



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: Analysis of transition metal (Mn, Co, Ni) dissolution in high energy density cathode active materials for Li-ion batteries	Experiment number: MA-5047
Beamline: BM23	Date of experiment: from: 18.11.2021 to: 23.11.2021	Date of report: 20.09.2022
Shifts: 15	Local contact(s): Cesare Atzori (email: cesare.atzori@esrf.fr) Olivier Mathon (email: mathon@esrf.fr)	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Mrs Guelen Ceren Tok, Technical University Munich Mr Leonhard Reinschlüssel, Technical University Munich Mrs Anne Berger, Technical University Munich Mr Philip Rapp, Technical University Munich		

Report:

Within the allocated beamtime MA-5047 a series of operando hard X-ray absorption spectroscopy experiments within Li-ion batteries was conducted, investigating the transition metal (TM) dissolution from lithium- and manganese rich cathode active materials (LMR-CAMs). In specific, two different CAMs were compared; Namely, a cobalt containing LMR-NMC and a cobalt free LMR-NM were investigated. For this, a special operando XAS electrochemical cell designed by our group was employed (see Figure 1a). Owing to the unique geometry of this cell, we were able to spectroscopically access and independently investigate both the anode electrode and the electrolyte within the separator. The implementation of a lithium reference electrode placed in a central position underneath the electrode stack enables to record the charge/discharge characteristics of the anode and cathode. The loadings of the electrodes were 5.3 mAh/g_{CAM} on the cathode and 6.5 mAh/g_{graphite} on the anode and the cells were built with two glass fiber separators and filled with 100 µl electrolyte, LP57 (1 M LiPF₆ in EC:EMC (3:7)). The first part of the experiments was focused on the activation of the investigated lithium- and manganese rich CAMs by charging the cell to a upper cut-off potential of 4.8 V vs. Li⁺/Li in a constant current (CC) charging step at a rate of C/10. This was followed with by a constant current discharge to 2.0 V vs. Li⁺/Li at a rate of C/2. After that two more cycles were conducted at a constant current constant voltage (CCCV) charge/discharge to 4.7 V vs. Li⁺/Li and 4.8 V vs. Li⁺/Li at a rate of C/2 (see Figure 1d and e).

A sagittally focusing double crystal monochromator consisting of two Si 111 crystals was used to select the incoming energy and the beam was focused using Si coated mirrors; then, the beam was cut with slits to achieve a beam size of 5 µm in the horizontal dimension (i.e., along the thickness of the graphite electrode and the separator) and approximately 5 µm in the vertical dimension (i.e., along the width of the graphite electrode/the separator). These dimensions allow focusing the beam exclusively on either the separator, or the graphite electrode. As we are using hard X-rays in the energy range of 6-8 keV the probing depth of the XAS method is rather high on the order of ~300 µm making the method bulk sensitive. Photon energies were calibrated using the first peak in the first derivative of the pure metal foils, which were measured in fluorescence before the operando study; background corrections of the spectra were carried out using the IFEFFIT software package. XANES was measured operando and alternated between two different positions in the cell (separator/electrolyte and graphite electrode) to obtain the total amount of dissolved transition metals from the respective CAMs. The acquisition time for each spectrum presented in this report was approximately 7 minutes.

To quantify the amount of dissolved TMs in the cell volume, the edge-jump (difference between post- and pre-edge region) was determined over the course of the experiments (see Figure 1b) by evaluating it with calibration curves for the respective TMs. These calibration curves were recorded prior to the operando measurements by preparing electrolyte solution with known amounts of the respective TM-TFSI salts, that were filled in the

described cell setup with two glass-fibre separators only and then evaluating the edge-jump, corresponding to a specific concentration of the respective TMs (see Figure 1c).

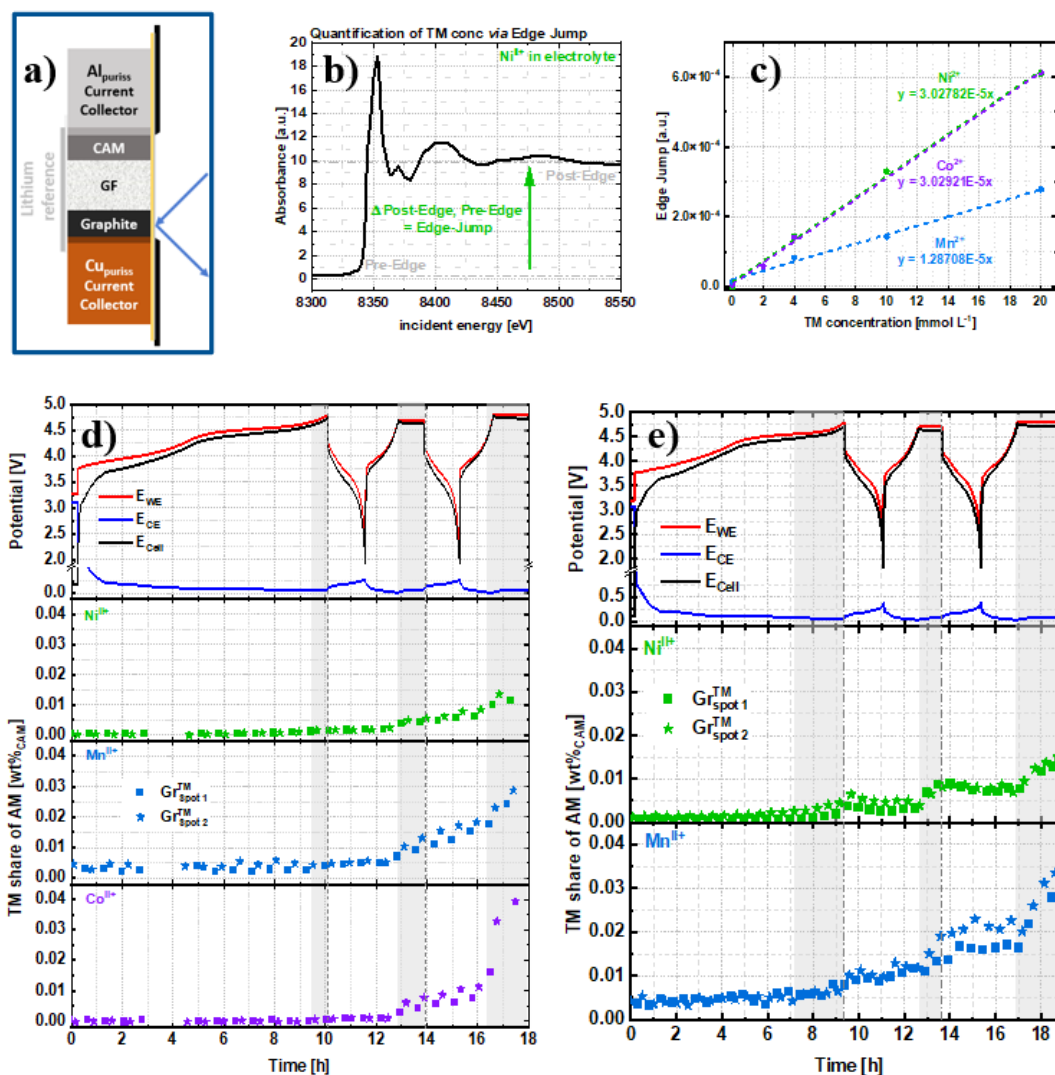


Figure 1. a) Schematic of the electrochemical cell for operando X-ray absorption spectroscopic investigation used within this beamtime. b) exemplary visualisation of the edge-jump method used for the quantification of transition metal ions within the electrochemical cell during cycling, that was applied within this study. c) Calibration measurements for the respective transition metals under investigation (Ni^{2+} in green, Co^{2+} in purple and Mn^{2+} in blue) determined by spiking electrolyte solutions (LP57 (1 M LiPF_6 in EC:EMC (3:7))) with known concentrations of the respective TM-TFSI salts and measuring those electrolytes in the abovementioned operando cell within two glass fibre separators. d) Potential profiles and respectively determined transition metal concentration measured within the graphite electrode for the Co-containing LMR-NMC. e) Potential profiles and respectively determined transition metal concentration measured within the graphite electrode for the Co-free LMR-NM.

Both investigated materials show a comparable behaviour in regards to the dissolution of Ni^{2+} and Mn^{2+} from their bulk structure. The main onset for TM dissolution is reached once surpassing a cathode potential of 4.6 V vs. Li^+/Li , whereby the time spent at the respective upper cut-off potentials seems to be specifically detrimental (exemplified by the constant voltage holds in cycle #2 and #3). At the end-of-test both materials show almost identical values regarding the weight percent (wt%) of TM-loss in regard to Ni^{2+} and Mn^{2+} , which is due to their highly comparable bulk-stoichiometry (not mentioned here). For the co-containing LMR-NMC (Figure 1d) a large overestimation of the dissolved Co^{2+} was observed, which, thus far, can't be explained.

Overall, the obtained results during the successful beamtime MA-5047 at BM23 shown to be highly promising and laid the foundation for an ongoing investigation of the impact of parasitic reactions occurring at high operation voltages in Li-ion batteries containing LMR-CAMs. A fundamental understanding of those will enable selective approaches to tackle the limiting issues of these high-energy materials to promote their implementation in Li-ion battery systems for high-energy applications. To conclude this study, the temperature dependence of the TM dissolution of state-of-the-art CAMs will be key subject of further operando hXAS studies (pending proposal MA-5685).