# Experimental report

30/09/2022

**Proposal:** DIR-221 **Council:** 10/2020

**Title:** Enabling in operando batteries measurement at D19 beamline

**Research area:** Methods and instrumentation

**This proposal is a new proposal**


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**Samples:** Li metal
NMC811

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D19 | 4 | 4 | 14/06/2021 | 16/06/2021 |
| | | | 12/07/2021 | 14/07/2021 |


## Abstract:

The Li-ion chemistry is thus far the most advanced chemistry employed in battery technology. To date, Li-ion batteries dominate the market of the electronics and portables devices. However, in the field of electric and hybrid vehicles further improvements are required in terms of performance, safety, and cost. High voltage cathode materials such as LiNi0.8Co0.1Mn0.1O2 (hereafter called NMC811) are suffering drastic volume changes and enhanced structural degradation caused by the Li insertion/de-insertion. Understanding the extend of the structural degradation during cycling will be an asset to improve the overall electrochemical performance. In operando measurement are thus crucial but it requires several days at beamline quite often saturating the beamtime demand. Here we identified that the D19 beamline generally used for single crystal diffraction on molecular and structural biology samples could be tuned to welcome batteries users and in operando measurement if some modifications at the beamline are undertaken. It will drastically increase the ILL capacity in term of battery investigation in the next future.

# In operando battery characterisation on D19

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*The Li-ion chemistry is thus far the most advanced chemistry employed in battery technology. To date, Li-ion batteries dominate the market of the electronics and portables devices. However, in the field of electric and hybrid vehicles further improvements are required in terms of performance, safety, and cost. High capacity cathode materials such as $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (hereafter called NMC811) are suffering drastic volume changes and enhanced structural degradation caused by Li insertion/de-insertion. Understanding the extend of the structural degradation during cycling will be an asset to improve the overall electrochemical performance. In operando measurement are thus crucial but requires several days at beamline quite often saturating the beamtime demand. Here we identified that the D19 beamline generally used for single crystal diffraction on molecular and structural biology samples could be tuned to welcome batteries users and in operando measurement if some modifications at the beamline are undertaken. It will drastically increase the ILL capacity in term of battery investigation in the next future.*

The ongoing demand for new generation energy storage being more powerful and energetic requires the development of novel type of batteries based on post Li-ion technology. Advanced Li-ion batteries and the pre-cited novel systems utilize less understood electroactive materials and thus show new reaction mechanisms during electrochemical cycling, the understanding of which requires characterization tools and techniques, among them, the usage of in operando techniques at large scale facilities. In the present case, we wanted to demonstrate that the Beamline D19 at the ILL, normally dedicated to crystal structure determination through single crystal diffraction can be properly tuned to welcome also in operando battery investigation, increasing then the capability of ILL beamlines to welcome advanced in operando energy research.

Beginning of September 2020, we were granted two days of test measurement to demonstrate the feasibility of in operando battery measurement at D19. We measured a Li-ion battery based on known material NCM523 vs. Li. For this test, we used the cell developed by Dr. E. Suard, Prof. C. Masquelier, Dr. L. Croguennec during the thesis of Dr. M. Bianchini, so call ILLBATT1, known to be a null matrix cell owing to the TiZr alloy employed for the casing.[1] This cell was mounted on D19 beamline to test the feasibility of operando measurement. Despite the fact that the cell was not optimized (non-deuterated electrolyte employed), it was possible to measure an electrochemical cell at D19 for a night. Those results help us to design a new collimation tube on the beamline to reduce the background due to the incoherent scattering coming from the TiZr, which was increasing the signal to noise ratio.

For DIR-223, an operando measurement with the collimation tube was performed on $LiNiO_2$ (LNO), end member of the Ni-rich NMC cathode using the ILLBATT1 cell filled with deutered electrolyte. As can be seen in Figure 1, we were able to fully charge the positive electrode (i.e. delithiation) and see the several phase transition that are ongoing inside this material.

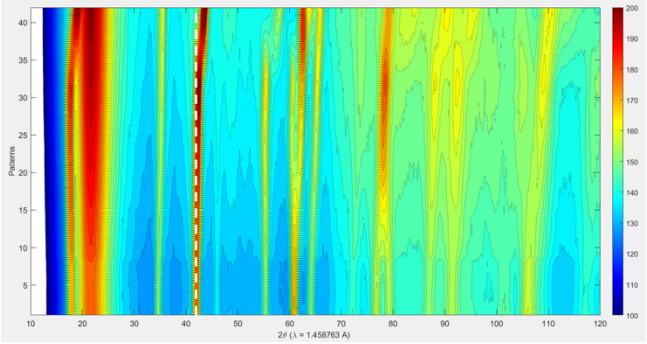


**Figure 1.** Contour plot representation of the neutron diffractograms collected during the in operando measurement of LNO cathode materials on D19

For a fair comparison and to check the quality of the data collected on D19, Rietveld refinement was performed using Fullprof suite and the extracted cell parameters were compared to the operando X-ray diffraction investigation performed by Janek et al.[2] and to the ex situ data collected on D2B beamline. The data as well as the electrochemical performance of the cell are displayed in Figure 2. Regarding the electrochemistry, we obtained a very similar signature between a coin cell and the operando cell, despite the difference in mass content in the cell. For the evolution of the *c* lattice parameter, we can see that early delithiation leads to a slight increase of *c*, while at the end of delithiation a phase transition is observed with a massive decrease of *c*. Those results are in agreement with the data obtained by an operando X-ray diffraction study and slightly different to the one obtained at D2b, especially at the end of the delithiation. This difference can be explained by the fact that the delithiation is different in the operando cell and in the ex situ sample, also in the ex situ sample, relaxation might have occurred.

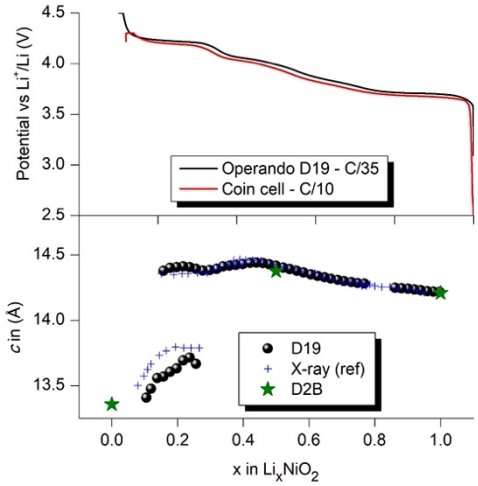


**Figure 2.** (top) Comparison of the electrochemical data obtained in the cell developed by Bianchini et al and a coin cell. (Down) Comparison on the evolution of the c lattice parameter between D19 beamline, D2B ex situ sample and the X-ray data from the literature.

At this stage, we demonstrate that D19 beamline is a robust beamline to perform long term cycling operando based measurement.

Work fully performed at ILL
Proposal-number: DIR 221
Instruments: D19

References :

1. Bianchini, M. *et al.* A New Null Matrix Electrochemical Cell for Rietveld Refinements of In-Situ or Operando Neutron Powder Diffraction Data. *J. Electrochem. Soc.* **160**, A2176 (2013).
2. de Biasi, L. *et al.* Phase Transformation Behavior and Stability of LiNiO2 Cathode Material for Li-Ion Batteries Obtained from In Situ Gas Analysis and Operando X-Ray Diffraction. *ChemSusChem* **12**, 2240–2250 (2019).