Ball milling synthesis of $Li_xTi_yP_4$: Electrochemical performances and mechanism.

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We have recently shown that up to 7 lithium can reversibly be extracted from Li_9TiP_4 leading to first cycle specific capacities reaching up to 1000 mAh/g at an average potential of 1V vs Li^+/Li. These raw characteristics suggest these phases as very promising negative electrode for Li-ion batteries. Today's drawback with these phases is the difficulty encountered in preparing single-phase powders. The crystallised powders prepared at high temperature (900°C) are systematically found to be contaminated by extra phases with impurity contents varying from less than 10mol% to more than 50mol%. The presence of such more or less electroactive impurities curtails the electrochemical performances of these materials.

To alleviate these issues, new synthetic routes have been investigated and we present in this paper our results obtained by ball milling (BM) syntheses. By this method, pure phases can be obtained even at room temperature. However, because of the morphological as well as crystallinity characteristics of the as prepared powders, poor electrochemical cyclabily was obtained. In contrast, BM powders annealed at 500°C present nicely cristallized particles as demonstrated by XRD (Fig. 1), thus allowing a strong improvement of the cyclabilities (Fig. 2) even at high scan rate (C/2).

We will discuss in this paper, the lithium reactivity of these pure phases through PITT, GITT and in situ X-ray diffraction revealing the amorphisation/recristallisation process upon cycling.

We will also demonstrate, the ability of BM synthesis for the preparation of new phases with low titanium content. This suggests these $Li_xTi_yP_4$ phases to be described as cubic Li_xP_4 phases doped with Ti. However, the poor resulting electrochemical performances of these low Ti content phases confirm the key-role of TiP_4 tetrahedrons in the electrochemical process.

On over hand, X-ray diffraction measurements on low Li content phases prepared by BM have confirmed the structural modifications arising from the lithiation - delithiation processes.

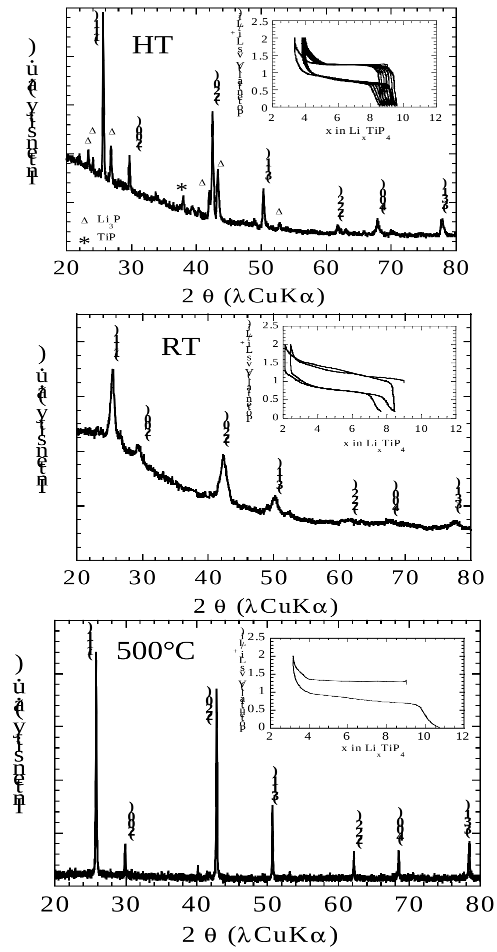

Fig.1: X-ray diffraction patterns (XRD) of Li_9TiP_4 prepared at high temperature (HT), by BM (RT), and by BM after annealing at 500°C for 1 week. Inserts show corresponding galvanostatic curves.

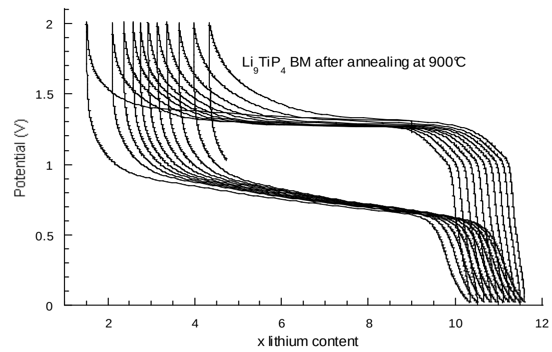

Fig.2: First 20 galvanostatic sweeps for Li_9TiP_4 prepared BM after annealing at 900°C for 1 week.

References:

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