ESRF	**Experiment title:** Real-time Structural Evolution of Si-Ge Nano Particles based Anodes during Lithium Battery Cycling	**Experiment number**: 02-01 896
Beamline: BM02	**Date of experiment**: from: 26/09/2018 to: 02/10/2018	**Date of report**: 02/03/2020
Shifts: 18	**Local contact(s)**: G. Chahine	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

We build on our previous experiment (MA3814) to successfully perform this experiment. As planned, we performed operando SAXS/WAXS measurements in (Si,Ge) nanoparticles formulated as electrodes for Li-ion batteries. The aim of the experiment was to study the lithiation of crystalline (Si,Ge) (which becomes amorphous upon the first lithiation), evidence the Si or Ge concentration dependence, and evaluate the concomitant morphological changes associated with the large volumes changes (up to 300% theoretically).

The electrochemical cells were prepared as pouch cells at CEA prior to the experiment, and mounted on their respective holders (Fig. 1). We used the standard SAXS/ WAXS geometry, with the SAXS detector at about 3m, and the WAXS detector at about 17 cm. We first calibrated the setup using the standards available on the beamline: Cr_2O_3, LaB_6, AgBh (Fig. 2) and Si powder from the NIST. The pyFAI software suite was used to perform the calibration. We also measured blank cells (i.e. everything but the electrode material) for later background correction.

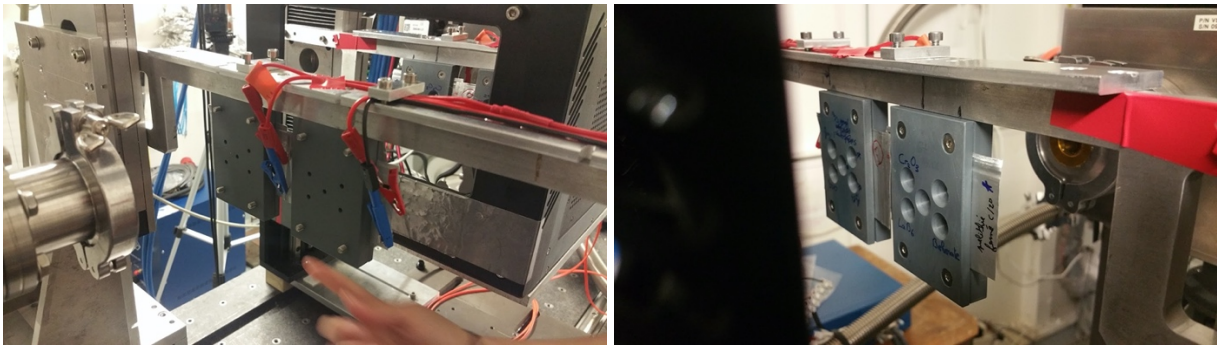


Fig. 1 : Pouch cell samples mounted on their respective holders, on the multi-sample holder that we had previously designed for BM02.

In total, we investigate up to 4 cells in parallel (NP191, NP193, NP198, NP228) corresponding to different (Si,Ge) composition and sizes distribution. During all the acquisition, we used pyFAI on the d2gpu2 computer for online data reduction, which proved extremely useful for fast online diagnostics. We also took advantage of the example jupyter notebooks developed by the beamline staff and collaborators, and available on the beamline.

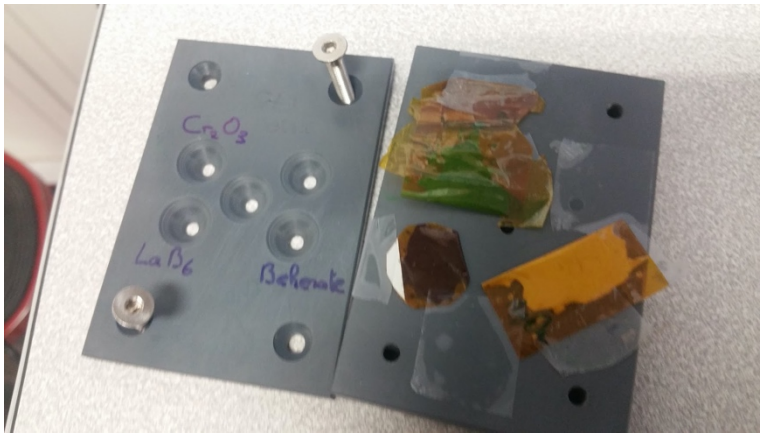


Fig. 2. Standards for alignments mounted on a pouch cell holder

We controlled the uniformity of the SAXS/WAXS over each measuring hole by performing a small mesh scan (Table 1). We found some inhomogeneous distribution of the signal in some cells, which we attributed to the difficulty to process some of the nanoparticles as an homogeneous electrode ink. In order to eliminate any non-representative effect, we chose to acquire such a mesh scan at each point in time. This also distributed the dose over a larger area, i.e. instead of counting 120s at the same location at each point, we measured during 13s over 9 locations for the same time resolution. The typical acquisition was thus a loop of successive mesh scans on each of the 4 cells. During the acquisition, cell NP191 failed and had to be replaced by the backup NP191b. We later also replaced cell NP228 by a composite of the same nanoparticles with graphite (NP228gr)

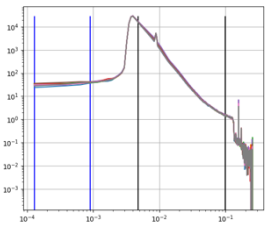
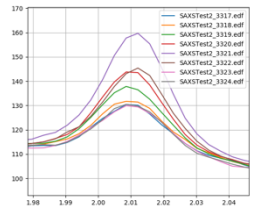
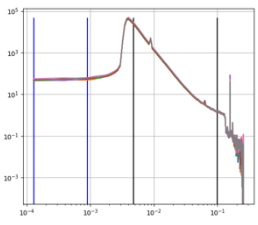
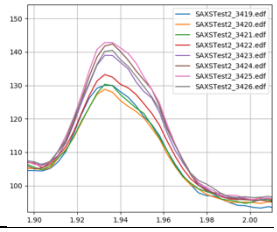
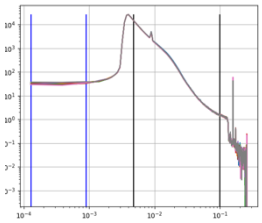
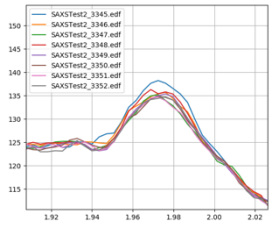
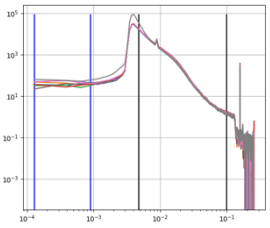
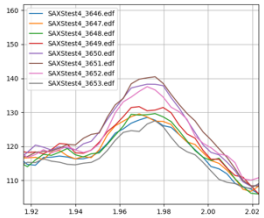
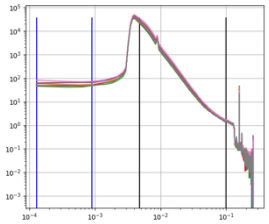
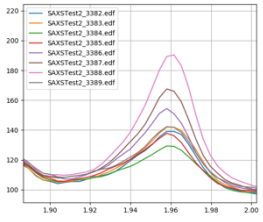
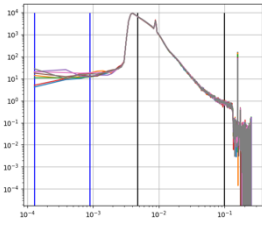
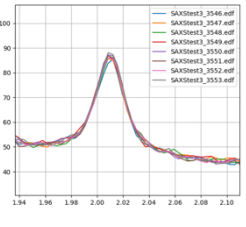
NP228			NP193	 
NP191			NP191b	 
NP198			NP228g	 

Table 1: Preliminary homogeneity check of the sample in SAXS (left) and WAXS (Si 111 reflection, right) over 8 locations. The x axis in $Å^{-1}$, the y axis is in arbitrary units.

Typical raw results are illustrated below in Table 2 and Fig. 3.

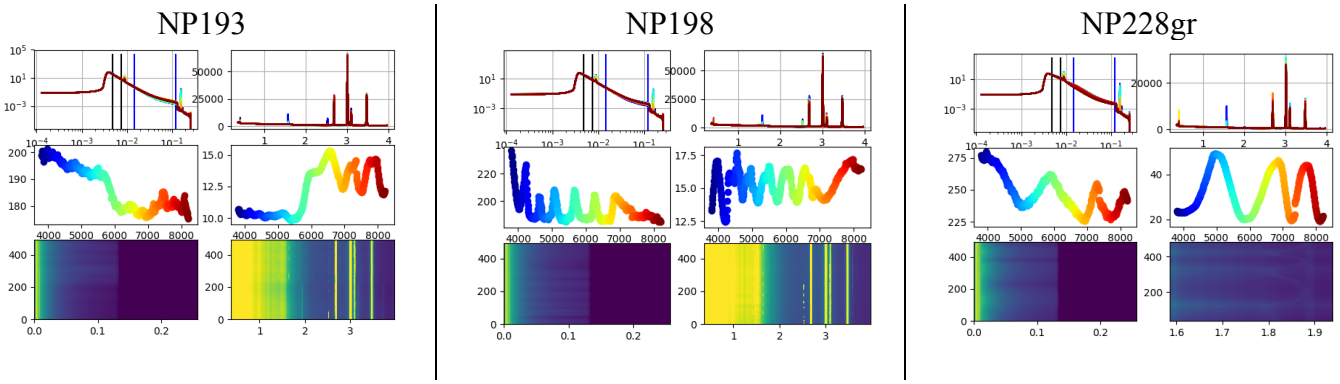


Table 2. Illustration of the results over several cycles in sample NP193, NP198 and NP228gr: (top left, right) SAXS, WAXS data: intensity as a function of momentum transfer, the color indicates the time, from blue to red ; (middle left, right) integration of SAXS between the black, blue lines (see top left) ; (bottom left, right) SAXS, WAXS data as colormaps.

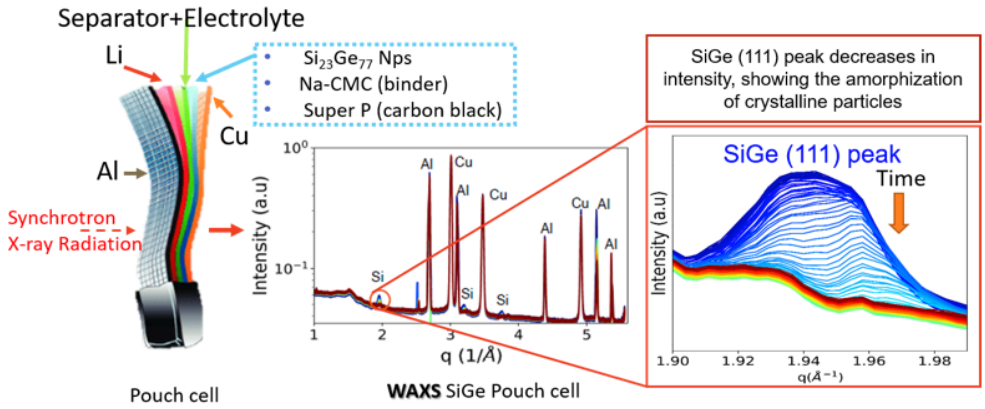


Fig. 3. Illustration of the lithiation-induced differential amorphization in SiGe nanoparticles. [D. Zapata-Dominguez et al., "Lithiation mechanism in SiGe alloys for lithium-ion batteries investigated by operando diffraction", Poster at ESRF F-CRG workshop (Dec. 2019)]

In conclusion we were able to measure the SAXS (= morphological changes) and WAXS (=atomic ordering) in alloyed (Si,Ge) nanoparticles. We could clearly see the evolution of the composite 111 Bragg reflection from the different composition within each sample, and observe how Ge-rich or Si-rich component would be lithiated depending on the cell potential. In depth analysis of the WAXS and SAXS data is in progress but some of the operando XRD data has already been published (see below). Complementary laboratory XRD, NMR and TEM-EELS measurements are in progress.

<u>Publications</u>:

- **Paper:**
  Part of the WAXS data was published in Desrues et al., Batteries & Supercaps **2019**, 2, 970–97 (see cover)
- **Poster:**
  D. Zapata-Dominguez *et al.*, "Lithiation mechanism in SiGe alloys for lithium-ion batteries investigated by operando diffraction", ESRF F-CRG workshop (Dec. 2019)