Tin Oxide Nanorods as Li-ion Battery Anodes

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Introduction

Nanorods are currently being explored for applications where the charge confinement effect due to one of their length scales being in the nanometer range may impart interesting and useful properties.¹ This work reports the preparation of highly crystalline SnO_2 nanorods by heating phenathroline-capped Sn nanoparticles in a NaCl-KCl flux at 700°C; and using the nanorods as an anode material for rechargeable Li-ion batteries. The SnO_2 nanorods so obtained are typically ~15nm in diameters with an aspect ratio of ~50-1000. They cycle well as a tinbased anode material; and in some cases show specific capacities higher than the theoretical capacity expected from the well-known stoichiometry of $\text{Li}_{4.4}\text{Sn}$. The morphology changes in the nanorods during cycling were followed by SEM and TEM examinations.

Experimental

0.1g pheathroline-capped Sn nanoparticles as prepared by a previously reported procedure² was mixed with 0.2g NaCl and 0.3g KCl; ground into a fine powder and heated at 700^oC for 1h in a furnace. The melt was then naturally cooled to the room temperature. The solidified mass was washed several times with water and methanol, and dried at 130° C for 3h to recover the nanorods. 70 wt% of the nanorods, 20 wt% of carbon black and 10% of polyvinylidene fluoride were used to formulate the working electrodes in two-electrode Li test cells. All cells were tested at the constant current density of 0.4 mA/cm² and were charged and discharged between fixed voltage limits (1V or 2 V-5mV) on a Maccor Series 2000 battery tester.

Results and discussion

Fig.1a is a typical SEM image of the products obtained. A large number of rod-like structures could be identified. The rods were nanoscale in diameters and several hundred nanometers to several micrometers in lengths. The SnO_2 nanorods were also examined by TEM under high magnification (Fig.1b) which showed good uniformity of diameters of ~15nm, and a highly smooth external surface.

Within the narrower voltage range of 5mV - 1V, a specific capacity of ~700mAh/g and a highly stable cycling performance could be achieved simultaneously as shown in Fig.2. The capacity is higher than the ~650 mAh/g reported for pristine SnO₂ nanoparticles.³ Good cyclability in a more restricted voltage window is a known phenomenon.⁴ A more notable point from the same Figure is that a specific capacity of ~1100 mAh/g could be obtained in the voltage range of 2 V- 5 mV, at least for the first five cycles. The specific capacity of 1100 mAh/g is significantly higher than the theoretical capacity of SnO₂ assuming Li ion storage according to the formation of Li_xSn alloy with x_{max} of 4.4.

References

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Fig.1 (a) SEM and (b) TEM images of SnO₂ nanorods.



Fig.2 Cyclability of SnO₂ nanorod anodes.