ESRF	**Experiment title:** Spinel/rGO aerogels as anodes in Li-ion batteries: unrevealing the fundamentals of remarkable enhancement of specific charge upon cycling	**Experiment number**: MA3048
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This is a preliminary report. Spectra analysis and the changes in comparison to the battery performance are in progress.

Report:

We have successfully fabricated an aerogel of spinel ferrite nanoparticles and rGO to use as anode material in Li ion batteries. The high surface area and open porosity of the aerogel is beneficial for fast Li ion diffusion. Additionally, the open volume of the aerogel allows the spinel nanoparticles to expand and contract during charging and discharging. Those structural advantages result in a high specific charge and cycling stability of more than 1000 cycles with an unsual electrochemical behavior. From various spinels, CoFe$_2$O$_4$/rGO showed exceptional battery performance but the interactions during cycling and the reason behind the unsual cycling stability are not clear yet.

The questions targeted with this experiments were: a) Which metal ion participates in the battery reaction? b) Does one of the metal ions participate at all? c) Do we observe local structural changes around the metal ions or is the local spinel structure stable? We targeted those questions with in-situ high-energy resolution fluorescence detected (HERFD) X-ray absorption spectroscopy (XAS), core-to-core (ctc) X-ray emission spectroscopy (XES), and valence-to-core (vtc) XES at the iron and cobalt edge. We performed the experiments in a new type of *in-situ* battery cell, in which we probed the material under realistic battery conditions.

Both the alignment of the spectrometer and and in situ experiments were very challenging. The spectrometer had to be aligned to measure at the same time at Co and Fe K-edges – in the initial alignment, one of the crystal was inproper. Also due to high concentration of carbon in the sample we observed in the vtc spectra high background possibly due to Campton scattering. In total the alignment of the spectrometer took app. 6 shifts hours. The alignment of the cell took 2 shifts (two stages were tested).

We observe that the batteries are not stable in the X-ray beam. The battery itself consists of the NP/rGO aerogel, which is impregnated with electrolyte. Lastly, optical fibers sperate this aerogel from the Li counteranode. Figure 1a shows a scan across the battery before XAS/XES measurements (red line) and after the measurements. The drastic decrease of the intensity in general is obvious. The sharp point in the green line marks (Figure 1a) the position where the XAS/XES experiments were carried out. Figure 1b shows the HERFD XAS experiments at this position. The red line corresponds to the first HERFD XAS measurement at a new spot and the green line to the same spot after numerous measurements.

We have tested in operando 6 batteries (7 shifts). The electrochemical performance of the batteries in the X-ray beam and without the beam varies dramatically (not shown here).

We finally could avoid the beam damage by measuring at a new spot for each energy point (not shown here). The aqusition time required to measure a single spectra at aerogel is very long (1 shift) and thus it was not possible to follow in operanod changes of the batteries. The measurements of different references took 2 shifts.

The detail analysis of data is in progress.

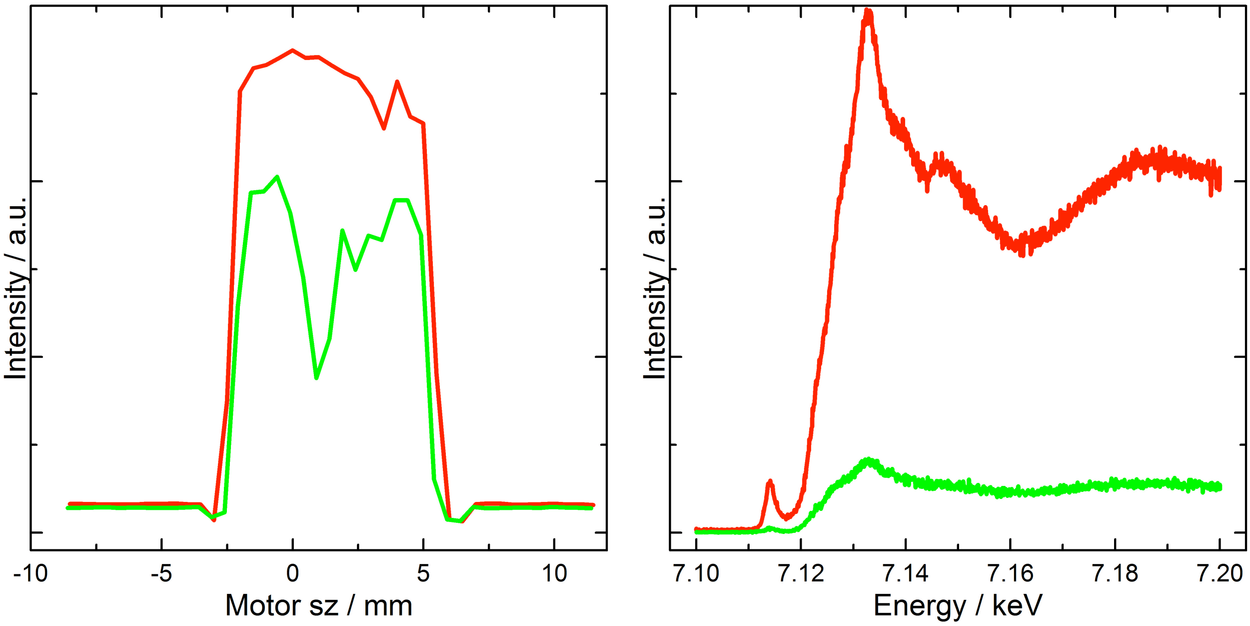

Figure 1. (a) Scan across the battery. (b) HERFD XANES at one spot on the battery. The red line corresponds to a fresh spot and the green line to the same scan at the same spot after extended measurements.