



	Experiment title: Investigation of the (de-)sodiation mechanism of O3/P2/P3-type $\text{Na}_{0.76}\text{Mn}_{0.5}\text{Ni}_{0.3}\text{Fe}_{0.1}\text{Mg}_{0.1}\text{O}_2$ for high-performance Na-ion cathodes via <i>in situ</i> XAS	Experiment number: MA-3437
Beamline: BM23	Date of experiment: from: 17/09/2017 to: 22/09/2017	Date of report: 10/09/2017
Shifts: 15	Local contact: Debora MEIRA	<i>Received at ESRF:</i>
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Report:

We have recently developed a mixed P3/P2/O3-type sodium-ion cathode material with an average elemental composition of $\text{Na}_{0.76}\text{Mn}_{0.5}\text{Ni}_{0.3}\text{Fe}_{0.1}\text{Mg}_{0.1}\text{O}_2$.^[1] This mixed-phase cathode allows for overcoming the intrinsic drawbacks associated to single-phase P2- and O3-type materials and, as a result, provides high specific capacity, superior rate performance, and excellent long-term cycling stability. The underlying mechanism of the occurring phase transitions, however, in fact, for all these materials but in particular for this new material class has not been fully revealed so far.

Therefore, we performed in this experiment a comparative *in situ* X-ray absorption analysis (XAS, K-edge) of the two single-phase and the mixed-phase material, to investigate the evolution of the oxidation states (XANES) and local environment (EXAFS) of the transition metal cations (Mn, Fe, and Ni; Mg is considered to be electrochemically inactive) and, thus, the overall structural changes as a function of the sodium content in the layered lattice. We may note here, that we studied only the charge process for the Fe edge due to time constraints. The general development of the *in situ* recorded XANES spectra, for the O3 sample, at the three edges is presented in **Figure 1**. The XANES changed for all edges during the charge and discharge cycles, indicating the reversible changes in oxidation state upon sodiation and desodiation. This edge shift was plotted as a function of time and specific capacity to compare it with the evolution of the cell voltage. As apparent from **Figure 2**, the edge shift nicely follows the potential profile, highlighting the successful implementation of this *in situ* technique for studying the evolution of the electronic structure upon charge/discharge for this material class – particularly for the electrochemically most active nickel.

EXAFS measurements were conducted in the pristine material and charged/discharged states (4.3 / 2.5 V vs. Na^+/Na , respectively). The local environment of the Ni, Fe, and Mn atoms was determined using the phase shift and amplitude functions for M-O, M-M and M-Na (where M corresponds to the metal), as calculated for the O3 structure and a cubic impurity. The EXAFS results reveal a decrease of the coordination number for the M-Na contribution upon charge (i.e., desodiation). This effect was more pronounced at the Ni-edge, which is contributing most to the recorded capacity. Also, a contraction for the M-O and M-M distances and an increase in the Debye Waller values were observed for the charge process. These effects were reversible when the sample was discharged. For all edges, it was necessary to include an M-O contribution related with the cubic impurity.

In sum, we may state that the experiment is considered very successful – not least with respect to the great amount of data, which are presently still treated and analyzed and will be reported in a corresponding publication in near future.

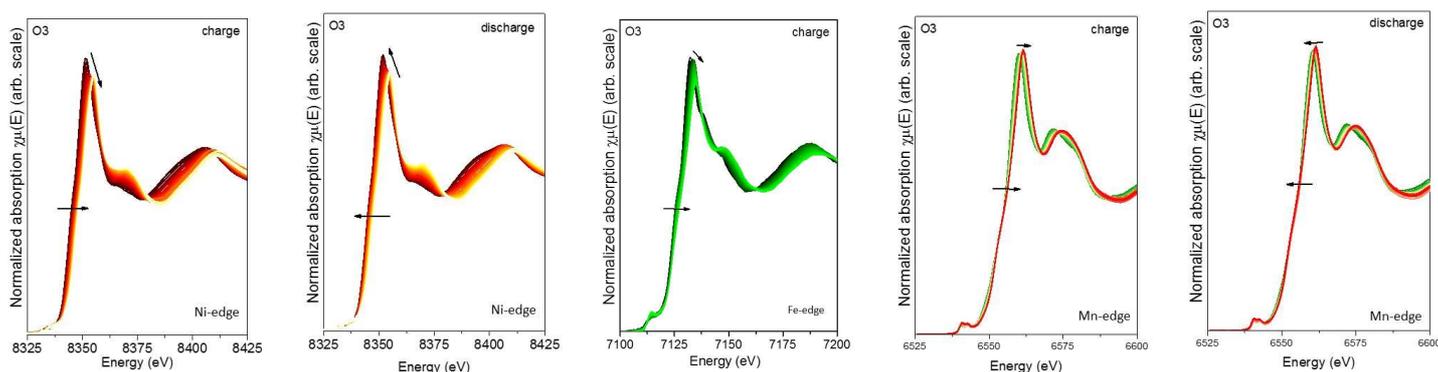


Figure 1. XANES spectra for the O3 sample during charge and discharge at the three different edges – Ni, Fe, and Mn.

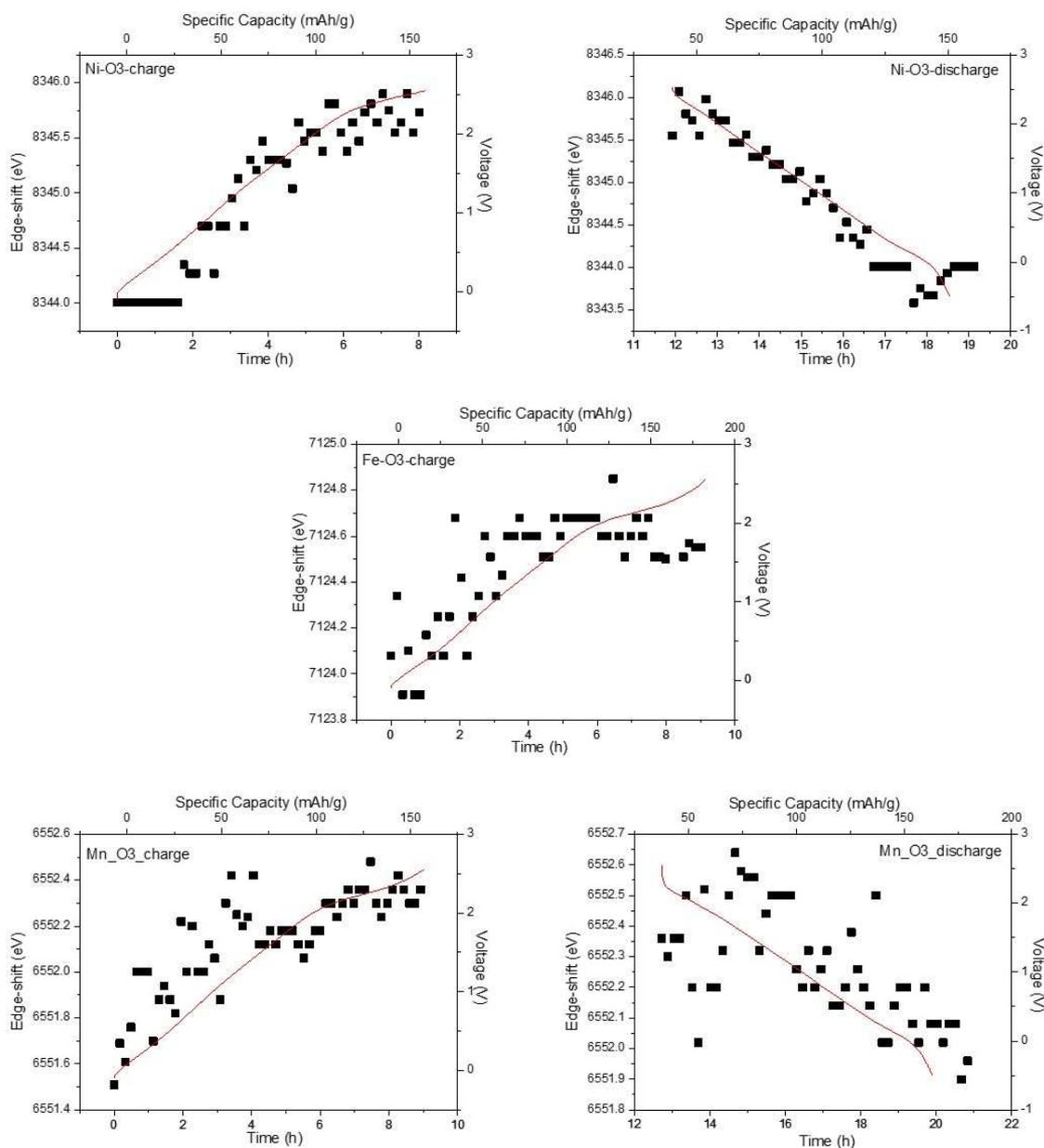


Figure 2. Edge shift deduced from the XANES data as a function of time and specific capacity compared with the cell voltage for the O3 sample at the three different edges – Ni, Fe, and Mn.