



Experiment title: In situ investigation of the reaction mechanism of oxyphosphate's family ($M_{0.5}TiOPO_4$, $M=Ni, Co, Cu, Mg, Fe\dots$) used as negative electrode for Li-ion batteries

Experiment number:
01-01- 914

Beamline: BM01B	Date of experiment: from: 23.1.14 to: 27.1.14	Date of report: 28.2.14
Shifts: 12	Local contact(s): Wouter van Beek	<i>Received at ESRF:</i>

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Report:

The aim of this beamtime was to test our newly developed in situ electrochemical cell and, by using this cell, to study the reaction mechanism of $Fe_{0.5}TiOPO_4$ upon lithation and delithiation. The main focus was on assigning the different plateaus and reactions detectable by the galvanostatic cycling to the reacting metal ion. This would allow understanding which reaction delivers how much specific charge in the material. An additional aim was to understand which reaction leads to an amorphisation in the sample.

We successfully tested our newly developed in situ electrochemical cell. We were able to follow the reaction mechanism of $Fe_{0.5}TiOPO_4$ upon lithiation and delithiation by observing the Ti K-edge in fluorescence, the Fe K-edge in transmission and an XRD of the same spot of the sample within less than 40 min. By using the motor of the sample stage, we were even able to measure alternating two cells. The two cells differentiated in the cycling program and the used window material. The galvanostatic curves of both cells are plotted in figure 1 (left). Cell 1 was equipped with a PE-window and was cycled first to 1.3 V and then to 3.0 V in

order to check the reversibility of the reaction mechanism with the first Li^+ per formula unit. Afterwards, this cell was cycled to 10 mV. A Kapton-tape was used as a window for cell 2. Cell 2 was cycled in a slow cycle to 10 mV, followed by a delithiation to 2.6 V.

It can be seen in Figure 1 (right) that there is a phase change before reaching the plateau at 0.8 V with minor changes of that phase during the plateau. After the plateau, the sample turns amorphous from XRD point of view. From the observation of the Ti- and Fe-K-edge for cell 2 (figure 2 right), it can be seen that the phase change can be associated with a reduction of Ti and the amorphisation with a reduction of Fe. Upon further cycling to 10 mV, Ti is reduced further. Upon delithiation to 2.6 V, Ti was oxidised but no significant change for the edge position of Fe was observed. Similar results were obtained with cell 1 (figure 2 left) for the lithiation to 10 mV. For the first cycle with the lithiation to 1.3 V, it could be seen that there is only a partly reversible reduction of Ti detectable. In general the data quality with the PE-window at the Ti-edge is much better due to the lower absorption of the window material.

A further investigation of the data is ongoing, especially the comparison of the absorption energies with measured ex situ references, as well as the comparison of the in situ data with ex situ data of samples cycled to key positions in the galvanostatic curve. Additionally the treatment and analysis of the intermediate in situ measurements is in progress.

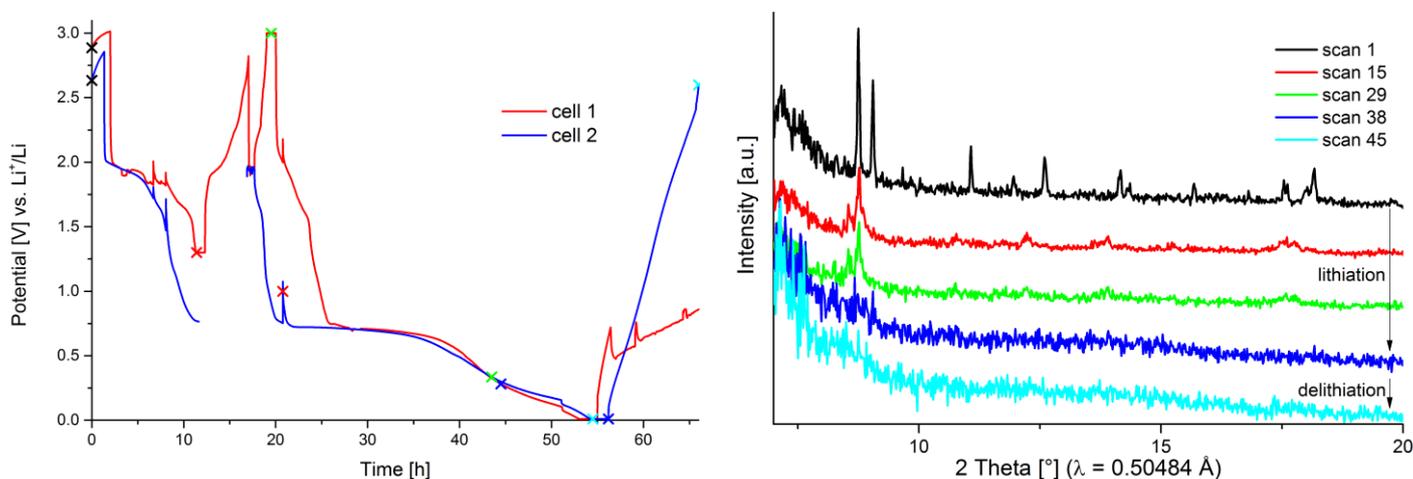


Figure 1: Galvanostatic curve of the two cells during the in situ experiment (left) and the XRD patterns of cell 2 collected at the marked points.

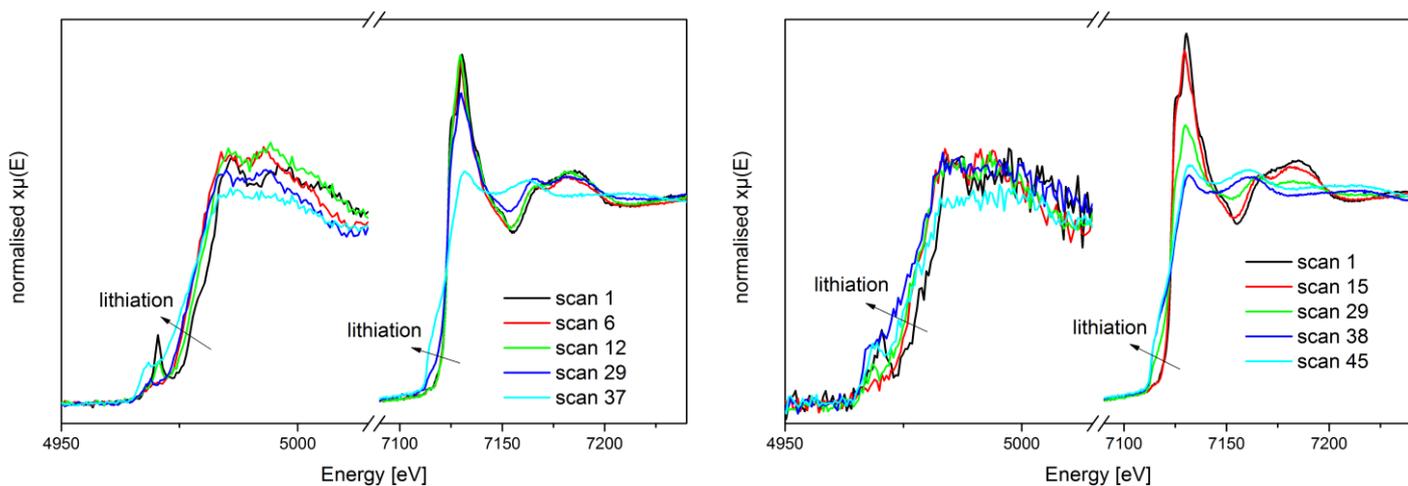


Figure 2: XANES spectrum of the Ti- and Fe- K-edge of cell 1 (left) and cell 2 (right) collected at the marked points of the galvanostatic curve in figure 1.