ESRF	**Experiment title:** Spinel-based intercalated electrodes for Li-ion and Na-ion batteries. Investigation of the local environment of Mn atoms.	**Experiment number**: MA 3845
Beamline: ID26	**Date of experiment**: from: 18/10/2017 to: 24/10/2017	**Date of report**: 05/01/2018
Shifts: 18	**Local contact(s)**: Rafal Baran	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dominika Baster[1*], Lukasz Kondracki[1*], Sara Lafuerza[2*] and Rafal Baran [2*]

[1]AGH University of Science and Technology, Faculty of Energy and Fuels, al. Mickiewicza 30, 30-059, Krakow, Poland

[2]Laboratory ESRF 6 rue Jules Horowitz B.P 220 FR - 38043 GRENOBLE Cedex (France)

Report:

The electronic and local structure changes of the Mn and Ni atoms in spinel oxides for cathode materials with different intercalating ions (Li and/or Na) were investigated by X-ray absorption and emission spectroscopies (XAS-XES). We performed high energy resolution fluorescence detected (HERFD) XAS measurements by setting the emission energy to the maximum of the transition metal $K\alpha_1$ line. Both the x-ray near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) were recorded. The experiment was performed on pellet samples made from few mg of of pollycrystalline material mixed with cellulose in about 1 wt % in order to minimize the self-absorption effects. A micro-tomo furnace from the ESRF sample environment and the He flow cryostat from ID26 were used to carry out the temperature-dependent measurements between 200 K and 353 K. In the following we present the main results focusing on the HERFD-XANES data, the analysis of the EXAFS spectra is currently in progress.

Firstly, we investigated the environment of the Mn atoms by means of room temperature measurements on samples $Li_xMn_2O_4$ (x = 0.1, 0.2, 0.3, 0.5, 0.7, 1) and $Na_xMn_2O_4$ (x = 0.1, 0.2, 0.3, 0.5, 0.7, 1) to follow the changes as a function of the intercalating ion content (x). Besides, we measured MnO (Mn^{2+}), Mn_2O_3 (Mn^{3+}), Mn_3O_4 (Mn^{2+}/Mn^{3+}), MnO_2 (Mn^{4+}), $LiMn_2O_4$ ($Mn^{3.5+}$), Li_2MnO_3 (Mn^{4+}), and λ-MnO_2 (Mn^{4+}) as references. A shift in the main rising edge of the HERFD-XANES spectra as well as intensity changes in the pre-edge are observed between the measured materials with different alkaline metal content (see Figure 1 and Figure 2), indicating changes in the valence state of manganese as a result of electrochemical deintercalation/intercalation process. In particular, the edge shifts to lower energies upon increasing x which reflects a reduction in the Mn oxidation state from +4 to +3.5. While the evolution is more continuous for $Li_xMn_2O_4$, greater changes are appreciated in $Na_xMn_2O_4$ for $x \geq 0.7$ which we ascribe to the fact for this content the structure is no longer cubic but cubic+monoclinic [1]. The temperature-dependent measurements revealed no changes on the HERFD-XANES spectra of $Li_xMn_2O_4$ and $Na_xMn_2O_4$ (not shown here) despite the fact that these compounds exhibit a structural phase transition from cubic to orthorhombic at around 280 K. This finding indicates that the Mn local structure remains unchanged through this transition.

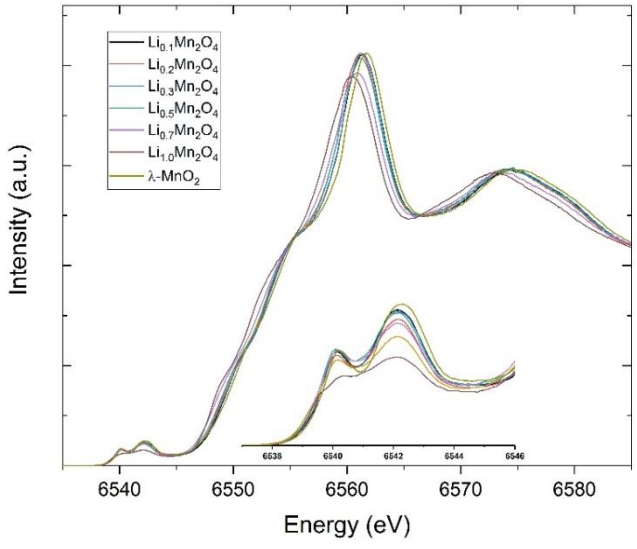

Fig. 1. HERFD-XANES spectra of $Li_xMn_2O_4$ together with λ-MnO_2, measured at 298 K as a function of lithium content (Mn K-edge).

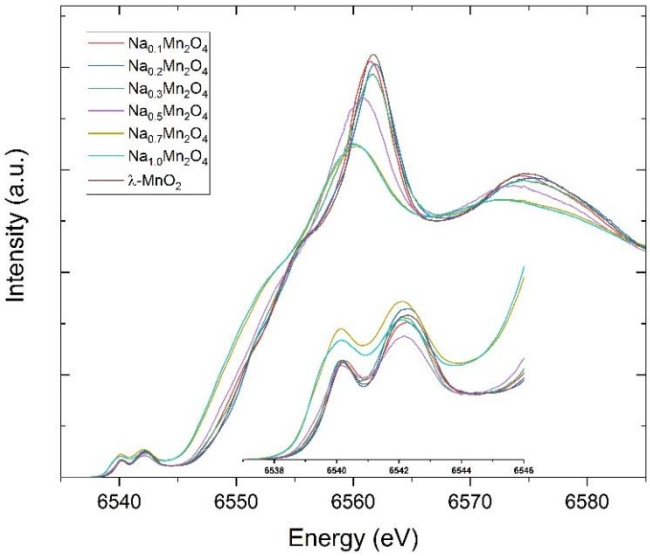

Fig. 2. *HERFD-XANES spectra of $Na_xMn_2O_4$ together with λ-MnO_2, measured at 298 K as a function of sodium content (Mn K-edge).*

We also studied the Ni-substituted spinels $Li_xMn_{1.5}Ni_{0.5}O_4$ (x = 0.3, 0.5, 0.7, 0.8, 1) obtained by electrochemical deintercalation of Li. These samples were first studied at room temperature at both Mn and Ni K-edges. We also measured the Ni-references: NiO (Ni^{2+}), $NiCO_3$ (Ni^{2+}), La_2NiO_4 (Ni^{2+}), and $LiNiO_2$ (Ni^{3+}). The absence of significant changes in the HERFD-XANES at both edges (see Figure 3 and Figure 4) as a function of Li content (x) compared to $Li_xMn_2O_4$ indicates that in Ni-rich spinels, manganese and nickel are not electrochemically active during battery operation. No temperature-dependent changes were observed in the Ni-substituted samples either.

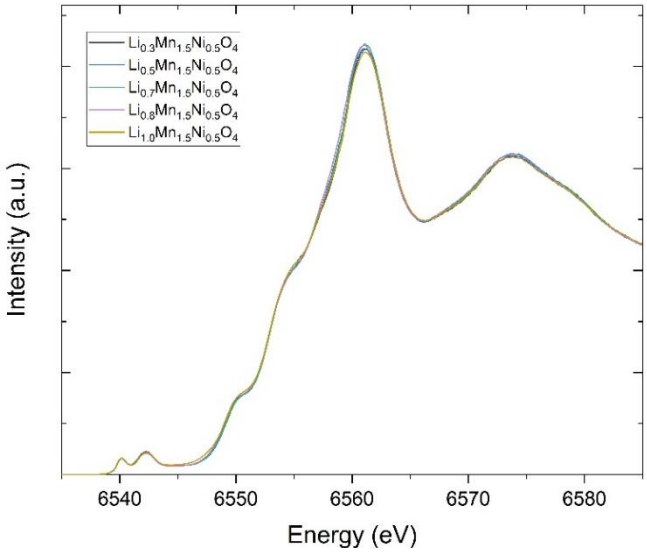

Fig. 3. HERFD-XANES spectra of $Li_xMn_{1.5}Ni_{0.5}O_4$, measured at 298 K as a function of lithium content (Mn K-edge).

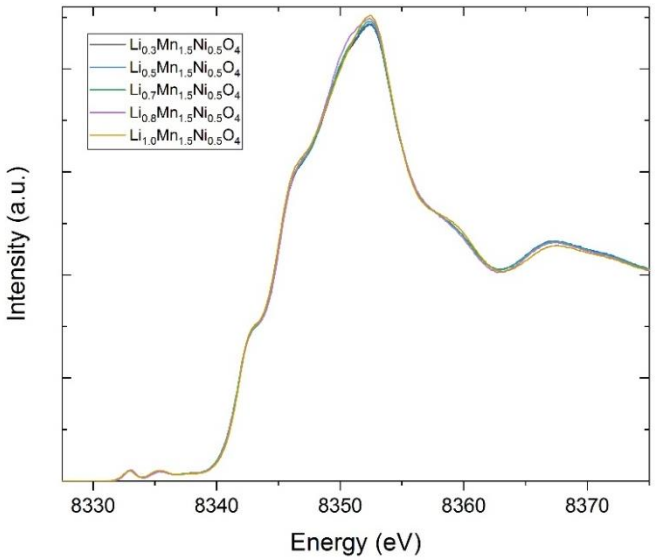

Fig. 4. *HERFD-XANES spectra of $Li_xMn_{1.5}Ni_{0.5}O_4$, measured at 298 K as a function of lithium content (Ni K-edge).*

References: [1] Tian, M., Gao, Y., Wang, Z., & Chen, L. (2016). Understanding structural stability of monoclinic $LiMnO_2$ and $NaMnO_2$ upon de-intercalation. *Physical Chemistry Chemical Physics*, *18*(26), 17345-17350.