



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: Determination of Solution-Phase Concentration Gradients in Solid-Polymer Electrolyte Li-ion Batteries

Experiment number:
CH-5698

Beamline: ID-31	Date of experiment: February 2020 from: February 4 th 8:00am to: February 9 th 8:00am	Date of report: 01/03/2021
Shifts: 15	Local contact(s): Isaac Martens, Marta Mirolo	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Jeremy I. G. Dawkins^a, Janine Mauzeroll^a, Steen B. Schougaard^b, Isaac Martens^c

^aDepartment of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal H3A 0B8, Quebec Canada

^bDepartment of Chemistry, NanoQAM, Université du Québec à Montréal, Case Postale 8888 Succ. Centre-ville, Montréal, Québec H3C 3P8, Canada

^cEuropean Synchrotron Radiation Facility, ID 31 Beamline, BP 220, F-38043 Grenoble, France

Report:

This experiment had one main objective with two subcomponents:

1. Develop a tandem X-ray fluorescence (XRF) and X-ray diffraction (XRD) methodology for measuring Li-ion batteries (LIB) *operando*.
 - a. Deliver proof of concept measurements on LiFePO₄ positive electrodes
 - b. Deliver proof of concept measurements on graphite negative electrodes
 - c. Deliver proof of concept measurements on solid polymer electrolytes

1a) Proof-of-concept XRF and XRD on positive electrodes

The first element was the tandem collection of XRF spectra and XRD diffractograms on LIBs *operando*. In order to obtain proof-of-concept on the feasibility of this system, we assembled a LiFePO₄ (LFP)/Li-metal half-cell using a 1M LiAsF₆ in EC:DMC in an X-ray transparent home made Swagelok cell. The cell was mounted on a translational stage and connected to a potentiostat for *operando* measurement (Fig. 1).

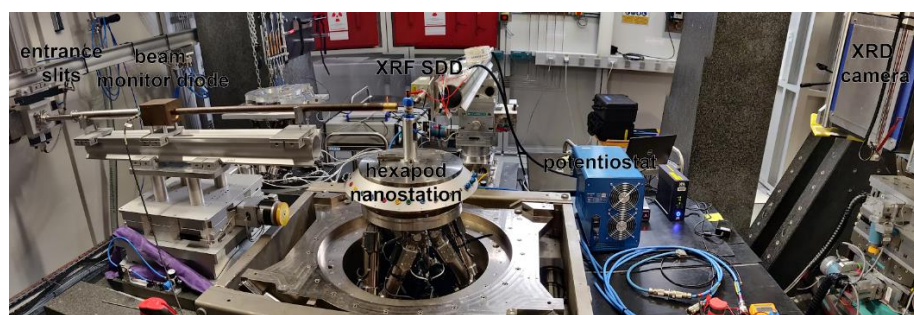


Figure 1 Simultaneous XRF/XRD setup for Swagelok LFP/Li cell

The incident beam was aligned with the knife-edge current collector (stainless steel) by using the Cr K α to ensure the sample had no tilt. Once aligned, the cell was charged and discharge while linescans were performed. Here the As K α gives the concentration gradient of AsF $_6^-$ (and therefore of Li $^+$) in solution and the LFP characteristic peaks are monitored in XRD (Fig. 2). These markers were monitored over the course of a (dis)charge at various currents. Although the data has not been completely processed yet, preliminary results confirm that we were able to observe the formation of a concentration gradient in the solution phase and monitor state-of-charge (SoC) in the solid phase. These data are critical for modeling LIBs accurately as well as for the development of new LIB electrode architectures.

1b) Full cell measurements

Once proof-of-concept for the method was established, the next goal was to mount and measure a full cell (including both an intercalation cathode and anode simultaneously). To this end, we mounted a pre-assembled LFP/Graphite cell in a modified Swagelok cell. Although data was successfully collected, we observed a conflicting Cu K α and Graphite characteristic XRD peak (Fig. 3). Our interpretation of this is that the Cu foil (the substrate on which the graphite electrode is placed) was bent, wavy or pinched in the cell. Measurement on a backup full cell yielded the same result. Given the LFP film was made freestanding (without underlying substrate) this problem did not arise for the cathode. For this reason, it was decided to extend the remaining beam time to performing measurements on the half-cell from Fig. 2. This problem will easily be avoided in the future by making the graphite film free-standing as well.

1c) Solid polymer electrolytes (SPE)

The final objective was to perform measurements on SPEs containing the LiAsF $_6$ electrolyte which is used as a fluorescent probe. Although functional SPEs incorporating the LiAsF $_6$ probe were developed successfully, ID-31 did not have heating/cooling capabilities for the dimensions of our cell (2 cm diameter, 15 cm height). The developed SPEs only operated above 50°C and this component of the proposal is therefore delayed until 1) room temperature SPEs with the LiAsF $_6$ salt can be produced or 2) a cell heating system developed.

Summary

In summary, the main objective of delivering proof of concept measurements involving simultaneous XRD and XRF measurements was accomplished. The subcomponent 1b) was partially accomplished through linescans performed at open circuit voltage. In order to gain quantitative information on the full-cell configuration (and specifically LIB anodes), freestanding graphite films can be made for a future beamtime. The SPE component will be reworked (as outlined in 1b) to accommodate the infrastructure available at ID-31.

The momentum of the progress made will be leveraged in a future proposal for beamtime. By applying the developed methodology to commercial LIB electrodes, valuable quantitative data will be acquired and made available for 1) improvement of numerical models and 2) industrial research and development of new LIB architectures.

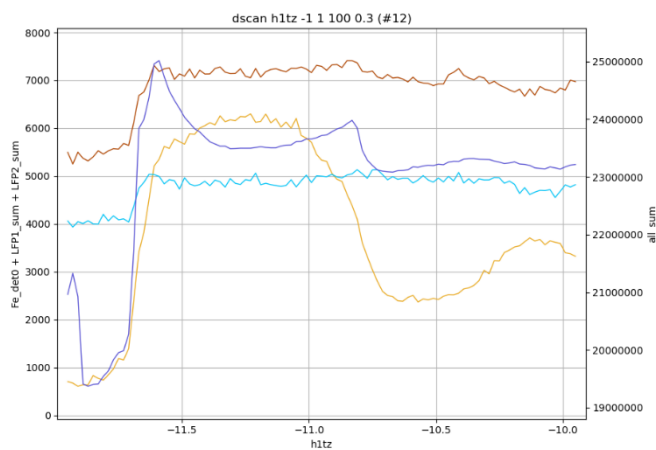


Figure 2 Linescan of LFP electrode and separator. Brown and cyan are LFP characteristic XRD peaks, yellow is As K α and blue is p3 all pixel sum

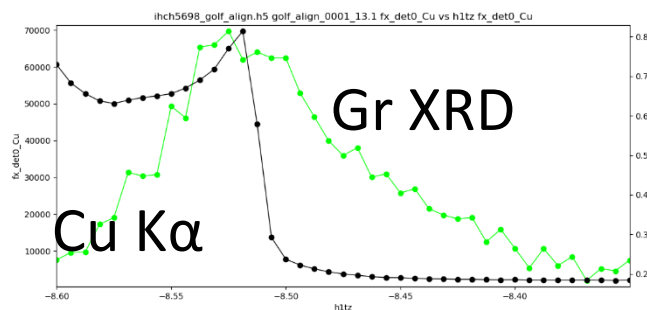


Figure 3 Graphite characteristic XRD peak (green) and integrated Cu K α as a function of position within the LFP/Graphite full cell