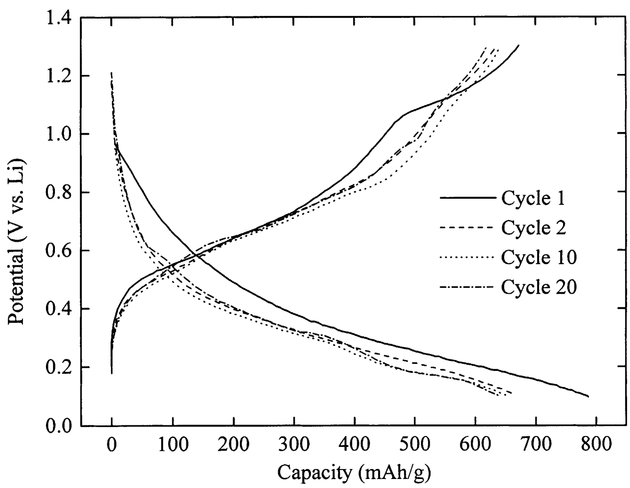

Fig. 3. Discharge–charge profiles for a electrode containing 20% Ni, 10% PE, 24.5% $Li_{2.6}Co_{0.4}N$, and 45.5% fine SnO.

compositions need to be adjusted according to SnO particle size to achieve an optimal cycle performance, because the specific surface and density of SnO powders change with the particle size.

In order to enhance the first cycle efficiency, $Li_{2.6}Co_{0.4}N$ powder is added into the SnO electrodes. The first Li-insertion capacity is ca. 100 mAh/g for $Li_{2.6}Co_{0.4}N$ electrode and its Li-extraction capacity is near 900 mAh/g. This big capacity difference is just useful for compensating the irreversible capacity of SnO electrodes. When active material consists of 35% $Li_{2.6}Co_{0.4}N$ and 65% fine SnO, the first cycle efficiency rises from 44% (for fine SnO) to 86%. A substitution of the coarse SnO powder for the fine powder can further enhance the efficiency to 97% for the same mix ratio of the two hosts. Fig. 3 exhibits cycling behavior of a fine SnO/$Li_{2.6}Co_{0.4}N$ composite electrode. The electrode has good cycle stability with reversible capacities more than 600 mAh/g. Although this capacity is higher than that of $SnSb_{0.14}$/$Li_{2.6}Co_{0.4}N$ composite as described previously [13], both the electrodes have a similar practical capacity (ca. 460 mAh/g on the basis of the total electrode weight). For SnO-containing electrodes, a higher content of Ni conducting additive is required.

X-ray diffraction measurements reveal that $Li_{2.6}Co_{0.4}N$ can entirely reduce the fine SnO to Sn and amorphous Li_2O, so long as $Li_{2.6}Co_{0.4}N$ content is high enough in the electrode. For the coarse SnO powder, it is found that the conversion of SnO is due to kinetic factor incomplete after mixing. The complete conversion can be realized by soaking the composite electrode into the electrolyte.

4. Conclusions

The cyclability of SnO electrodes is strongly dependent on the particle morphology of the SnO powder. Decreasing the particle size can improve the cycle performance. High irreversibility of the SnO electrodes in the first cycle can be effectively compensated by adding a certain amount of $Li_{2.6}Co_{0.4}N$ into the electrodes. The composite electrode based on the fine SnO and $Li_{2.6}Co_{0.4}N$ possesses good cycle stability.

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