



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

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th 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.



Experiment title: Ultra-fast Operando Characterization of Li-ion Battery Ionic and Electronic Limitations

Experiment number:
CH-6081

Beamline: ID-31	Date of experiment: February 2020 from: February 9 th 8:00am to: February 16 th 8:00am	Date of report: 28/02/2021
Shifts: 15	Local contact(s): Isaac Martens, Marta Mirolo	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

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Preliminary Report (Data collection was completed less than two weeks ago):

The goal of this beamtime at ID-31 was to further develop our new X-ray diffraction (XRD) and X-ray fluorescence (XRF) Li-battery analysis methodology. The main goals were to:

- 1) Obtain full datasets using XRF/XRD on a high power $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO)/ LiFePO_4 (LFP) full-cell battery.
- 2) Compared fast-charging algorithms and analyzed real-world data from electric vehicle discharge profile.
- 3) Spatially resolve the LTO state-of-charge with XRD.

1) Obtain full dataset using XRF/XRD method on a full cell configuration $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) vs. LiFePO_4 (LFP)

In this experiment we performed vertical linescans collecting simultaneous XRD and XRF data on full cells of LTO/LFP in a spiked solution of 1M LiPF_6 + 0.1M LiAsF_6 in EC:DMC (1:1). The As $\text{K}\alpha$ peak was monitored as it is directly proportional to the concentration of Li^+ in the solution phase of the cell. The LFP being a 2-phase material has separate reflexions for the discharged state (LFP) and its delithiated charged state (FP). The ratio of 2 characteristic reflexions from either structure gives the local state of charge (SoC) which is spatially resolved along with $[\text{Li}^+]$ in solution. Two separate cells were measured (India and Lima).

Lima, fast: Cycling was performed at large and increasing currents, initially with full (dis)charge in 60 minutes, ending with less than 15 minutes. A return to the initial current was made at the end of the measurement cycle to ensure there was no sample degradation. The XRD and XRF results (Fig. 1) show an expected concentration gradient forming in both the solution and solid phase of the sample. The solution phase

gradient is stronger near the current collector which is reasonable for a sample limited by mass transport in the electrolyte. The XRD results (Fig. 1a) initially show a stronger gradient near the separator, and later close to the current collector. This could be the result of the charge being initially limited by mass transport in the electrolyte (gradient near separator). Once the separator side is fully delithiated, the local charging current density increases towards the current collector.

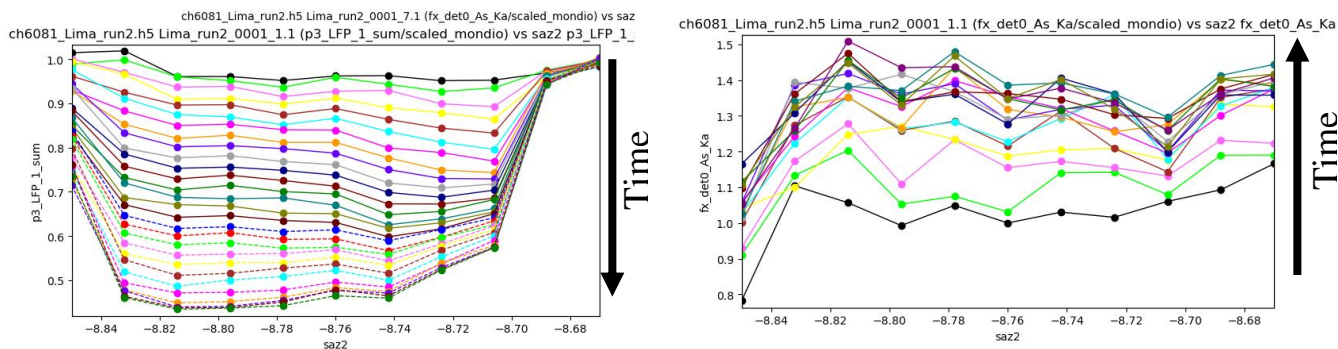


Figure 1: a) XRD - ratio of LFP(dis)/FP(charged) during charge at 1C representing the state of charge in the solid phase as a function of position within LFP electrode. b) XRF - As K α peak integral as a function of position within LFP electrode and normalized to response at rest. In both cases, the current collect is positioned to the left of the collected data and the separator to the right. Distance indicated in mm.

India, first: This cell had **not** undergone any previous electrochemical measurements. As such we could investigate the “breaking-in” of the cell during the first charge/discharge cycle. The XRF/XRD method provides a crucial insight into early cycling effects that could be symptomatic of cell failure later. In particular we can closely monitor the electrolyte concentration throughout early cycles for early decomposition or SEI formation. Although the LTO anode used should be “SEI-free”, we observe an increase in the solution phase As signal in **both the cathode and anode** during the first charge at a current of C/5 (Fig. 2a). Normal behaviour would see a drop in As signal (and therefore a decrease in [Li⁺]) in the anode during charge. During the rest period after the first charge (Fig. 2b), the As signal does not return to its initial state implying that the As has been deposited at the anode in the form of decomposition products or through precipitation. The majority of this deposit is present near the separator which could imply that this is a form of SEI which is reported for LTO but is known to degrade upon further cycling. A deeper investigation of the preliminary result will be required to understand the implications this has on the performance of the studied cell.

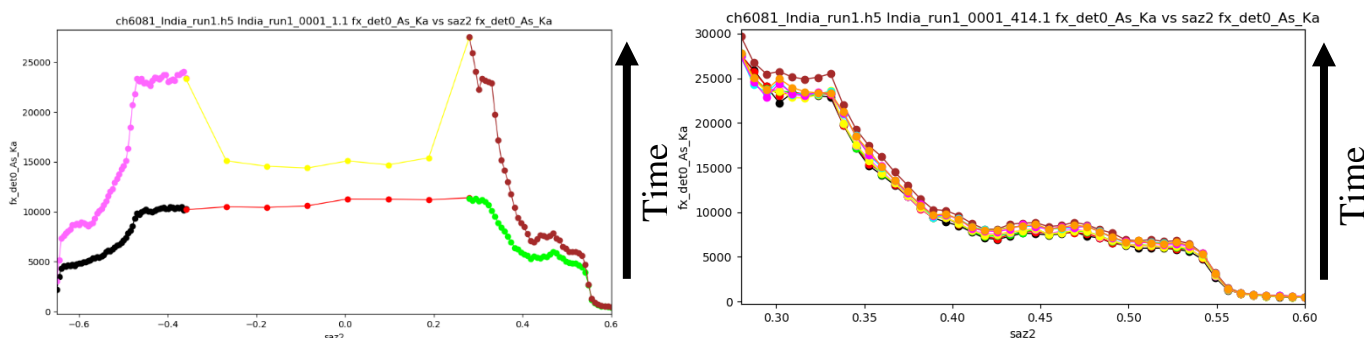


Figure 2: a) Integrated As K α peak as a function of position throughout the cell. Black/pink in LFP, red/yellow in the separator and green/maroon in the LTO before/after charge at C/5 respectively. b) As K α peak integrated as a function of position through LTO electrode during the rest cycle after the first charge at C/5. To the left, the separator and to the right the current collector. Distance indicated in mm.

2) Compared fast-charging algorithms and analyzed real-world data from electric vehicle discharge profile

One of the main motivations for developing the XRF/XRD method, is that it is currently difficult to assess the effect inside the battery of various fast-charging algorithms for electric vehicles. Specifically, *the combined*

local solution phase concentration gradient and the state of charge in the solid material is not currently available. Pulsed charging techniques were the first target since these methods are designed to reduce the formation of concentration gradients. Two pulsed charging techniques were applied to the same cell: 1) a charging current of 1C with a 80% duty cycle and b) 2C at 40%. Analysis of the data (not shown) will answer the following questions:

- 1) Does the bulk electrochemistry (capacity, overpotential etc.) correspond to the measured solution/solid phase gradient information?
- 2) Which algorithm is better for mitigating concentration gradient formation?
- 3) Does the material charge more homogeneously than in constant current charging at equivalent currents?

3) Spatially resolve the LTO state-of-charge with XRD

Determining the SoC in LTO is difficult as it is considered to be a “zero strain” solid solution material. The cell lattice fluctuates by 0.07% from the fully charged to fully discharged state. As such there has been no XRD report to our knowledge of the spatially resolved LTO state of charge given the resolution requirements. Our preliminary results show that we can qualitatively detect the LTO SoC over the course of 3 charge/discharge cycles at a rate of 1C (Fig. 3). The peak position of a characteristic reflexion is monitored as a function of time and is seen to correspond to the imposed current. Further analysis will lead to *operando* quantification of the LTO SoC with spatial and time resolution relevant for practical batteries for the first time.

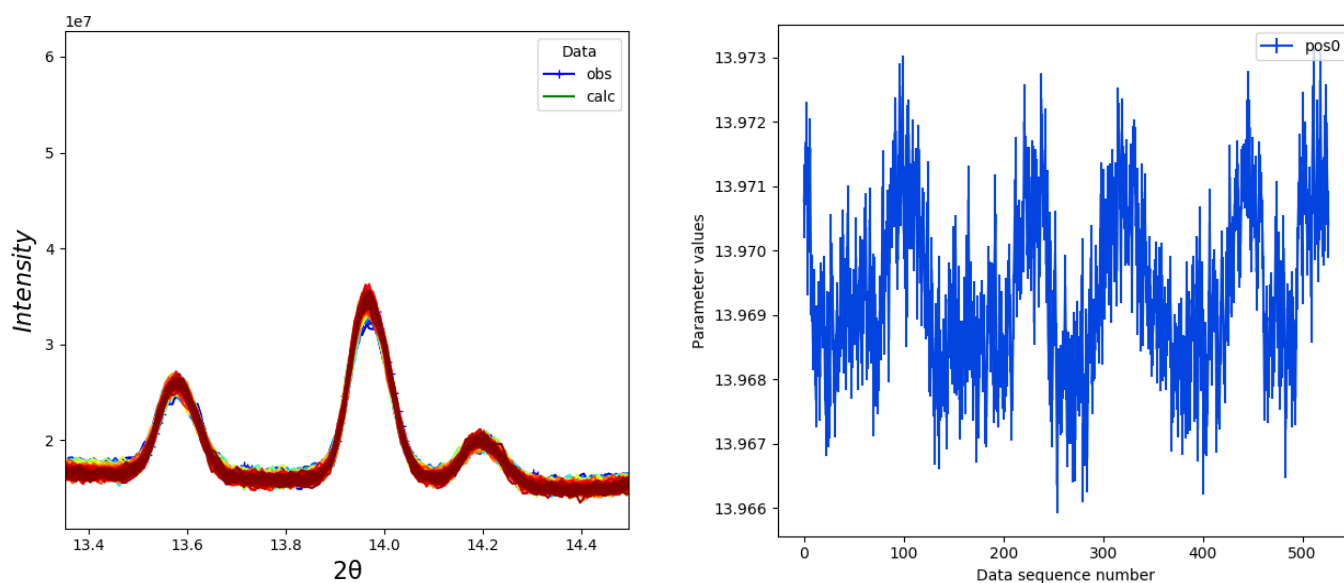


Figure 3: a) Diffractogram of characteristic LTO peak as a function of time during charge/discharge at a rate of C/5 followed by 2C/5 (2 full (dis)charge cycles). b) Characteristic reflexion peak position as a function of time during same period.

Summary

The data collected has enormous implications for furthering our understand of Li-ion batteries. The development of the XRF/XRD method opens the door to analysis of novel electrode architectures to determine performance limitation. Immediately, the data we have collected can be used to validate numerical models that have simulated LIB development for decades. We also report the first XRD *operando* spatially resolved determination of the LTO state of charge which is necessary for understanding the (dis)charge behaviour of this material, which is *the* “go to” commercial anode when high power is needed. Finally the practical comparison of fast-charging techniques using this method should once the data is fully analysed allow us to discern their performance improvement mechanism leading to rational design of superior algorithms.