EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

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

ESRF	**Experiment title:** Transition Metal Dissolution in Promising Future Lithium-Ion Battery Systems investigated by Operando X-Ray Absorption Spectroscopy	**Experiment number**: CH5202
Beamline:	**Date of experiment**: from: 19.10.2017 to: 24.10.2017	**Date of report**: 23.04.2018
Shifts:	**Local contact(s)**: Debora Motta Meira	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Anna T.S Freiberg*

Sophie Solchenbach*

Benjamin Strehle*

Moniek Tromp

Hubert A. Gasteiger

Not part of original proposal but experimentalist: Armin Siebel*

Report:

While the complete data set obtained from this beamtime (experiment CH5202) can not be set online due to confidentiality, the basic success of these experiments shall be summed up. A detailed report displaying all data and quantitative analysis was sent to the user office after clearance was given from the material manufacturer.

Goal of our experiments was the analysis of transition metal dissolution for promising future Li-Ion battery materials in comparison to commercially employed NCM111. We were able to gather operando data on the dissolution behavior of NCM111 in comparison to NCM811 material for all transition metals of interest, e.g. manganese, nickel and cobalt. Due to our unique spectro-electrochemical cell, the concentration in the electrolyte and on the graphite anode could be followed throughout cycling. By a sophisticated electrochemical cycling procedure of the battery cells, we were able to deconvolute the two major dissolution mechanisms for layered transition metal oxide cathode materials: Electrochemical destabilization of the lattice at high state-of-charge and chemical leaching of transition metals by protic species formed out of electrochemical oxidation of the electrolyte at high potential.

The on-set of transition metal dissolution is caused by electrochemical destabilization of the lattice and sets in at a constant SOC, independent of the potential at which this SOC is reached for different materials. This behavior is of great importance for application of those materials, as they are currently only employed up to a maximum SOC of 70%. Pushing the upper limit above that value, aging of the cell aggravates disproportionally, which can now be linked (among other mechanisms) to the dissolution of transition metals out of the cathode active material, leading to loss of active lithium on the graphite counter electrode and increased cell impedance. Cycling at higher SOC will only be possible if one solves the inherent crystal destabilization problem of the particle surface.

The main transition metal dissolution however sets in at high potentials, which can be explained by electrochemical electrolyte oxidation forming protic species that leach out transition metals out of the active materials. Onset of this transition metal dissolution very well coincides with the detection of gaseous electrolyte oxidation products. By carefully setting the upper charge cut-off potential and overcharge protector, this region can be avoided in application but will have to be determined independently for different electrolytes.

Further operando measurements for Li-rich HE-NCM and the high voltage spinel LNMO (as written in the proposal) could not be executed due to two beam drops lasting for several hours, which made us repeat operando measurements as they were interrupted. However, further ex-situ data could be gathered studying the effect of electrolyte solvent, aging cycling at currently employed upper cut-off potential, and purity of the battery casing that is exposed to high potentials and corrodes as well. This data will only be shown in the confidential report sent to the user office as mentioned earlier.

The great optics enabling a stable, high quality micro-sized X-ray beam inspired us to submit a new proposal (CH 5555) where this characteristic will be fully utilized. Preliminary data for this new experiment series was gathered during experiment CH 5202 and present a good starting point for a sophisticated homogeneity study.

A manuscript of the high-quality data gathered during CH 5202 is in preparation. Parts of the results will be presented on an international conference in October 2018.