ESRF	**Experiment title: In situ study of lithium insertion-deinsertion in lithium rich layered oxide.**	**Experiment number**: 20-02-706
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Report:

The goal of this experiment was to study the mechanism of lithium insertion-deinsertion in a high capacity electrode material : $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$. We aimed to get more information on the origin of the extra capacity observed during the first charge and which cannot be explained by the oxidation of metals to tetravalent state.

For this purpose we cycled this material in a pouch cell containing lithium as counter electrode. During this cycling, difffractogramms were taken in a transmission mode every 3 minutes at the energy of 25 keV and using an image plate detector. This allowed us to collect 900 diffractogramms along the first 1.5 cycle, giving us a high time resolution.

The whole pattern matching refinement was carried out every ten patterns to follow the structural changes. Each result was then attributed to one voltage. These results are provided in figure 1

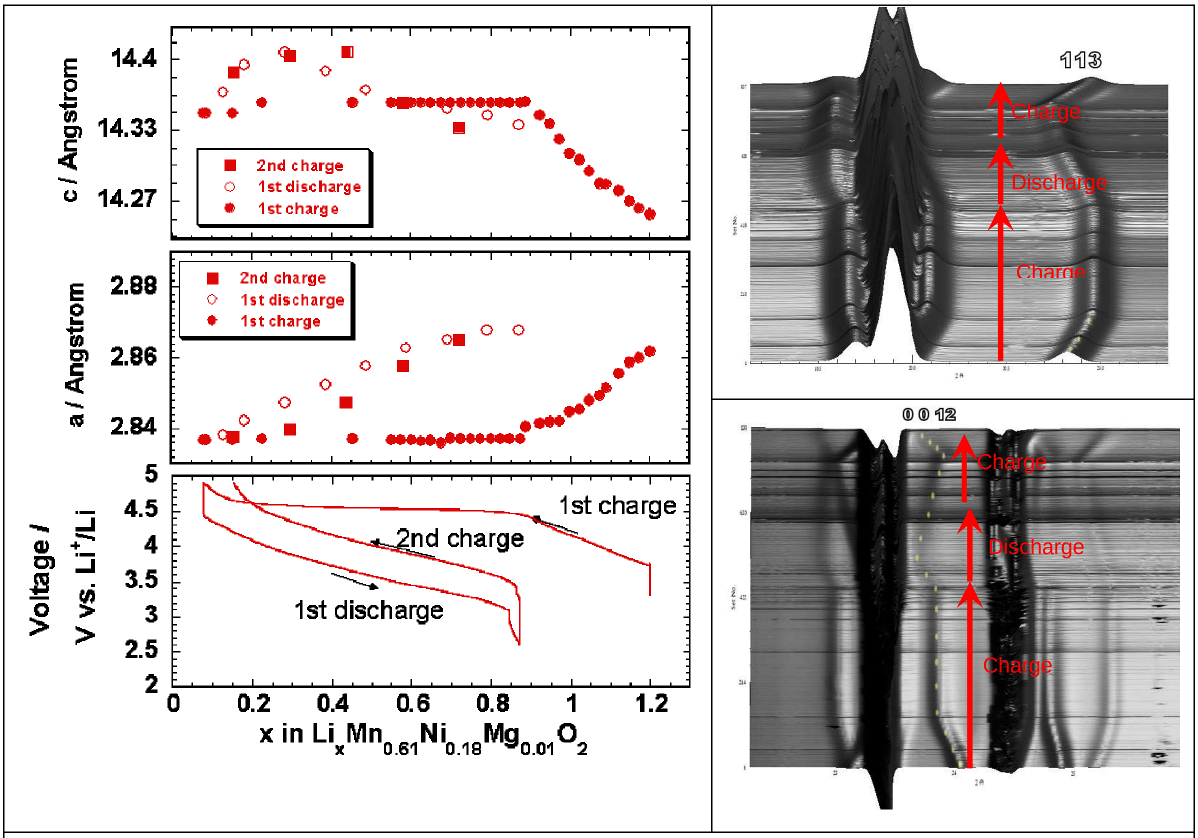

Fig. 1 : Evolution of cell parameters related to electrochemical curve and evolution of caracteristic reflexions

As one can observe, during the first step of the charge, the cell parameters evolve linearly as well as the potential. This is attributed to the oxidation of metals which gives smaller ionic radii explaining the decrease of a and b parameters, and to the lesser content of the lithium layer that lead to a diminishing screening effect between the oxygen of the metals layers and then to an increase of the c parameter.

When the potential reach the high voltage plateau, no further evolution of cell parameters is observed. This would be expected for a biphasic process, but surprisingly no new phase is observable. Then we can suppose the second phase is amorphous or so close from the first one that we can not distinguish them simply. An analysis of the FHWM is under progress do determine if the peak broadening observed can be due to this second phase.

However after this first charge, we observe a completely different mechanism, allthough the a and b parameters come back to values close from the starting one during the discharge, indicating the reduction of the metals, the c parameter does not show a reversible behaviour. This new mechanism is reversible during the second charge with almost no hysteresis. This would mean, that the first charge acts as an activation which creates a new structure. This structure would then be cycle reversibly.

During this measurement campaign we also took an *ex situ* pattern of the starting compound in a capillary geometry, to be able to refine the complex structure of this compound where metallic cationic site are occupied by 3 different atoms. Coupled with an ex situ neutron measurement, it allowed us to refine the repartition of the cations in the layers giving us a reliable starting point for further refinement on cycled compounds. We particularly observed a statistic ordering of metals decresing the symmetry from $R\bar{3}m$ to $C\,2/m$ with cell parameters a=4.961Å, b=8.588 Å, c=5.038 Å, β=109.30°, and a 3.85 % Ni/Li exchange in the lithium layers (fig.2) .

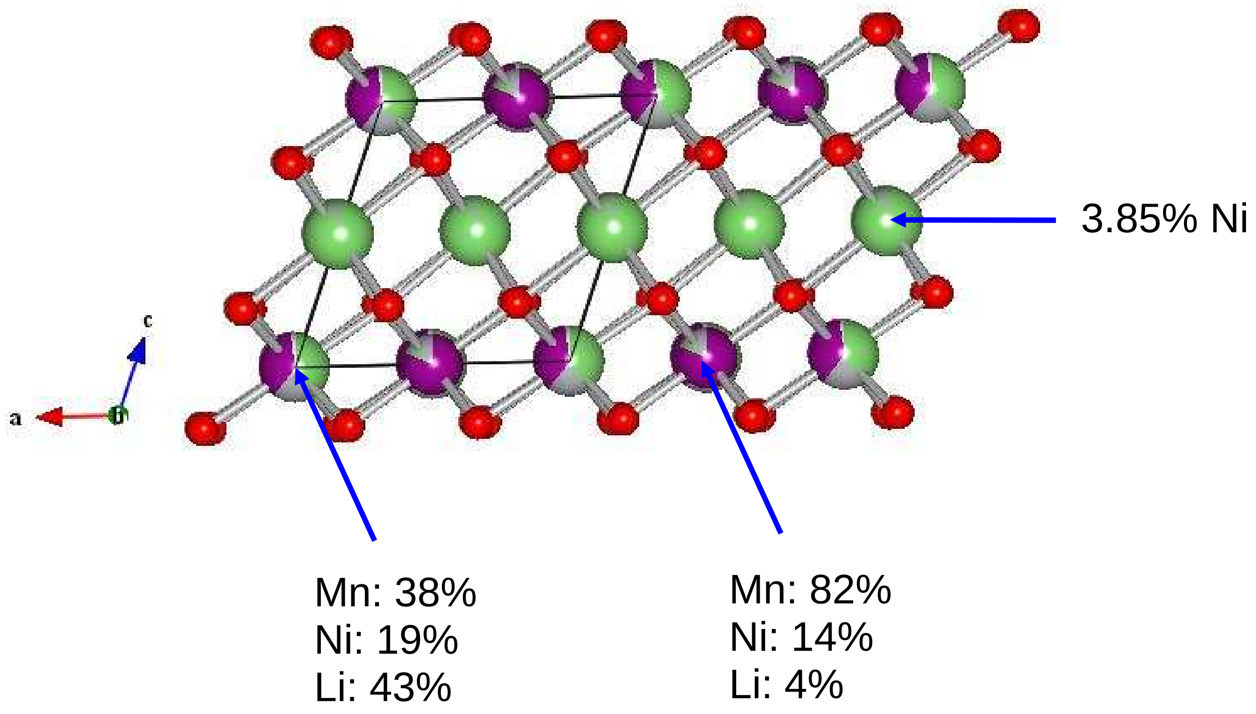

Fig. 2 : Structure of the starting compound and repartition of the metals

To summarize, this study allowed us to enlight an activation step at high voltage in this material and to obtain more information on the starting compound. The caracterization of the compound at the end of the charge is still to be done and it would certainly require new experiment (*ex situ* neutron diffraction has already been carried out).