Experimental report

24/02/2022

Proposal:	**5-23-765**	**Council:**	10/2020

Title: Operando study of high-voltage positive electrode spinel materials Li1Ni0.5-xMn1.5-yO4-z for lithium-ion batteries

Research area: Materials

This proposal is a new proposal

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Local contacts:	Nebil AYAPE KATCHO Laura CANADILLAS DELGADO Emmanuelle SUARD

Samples: 3 samples of distinct LiNi0.5Mn1.5O4 mixed with C (to improve electrochemical response)

Instrument	Requested days	Allocated days	From	To
D2B	1	1	31/08/2021	01/09/2021
D20	4	0		
D19	4	0		

Abstract:

Three different samples of spinel LiNi0.5Mn1.5O4 used as high-voltage positive electrode materials for next generation of Li-ion batteries have been selected because they show distinct electrochemical performance. Although their XRD patterns are very similar, such differences in their electrochemical properties are probably related to structural features (off-stoichiometries, metal ordering, antiphase boundaries, antisite defects, etc) which will be better characterized from their NPD patterns. From this operando NPD experiment, we aim here at understanding the differences in their reaction mechanism and establishing the correlations existing between composition, (micro)structure and electrochemical properties of these spinel materials, which are attracting strong interest as being one of the best candidate to replace cobalt-based cathodes in the next generation of Li-ion batteries developped by the European Community.

Proposal D2B 5-23-765/ D19 DIR223 – Experimental report

Main proposer: Marine Reynaud, Co-proposer: Marcus Fehse, Iciar Monterrubio
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Operando study of high-voltage positive electrode spinel materials $Li_1Ni_{0.5-x}Mn_{1.5-y}O_{4-z}$ for lithium ion batteries

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) spinel is the most promising candidate as cathode material for 3b-generation Lithium ion batteries (LIB) that can meet the high energy density demands set by the automotive sector, while at the same time avoiding environmentally and ethically burdened cobalt. Its high energy density stems primarily from the elevated operating voltage of the $Ni^{2+/4+}$ redox couples at 4.7V vs. Li^+/Li. However, LNMO exhibits a very complex crystal chemistry, owing to Ni/Mn ordering, non-stoichiometry, defects and rock salt impurities. In non-stoichiometric materials the $Mn^{3+/4+}$ redox couple at 4.1V vs. Li^+/Li can contribute to the total capacity obtained. The presence of Mn^{3+} is linked to the deficiency of Ni and/or oxygen by charge neutrality. Two crystal structures of LNMO are reported, the ordered $P4_332$ phase and the disordered $Fd\overline{3}m$ phase. In the latter Ni and Mn are randomly distributed in the 16d sites while in the $P4_332$ phase they occupy 4b and 12d sites in an ordered fashion. The disordered phase has been reported to have higher charge mobility hence yielding to superior rate capability. However, the crystallization of LNMO in the disordered phase is often linked to formation of Mn^{3+} which can compromise the cycling stability, vide supra. The ubiquitous formation of rock-salt-type secondary phases during the synthesis process of LNMO is another intrinsic challenge of this material as it has detrimental effects on the charge transport properties. Different cycling mechanism have been proposed for TM ordered and TM disordered phase based on XRD and electrochemical signature (two phase mechanism vs solid solution), but a detailed picture is still pending.

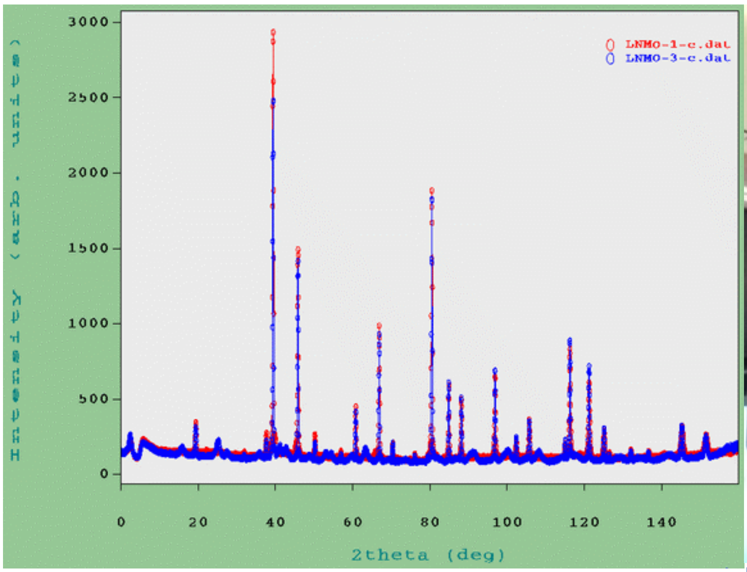

Illustration 1: Diffraction pattern of pristine LNMO spinel phases, with transition metal ordered (blue) and disordered (red) measured at D2B.

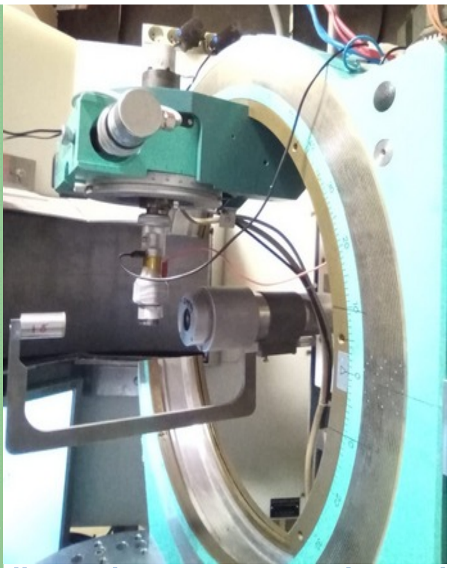

Illustration 2: Experimental setup of operando cell at D19

The measurement of pristine $P4_332$ and $Fd3m$ LNMO samples revealed well defined pattern corresponding to LNMO spinel phase. Moreover, neutron diffraction clearly depicts additional features for the $P4_332$ phase originating from the transition metal ordering, see Fig. 1, which underlines NPD’s sensitivity to TM superstructures. Interestingly these additional features show an increased FWHM compared to mutual diffraction features which suggests a significantly smaller domain size of TM ordering compared to crystallite size. The high quality of the data will allow us to extract additional information regarding stoichiometry which will help us understand the differences in electrochemical cycling performance of these materials.

Subsequently a LNMO ordered electrode was mounted on D19 in a specially designed electrochemical cell equipped with a neutron transparent body allowing the acquisition diffraction patterns while being subjected to electrochemical cycling. The experimental setup with the cylindrical operando cell is depicted in Fig . 2

Due to strong electrochemical overpotential which led to premature cut-off of the charge reaction the charging speed was drastically decreased from C/10 to C/30. This allowed to reach acceptable capacities, however the very slow cycling impeded measurements of additional samples. The evolution of NPD pattern for LNMO ordered upon electrochemical delithiation and lithiation is depicted in Fig. 3. About 150 diffraction patterns were acquired which are of acceptable quality and reveal reversible shift and intensity growth of several diffraction features, underlining the feasibility of this approach to monitor crystal structural changes. A detailed analysis of these reversible changes will be necessary for more conclusive results. The ex situ patterns of LNMO phases at the end of charge and discharge reaction acquired during previous beamtime (D2B 5-23-751) will serve us reference in the analysis

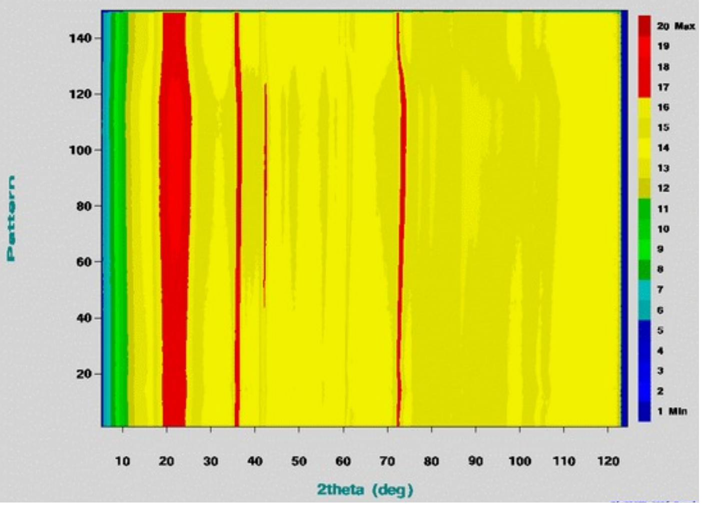

Illustration 3: Evolution of diffraction patterns of ordered LNMO upon de-insertion and insertion of Li under operando conditions at D19

We would like to warmly thank Emmanuelle Suard & Nebil Katcho Ayate for their dedication and professional support in the preparation and during our beamtime which greatly contributed to its success.