

Disproportionation hindrance of Mn³⁺ ion due to nanoparticles surface interaction with Alumina coating

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LiMn₂O₄ (LMO) is an interesting cathode material offering Li-ion storage in the spinel structure by insertion of Li⁺ in the 8a sites and exchange of the position with the empty octahedral 16c sites, in this way keeping the extraction/insertion rate as high as possible [1]. On one side such a cathode material would be preferable among other because of its high voltage operation, low cost, light weight and minor environmental impact. On the other, capacity fading has been found when surfaces oriented along {110} showing the highest Li diffusion are found the most prone to dissolution of Mn³⁺ ions into Mn²⁺ and Mn⁴⁺ [2] in presence of the electrolyte, reported as the major hinder against battery safety and durability. Such a disproportionation is enhanced by the structural phase transition occurring from the cubic spinel to the cubic rock-salt at about 3 V when Li⁺ ion is first occupying the empty 16c and then the 8a tetrahedral sites [1,3].

In this work LMO nanoparticles by solid state synthesis [4] are used in the fabrication of cathodes during various phases of delithiation and lithiation. Here, a way to avoid Mn dissolution is coating the nanoparticles with amorphous alumina (Al₂O₃).

At present it is still not clear if Alumina coating is also acting chemically by charge transfer reduction of the Mn, and vice versa and to what extent. In particular it would be important to understand if such reduction is dependent on the coating thickness or it is activated only at some particular stage during the charge. Recently the suggestion that charge transfer is mainly due to Alumina towards the LMO to make it more stable rather than the reverse [3] is still looking for a confirm. Soft XAS can be useful to spread light on this material, that like any other transition metal is a difficult tasks for DFT.

There is a second reason for using SOFT XAS for the present investigation to understand what is the role of the coating during the Li⁺ transfer, as DFT methods are definitely inefficient to reproduce such ordered/disordered interfaces. In Fig. 1 the Mn L_{2,3} series of an uncoated (green) and coated (red) batch of LMO nanoparticles used for cathodes according to the experimental procedure described in ref. [4], at various level of delithiation (up to 4.35 eV) and subsequent full lithiation (3V) are shown together with the cycling up to the final voltage of 3.6 V. What it is immediately observed is the predominance of the valency of Mn³⁺ in the case of coated samples and of the Mn⁴⁺ in the case of the uncoated samples.

A strong phase transition is visible. With a clear Mn⁴⁺ component at 643 eV and the Mn³⁺ at 640 eV. Such a Mn component while is evident in the case of full lithiation in the coated samples, it is less evident for non coated samples because of the disproportionation in Mn⁴⁺ / Mn²⁺ and related dissolution within the electrolyte of the latter Mn²⁺. It does prove that the coating is effectively preventing such chemical damaging.

It is also found that Mn⁴⁺ valency is not easy to be reached during the delithiation in uncoated samples. This is an indication that lithium is hardly removed from the structure and it is a clear proof that the cathode cyclability is limited. By using CMT4XAS [5] we determined not only the valence of the Mn states but also the local Mn coordination. We found that the cathodes assume a coordination that is different from the octahedral one at the first stages of the electrode (fresh samples) and it is transformed to a more octahedrally coordinated Mn during the operation of charge. This counterintuitive behavior is rationalizable if we consider that the coating helps the structural stability of the whole nanoparticles hindering the Jahn teller distortion.

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Fig.1 Comparison of coated(red) vs uncoated (green) LMO nanoparticles in delithiation/lithiation of LiB cathodes.

Fig.2 Multiplet simulation by CTM4XAS of lithiated coated and uncoated cathodes MnL_{2,3} experiments (black curves).

