	Experiment title: COMBINED SAXS/WAXS OPERANDO CHARACTERIZATION OF SILICON BASED ANODES FOR LITHIUM-ION BATTERIES	**Experiment number**: MA-3814
Beamline: BM02	**Date of experiment**: from: 08/02/2018 to: 12/02/2018	**Date of report**: 02/03/2020
Shifts: 12	**Local contact(s)**: G. Chahine, N. Boudet	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The aim of the experiment was to study the structural (atomic-scale) and morphological changes upon lithiation in composite amorphous Si + graphite anode materials. This experiment was part of the SINBAT H2020 project (Grant Agreement 685716). We measure the state of lithiation of the graphite by measuring the position of the 002 reflection upon reflection: insertion of Li atoms increases the distance between the graphene sheets of graphite. The silicon was amorphous (and we never cristallized any of the Li-rich (Li,Si) alloys), however the Si domains were nanostructured and their volume expansion could thus be tracked using small-angle scattering. *See experiment report MA-3280 for further details on the technique.*

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). 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.

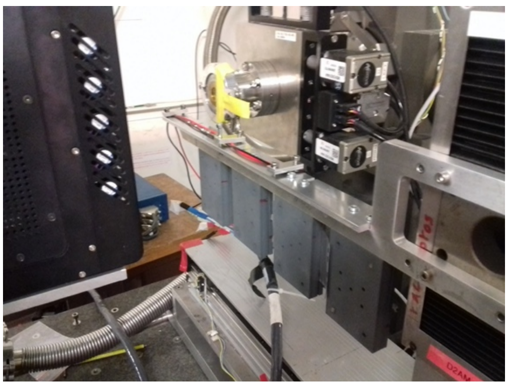

Fig. 1 : Pouch cell samples mounted on their respective holders, on the multi-sample holder that we had specifically designed for BM02.

In total, we investigate up to 4 cells in parallel, corresponding to different electrode composition or ageing (preliminary laboratory cycling). In order to gather information on large-scale spatial effects, we collected data at different prepared positions (up to 5 on each holder). 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.

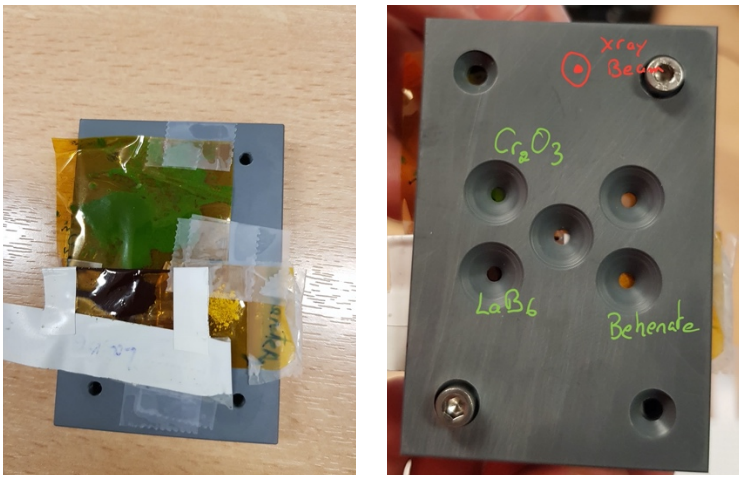

Fig. 2. Standards for alignments mounted on a pouch cell holder

We enjoyed excellent beam and beamline stability throughout the experiment, and we thank the beamline staff for their continuous support. We could perform all the required measurements and more. A detailed analysis of the data has been published in Berhaut et al., “Multiscale Multiphase Lithiation and Delithiation Mechanisms in a Composite Electrode Unraveled by Simultaneous Operando Small-Angle and Wide-Angle X-Ray Scattering”, ACS Nano 2019, 13, 10, 11538-11551. For simplicity, the main results from our paper are reproduced hereafter. Additional results have been submitted to Energy Storage Materials.

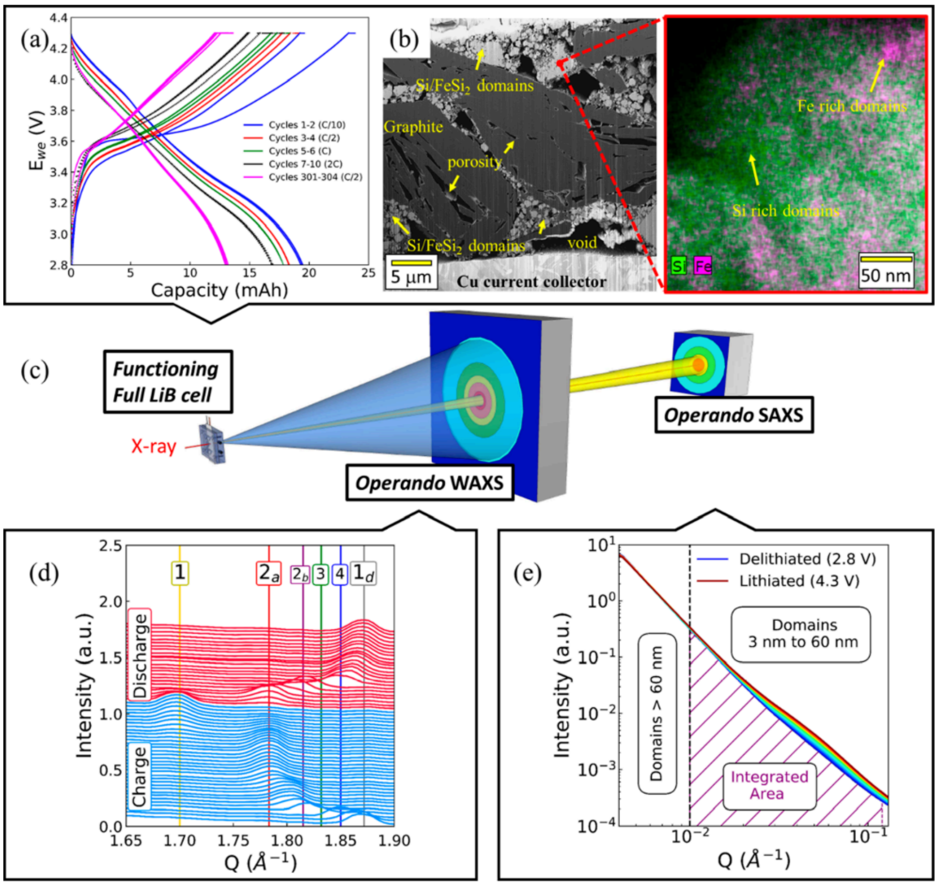

Figure 1. (a) Fresh and aged full-cell charge/discharge profiles. The fresh cell was cycled at several C-rates: cycles performed at C/10, C/2, C, and 2C are respectively represented in blue, red, green, and black. The aged cell was cycled at C/2. Each cell charge ended with a constant voltage (4.3 V) step. (b) FIB-SEM slice of the pristine a-Si/c-$FeSi_2$/graphite composite negative electrode along with a scanning transmission electron microscope energy-dispersive X-ray (STEM-EDX) nanoscale chemical mapping of an a-Si/c-$FeSi_2$ domain. The iron-rich and silicon-rich phases are respectively colored in magenta and green. (c) Scheme presenting the BM02 beamline setup at ESRF. (d) Variations of the WAXS intensities of the Bragg reflections of the graphite lithiation stages: 1_d, 4, 3, 2_b, 2_a, and 1 during one cell charge/discharge cycle, from the LiC_6 (001) to the graphite (002). (e) SAXS intensity profile variations over the course of one cell charge (2.8 to 4.3 V).

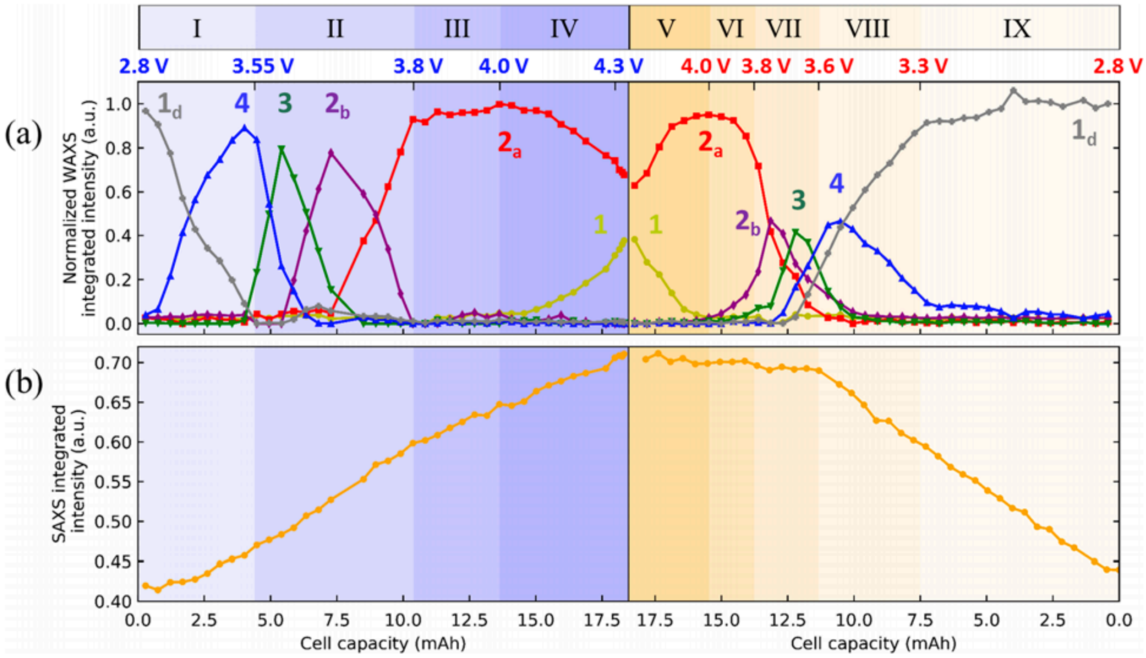

Figure 2. **(a) Normalized peak areas of the Li_xC_6 stages: 1_d (gray), 4 (blue), 3 (green), 2_b (purple), 2_a (red), and 1 (yellow), and (b) SAXS integrated intensity variations measured during the a-Si/c-$FeSi_2$/graphite composite electrode lithiation (purple regions) and delithiation (orange regions) at C/2 as a function of capacity.**

<u>**Publications**</u>:

- **Paper:**
  - Berhaut *et al.*, "*Multiscale Multiphase Lithiation and Delithiation Mechanisms in a Composite Electrode Unraveled by Simultaneous Operando Small-Angle and Wide-Angle X-Ray Scattering*", ACS Nano 2019, 13, 10, 11538-11551

  - Berhaut *et al.*, "*Prelithiation of silicon/graphite composite anodes: benefits and mechanisms for long-lasting Li-ion batteries*", submitted to Energy Storage Materials

- **Highlight ESRF 2019**
  - Berhaut *et al.*, "*Multiscale Multiphase Lithiation and Delithiation Mechanisms of a Promising Li-Ion Battery Cell Anode Composite Material*" p.153