

Carbon Nanotube Composites of Sb, Sn₂Sb and Sn₂Co Alloys as Li-ion Battery Anodes

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Introduction

Carbon nanotubes (CNT) are interesting one-dimensional hosts for the intercalation of Li and alkali metals. It has been reported that their storage capacities are often dependent on their microstructure, with reversible capacities typically in the range of 80-640 mAh/g [1-2]. On the hand, metals such as Sn and Sb are known Li storage compounds with very high capacities. However, the large specific volume change in Li insertion and extraction reactions causes mechanical disintegration of the electrode, and rapid capacity fading is observed. In our previous work [3], a high dispersion of tin oxide on graphite exhibited improved fading characteristics relative to pristine tin oxide and higher specific capacity relative to graphite. Here we present our preliminary findings on the preparation of CNT nanocomposites with Sb, Sn₂Sb and Sn₂Co alloys; and their electrochemical activities in Li insertion and extraction reactions.

Experimental

The composites of CNT with Sb, Sn₂Sb and Sn₂Co were prepared using SnCl₂, SbCl₃ and CoSO₄ as precursors and KBH₄ as the reducing agent. Their electrochemical activities for Li storage and retrieval were determined from constant current discharging/recharging at room temperature. The working electrode consisted of the active material with 10wt % each of acetylene black and PVDF. Half-cells with Li disks as counter electrodes were assembled in an Ar filled glove box. Celgard 2400 was used as the separator and a 1M LiPF₆ solution in a 1:1 v/v mixture of ethylene carbonate and diethyl carbonate was used as the electrolyte.

Results and discussion

Fig. 1 shows the typical SEM and TEM images of CNT-Sb nanocomposites, in which the Sb deposit on the outside surface of the CNTs was fairly well dispersed in most of the areas. As shown in Table 1, the CNT-metal composites exhibited higher reversible capacities and coulombic efficiencies than the CNT electrode alone. Fig.2 compares the cyclability of these electrodes in electrochemical lithiation and

de-lithiation reactions. Except for low reversible capacity, the CNT electrode showed good cycle stability, retaining 74% of the initial capacity at the 50th cycle. Although the unsupported Sn₂Sb alloy electrode had high initial capacity, rapid capacity fading caused its capacity to decline below that of CNT in the 31st cycle. The rapid capacity fade is typical of the pulverization problem in Sn-based alloy electrodes. Pulverization was likely to be less severe after the dispersion of metal and alloy particles in the CNT network, which could maintain the former in smaller dimensions. The soft CNT network could also be a good medium to cushion the mechanical stress arising from the volume change in the reactions. These factors probably worked collaboratively to improve the overall cyclability.

Table 1 A comparison of the capacities for electrochemical Li insertion and extraction at 1st cycle and 50 mA/g between 0-2.0V

Electrode	Li-insertion /mAh g ⁻¹	Li-extraction /mAh g ⁻¹
CNT	822	199
CNT-Sb (36wt.%)	1266	462
CNT-Sn ₂ Sb (56wt.%)	1092	518
CNT-Sn ₂ Co (53wt.%)	1040	462
Sn ₂ Sb	951	726
Sb	1023	648

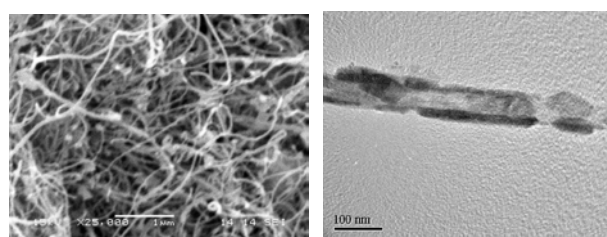


Fig. 1 SEM and TEM images of CNTs-Sb

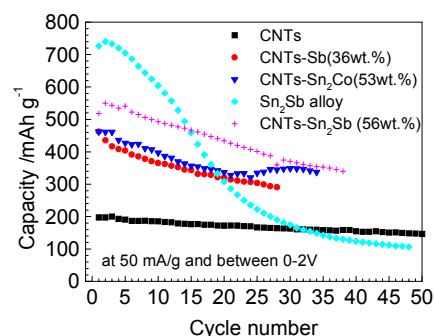


Fig. 2 Cyclability of CNT and their metal nanocomposites electrodes

References

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