

ESRF Beamtime report

ESRF Project: 26-01 1136

main proposer: Erik Kelder

## **“Study of microstructural and morphological changes in Li<sub>2</sub>FeSiO<sub>4</sub> during battery cycling”**

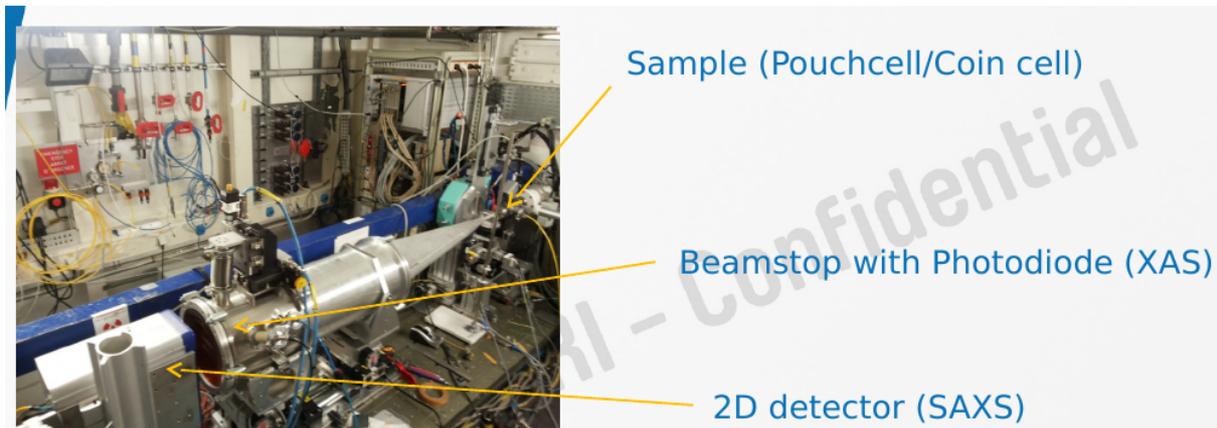
### Objectives:

The aim of this experiment was to establish a combined measurement of SAXS -XANES for operando investigation of electrode materials for batteries. The simultaneous acquisition of small angle scattering (SAXS) and X-ray absorption near edge structure (XANES) during battery operation will allow us to correlate morphological, interphase and mesoscale changes with the electronic structure changes upon electrochemical cycling.

As a material system for the first measurements we propose the well established Lithium iron silicate Li<sub>2</sub>FeSiO<sub>4</sub> cathode material. It is an insertion type material which means that the host structure is largely preserved during electrochemical cycling. We are expecting to gain new insights on the irreversible structural rearrangement linked to the first charge as well to get insights on the impact of reversible cycling on the morphology and microstructure. If successful we are hoping to apply this technique to other electrode materials.

### Results:

Combined SAXS XANES operando measurements were carried out successfully @7keV with the setup shown in Illustration 1.

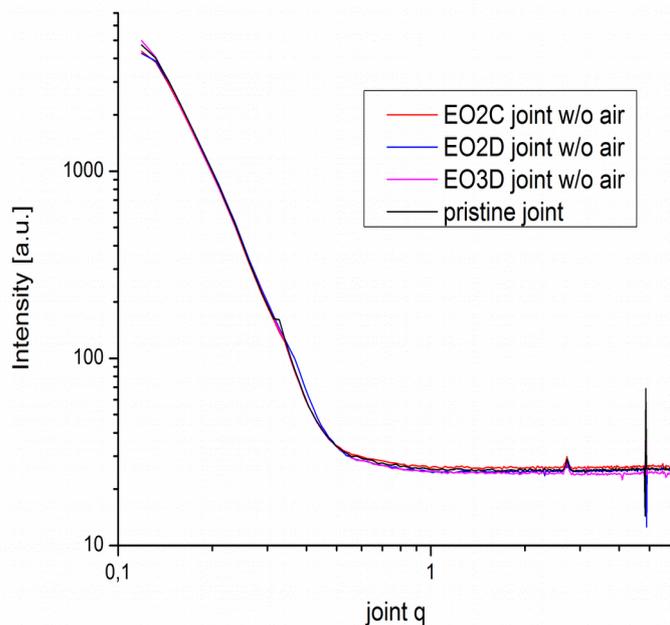


*Illustration 1: Joined SAXS-XANES setup at BM26A during beamtime 10-2017*

The XANES spectra revealed expected evolution of Fe k-edge according to the reversible formation from Fe<sup>2+</sup> → Fe<sup>3+</sup> upon charge, which has been shown in previous reports (26-01-1091, 26-01 1050, 28-01 1122).

In order to enlarge the q range we carried out an additional electrochemical cycle while measuring SAXS at 13keV. After careful background removal and scaling the obtained SAXS spectra for the two separate energy runs were merged to allow a broad picture of q- range, from 0.015-6 nm<sup>-1</sup>.

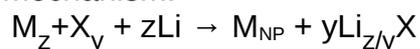
Illustration 2 shows the scattering plot of LFS cathode at various stages of cycling, end of charge (EOC) and end of discharge (EOD), respectively. There are only slight differences noticeable, which are located in the region of 0.3-0.4nm<sup>-1</sup> which is the region in which low and high energy scattering plot were merged and can therefore not be used for precise data interpretation. Besides these differences no other significant deviations of the different scattering at distinct points of cycling are visible. We can therefore conclude that the LFS does not undergo any significant morphological changes on the nanoscale, neither during the first charge nor during subsequent cycles. Also no coarsening or interphase alterations were observed.



*Illustration 2: Joined SAXS spectra of high and low energy measurement for LFS cathode at end of 2nd charge (EO2C), end of 2nd and 3rd discharge (EO2/3D)*

#### Outlook:

Now that the set-up of the simultaneous SAXS-XANES has been proven successful operation, the aim is applying it to an electrode materials that undergo more drastic structural and morphological changes during electrochemical cycling, such as conversion type materials. The latter are of particular interest for SAXS due to the reversible formation of metallic nanoparticles ( $M_{NP}$ ) upon lithiation, following reaction mechanism:



(where M stands for a cation and X an anion)