ESRF	**Experiment title:** COMBINED GISAXS/GIXRD OPERANDO CHARACTERIZATION OF CARBONCOATED SILICON NANOPARTICLES ANODES FOR LITHIUM-ION BATTERIES	**Experiment number**: **MA-3280**
Beamline: BM02	**Date of experiment**: from: 27 Jan 2017 (8h) to: 31 Jan 2017 (8h)	**Date of report**: 27 February 2017
Shifts: 12	**Local contact(s)**: BLANC Nils, BOUDET Nathalie	*Received at ESRF:*

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Report:

The aim of the experiment was to follow in situ/operando the process of lithium insertion and deinsertion in a Silicon based lithium-ion battery along charge/discharge. Combined GISAXS/GIXRD was proposed to follow simultaneously i) the evolution in size and shape and ii) the process of amorphization of silicon nanoparticles (Si-NPs). We had different types of Si-NPs to probe, e.g. possibly different sizes and polydispersity, with and without carbon coating. We planned to use our home-made battery cell developed for X-rays reflectivity.

GISAXS/GIXRD->SAXS/WAXS and choice of battery cell designs

Our initial plan was to combine Grazing Incident Small-Angle Scattering X-ray (GISAXS) and Grazing Incident X-ray Diffraction (GIXRD). We discussed with our local contacts prior to the measurements to optimize the design of our home-made reflectivity battery cell (a round cell that was designed, tested and used by us for operando synchrotron reflectivity experiments at BM32, exp. N° MA-2646). This cell is made in PEEK, with lithium as counter-electrode. It can be positioned in GISAXS/GIXRD configuration using grazing incidence geometry. However, issues related to i) the coating of Si-NPs electrode onto a well-defined surface (e.g. wafer) and ii) available diffraction angles were raised. Therefore, we decided to perform combined Wide-Angle (WAXS) and Small-Angle X-ray Scattering (SAXS) in order to i) avoid the surface coating issue and ii) optimize the accessible Q-range domains. For this purpose we adapted the neutron cells developed for SANS and successfully tested in Dec. 2016 at ILL. These cells are made of Titanium parts (300µm thick) which were reduced to 100 µm. We also prepared pouch cells to anticipate difficulties to resolve the Silicon Bragg peaks.

SET-UP. The SAXS/WAXS configuration was optimized in terms of balance between Q-range and transmission requirements:

- Energy = 18 keV (λ=0.6886 Å)
- Distance sample-D5 detector (SAXS) = 350 cm ($0.003 < q < 0.1$ Å^{-1})
- Distance sample-WOS detector (WAXS) = 14 cm ($1 < q < 5$ Å^{-1})
- Beam-stop = 2 mm
- Beam size = 500*500 µm

BATTERY CELLS ASSEMBLY

Two types of cells were prepared:

- ***Titanium-based SANS cell*** **(***Fig. 1a*). The design of this cell has been adapted to small sngle scattering (SAS) experiments, e.g. there is no polymer separator (to avoid small angle parasitic contributions). The theoretical transmission was calculated to 13.5% in the selected BM2 set-up. Unfortunately, the transmissions turned out to be much lower, due to difficulties to control the titanium thickness below 150 µm. Only one Silicon Bragg peak, i.e. (111) peak, was detectable by WAXS. This situation impeded to proceed to the combined SAXS/WAXS operando characterization and the pouch cell option was therefore preferred.

- ***Pouch cells.*** (*Fig. 1b*) The cells were assembled as pouch bag cells (i.e. a multilayer of Nylon, aluminum and polypropylene) with the Silicon slurry coated on a copper foil (anode), a lithium counter electrode (cathode), separated by a layer of Celgard. Before sealing, 700 µL of 1M LiPF6 dissolved in EC: DMC (1:1) were added as electrolyte. We prepared 3*2 cells using different Si-NPs: CEA-made monodisperse coated and uncoated NPs (30 nm in size) and polydisperse uncoated commercial NPs (20-30 nm in size). Each system was doubled because we wanted to operate the battery at full and limited capacities.

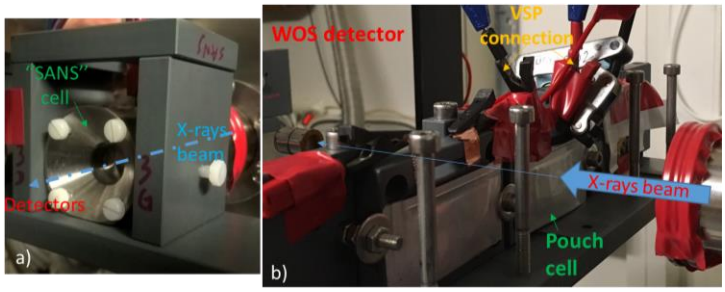

Figure 1: a) Titanium-based SANS cell, adapted for X-rays. b) Two pouch cells mounted in parallel on BM2 with the WAXS/SAXS set-up (WOS and D5 detectors).

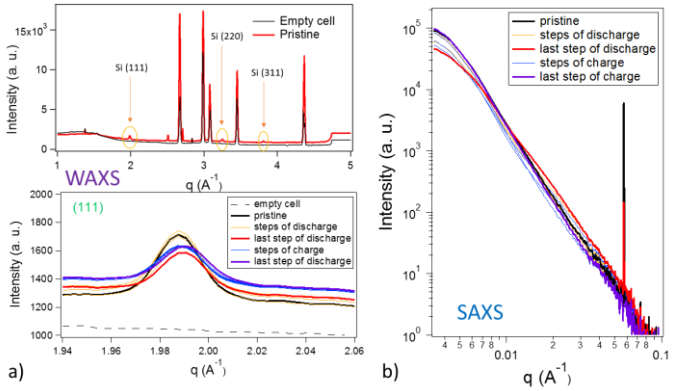

Figure 2: a) WAXS data show all the Bragg peak positions of the pouch cell. Focus made on the (111) Si-NPs peak range along charge and discharge evidencing shifts in position due to lattice parameters variations. b) SAXS data showing the nanoscale structural evolution of the NPs.

RESULTS.

The first day of our experiment was dedicated to beamline alignment. The second day, we tested the titanium-based SANS cells. During the last 2 days, we were able to operate in parallel two pouch cells (using specially designed rack) during 1.5 cycles (*Fig. 3a*). We performed the operando SAXS/WAXS on the reference uncoated commercial samples at full and limited capacity. Some data are shown on *figure 2*. During lithiation, the Si-NPS get progressively amorphized (fully (partially) if it is cycled at full (limited) capacity) and they grow in size due to alloying of silicon (formation of Li_xSi_y). Hence, we expect to have core-shell lithiated particles during the cycling. During delithiation, the particles shrink.

- **We were able to follow the evolution of the three Bragg peaks of silicon**, namely (111), (220) and (311), by WAXS (*Fig. 2a*). Observation and quantitative fitting of these peaks is possible thanks to the high brilliance synchrotron. We could resolve the variations of the Si Bragg peaks positions (typically 1%, *Fig. 3b*), which allows us to evaluate the strain state of the crystalline core of the NPs. Quantitative analyses of the intensity and width variations are under progress to possibly quantify the amount of crystalline material and size of grains.

- **We evidenced the continuous evolution of the SAXS profiles** upon lithiation/delithiation (*Fig. 2b*), which is related to the volume changes of the NPs. A distinct behavior is obtained in the very low and medium angle region (*Fig. 3c*), which could be related to the formation of the unstable Solid

Electrolyte Interphase (SEI) and the particles growth, respectively. Quantitative analyses of the SAXS data are under progress, in particular modelling with selected form/structure factors to obtain average core-shell sizes, shape, aggregation and composition.

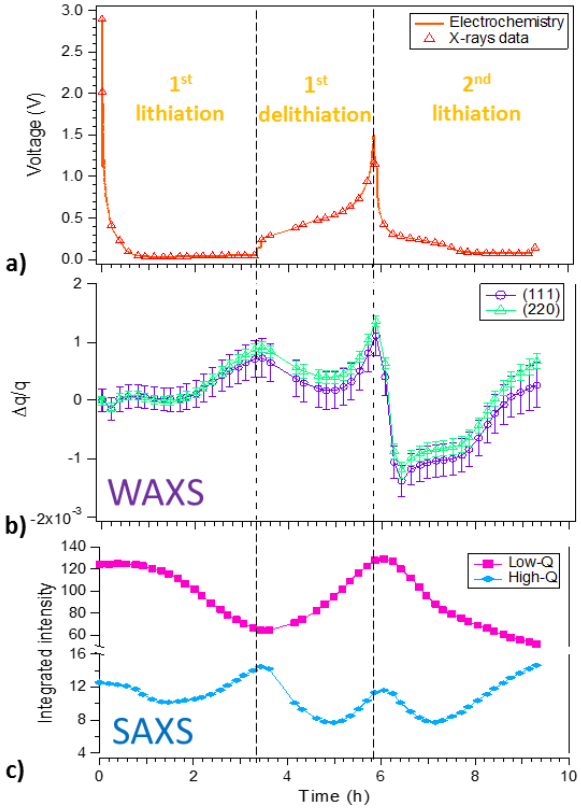

Figure 3: Limited capacity cycling data.
a) Electrochemical sequence (voltage vs time during 1.5 cycles) applied to a Commercial Si-NPs anode mounted in pouch cell on the BM2 beamline. b) Variations of the (111) and (220) Si Bragg peaks positions vs time.
c) SAXS integrated intensity related to the evolution of SEI (low-Q) and Si-NPs growth (high-Q).

Conclusions

We have successfully performed operando combined WAXS/SAXS experiment on silicon-based nanostructured anodes in the course of battery cycling. We could cycle in parallel two cells at full and limited capacities. We are currently comparing the results of these two measurements. The process of amorphization (full vs limited capacities) seems to affect the (ir)reversibility of the Si-NPs volume changes, which could be correlated to the capacity loss in the course of battery cycling.

The time needed for measuring 1.5 cycles is 2 full days (the first cycle requires a C/20 rate meaning 40h, the next cycles being done at C/10). It would be very interesting to pursue the operando investigation up to 3 full cycles, in order to get further information on the battery stabilization regarding the particles size evolution (quantification of irreversible changes on the size detected by SAXS) and the crystalline strains (especially for limited capacity, detected by WAXS).

We could not measure in this experiment the CEA-made samples, because we had to optimize the beamline set-up, the cells used, the protocols (electrodes are not homogeneously cycled, transmission meshes were made in order to focus on the best spots) during this first run. However, we demonstrated the feasibility and suitability of combining these techniques to bring real-time information on the structural evolution of the Si-NPs, in relation to the electrochemical behavior of the cell. Now, we need to complete our full program and we are in position to study the coating on the structural evolution and the electrochemistry.

What can be improved: The pouch cell design should be improved in particular for SAXS data. Indeed, the polymer separator and polymer multilayers give parasitic contributions in particular at q=0.56 $Å^{-1}$. Possibilities for improving the pouch cell consist in making holes for the X-ray beamline through the separator but also using Kapton windows on the multilayers of nylon, aluminum and polypropylene foil. The rack could also be improved in order to cycle more than 2 pouch cells and facilitate the passage of electric wires.