EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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

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 form 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.

ESRF	**Experiment title:** Role of Zr-doping for stabilization of next generation positive electrode materials in Lithium Ion Batteries	**Experiment number**: CH-6389
Beamline: ID31	**Date of experiment**: from: 03/12/2022 to: 07/12/2022	**Date of report**: 12/09/2023
Shifts: 12	**Local contact(s)**: Dr. Marta Mirolo	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Abstract:

Layered Ni-rich lithiated metal oxides such as LiNi0.8Mn0.1Co0.1O2 (NMC811) are attractive candidates as next-generation Li-battery (LiB) positive electrode materials due to their high capacities and reasonable price. Unfortunately, the cycle life of these materials is relatively short due to structural instability. However, the loss in performance over time can be delayed by either bulk or surface Zr-doping. The goal of this experiment is to perform operando HE-XRD on different Zr-doped/coated and undoped electrodes in fresh and aged assembled cells to understand the exact role and behaviour of the dopant in the host NMC structure during cycling.

Setup and Sample Preparation:

In this experiment we performed vertical and horizontal linescans collecting 2D XRD patterns of 3 Swagelok cells, composed of 3 different cathodes: *Undoped*, *Zr-doped* and *Zr-coated NMC811* in electrolyte solution of $LiFP_6$ in EC:DMC 1:1 and Metal Lithium as a counter anode.

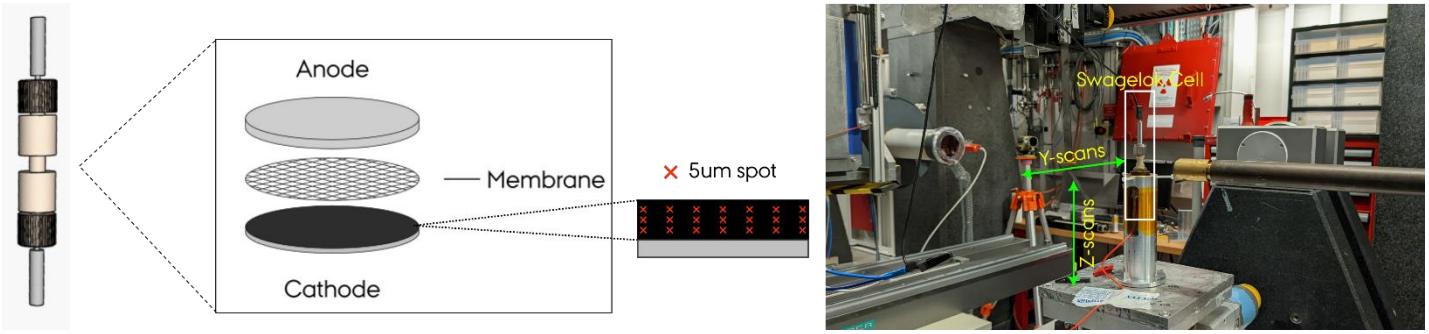

***Figure 1**: Sketch of the Swagelok cell used for the Beamtime on the left. 5um beam measurement for different spots on the NMC cathode in the center. Picture of the real setup inside the experimental hutch can be seen on the right.*

Results:

The initial idea of the proposal was to cycle the cells up to 4.4V first and then rise the voltage to 4.5V to speed up the degradation process of the cathode material while monitoring its evolution. Processing the data during the beamtime, we noticed that, at 4.4V, the *Undoped NMC* sample owned an unreacted phase, as shown in **Figure 2**. Since we did not know the nature of its sudden appearence, we decided to increase the upper voltage limit of the subsequent cycle not anymore to 4.5V as declared in the proposal, but to 4.6V. In this way we stressed and pushed the delithation process at the expenses of possible permanent collapse of the structure. At 4.6V (while keeping the voltage costant) we noticed that the permanent phase started to slowly react and transition. A third cycle up to 4.8V was performed, showing that the material needed a much higher overpotential to fully react at 1C. This happened also for the *Zr-Coated NMC* sample. Whereas, the *Zr-Doped NMC* sample even at 4.4V was able to fully react without applying any overvoltage. This evidence tell us that in a comparable voltage window from 3.0 to 4.4V, the doped sample is able to withdraw 100% amount of Li^+ ions from the cathode material. What has to be underlined is that the cells were all equally cycled at the same C-rate (1C). The unreacted phase is present because the Li^+ removal from the host structure is kinetically limited by the fast C-rates, however, this did not happen for the *Zr-Doped NMC* sample. The doping is likely to ease the Li^+ diffusion, therefore, the material could find applications on devices that require faster charging rates.

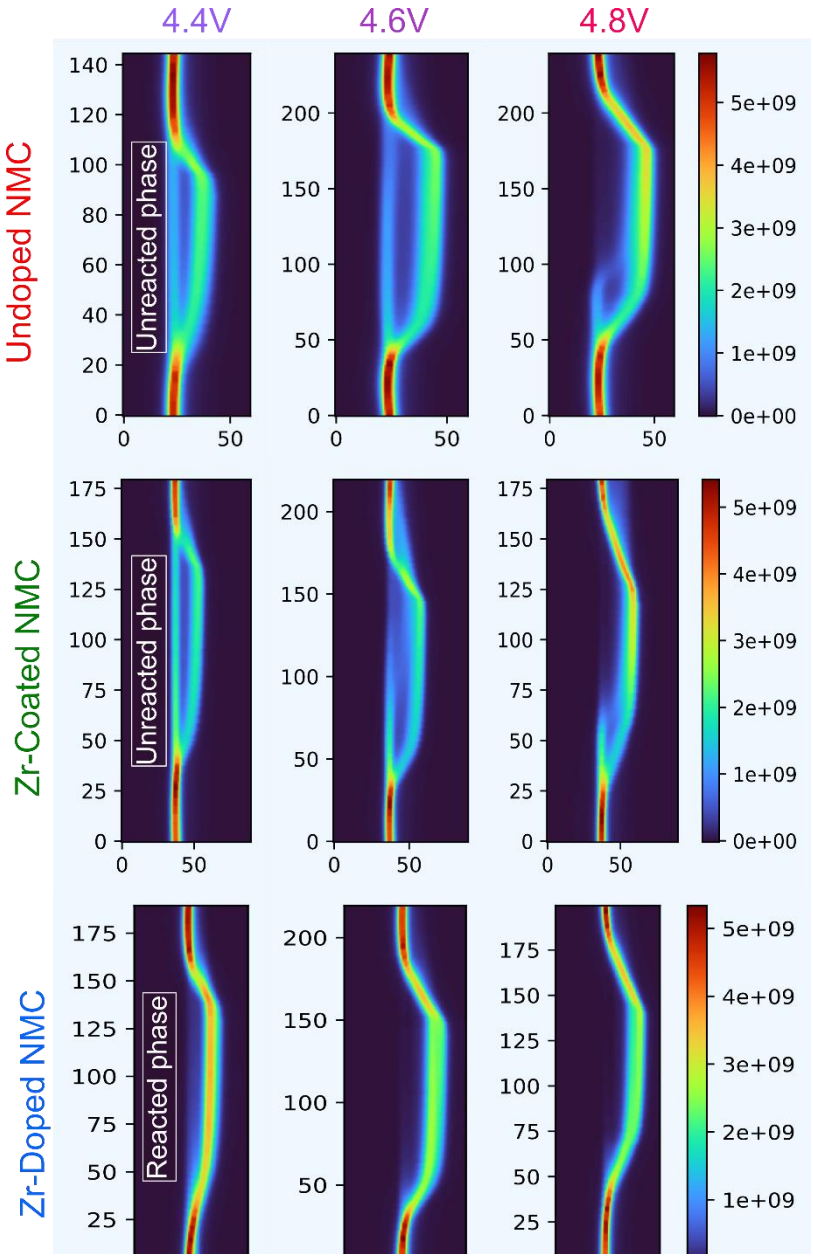

***Figure 2**: Evolution over cycling at different voltages of the 003 reflection. Displayed the center of the electrode height.*

In the literature we usually find works where cycling rates are rather slow (0.1C/0.2C), mostly limited by Bragg-Brentano geometries and slow acquisition times at laboratory scale. The cell electrochemistry can not be faster than XRD acquisition time. But this has been possible at ID31 where energies were high enough to probe inside the PEEK body of the cell, and thanks to 2D Pilatus 2M Detector we were able to take full XRD snaposhots in 1s.

Problems Encountered:

The change of plans that brough us to cycle the cells 3 times and not 2, prolonged the overall time for measuring each sample which ended up only on the fresh and not being able to study the aged one. It happens pretty often in electrochemical in-operando studies that the cells fail, which led us to open, wash, bake and reassembling them few times (requires from 6 to 8hrs). Sine the priority was given to the fresh samples to have a consistent rack of data, aged electrodes were left behind. This, unfortunately, kept out still few unanswered questions.

Next-Plans-To Be Done:

1) Reduce the number of filters for *Zr-Coated NMC* aged electrode to see whether Li_2ZrO_3 is visible and reactive.
2) When samples are cycled at least 100 times, inevitably, fatigued phases will appear. The idea is to look again at *Undoped NMC*/*Zr-Doped NMC* aged samples and check whether the doped one is still able to fully delithiate (100%) and in case of unreacted phase, quantify it and estimate when the fatigued phase might appear.