Structural evolution of the $LiNi_{0.5}Mn_{1.5}O_4$ cathode material upon ex-situ and in-situ cycling by (S)TEM

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$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is considered to be a promising cathode material for the application in the new generation of high voltage lithium-ion batteries. However, various factors such as oxidation state, atomic coordination of Mn and Ni cations and the morphology of the particles influence the performance of LNMO as cathode material [1], [2]. Previous results have shown the presence of different crystallographic phases at different cycling stages using high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) imaging techniques [3] which is mainly sensitive to Mn and Ni in LMNO. The distortion at the oxygen sites and the oxidation state of the Mn and Ni have not been investigated. In this work, our purpose is to investigate structural and chemical changes in LNMO at different state of charge using a broader range of TEM techniques, including annular bright-field (ABF) STEM and electron energy-loss spectroscopy (EELS).

The battery electrochemical cells were assembled in a Swagelok-type cell and were tested at a current rate of 20 $mA.g^{-1}$ and cycled between 3.5-5 V (vs. Li/Li^{+}). Two cells (labeled 1 and 2) were stopped at 5 V (charged) and 3.5 V (discharged) respectively and their respective active materials sealed to prevent atmospheric contamination. HAADF-, ABF-STEM and selected area electron diffraction (SAED) imaging methods were used to determine changes in crystal structures at different cycling states (pristine, charged, discharged). It was found that depending of the state of charge, LNMO undergo atomic structure transformations. The SAED pattern and HAADF-STEM data of as-synthesized nanoparticles (Fig.1) shows a perfect periodic arrangement of atoms in spinel crystal structure with a little amount of the rocksalt phase. Upon delithiation the migration of transition metals (TM) occurred into the lithium tetrahedral sites, which is seen as the additional contrast in this sites on HAADF- and ABF-STEM images along [110] direction (Fig.2). After the first discharge, the spinel is still the predominant phase (Fig.3b) while a small amount of the intermediate phase is present at the edge of the particles (Fig.3c) and rocksalt phase in the bulk part (Fig.3d). The position of the oxygen column, visible in ABF-STEM imaging mode will be correlated with the oxidation states of Mn and Ni measured by EELS. In the next stage, the *in-situ* in a TEM liquid experiment will be started in order to fully understand and characterise the formation and evolution of different phases of LNMO during electrochemistry cycling at the atomic scale.

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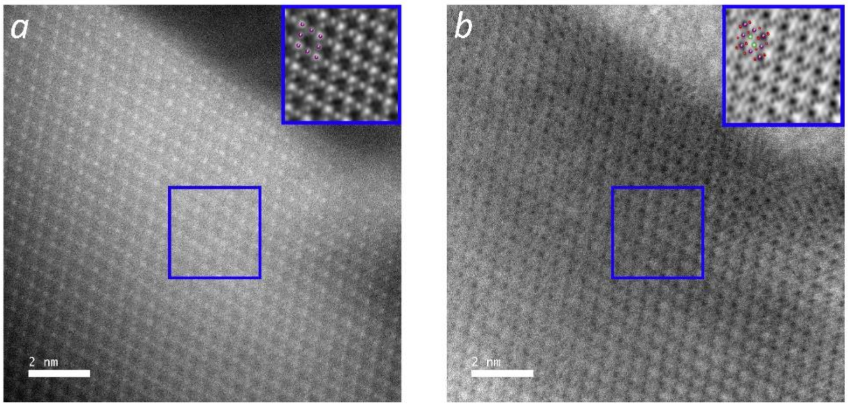

Figure 1. HAADF-STEM (a) and ABF-STEM (b) micrographs of the pristine LNMO nanoparticle along [110] zone axis. Insets show enlarged areas overlaid with the corresponding spinel crystal structure (O - red atoms, Mn – purple, Ni – gray, Li – green).

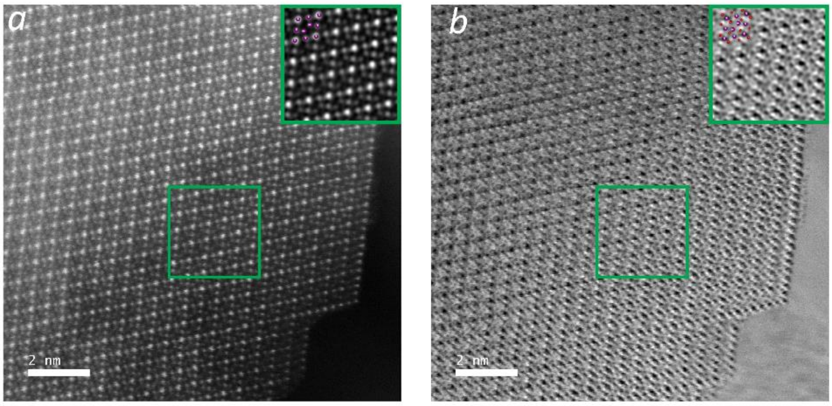

Figure 2. HAADF-STEM (a) and ABF-STEM (b) micrographs of the charged LNMO nanoparticle along [110] zone axis. Insets show enlarged areas overlaid with the corresponding crystal structure (O - red atoms, Mn – purple, Ni – gray, Li – green). Additional contrast can be seen in the tetrahedral sites.

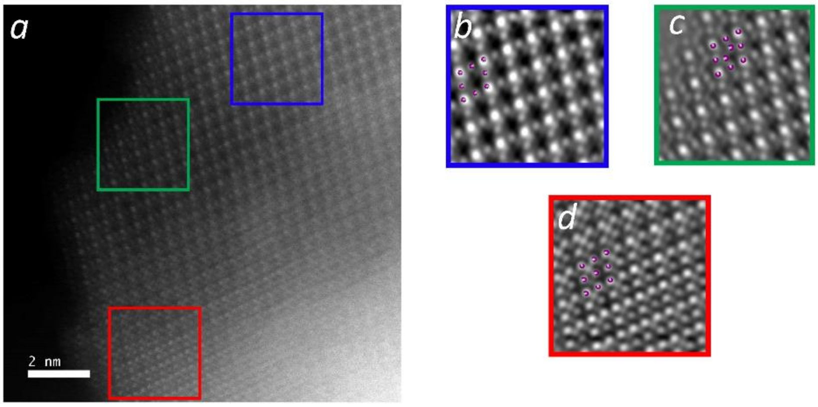

Figure 3. a) HAADF-STEM micrograph of the discharged LNMO nanoparticle along [110] zone axis. Enlarged areas overlaid with the corresponding crystal structures of b) spinel, c) intermediate with TM atoms in the tetrahedral sites, d) rocksalt-like structure with TM in octahedral site (Mn – purple, Ni – gray, Li – green).