Experimental report

20/01/2022

Proposal:	**5-23-751**	**Council:**	4/2020

Title: Effect of stoichiometry, ordering and defects on the electrochemical properties of high-voltage spinel LNMO for Li-ion batteries

Research area: Materials

This proposal is a new proposal

Main proposer: **Marine REYNAUD**

Experimental team:
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Local contacts: Emmanuelle SUARD

Samples:
4 delithiated samples of LixNi0.5Mn1.5O4
4 pristines samples of LiNi0.5Mn1.5O4
1 air-aged sample of LiNi0.5Mn1.5O4
8 electrochemically aged samples of LiNi0.5Mn1.5O4
1 re-annealed sample of LiNi0.5Mn1.5O4
5 samples of LixTiNb2O7 (0<x<4)

Instrument	Requested days	Allocated days	From	To
D2B	3	3	26/02/2021	01/03/2021

Abstract:

Four 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. We aim here at 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 EXP5-23-751– Experimental report

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

Local contact: Emanuelle Suard

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 8 different samples of LNMO based materials were measured at D2B. Due to Covid restriction, sample change was handled by the local contact while the data acquisition was partially controlled remotely by the users. Among the measured samples where pristine LNMO with tailored stoichiometry. Preliminary results confirm the $Fd\bar{3}m$ spinel crystal structure and marginal amounts of rocksalt impurities, see Figure 1.

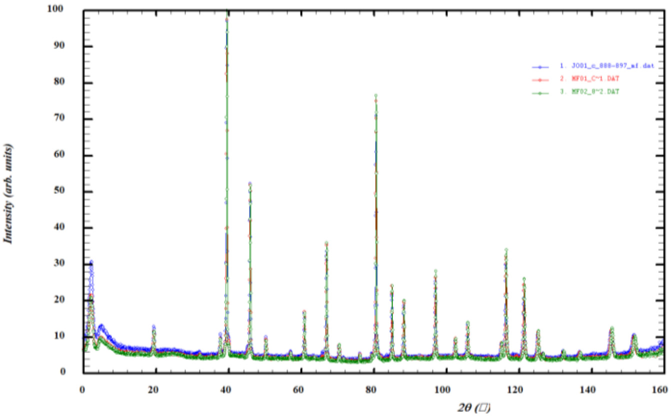

Figure 1 LNMO pristine material with tailored stoichiometry confirming prevalence of Fd3m spinel structure

For cycled LNMO electrodes, which composed the majority of the samples, obtaining of high-quality diffraction pattern was more challenging. Nevertheless, thanks to experience of local contact, satisfactory results could be obtained which enabled us to determine the lattice parameter as well oxygen and Ni stoichiometry at different stages of electrochemical cycling, see Figure 2 . From this it is salient that delithiation is accompanied by a strong contraction of the lattice. Interestingly, a contraction of the lattice is also observed for longer cycled electrodes. How this contraction is linked to changes in the elemental occupancy is currently under investigation. It is also noteworthy that we do observe some discrepancy in the evolution of transition metal ordered (*P*4332) and TM disordered (*Fd3̄m*) LNMO cycled samples which deserve further investigation.

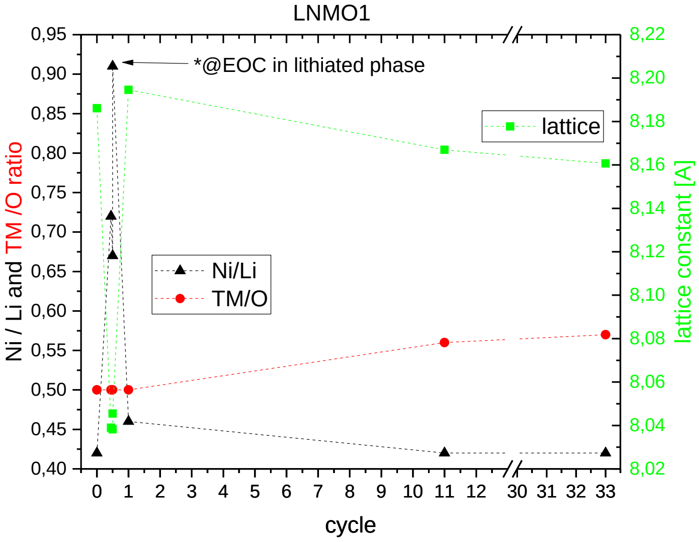

Figure 2 Evolution of elemental occupancy and lattice parameter upon electrochemical cycling of LNMO cathode material.

In conclusion, this beamtime at D2B diffractometer allowed us to obtain high quality diffraction patterns that will allow us to link stoichiometry to electrochemical performance link as well as to study degradation of LNMO samples. We would like to warmly thank Emanuelle Suard for her dedication and professional support during our beamtime which enabled its success.