

Electrochemical behavior of tin hydrogen phosphate in lithium batteries

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The recent intense research activity aimed at the study of Tin-based oxides and related materials as anodes in Li-ion batteries is motivated by their high capacities in comparison with the conventional carbon-based materials.¹⁻⁵ The performance of such compounds results from their aptitude to form reduced-size and well-dispersed Sn/Li alloys domains through the matrix which facilitate the alloying/de-alloying process governing the performance of the material in term of the capacity-retention.

Here we report a study on SnHPO₄ prepared by a soft-precipitation route. The electron microscopy examination of this phase shows an homogenous porous aspect with elongated “cigar”-like particles (Figure 1). Moreover, the crystallographic structure exhibits channels of ca. 0.4 nm diameter (Figure 2) which facilitate the reaction with lithium during the first steps of discharge in lithium anode cells.

Lithium cells of the type Li/LiPF₆ in EC:DMC/SnHPO₄ thermototized at different temperatures and a MacPile multichannel system were used in the electrochemical experiments. The galvanostatic experiments on these cells demonstrate a high capacity (>1700 mAh/g Sn) when the first discharge is recorded at 20° C and at 10C rate (Figure 3). However, the reversible capacity is limited to ca. 400 mAh/g Sn. A better cycling behavior was found by working at 40°C.

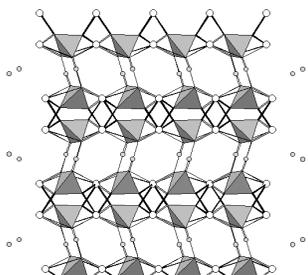
A step by step characterisation of the Li-network interaction will be presented in the light of the short and long-range modifications examined by means of X-Ray diffraction and ⁷Li, ³¹P MASNMR at different stages of the reaction with lithium. A significant conclusion of the joint XRD-NMR study is that the structure of the phosphate group is basically preserved during discharge to 0 V vs. lithium, while the formation of lithium-tin alloys with a high level of dispersion is confirmed.

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Figure 1. Electron micrograph showing the shape of the



tin hydrogen phosphate particles.

Figure 2. The structure of SnHPO₄ showing the PO₄, SnO₅ groups and the interlayer available space.

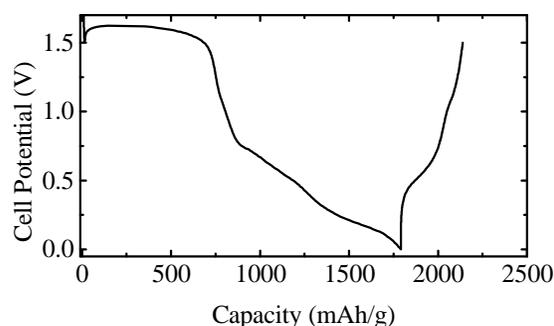


Figure 3. First discharge-charge cycle of a lithium cell using tin hydrogen phosphate electrode obtained at 20°C and a 10C rate.

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