

Strain-free structural transition during Li-ion rocing chair battery operation based on LTO anodes

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LTO (Li₄Ti₅O₁₂) spinel to cubic transformation [1] induced by Li insertion in octahedral sites and concomitant migration of pristine lithium from tetrahedral sites, is in principle strain-free; correspondingly can guarantee a longer life-time and cyclability, in spite of a lower energy density, for higher frequency applications. The transformation to a cubic structure though apparently does not affect the volume, creates at the level of the surface a strong rearrangement of the electrode changing morphology and chemical composition [2],

Cubic phase valence of Ti (3+) can be better stabilized assuming a (4+) character by transforming to a Li₂TiO₃ phase acting as a barrier against electrolyte decomposition. The role of the surface is still unknown and the possible use of it as an additional reversible capacitance source is under scrutiny. It is also debated the role of separation of the present LTO material because it is often found the clear signature of anatase or rutile TiO₂ in the raman and other structural methods like X-ray absorption or diffraction.

The structure of the device is controlled, during batteries charge and discharge cycles, at the atomic level as a function of time by using XAS [4], a chemical sensitive and short range probe, and by selectively tuning the detection depth by collecting electrons, total and partial yield, and photon fluorescence yield. X-ray absorption experiments have been conceived and realized to study the modification of the signals related to the various atomic species in LTO electrodes selected at different states of charge during the first Li insertion process and thickness.

O-K edge absorption spectra are reported for a Total yield detection. Conduction band is probed by the O 1s → O 2p-like transition, a weak two-peak separation is recognizable for rutile and much less prominent for anatase and brookite. The O2p band splitting in rutile results from the sp²-like hybridization in the planar (Y-shaped) OTi₃ building blocks. In the LTO a signature of rutile TiO₂ is clearly evident especially in the two peaked resonances below 530 eV. The transformation to the cubic phase is evident in the charged (1.0 eV) sample while the complete reversibility of the Cycled sample is an hint that the formation of the Li₂TiO₃ is not limited to the first charge discharge cycle. Also the impossibility to retrieve the exact spinel structure is due to the modification of the surface nanoparticles adopting a more Li₂TiO₃ thick configuration enough to be mostly detected by the present probing total yield detection. We also observed quite clearly the cubic structure does not seem to get covered by the titanate layer but is consumed during the charge at the first cycle possibly because still unstable, can exceed the theoretical capacitance [3].

XAS experiments at the L_{2,3} edge can be accompanied out by calculating the multiplet structure determined by the Coulomb and exchange interaction between 2p holes and 3d electrons, the splitting by the crystal field and the spin-orbit interaction [5].

The dominant contribution is the Ti⁴⁺, even if the different branching ratio cannot be entirely understood. When present the cubic charged phase the contribution of the Ti³⁺ should be more visible especially for the sample at 1.0 V.

The detailed structure and chemical composition of the nanoparticles actively incorporating Li⁺ ions in electric batteries can be obtained by means of XAS at soft and hard photon x-ray by probing the different structural transition occurring at various phases of charging and discharging of the anodes.

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