# Experimental report

30/09/2022

**Proposal:** DIR-233 **Council:** 4/2021

**Title:** Lithium gradients in high energy cathode material cycled vs. Li metalusing a standardised neutron radiography operando cell

**Research area:**

**This proposal is a new proposal**


**Main proposer:** **Sandrine LYONNARD**

**Experimental team:** Sandrine LYONNARD
Quentin JACQUET
Guilhem PARADOL

**Local contacts:** Lukas HELFEN


**Samples:** LiNiO2

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| NEXT | 2 | 2 | 06/03/2021 | 08/03/2021 |

**Abstract:**

**DIR – 223. Operando neutron imaging of Li-ion batteries: Tracking Li concentration gradients**

*Quentin Jacquet[a], Lukas Helfen[b], Claire Villevieille[c], Sandrine Lyonnard[a]*

*[a] Univ. Grenoble Alpes, CEA, CNRS, IRIG-SyMMES, 38000 Grenoble, France*

*[b] Institut Laue-Langevin (ILL), BP 156, 71 Avenue des Martyrs, 38042 Grenoble, France*

*[c] Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France*

*E-mail: quentin.jacquet@cea.fr*

**General objective :** Mastering fast charging conditions of high energy density Li-ion batteries is key to accelerate market penetration of electric vehicles (EV). This will be achieved by better understanding lithium concentration heterogeneities developing under high current densities. However, this requires operando characterisation capable of quantifying lithium concentration at the scale of some micrometres in solid and liquid phases within minutes. This is often only accessible combining several technics such as Neutron Imaging(NI)/Wide angle X-ray scattering (WAXS). To circumvent the well-known issue of limited reproducibility over different cell designs especially at high charging rate, combined characterisations need to be performed on the same operando cells. Therefore, we tested neutron imaging a PFA Swagelok type cells is compatible with synchrotron beamlines – especially ID31 at ESRF to perform micro resolved WAXS/SAXS (Figure 1).

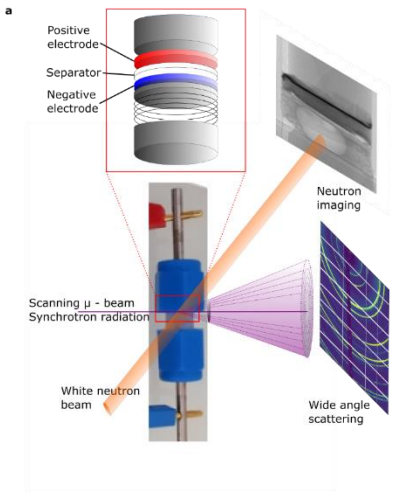


*Figure 1 : a – schematic of the correlated WAXs (wide angle X-ray scattering) and NI experiment on a $LiNiO_2$/Graphite cell*

**Experiment goals:** Neutron being absorbed by $^6$Li which is 8% neutrally abundant and strongly scattered by hydrogen, there are typically two possible strategies to perform *operando* neutron imaging of batteries. The first strategy consist in using commercial grade battery components without any isotope exchange, in this case $LiNiO_2$, Li metal, LP57 (1M LiPF6 in EC/DEC) as the cathode, anode and electrolyte materials. Data collected in this set up are representative of a realistic battery chemistry, but the low concentration of $^6$Li together with the abundance of hydrogen in the LP57 electrolyte makes Li concentration potentially difficult to measure. The second strategy is to use $^6$Li-enriched materials with deutered electrolyte, being a model battery system ideal for neutron imaging. In DIR-223, we decided to use commercial materials.

**Experimental details:** Materials were provide by BIG-MAP partners (https://www.big-map.eu/). The high-flux white neutron beam available on D50/NeXT was collimated by a slit aperture of 30 mm height

and 15 mm width. The spatial resolution achieved was 14 microns in the direction of the depth in the electrodes, with a pixel size of 7 microns. Images of the cells have been continuously collected during battery operation at charging rates ranging from C/5 to 2C and with a time resolution of 30 sec.

**Results :** Typical neutron transmission image of the battery before cycling is shown figure 2 in which the thick Li electrode appears in black, the separator in grey, and the $LiNiO_2$ in light grey, as expected from the relative Li content. Electrochemical performance of the cell during the experiment is shown Figure 2, and are in good agreement with literature for C/5, C/2 cycles[1]. However, voltage holds during C and 2C charges are abnormally long suggesting the presence of Li dendrites. During charge (corresponding to the delithiation of $LiNiO_2$ and Li plating), $LiNiO_2$ electrode becomes darker, while the Li electrode grows. These changes are reversible during discharge showing qualitatively the sensitivity of the technique to track Li concentration.

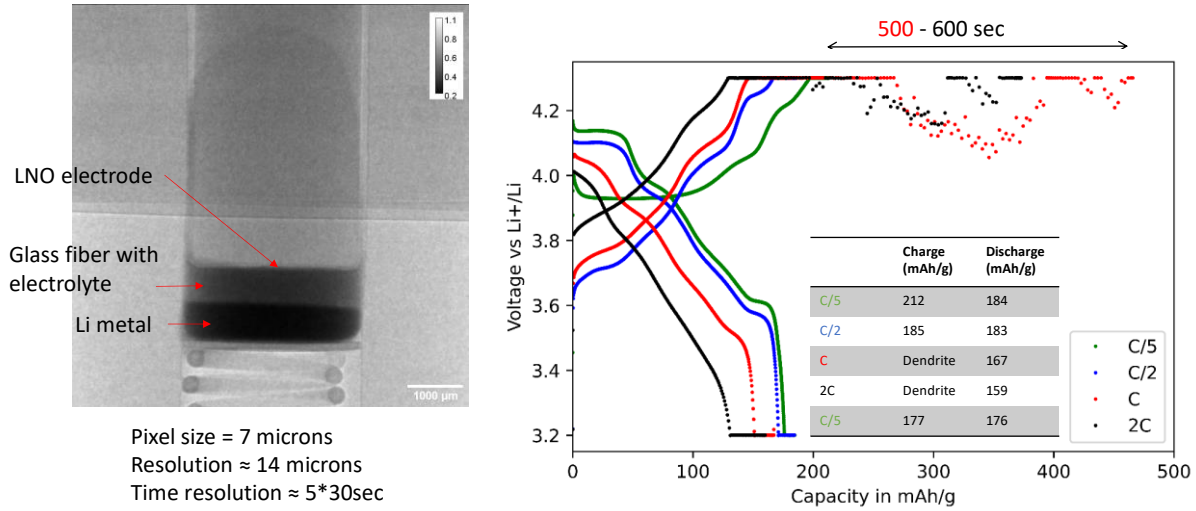


*Figure 2 : left, neutron imaging of the cell in which the grey scale is the transmission, right, voltage versus capacity plots of the operando cycling with a table summarizing major observations.*

Moving towards a more quantitative analysis, after typical image correction enlisting, dark and flat removal and image drift correction, the attenuation difference between $Li_xNiO_2$ and $LiNiO_2$ can be calculated as shown Figure 3. Differential attenuation is positive during delithiation because the attenuation of $Li_xNiO_2$ is less than $LiNiO_2$ and reaches up to 0.6 at the end of discharge. Interestingly, the electrode appears to spread over 30 pixels (210 microns) which is much thicker than expected. This is probably due to a tilt of the cell with respect to the neutron beam as calculated Figure 3 (center panel). From the attenuation change, Li content in $Li_xNiO_2$ can be calculated and is shown Figure 3 (right) for different depth in the electrode and compared to $Li_xNiO_2$ expected from electrochemistry. Excellent agreement between the expected and calculated Li concentration from neutron imaging is obtained proving that Li concentration can be quantitatively measured. However, no significant difference in the depth of the electrode is observed presumably due to the noise level.

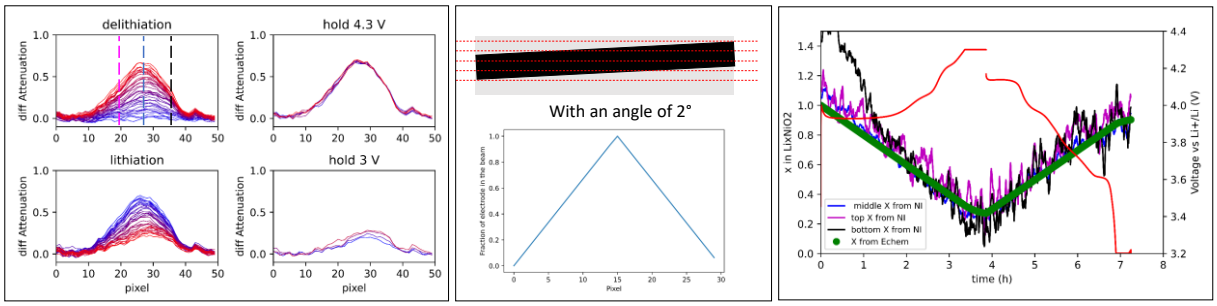


*Figure 3 : Left, differential attenuation as a function of $LiNiO_2$ electrode thickness (in pixel). Center : simulation of the effect of an angle of 2° between the electrode and the neutron beam on the vertical size of the electrode. Right, x in $Li_xNiO_2$ estimated from the differential attenuation at different depth of the electrode (in blue, magenta, black) compared to x expected from electrochemistry. Data is shown for the cycle at C/5.*

**<u>Conclusion:</u>** *Operando* neutron imaging with commercial cell component was successfully performed and lead to the decent quantification of average Li concentration in $LiNiO_2$ electrode during cycling, together with the identification of challenges to quantify Li heterogeneities in the depth of the electrode. These challenges are : 1 – reduce the noise level, 2 – improve flatness and alignment of the cell, 3 – explore higher C-rates, avoiding Li dendrite formation.