

Tin Oxalate Modified Graphite Anodes for Lithium-Ion Battery Applications

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Introduction

While various forms of carbon are still exclusively used as the anodes of lithium-ion batteries, the search for an alternative material continues because of the un-ending need for higher capacity, and hence higher energy density in a battery. Metals and semi-metals that alloy with lithium are good candidates, but they deliver high capacities at the expense of cyclability [1-2]. This is due to changes in the specific volumes of these materials during lithiation and de-lithiation, leading to anode pulverization and the loss of particle connectivity.

Here we intended to combine the good cyclability of carbon anode with the high capacity of SnO₂ to produce a composite anode material with better application performance. The results show that such objective could be achieved with the right synthesis chemistry, and with careful control of the synthesis conditions.

Sample preparations

A known amount of tin (II) oxalate (Aldrich, 98%) was dissolved in ethanol (Hayman, 99.9%) and vigorously stirred for 2h. Graphite (KS6 from TimCal, 19 m²/g) was then added and stirring continued for another hour. This was followed by the drop-wise addition of 0.2 M LiOH aqueous solution to precipitate Sn²⁺ as mixture of Sn(OH)₄.xH₂O and Sn(OH)₂ on the graphite surface and inside the graphite layers. 30 min latter, the solid phase was removed by filtration and heated in a tube furnace at 350 °C for 3h. The procedure was repeated for different ratios of the ethanolic solution to graphite to produce different composite samples.

Result and discussion

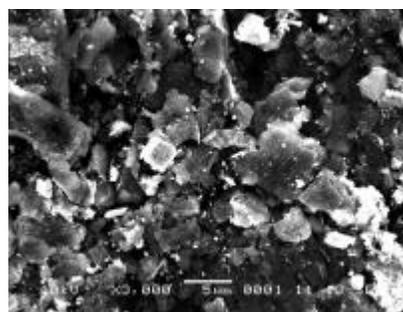
The scanning electron micrographs (SEM) in Fig.1 show the oxides as faceted particles on the graphite surface, with increasing uniformity for higher tin content samples. There is also an apparent reduction in the size and textural smoothness of the graphite flakes between pure graphite and the graphite laden with tin oxides (samples A, B, C). For samples A and B which have lower tin loadings, some tin oxide may reside within the graphite layers. The preference for the oxide particles to decorate the graphite surface rather than to exist as an independent phase is also more evident in the high tin content samples.

A comparison of cyclability is carried out in Fig. 2. Sample A with the Sn content of 1.1wt% has the best cyclability, maintaining an average capacity of about 400 mAh/g for 30 cycles. This experimentally measured capacity is significantly higher than the weighted sum of specific capacities from graphite and tin oxide (the capacities of graphite and SnO₂ are 270 mAh/g and 500 mAh/g under the experimental conditions. Collectively

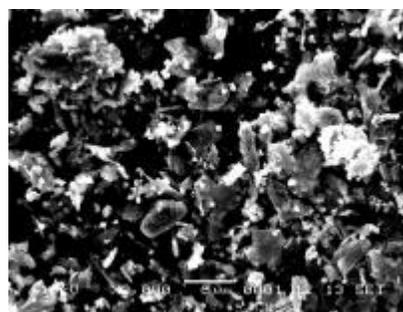
they would produce no more than 300 mAh/g if their contributions were independent and purely additive). Samples B and C with higher tin contents have fared much less satisfactorily. Not only are they poorer in cyclability, they are also lower in capacities compared to sample A.

References

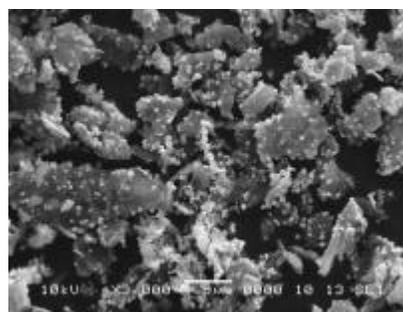
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Sample A



Sample B



Sample C

Fig. 1 SEM images of samples of different tin oxide contents

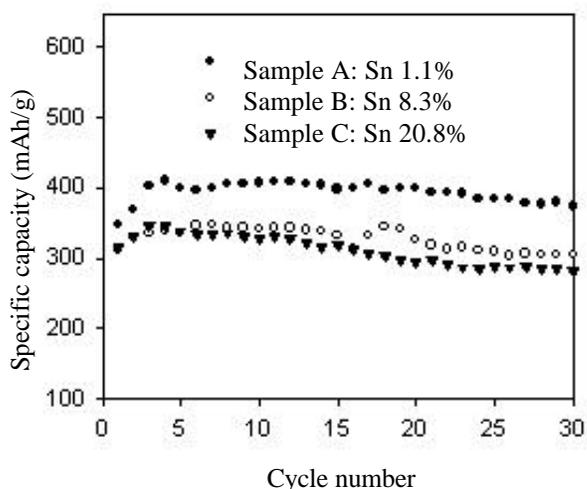


Fig.2 Cycling performance of samples with different tin oxide contents