



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:**

High-Energy X-ray Diffraction to Understand Desalination Batteries

Experiment number:

CH-6565

Beamline: ID31	Date of experiment: from: 12.07.2023 to: 17.07.2023	Date of report: 30.08.2023 <i>Received at ESRF:</i>
Shifts: 15	Local contact(s): VINCI, Valentin	

Names and affiliations of applicants (* indicates experimentalists):

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Report:

During our 15 shift beamtime CH-6565 in July 2023, we carried out time- and spatially resolved *operando* high-energy X-ray diffraction experiments of desalination battery cathodes. These experiments were carried out in duplicate using realistic flow-by reactors for three distinct active materials across six varied aqueous salt solutions. Our overall aim was to unravel the ion intercalation mechanisms, as well as associated degradation processes and structural heterogeneity, and to correlate these to the desalination performance.

The experimental setup (Fig. 1) was a three-electrode configuration featuring an AgCl quasi-reference electrode and an activated carbon cloth counter electrode parallel to the working electrode. The salt solution was pumped through the reactor between the electrodes ('flow-by' mode) at 15 mL/min. A stirred reservoir of the salt solution allowed for simultaneous conductivity and temperature measurements during desalination. Initially deintercalated LiMn_2O_4 , $\text{Na}_{0.44}\text{MnO}_2$ and LiFePO_4 served as working electrodes in 0.1 M chloride salt solutions of Li, Na, Li:Na 1:1, and Li:Mg 1:1 as well as synthetic seawater (SSW) and SSW with 0.014 M LiCl. The electrodes were cycled at a (dis-)charge rate of 4 hours and 10 hours (relative to the theoretical capacity) in constant-current mode with potential limits (GCPL) and using constant-current constant-voltage mode with time limits (CCCV). The reactors were placed into a high-throughput setup allowing the quasi-simultaneous measurement of three independent reactors at a time, each of which was measured at 36 points across the electrode surface with a resolution of 6 minutes over a course of 8 hours. In the following, we describe our preliminary findings, noting that in-depth data analysis is ongoing.

The figures below present the X-ray diffraction patterns, working electrode voltage and conductivity as a function of time. Figure 2 illustrates the distinct phases that emerge during the intercalation and deintercalation processes: the formation of Li-rich LiFePO_4 and the Li-poor FePO_4 . Both species exhibit the olivine phase with

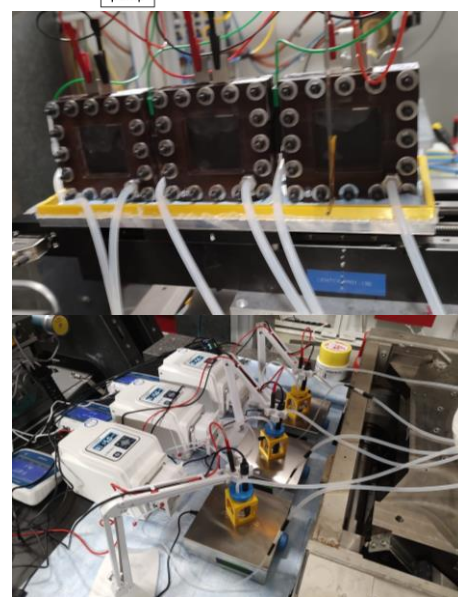
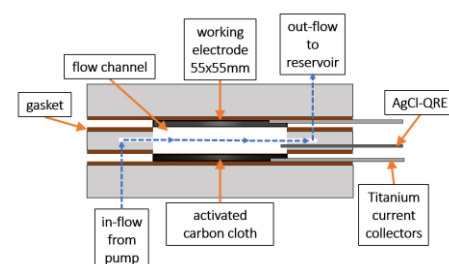


Figure 1: Schematics of the flow-by reactor and photographs of the setup installed at ID31.

different lattice parameters, leading to the distinct decrease and increase in peak intensities. When considering the NaCl solution, these processes face both thermodynamic and kinetic hinderance due to the larger ionic radius of Na. To overcome thermodynamic barriers, an extension of the potential window was used, while addressing kinetic constraints were addressed by operating at a lower C-rate. In Li:Na mixed solution (not explicitly shown here), a preferred formation of LiFePO_4 was observed compared to the formation of NaFePO_4 . Furthermore, employing a three-step potentiostatic method revealed subsequent deintercalation of Na^+ and Li^+ . In SSW, the deintercalation and intercalation plateaus exhibit significant separation, accompanied by the evolution of several peaks. These observations are ascribed to the complexity of the SSW.

LiMn_2O_4 (LMO) cycled in LiCl (Fig. 3) shows the anticipated shift in d-spacing, indicating contraction during deintercalation and expansion during intercalation. In SSW with additional Li presented good cycling behaviour. A preliminary analysis of the data suggests a strong selectivity towards Li, with an additional intercalation of magnesium at low potentials ($<0\text{V}$ vs. AgCl). $\text{Na}_{0.44}\text{MnO}_2$ (NMO) in SSW demonstrated good cycling behaviour (similar to pure NaCl electrolyte, Fig. 4) and displays enhanced salt removal with successive cycles. This suggests an activation process of the electrode material specific to the SSW environment, which was not observed in NaCl electrolyte. CCCV testing of this electrode/electrolyte setup exhibited no further intercalation occurring during the constant-voltage step.

The upcoming stages of analysis encompass removal of background, phase identification, calculation of unit cell parameters, calculation of intercalated ion mass and the creation of quantitative phase maps of the electrodes. We anticipate that our analysis will shed light on intercalation mechanisms, degradation processes, and structural heterogeneity resulting from ion distribution along and adjacent to the flow path.

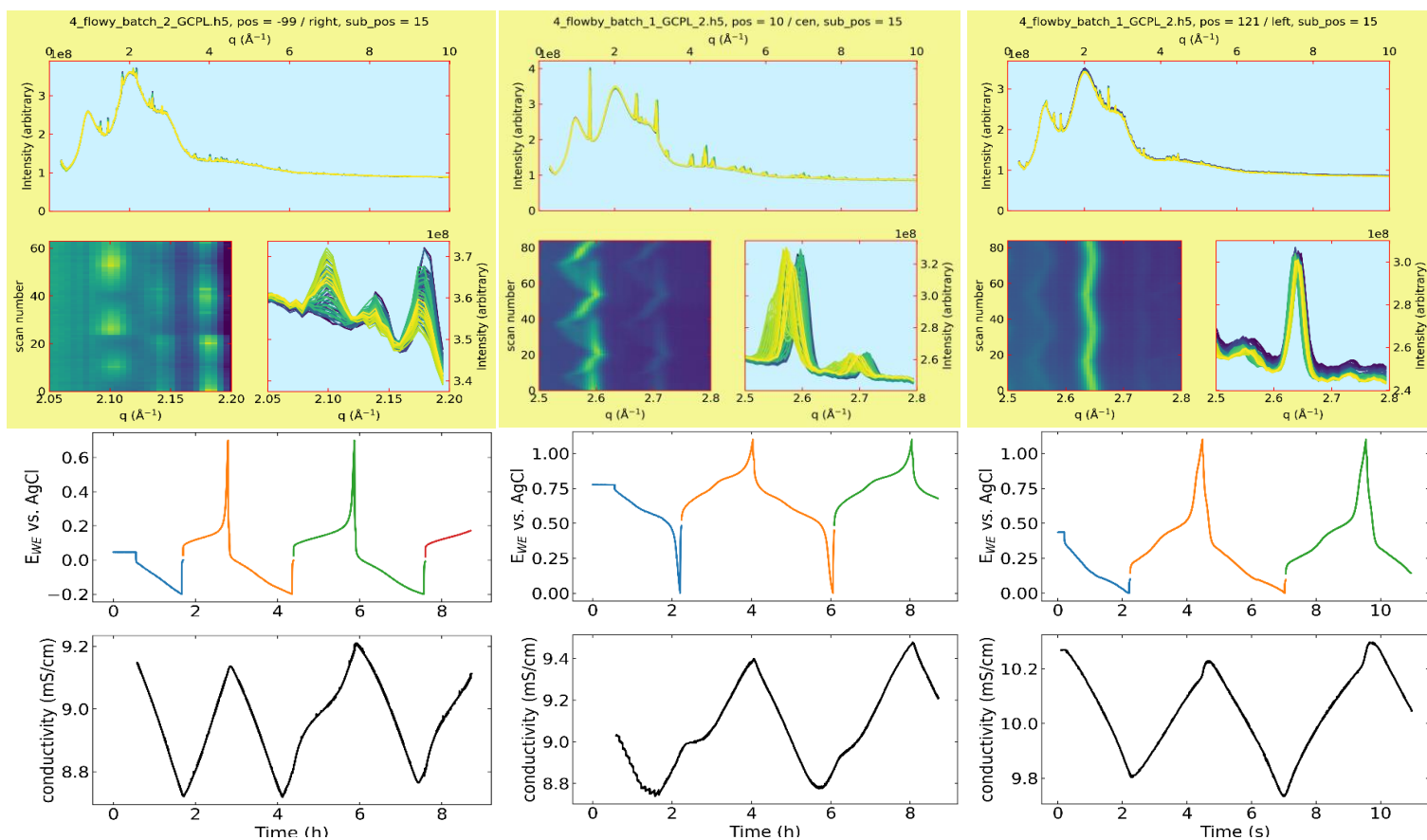


Figure 2: Operando HEXRD, electrochemistry and conductivity of a LiFePO_4 electrode in 0.1M LiCl electrolyte in a flow-by reactor at C/4. Measurement near the center of the electrode.

Figure 3: Operando HEXRD, electrochemistry and conductivity of a LiMn_2O_4 electrode in 0.1M LiCl electrolyte in a flow-by reactor at C/4. Measurement near the center of the electrode.

Figure 2: Operando HEXRD, electrochemistry and conductivity of a $\text{Na}_{0.44}\text{MnO}_2$ electrode in 0.1M NaCl electrolyte in a flow-by reactor at C/4. Measurement near the center of the electrode.