Experimental report

30/09/2022

Proposal:	**1-05-59**	**Council:**	10/2020
Title:	6Li/7Li isotopic contrast to imagelithium gradients in high energy cathode cycled vs. Li metal cell using a standardised operando cell		
Research area:	Materials		

This proposal is a new proposal

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Samples:	LiNi0.8Mn0.1Co0.1O2 Li metal carbonate electrolyte + lithium salt

Instrument	Requested days	Allocated days	From	To
NEXT	4	4	21/05/2021	25/05/2021

Abstract:

Standards, protocols and electrochemical reliability are key parameters for operando type measurements in batteries, as the electrochemical response obtained in an operando cell is often far away from the one obtained in standard coin cell, potentially biasing the acquired knowledge. Here, we developed a special electrochemical cell for neutron and synchrotron operando imaging experiments, to demonstrate that standards and protocols can be obtained using a proper cell design. We would like to test this new electrochemical cell with known challenging high-energy material (LiNi0.8Mn0.1Co0.1O2 cathode vs. Li metal in organic based electrolyte) at D50/NeXT at ILL and, in parallel, at the ID31 beamline at ESRF. Our goal is to obtain a deep understanding of lithium gradients developed across the electrodes and electrolyte (specifically using Li isotopic contrast by neutron imaging), as well as microstructure changes during electrochemical cycling by combining X-ray and neutron techniques. The validation/optimization of neutron/x-rays standardized cell and correlated data analysis is a major target in battery research (BIGMAP European project, Batteries 2030+).

Proposal n°1-05-59. 6Li/7Li isotopic contrast to image lithium gradients in high energy cathode cycled vs. Li metal cell using a standardised operando cell

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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).

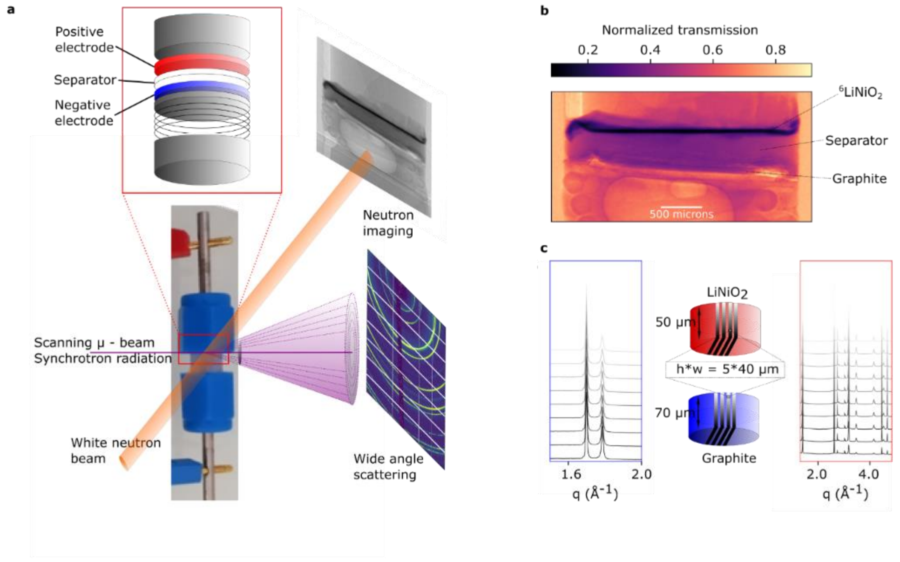

Figure 1 : a – schematic of the correlated WAXs (wide angle X-ray scattering) and NI experiment on a $LiNiO_2$/Graphite cell, b) typical neutron imaging for the pristine cell, c) schematic of the micro X-ray beam scanning protocol together with typical XRD patterns of LNO across the depth of the electrode.

Experiment goals: This proposal is a direct continuation of DIR-223, in which we successfully performed o*perando* neutron imaging with commercial cell components and could quantify average Li concentration in $LiNiO_2$ electrode during cycling. Challenges regarding the possibility of quantifying Li heterogeneities in the depth of the electrode are identified : 1 – reduce the noise level, 2 – improve flatness and alignment of the cell, 3 – explore higher C-rates, avoiding Li dendrite formation.

Therefore for this experiment, we have used ^{6}Li-enriched $LiNiO_2$ material together with deutered electrolyte hence drastically increasing the contrast between Li-rich and Li-poor regions. Regarding the cell components, they have been flattened, and sample alignement is performed really carefully during beamtime. Li metal anode is replaced with graphite limiting the formation of dendrite leading to electrical shortcuts. Finally, we have also increased the resolution from 14 microns to 5 microns by reducing the slit sizes. This enhanced resolution will allow a more precise determination of the gradient concentration of the ≈ 60 microns thick electrodes.

Experimental details: All electrode 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 5 mm width. Images of the cells have been continuously collected during battery operation at charging rates ranging from C/5 to 5C and with a time resolution of 30 sec.

Results : The electrochemical performance of the operando cell are similar to coin cell tests performed in the lab (Figure 2). Moreover, no sign of dendrite is observed, validating the strategy of replacing Li for graphite to allow high-rate measurement

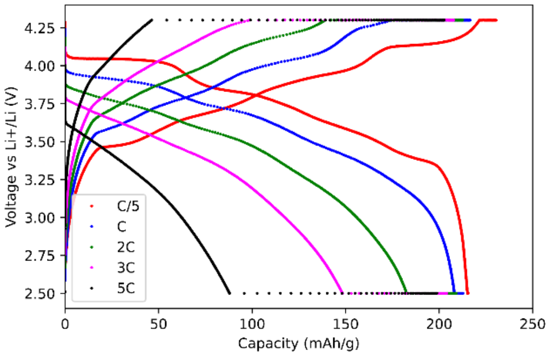

Figure 2 : Electrochemical performance of the operando cell at different C-rates

Turning to neutron images, typical pristine cell images can be seen from the Figure 1-b in which $^{6}\mathrm{LiNiO}_2$ appears dark due to the higher concentration of highly attenuating $^{6}\mathrm{Li}$ while the graphite electrode, free of lithium at this state of charge, is barely visible. During charging, the accumulation of $^{6}\mathrm{Li}$ in the graphite can be qualitatively observed Figure 3, from the decrease of the graphite electrode transmission located at 1.8 mm while the LiNiO_2 electrode (at 2.25 mm) transmission increases. From the transmission and with some assumptions regarding the electrode porosity and isotopic enrichment, Li concentration variation in both electrodes were calculated and are generally in good agreement with the expected values from electrochemistry. This is particularly true for the graphite electrode for which the predicted (NI) and expected (Echem) Li concentration overlap. For the LiNiO_2 electrode however, there are some differences. Such differences were not observed in the previous experiment, for which neutral abundant Li was used, suggesting that the origin of this discrepancy could be due to data acquisition (neutron scattering for example).

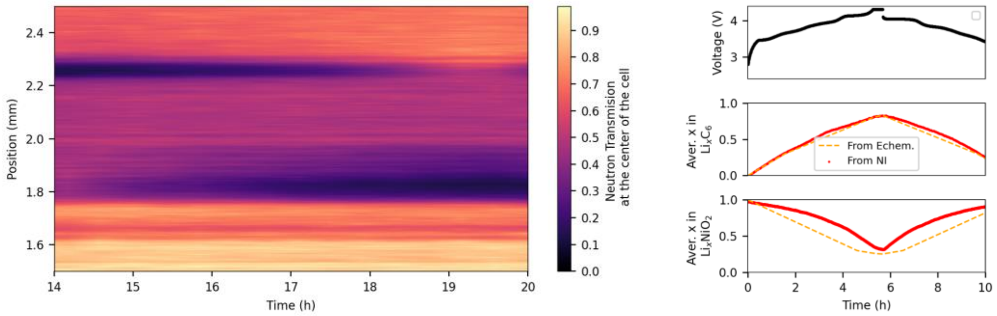

Figure 3 : Left panel, evolution of the (average) cell transmission profile across the vertical direction with time during a charge at C/5. Right panel from top to bottom, voltage vs time profile of the operando cell, Li quantification in graphite electrode, and LiNiO$_2$ electrode.

Regarding Li heterogeneities, on Figure 4-b, the intensity of the black curve is a proxy for the amplitude of Li heterogeneity in the graphite electrode during the 1st cycle at C/5. Li heterogeneity can be clearly resolved from the noise level, depends on the state of the charge, as reported previously[1], but also on the charge/discharge.

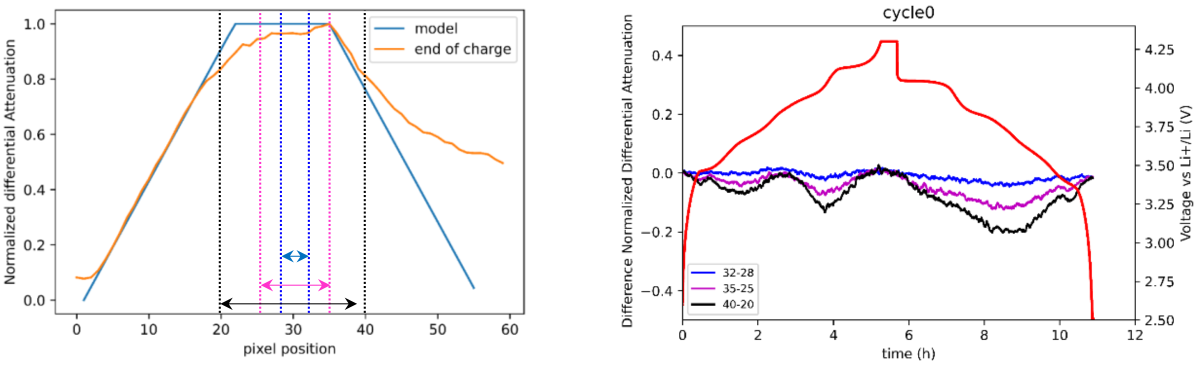

Figure 4 : left. Experimental and expected normalized differential attenuation of graphite electrode at the end of 1st charge in orange and blue respectively, as a function of depth in pixel (x axis). Right, difference of normalized differential attenuation between two depths – schematically marked as dotted line in the left panel.

<u>**Conclusion:**</u> After tackling the challenges identified during the first experiment, in this second experiment, we are able to qualitatively measured Li heterogeneities inside commercial electrodes using a cell compatible with synchrotron X-ray techniques. Correlated analysis of the SXRD and Neutron imaging experiment is currently been performed offering a complete view on the challenging problem of understanding heterogeneities during fast charging.