Experimental report

18/07/2024

Proposal: 5-23-792 **Council:** 4/2023

Title: Study of cation distribution in high voltage Li1Fe0.5Mn1.5O4 spinel with different structures by ex situand operando neutron diffraction

Research area: Materials

This proposal is a resubmission of 5-23-788

Main proposer: **Ivan BOBRIKOV**

Experimental team: Maha ISMAIL
Ivan BOBRIKOV
Jon SERRANO SEVILLANO

Local contacts: Emmanuelle SUARD

Samples: LiFe0.5Mn1.5O4

Instrument	Requested days	Allocated days	From	To
D19	7	7	25/10/2023	02/11/2023
D2B	1	1	30/10/2023	31/10/2023

Abstract:

The main goal of the experiment is to determine the distribution of Li, Fe, and Mn cations over octahedral and tetrahedral positions in LiFe0.5Mn1.5O4 positive electrode material in the initial state as well as during the lithium insertion and deinsertion process. To achieve this objective we intend to carry out ex situ high-resolution neutron diffraction experiments at the D2B diffractometer with as-synthesized powders and neutron high-intensity diffraction experiments under operando conditions at the D19 diffractometer with the samples in an electrochemical cell.

Proposal D2B 5-23-792/ D19 5-23-792 and EASY1249-1251 – Experimental report

Study of cation distribution in high voltage $LiFe_{0.5}Mn_{1.5}O_4$ spinel with different structures by ex situ and operando neutron diffraction

Main proposer: Ivan Bobrikov, Co-proposers: Marine Reynaud, Maha Ismail, Jon Serrano, Marcus Fehse, Iciar Monterrubio
Local contact: Emmanuelle Suard

Abstract: $LiFe_{0.5}Mn_{1.5}O_4$ (LFMO) spinel material crystallizes in the Fd-*3*m space group, with Li occupying the tetrahedral site (8a Wyckoff position) and the transition metals occupying the octahedral site (16d Wyckoff position).

Depending on the synthetic parameters, the Fe of the LFMO can migrate from the octahedral site to the tetrahedral one, where the lithium is normally placed in the structure; i.e. antisite defect. The consequence of this defect on the Li diffusion channels and hence on the electrochemical performance is not understood yet. Such cation exchange between these two sites in the spinel can also occur during cycling having a direct influence on electrochemical properties of LFMO. The cycling behavior of LFMO exhibits two separate plateaus: the first one corresponding to the Mn^{3+}/Mn^{4+} redox couple in the 4V region vs Li^+/Li and the latter in the 5V area attributed to the Fe^{3+}/Fe^{4+} redox activity.

An extensive structural investigation of the LFMO electrode materials before, after, and during cycling is required to elucidate the impact of Li, Fe, and Mn cation exchange on the electrochemical behavior of the material.

We currently have several critical questions whose resolutions will be crucial to understanding the electrochemical and structural behavior of LFMO: Does transition metal ordering occur in the LFMO depending on the synthesis method or state of charge? Does the compound contain some lithium in the octahedral site when Fe is in the tetrahedral site? Does only Fe move to the tetrahedral position or Mn as well? Do the Fe and Mn cations move between octahedral and tetrahedral positions during cycling? How does Fe in the tetrahedral site affect the Li insertion /deinsertion?

Goal: The main goal of the experiment is to determine the distribution of Li, Fe, and Mn cations over octahedral and tetrahedral positions in $LiFe_{0.5}Mn_{1.5}O_4$ positive electrode material in the initial state as well as during the lithium insertion and de-insertion process. To achieve this objective, we intend to carry out high-resolution neutron diffraction experiments at the D2B diffractometer with as-synthesized powders and neutron high-intensity diffraction experiments under Operando conditions at the D19 diffractometer with the samples in an electrochemical cell.

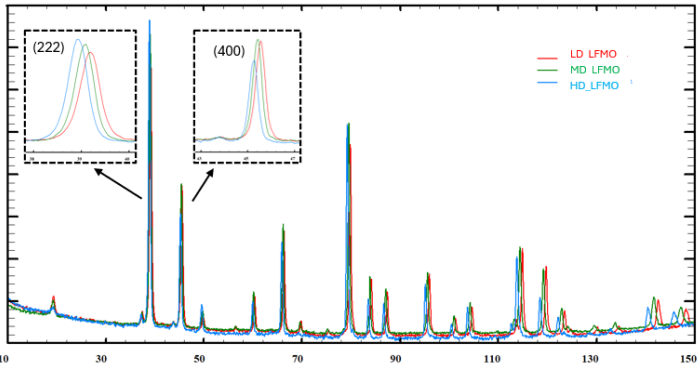

Figure 1: Neutron diffraction patterns of 3 pristine LFMO spinel materials with Low Defects (LD) in red, Moderate Defects (MD) in green, and High Defects (HD) in blue measured at D2B.

Table 1: Cell parameters and Atoms occupancy of the 3 pristine LFMO spinel materials revealed from Rietveld refinement of the NDP data.

	LD	MD	HD
Cell parameters	**8.246**	**8.268**	**8.297**
Mn octahedral	1.5	1.5	1.5
Li tetrahedral	0.974	0.954	0.861
Li octahedral	0.026	0.047	0.139
Fe octahedral	0.474	0.454	0.361
Fe tetrahedral	0.026	0.047	0.139
% Fe tetrahedral	**5.2%**	**9.4%**	**27.8%**

Experimental progress: 3 different samples of LFMO with different synthetic parameters affecting the amount of Fe antisite defects were selected for this study named as LD-LFMO (low defect), MD-LFMO (moderate defect), and HD-LFMO (high defect). The measurement of the pristine samples in D2B presented in Figure 1 reveals clearly different degrees of Fe in the 8a tetrahedral site of Li as indicated in table 1 below obtained from the refinement of the NPD patterns.

Subsequently, the LFMO electrodes of the 3 different materials were mounted on D19 in a specially designed electrochemical cell equipped with a neutron transparent body allowing the acquisition of diffraction patterns while being subjected to electrochemical cycling.

The main challenge in these experiments is to minimize the parasitic site reaction at the elevated operating voltage needed for the iron redox couple, such as electrolyte oxidative decomposition. As a compromise between overpotential and retention period at elevated potential a cycling rate of C/15 was selected. In this regard the elevated internal resistance of the thick and self-standing electrodes to reach critical electrode mass required, is a noteworthy obstacle. Besides these expected difficulties we also encountered issues of sulfur contamination inside of the glovebox located in the ILL hall, but thanks to help of beamline staff were able to circumvent this obstacle.

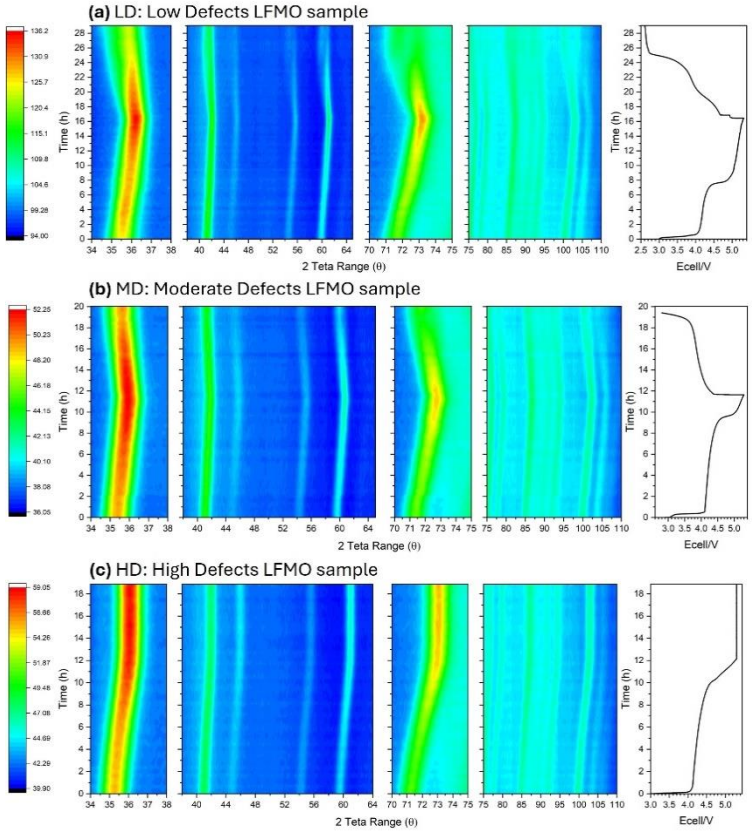

Figure 2: Evolution of neutron diffraction patterns of the 3 samples of LFMO (a) Low Defects (LD), (b) Moderate Defects and (c) High Defects upon de-insertion and insertion of Li under Operando conditions at D19

The evolution of the NPD pattern for the 3 samples of LFMO (LD, MD, and HD) upon electrochemical delithiation and lithiation is depicted in Figure 2. About 80 diffraction patterns were acquired for the first 2 cells (LD and MD) during charge and discharge while the 3rd cell (HD) was recorded only during charge due to technical issues. As presented, the recorded data 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 results obtained are planned to be published and presented at conferences.

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