Experimental report

20/01/2022

Proposal: **CRG-2789** **Council:** 4/2020

Title: Elucidating the effect of stoichiometry, Ni/Mn ordering and defects onthe electrochemical properties of high-voltage positive electrode

Research area:

This proposal is a new proposal

Main proposer: **Marine REYNAUD**

Experimental team: Iciar MONTERRUBIO

Local contacts: Oscar Ramon FABELO ROSA

Samples: LixNi0.5Mn1.5O4

Instrument	Requested days	Allocated days	From	To
D1B	3	3	18/09/2020	21/09/2020

Abstract:

Proposal CRG-D1B-20-388 – Experimental report

Main proposer: Marine Reynaud, Co-proposer: Marcus Fehse, Iciar Monterrubio

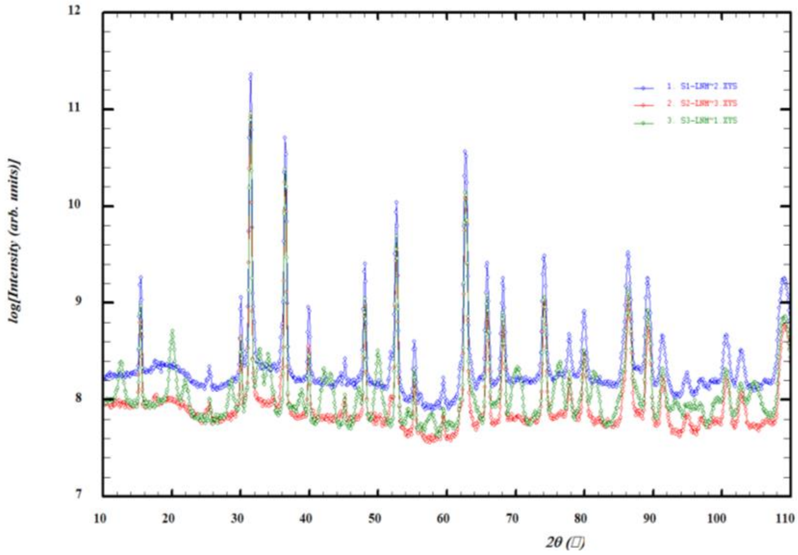
Local contact: Oscar Fabelo Rosa

Effect of stoichiometry, ordering and defects on the electrochemical properties of high-voltage spinel LNMO for Li-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 *P*4332 phase and the disordered $Fd\bar{3}m$ phase. In the latter Ni and Mn are randomly distributed in the 16d sites while in the *P*4332 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.

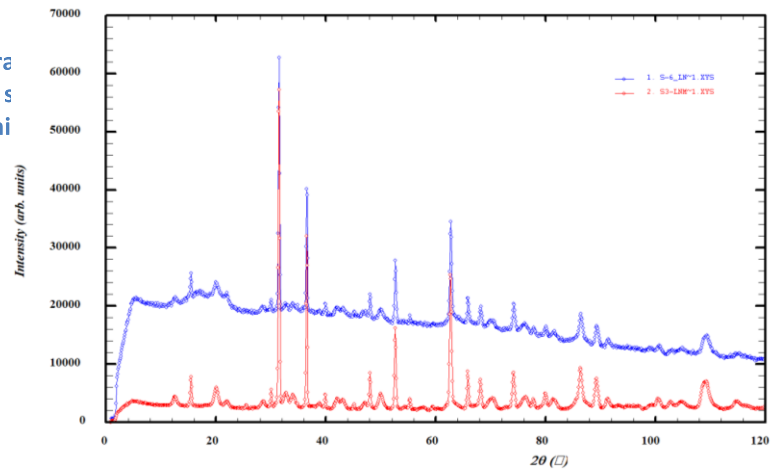
In our beamtime 13 different samples of LNMO based materials were measured at D1B. Due to Covid restriction, the data acquisition was controlled remotely by the users while the sample change was handled by the local contact. The measurement of pristine *P*4332 and *Fd*3*m* LNMO samples revealed well defined pattern corresponding LNMO spinel phase. Moreover, neutron diffraction clearly depicts additional features for the *P*4332 phase originating from the transition metal ordering, see Illustration 1. 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.

Illustration 1: Diffraction pattern of different pristine LNMO spinel phases, with transition metal ordering (green) and without (blue and red).



Furthermore, *ex situ* samples of cycled electrodes were measured. Although signal-to-noise ratio is much lower for these *ex situ* samples they contain valuable information on the reversibility of elecrochemical mechanism and material degradation. By comparing their diffraction pattern with those of pristine materials we observe that spinel phase as well as TM ordering are maintained throughout repeated electrochemical lithiation and delithiation.

Illustration 2: Diffra ordering in pristine s lithiation and delithi



In conclusion, this beamtime at D1B diffractometer allowed us to obtain high quality diffraction patterns that will allow us to study transition metal ordering domains, degradation as well stoichiometry of LNMO samples. This will provide better understanding of material properties and link them the the observed electrochemical performance. We would like to warmly thank Oscar Fabelo Rosa for his dedication and professional support during our beamtime which greatly contributed to its success.