ESRF	**Experiment title:** Investigation of heterogeneous lithiation occuring during operation in graphite electrodes of Li-ion batteries using operando micro-XRD	**Experiment number**: MA-4110
Beamline: ID13	**Date of experiment**: from: 21/04/2018 to: 23/04/2018 & from: 20/07/2018 to: 22/07/2018	**Date of report**: 02/03/2020
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Report:

The aim of the experiment was to use operando micro X-ray diffraction to follow the local lithiation states of graphite particles at different positions along the electrode thickness, i.e. between the electrode surface and the current collector, during constant current charges and discharges. The results would then be compared to the output of our physics-based model, which can predict such inhomogeneities as a function of the electrode properties and cycling parameters and the accuracy of which was verified at the macro scale.

Since we could perform the different parts of the experiment (charge/discharge) independently, we decided after discussion with the beamline staff to have the 4-day beamtime split into 2 runs of 2 days each. That way we would get a chance to reconsider and correct anything that could go wrong during the first run.

We designed a custom operando cell to allow the beam to pass through the thickness, over a distance short enough to minimize absorption and parallax effects, but long enough so that the electrode could be manually manipulated in a glovebox for preparation (Fig. 1). We obtained all the necessary information (drawings, measurements, etc…) from the beamline staff ahead of time to design a cell compatible with the beamline setup. We also receive support from the Soft Condensed Matter Group who kindly accepted to 3D-print the interfacial part between the cell and the gonio head of ID13. The cells (2 full systems) were tested at the CEA facility. We were granted our request to access the ESRF EC-lab, so we could prepare the sample for the experiments onsite, which proved very useful.

Beamline alignment and calibration was performed at the beginning of each run with the help of the beamline staff. We aligned the EIGER 4M detector behind the sample so that it the graphite 002 ring would lie near the middle. We set up our own galvanostat inside the hutch with a remote control over IP. For each run, after each sample mounting, the surface of the electrode was aligned flat in the horizontal plane using the micro-focused beam and the absorption of the copper current collector/stainless steel electrode. The acquisition was performed as a series of z-scans at different y-

positions. Data reduction was run in parallel using scripts from the beamline staff on the nanofocus station.

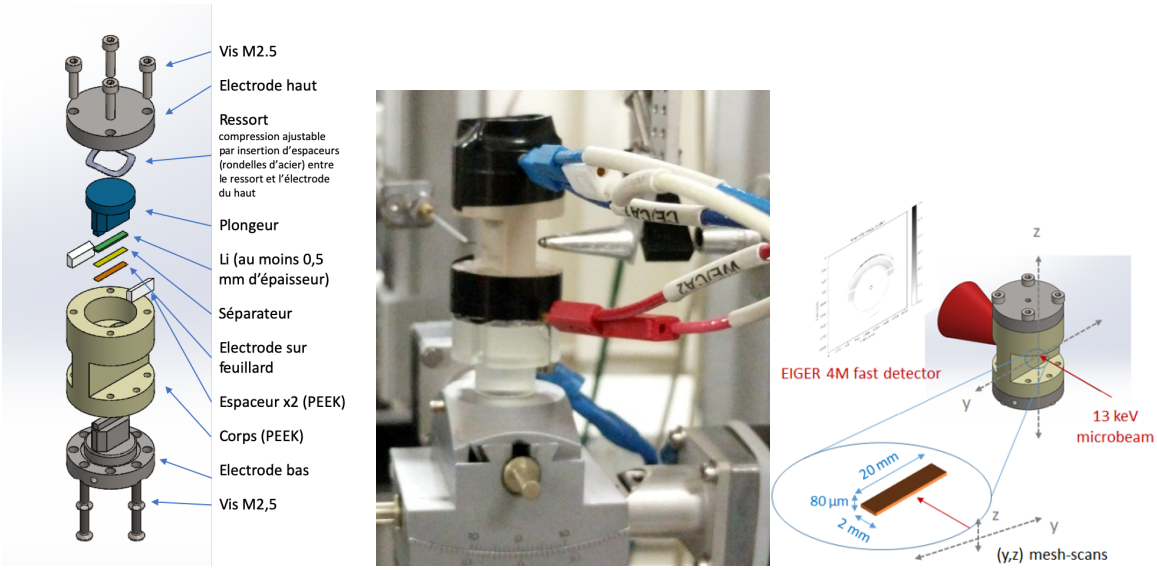

Figure 1. *(left)* Schematic view of the operando EC cell, the diameter is 25 mm, *(center)* actual cell mounted on ID13, *(right)* principle of the operando microXRD experiment.

During the first run we encounter a problem that we did not see at first: the value sent to the z motor suffered a rounding error, that slowly build up until the point that the electrode was out of the scanning range. We thus could obtain only partial results on only one sample (during the lithiation), but the principle of the experiment was validated. We also retained the follow lessons for the second run: (1) avoid irrationnal step sizes and prefer nicely rounded values, and (2) develop online analysis scripts to detect errors in the acquisition.

During the second run, we could check almost in real time the acquisitions using previously prepared python scripts. We also lithiated the sample before the experiment, to study the delithiation process. We suffered several beam loss during the first day and night, and since the electrochemistry was not interfaced with the acquisition we had to restart the second day. We added an additional fast mesh measurement every 50 z,y scans to cover the full electrode. Overnight the delithiation measurement in the new sample went fine, but the EIGER detector crashed during the following measurement, for causes unknown.

In conclusion we could obtain one full delithiation measurement in one sample, and the quality of the data was sufficient to achieve our primary goal and quantify the lithiation heterogeneities across the thickness of the electrode. The main results are shown hereafter in Fig. 2 and Fig. 3. Quantitative analysis has been performed and our Newman-type model already benefited from our experimental observations. A publication is being prepared on the topic. We are very thankful for the continuous and high level of support from the beamline staff, which enabled us to finally achieve a successful experiment.

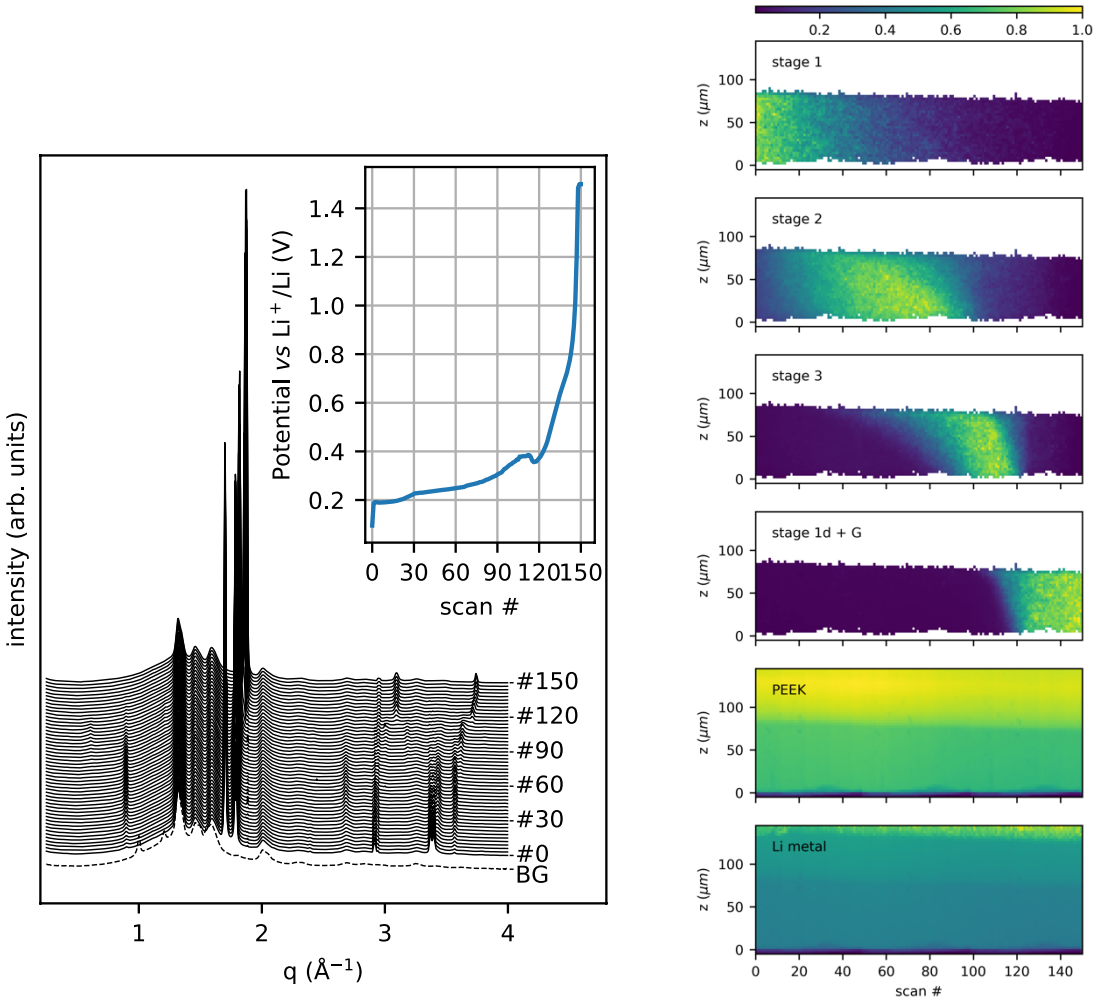

Figure 2. *(left)* Electrode-averaged diffraction pattern (y,z average) over the delithiation (inset). *(right)* z-resolved (y-averaged) maps of the different phases of Li-intercalated graphite, PEEK from the cell windows and Li metal counter electrode.

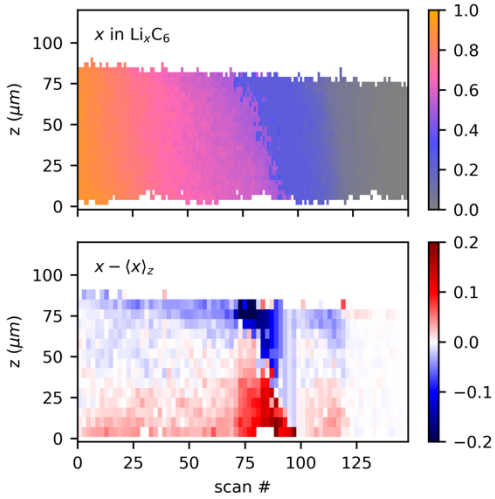

Figure 3. *(top)* Calculated Li concentration from the experimental data, *(bottom)* comparison the average value over the thickness for each point in time, showing large heterogeneities near scans 80 and 110.

Publications: In preparation