



## 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://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

#### Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

### Deadlines for submitting a report supporting a new proposal

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> September**

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.

### Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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.



	<b>Experiment title:</b> <b>Evolution of Li Dendrite Growth on Graphite Anodes Under Fast-Charging Conditions</b>	<b>Experiment number:</b> MA-5068
<b>Beamline:</b> ID19	<b>Date of experiment:</b> from: 2021-10-29 to: 2021-11-02	<b>Date of report:</b>
<b>Shifts:</b> 12	<b>Local contact(s):</b> Ludovic Broche ( email: broche@esrf.fr )	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>Matthew Sadd*</b> <b>Nataliia Mozzhukhina*</b> <b>Shizhao Xiong*</b> <b>Aleksandar Matic*</b> <b>Antoine Klein*</b> <b>Martina Olsson*</b>		

### Report:

The aim of this experiment was to monitor the lithiation/delithiation (charge/discharge) process of graphite anodes using an *operando* X-ray Tomographic Microscopy experiment. The plating of metallic lithium on graphite anode is a key issue that needs to be tackled in Li-ion batteries, as the formation of Li dendrites can affect the reversibility of the batteries and potentially lead to internal short circuiting, posing critical safety issues like ignition of the battery. In particular the experiment targeted the behaviour of the lithiation and delithiation process under 'fast-charging' conditions in a series of electrolyte formulations, linking electrolyte properties and applied current density on the formation of Li-metal on the graphite material during the intercalation process. The information provided from this experiment has given direct insights of the plating process on graphite anodes, with metrics gathered including the volume of plated Li-metal, the location of the plating process within the cell, and effect of applied current density on the extent of the plating.

In the experiment the PCO Edge 5.5 detector was used with a 20 times objective, resulting in a voxel size of 0.332  $\mu\text{m}$ . The 'half-acquisition' method was used to increase the field of view to 4450 x 2160 pixels with 1477.4  $\mu\text{m}$  x 717.12  $\mu\text{m}$ . Tomograms were gathered using rapid exposure, 15 ms per projection, owing to the high flux of the ESRF x-ray source. To acquire a tomogram with 4000 projections, the measurement time was 60 s. This rapid measurement time enabled the *operando* nature of the measurement where tomograms could be taken during battery operation, without the electrochemical measurements being paused. All acquired tomograms were reconstructed using the paganin phase reconstruction method. The reconstructed data was of high quality, with graphite, glass fibre separator, and plated Li-metal clearly observed. Only very minor ring artifacts were observed in the reconstructed data, enabling accurate analysis of the acquired images. During the beamtime there was some machine downtime and it led to the loss of 8 hours beamtime, resulting in the partial loss of data for one sample. However despite this issue *operando* data sets were successfully gathered for 6 cells, with the progressive cycling at rates of 1C, 2C, and 3 C. Further data sets were gathered for a series of *ex situ* samples.

The measured cells used 3 different electrolyte formulations:

- LP57 1 M LiPF<sub>6</sub> in ethylene carbonate and ethylmethyl carbonate (1:1v)
- LP57 + VC 1 M LiPF<sub>6</sub> in ethylene carbonate and ethylmethyl carbonate (1:1v) with vinylene carbonate
- LP57 + LiFSI 1 M LiPF<sub>6</sub> in ethylene carbonate and ethylmethyl carbonate (1:1v) with lithium bis(fluorosulfonyl) imide salt

The operando cells used for a majority of the experiments had a diameter of 1.58 mm, meaning that an 86% coverage of the total electrode volume was achieved when the half-acquisition method were applied. This allows quantitative analysis of the tomographic data, including correlative analysis with electrochemical data acquired simultaneously.

Figures 1 and 2 show the lithiation of graphite in cells containing the LP57 and the LP57 + VC electrolytes in the pristine, post lithiation at 1C, and post lithiation at 3C. In both figures the identifiable phases are that of the graphite particles, which are clearly resolved, the glass fibre separator that sits above the graphite, and lithium metal which is observed as the black phase that forms between the graphite and glass fibre layers (observed in Figure 1c and Figures 2b and c).

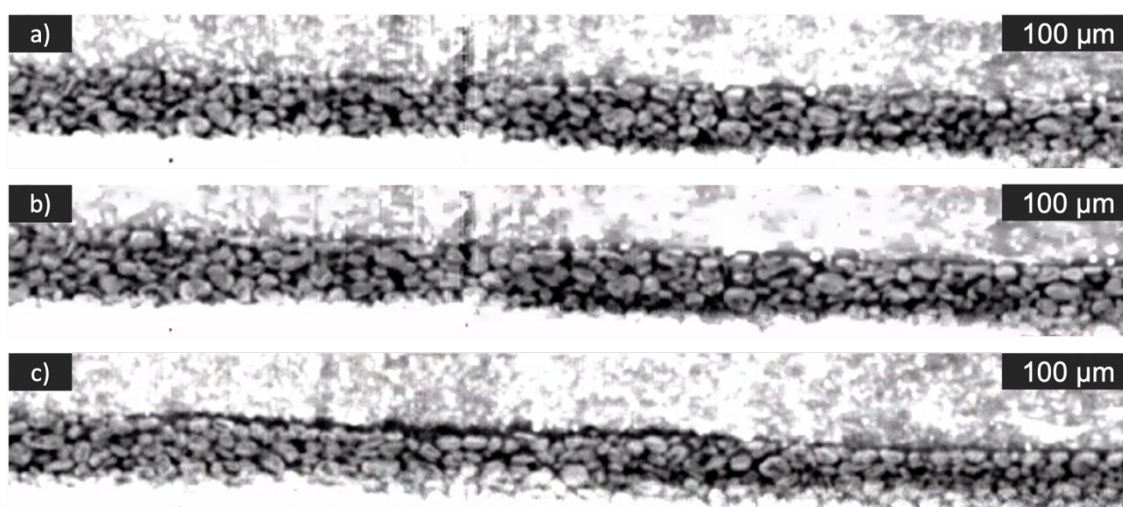


Figure 1 Vertical slices of graphite in cell contain the LP57 electrolyte a) in the pristine (uncycled) state b) after lithiation at 1C c) after lithiation at 3C. Scale bars of 100 μm.

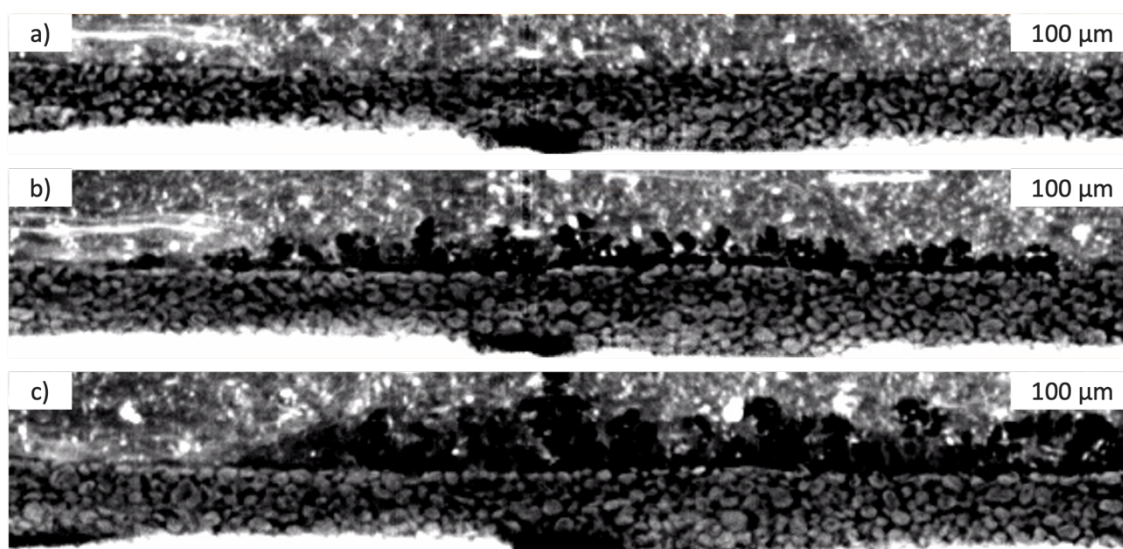


Figure 2 Vertical slices of graphite in cell contain the LP57 + VC electrolyte a) in the pristine (uncycled) state b) after lithiation at 1C c) after lithiation at 3C. Scale bars of 100 μm.

Our results show the difference in morphology of the plated lithium metal phases between systems with the two electrolytes. Figure 1c shows that when a Li phase forms, it mainly remains close to the graphite surface, with a morphology identified as “mossy” Li. In clear contrast Figures 2 b and c show plated Li that is prograding through the separator material, which would potentially lead to the short circuit and battery failure.

To gain further insights into the Li-plating process, the *operando* experiment has provided tomograms during the plating process, allowing the onset of plating to be correlated with the cell’s voltage and state of charge. Figure 3 shows that during the first 25 minutes (a-c) of lithiation there is no evidence of Li-plating on the graphite material. However, after 45 minutes of lithiation, when the cell’s voltage reaches an almost constant value, Li-plating starts. Furthermore, from the point where Li-plating is first observed it rapidly propagates, with the Li phase appearing to reach heights of ~50  $\mu\text{m}$  above the surface of the graphite electrode.

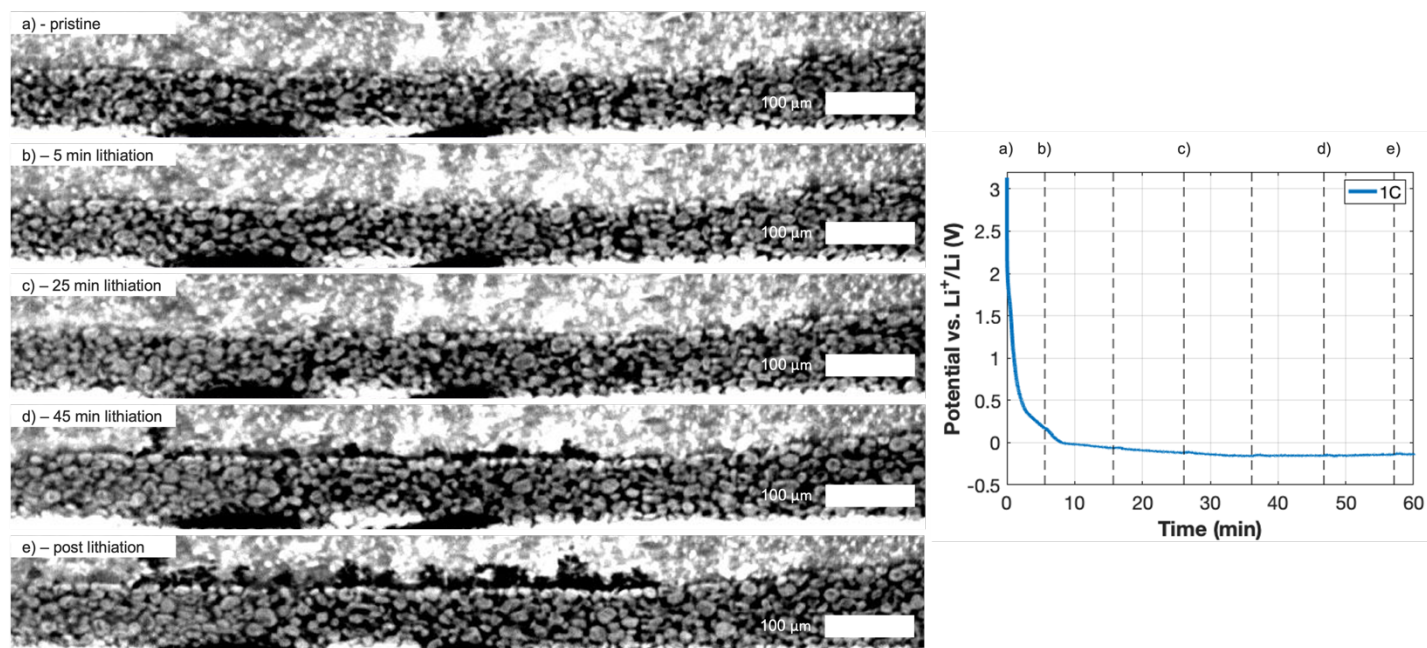


Figure 3 Vertical slices of graphite in cell contain the LP57 + VC electrolyte taken during cell cycling at 1C, *operando* measurement. a) in the pristine (uncycled) state b) 5 minutes of lithiation c) 25 minutes of lithiation d) 45 minutes lithiation e) post lithiation. With the electrochemical voltage profile shown as the inset graph on the right. Scale bars of 100  $\mu\text{m}$ .

The application of Paganin phase contrast reconstruction algorithms, along with the coherent x-ray source of ESRF have been instrumental in the successful identification of Li phases with the measured cells. Further work is underway on the segmentation of the Li phases to provide a quantitative analysis, gaining metrics of the Li-metal volume, and the kinetics of the Li phases growth during discharge. Finally, due to the materials and protocols used during this experiment, it is expected that the data acquired from this experiment will be provided for the BIGMAP project. The dissemination of the acquired data will be used not only for analysis of Li-metal plating, but also for modelling purposes, accelerating our knowledge of the processes in Li-ion batteries and further maturing the technology.