



	Experiment title: In situ XAS during lithium insertion-de-insertion in lithium rich layered oxide.	Experiment number: HS-4261
Beamline: BM30B	Date of experiment: from: 27/10/2010 to: 01/11/2010	Date of report: 08/02/2010
Shifts: 18	Local contact(s): Vincent Ranieri, Olivier Proux	<i>Received at ESRF:</i>
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Report:

The goal of this experiment was to study the mechanism of lithium insertion-deinsertion by X-ray absorption spectroscopy in a high capacity electrode material : $\text{Li}_{1.2}\text{Ni}_{0.18}\text{Mn}_{0.61}\text{Mg}_{0.01}\text{O}_2$. 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, X-ray absorption spectra were taken in a transmission mode at the Ni and Mn *K* edge. In the case of references and starting material, the spectra were acquired on pellets prepared by mixing them with boron nitride (BN).

Figure 1 provides XANES spectra of Mn and Ni at different states of charge during the first cycle. Dotted line spectra are XANES spectra of reference samples. It is clear, looking at the maximum of the edge, that for both Mn and Ni, a shift toward higher energies during charge is observed. However, although it seems that Ni valence moves from around +II at the initial state to almost +IV at fully charged state, it is more uncertain to interpret quantitatively the valence of Mn due to big changes in width and relative intensities of the different absorptions. Nevertheless, the shift of the Mn edge can be explained by a valence lower than +IV at the beginning of the charge.

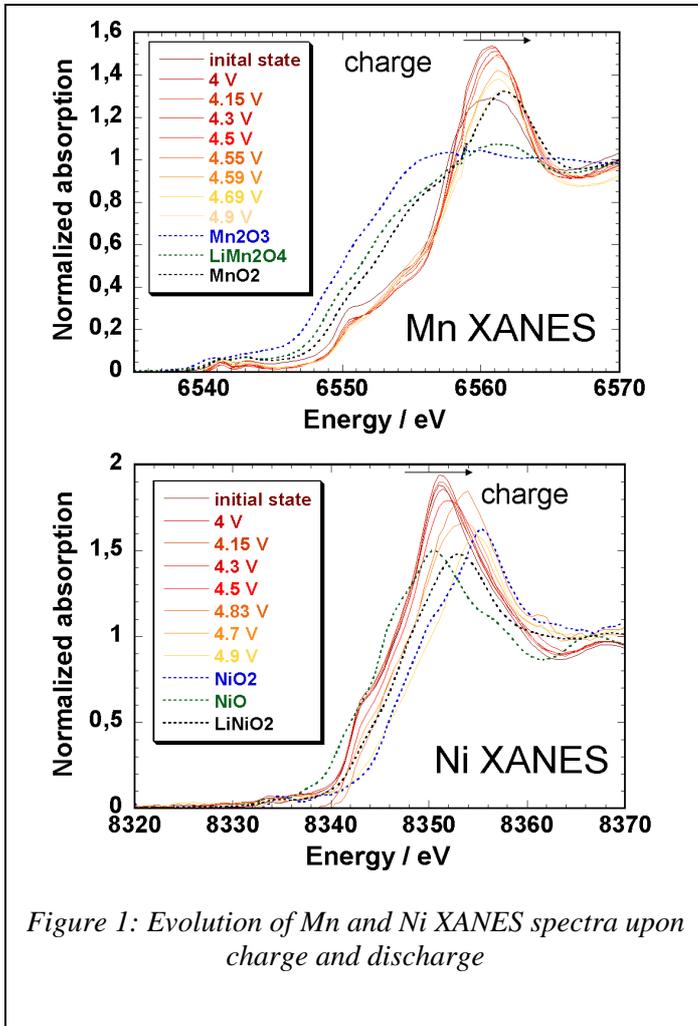


Figure 1: Evolution of Mn and Ni XANES spectra upon charge and discharge

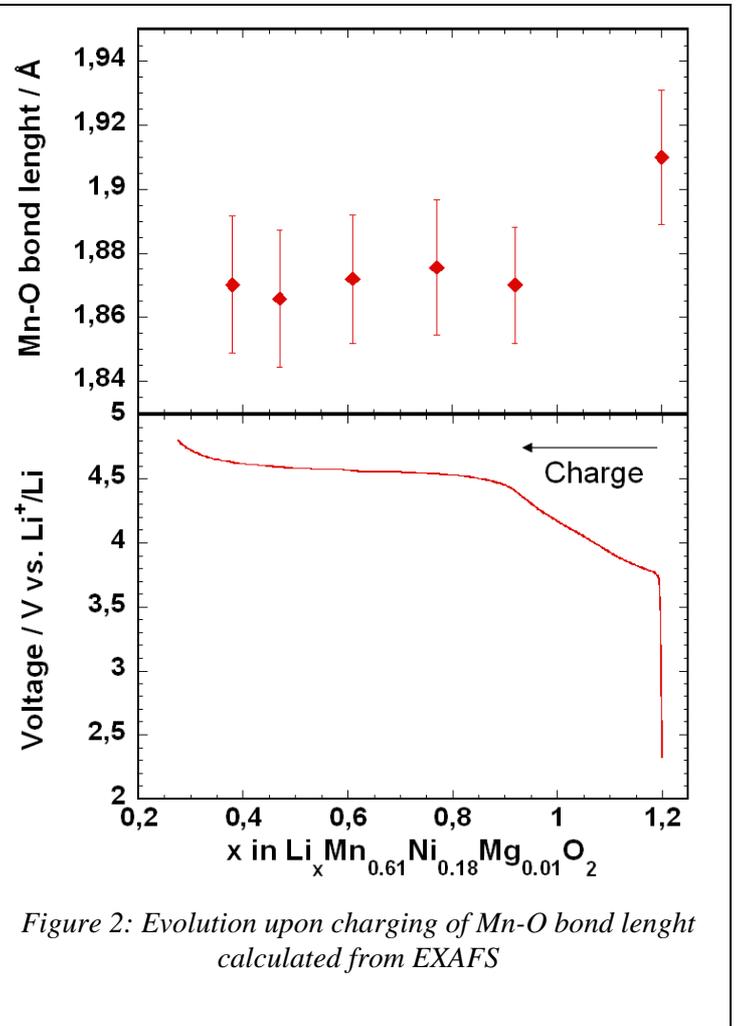


Figure 2: Evolution upon charging of Mn-O bond length calculated from EXAFS

Concerning the EXAFS part, only Mn spectra could be analysed, because of the poor quality of the Nickel spectra.

As an example, fig 2 presents the evolution of the Mn-O bond length upon charge. It is observed that Mn-O bond is decreasing during the charge, this tends to confirm that Mn is oxidising during charge. Moreover, this decrease seems to occur during the first slope of the charge, then it remains constant on the plateau. From this point of view, oxidation of Mn seems to occur during the first slope.

This is a very important observation for the comprehension of the first cycle mechanism of such materials considering that, so far, it was generally assumed that Mn valence was +IV [1]. The presence of oxygen vacancies in the initial material can be an explanation. Further investigations on this subject have to be performed on the initial material.

This first experiment provided very interesting results and showed that *in situ* XAS is a powerful tool to study the valence and the local structure around Ni and Mn atoms during cycles. However, the set up has to be improved (design of the cell, quantity of material, absorption of packaging...) in order to obtain better spectra especially at the Ni K edge. Some solutions are being considered for future experiments.

[1] Atsushi Ito, Decheng Li, Yuichi Sato, Masazumi Arai, Manabu Watanabe, Masaharu Hatano, Hideaki Horie, and Yasuhiko Ohsawa. Cyclic deterioration and its improvement for li-rich layered cathode material $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$. Journal of Power Sources, 195(2):567 – 573, 2010.