EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.

- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** In *operando* X-ray diffraction computed tomography for the investigation of lithium/sulfur batteries	**Experiment number**: CH4787
Beamline: ID15A	**Date of experiment**: from: 16 nov. 2016 to: 22 nov. 2016	**Date of report**: 26/04/2017
Shifts: 18	**Local contact(s)**: Gavin Vaughan (vaughan@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The aim of this experiment was to investigate the behavior of lithium/sulfur batteries, and more precisely to follow *operando* the active materials morphology and composition while cycling. Combined XRD and tomography was proposed to follow simultaneously: i) the evolution of crystalline species and potentially amorphous species and ii) the changes in the global morphology of both electrodes (lithium and sulfur) and electrolyte.

In order to characterize the batteries while cycling, and not to compromise the electrochemical behavior and standard cycling rates, initial experiments were carried out combining two-dimensionally resolved XRD and tomography.

Four cells were fully characterized both by tomography and XRD technics. We aim at investigating important parameters such as different c-rate, pressure and loading (see table 1) in order to see their influence on the system.

Cell	Pressure (bar)	Sulfur loading (mg_s /cm²)	Analysis	Electrochemistry (C rate)
Cell 1	1,2	4,85	Tomography & XRD	C/20 + C/10 + 4x C/5
Cell 2	2,4	6,29	Tomography & XRD	C/10 + C/5
Cell 3	Not controlled but > 2,4 bar	5,47	Tomography & XRD	C/10 + C/5 + C/2 + C/5
Cell 4	1,2	5,76	Tomography & XRDCT	C/20 + C/5

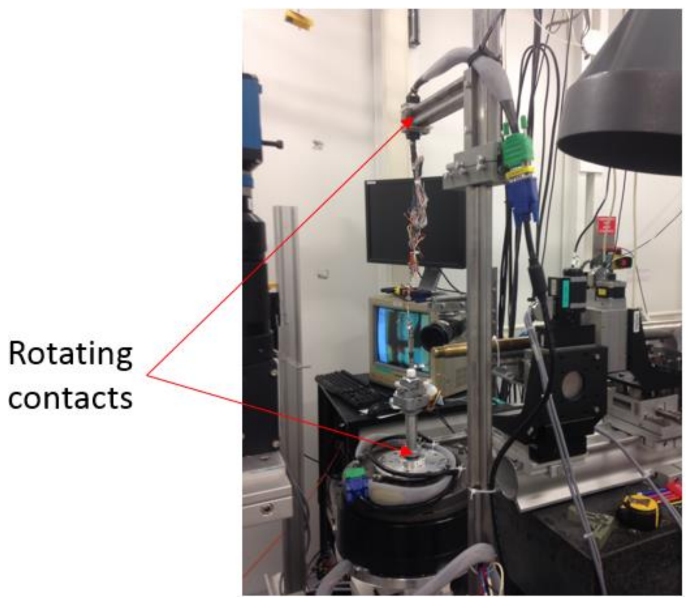
Table 1 : Sum up of the analyzed cells

Set-up:

The tomography and XRD configuration were optimized in terms of balance between spatial and temporal resolution.

- Energy = 78 keV
- Beam size = 3.18*3.18 µm (3.18 µm per pixel) for (x,y)-resolution
- "z resolution" : region of interest were probed (approximately 20 slices for 700 µm high)
- Temporal resolution : 20 minutes for a cycle (tomography + XRD)

The new rotative electrical contacts present in the beamline was tested in order to carry out electrochemical testing while rotation of the cell for tomography and XRDCT measurements. (See figure 1).

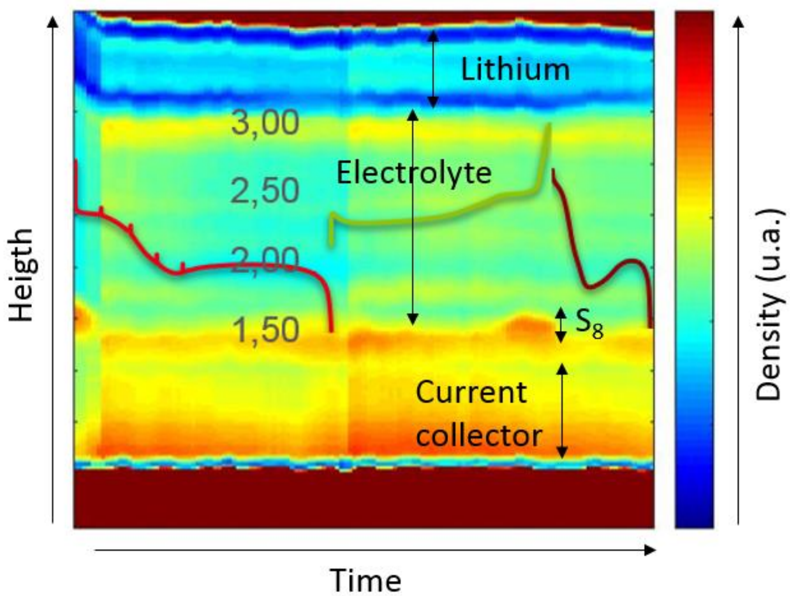


Results:

The two first days of the experiment were dedicated to beamline alignment and setting up of the cell and characterizing the system. . During third and fourth days, we performed the *operando* XRD/tomography on the "Cell 1" by varying the C-rate. "Cell 2" was characterized during the fourth day and the increase of the pressure could be analyzed. In the fifth and the sixth days, we analyzed the "Cell 3" by varying the cell assembly with a highly but not controlled pressure. In the last day, we performed XRDCT by probing only the solely region of interest, such as positive and negative electrode, and limit the scan for the electrolyte part, in order to collect data at adequate rates.

- **We were able to follow the morphological changes while cycling,** a segmented image allows to follow the evolution of the different active species (see figure 2). For this preliminary analysis, we clearly see the precipitation/dissolution of active sulfur (S_8) and the evolution of sulfur which is reproducible while cycling. The lithium electrode could also be followed notably in term of density and thickness. However, all tomographic data are not fully analyzed yet, and we hope to quantify and map the complete and complex state of the species in the battery more deeply.

- The XRD analysis is still ongoing and the Pair Distribution Function (PDF) in the electrolyte region (mostly) will also be carried out.



Conclusions:

We have successfully performed operando combined tomography/XRD experiment on four Li/S batteries while cycling. Different parameters were tested and we better understand the influence of each on the system, such as electrochemistry, morphological change and evolution of active species. In addition, it would be very interesting to pursue the *operando* investigation up to prolonged cycle (10th – 30th or 50th cycles), in order to see the impact of ageing on the processes occurred in the cell. Probing solely important slices with higher resolution (sub-µm) could allow extracting dynamic parameters

(kinetic of sulfur particles dissolution and precipitation for instance) by analyzing quantatively the cell and thus getting a deeper understanding of the active material behavior.

This experiment opens up the possibility to characterize the batteries on length scale from microscopic to macroscopic and we believe that this coupled approach will permit to get a deeper understanding of the performance limiting degradation phenomena that occur in batteries in general.

What can be improved:
The rotative contacts have to be improved in order to limit their impact on the electrochemical performance (noise, disconnections). This will be the case when the new diffractometer with build in rotating contacts will be installed later this year. In addition, an improved data acquisition method now available allows a huge increase in data collection rates without loss of quality, and will allow the characterization of the entire battery by XRDCT in future measurements.