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New composite anode systems combined with $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$

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Abstract

Ultrafine $\text{SnSb}_{0.14}$ and SnO powders as hosts for lithium insertion show high irreversibility in the first cycle. A combination of the tin-containing hosts with $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ has been examined for composite anodes in lithium ion batteries. The new anode systems reduce or eliminate the first irreversible capacity and improve the cycle performances. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Li-alloy composite anodes; $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$; Irreversibility compensation; Lithium ion battery

1. Introduction

In an effort to make the higher capacities of lithium secondary batteries, various new anode materials have been proposed. Among them, the revival of Li-alloy systems with Sn, Sb, Si, etc., as insertion hosts is especially noticeable. Recent studies show that the electrode performance can be significantly improved by decreasing the host particle size to sub-micron or nano scale [1,2] and using multi-component composite structures, in which active domains are embedded in a less-active or inactive matrix [3,4]. For example, amorphous tin composite oxides demonstrated high reversible capacity and excellent cycling life [5]. Sub-micro Sn/SnSb two-phase alloy powder also presented improved cycling stability under high lithium utilization [6]. Unfortunately, a serious disadvantage for the practical use of these materials is the high irreversible capacity in the first cycle attributed to the formation of irreversible lithium compounds.

As another class of new anode material with high capacity, lithium cobalt nitride, $\text{Li}_{3-x}\text{Co}_x\text{N}$ ($x = 0.4\text{--}0.5$) has been studied [7,8]. $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ shows a high capacity of more than 700 mAh/g with good cycle performance (0.7 V versus Li on average). One difficulty for the practical use is that the high potential cathodes such as LiCoO_2 cannot directly be combined because this nitride has already contained the full amount of lithium in the structure. However, if $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ is mixed with the lithium storage metals or

oxides, it is expected that active lithium in $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ can compensate the first irreversible capacity.

2. Experimental

Ultrafine Sn/SnSb two-phase alloy powder (nominal composition: $\text{SnSb}_{0.14}$, typical particle size $< 0.2 \mu\text{m}$) and SnO powder ($< 0.1 \mu\text{m}$) were prepared by chemical precipitation as described elsewhere [2,9]. $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ powder (typical particle size, 1–6 μm) was synthesized by traditional ceramic method [7]. Ni powder (99.9%, ca. 0.03 μm) and polyethylene (PE) with ultra-high molecular weight (m.p. 144°C) were obtained, respectively, from Nilaco and Aldrich. Electrodes were prepared by mixing the component powders in mortar agate in glove box and then pressing the powder mixture onto 280-mesh stainless steel grid.

Electrochemical measurements were carried out in laboratory-type glass cells containing sufficient organic electrolyte of 1 M $\text{LiClO}_4/\text{EC} + \text{DEC}$ (1:1). The electrode cycle performance was evaluated with lithium as counter electrode at a current density of 0.4 mA/cm². Cells with $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode were also measured. The $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode was composed of 6% acetylene black, 9% PTFE and 85% $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

3. Results and discussion

A decrease in the particle size of metallic hosts can enhance cycle capacity and stability. However, the use of

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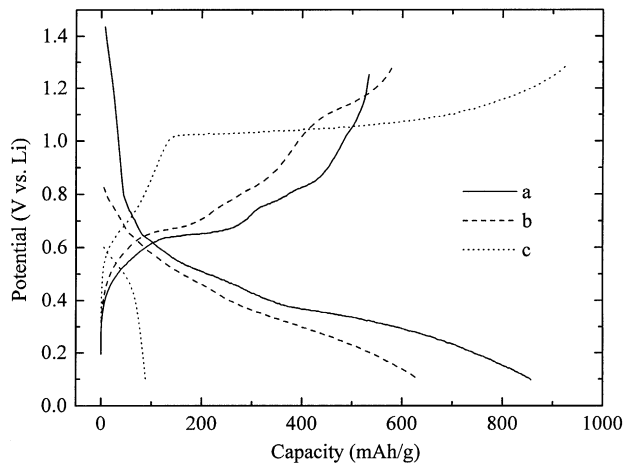


Fig. 1. The first cycle profiles for three types of electrodes: (a) 10% PE, 10% Ni, 80% SnSb_{0.14}; (b) 10% PE, 10% Ni, 20% Li_{2.6}Co_{0.4}N and 60% SnSb_{0.14}; (c) 10% PE, 14% Ni and 76% Li_{2.6}Co_{0.4}N.

the ultrafine host powders is often correlated to the high irreversibility in the first cycle owing to increased oxide impurity and the film formation over the large surface by electrolyte decomposition. The high irreversibility is also unavoidable for metallic oxide-based anodes because of an irreversible conversion from the respective oxides to Li₂O. Fig. 1 shows that such irreversibility can be compensated by adding Li_{2.6}Co_{0.4}N into the electrodes. Li_{2.6}Co_{0.4}N electrode has a low discharge capacity (ca. 100 mAh/g), but high charge capacity (ca. 900 mAh/g). On the contrary, the discharge capacity of SnSb_{0.14} electrode is much higher than the charge capacity ($\eta_1 = 62\%$). Therefore, a combination of these two active materials and control over the ratio of SnSb_{0.14} to Li_{2.6}Co_{0.4}N can adjust the charge and discharge capacity balance and achieve a high coulombic efficiency close to 100% in the first cycle. The half-cell cycling results reveal that the addition of Li_{2.6}Co_{0.4}N cannot only compensate the initial irreversible capacity, but also improve the electrode cyclability. The better cycling stability can, at least in part, be attributed to a small volume change of Li_{2.6}Co_{0.4}N structure during cycling. Its dispersion in the electrode alleviates the volume effect of the whole electrode.

Fig. 2 shows charge and discharge profiles of a cell using SnSb_{0.14}/Li_{2.6}Co_{0.4}N composite anode and LiNi_{0.8}Co_{0.2}O₂ cathode. The cell gives a good cycle performance under limited charge and discharge depth.

The combination of the Li-alloys with Li_{2.6}Co_{0.4}N can effectively compensate the first irreversible capacity. This offers a solution for the similar problems for Sn- or Si-based composite oxides and high capacity hard carbons. For ultrafine SnO powder as active material, the first efficiency is increased from 44 (only SnO) to 86%, when 65% SnO is mixed with 35% Li_{2.6}Co_{0.4}N. Since the potential for the SnO conversion into Sn and Li₂O is higher than the potential for Li-extraction from Li_{2.6}Co_{0.4}N, a direct lithium transfer from Li_{2.6}Co_{0.4}N to SnO is possible. X-ray diffraction

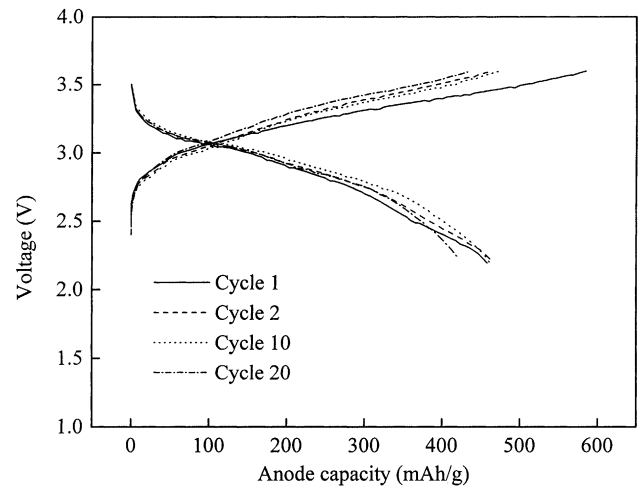


Fig. 2. Charge and discharge profiles for a cell with LiNi_{0.8}Co_{0.2}O₂ cathode and the SnSb_{0.14}/Li_{2.6}Co_{0.4}N composite anode. The weight ratio of cathode to anode active material = 5.

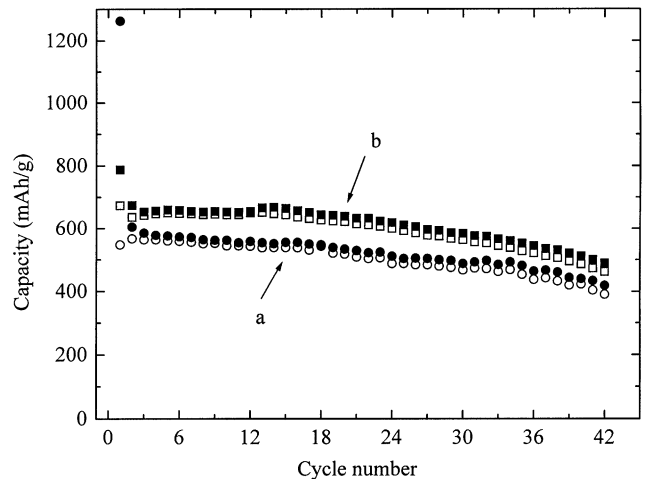


Fig. 3. Cycling behavior of SnO and SnO/Li_{2.6}Co_{0.4}N composite electrodes in a potential range from 0.1 to 1.3 V vs. Li: (a) 10% PE, 20% Ni and 70% SnO; (b) 10% PE, 20% Ni, 24.5% Li_{2.6}Co_{0.4}N and 45.5% SnO. Filled symbols: Li-insertion; open symbols: Li-extraction.

measurements indicate that such lithium transfer really occurs, even before the electrode is soaked in the electrolyte. Fig. 3 gives a comparison of cycling performance between the SnO electrode and the SnO/Li_{2.6}Co_{0.4}N composite one. Both the electrodes present similar cycle stability, but the composite offers a little higher cycle capacity.

4. Conclusions

The high irreversible capacity of ultrafine SnSb_{0.14} host powder can be effectively compensated by adding Li_{2.6}Co_{0.4}N powder into the electrodes. The mixed-host composite anode shows an improved cycle performance. This also offers a solution for the similar problems concerning Sn- or Si-based composite oxides and high capacity hard carbons.

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