Experimental report

14/09/2022

Proposal: 5-25-256 **Council:** 4/2017

Title: In-situ / operando structural study of Li1+x(Mn1-y-zNiyMz)1-xO2 as promising positive electrode materials for Lithium-ion batteries

Research area: Chemistry

This proposal is a new proposal

Main proposer: Tatiana RENZI

Experimental team: Ilia TERTOV
Laurence CROGUENNEC
Christian MASQUELIER
Tatiana RENZI

Local contacts: Thomas HANSEN
Emmanuelle SUARD

Samples: LiNi0.5Mn1.5O4

Instrument	Requested days	Allocated days	From	To
D2B	3	3	17/02/2017	20/02/2017
D20	5	3	27/02/2017 29/09/2021	28/02/2017 01/10/2021

Abstract:

We have recently developed four compositions of general formula Li1+x(Mn1-y-zNiyMz)1-xO2 for Li and Mn-rich layered oxides (M can be Al, Co), all of them showing electrochemical activity at high voltage (up to 4.8 V vs Li+/Li). Futhermore, four new compositions such as Li(NiIIx;yMnIVx+3yCoIII1-2(x+2y))O2, with (x+2y) around 0.425 are under study in our group, for which creating cationic deficiencies within the slabs allows developing Li and Mn-rich layered oxides with minimized first cycle irreversible capacity.
The first goal here is to determine changes in the anionic and cationic environments of each cation (Li, Ni, Mn and M) in the four compositions Li1+x(Mn1 y-zNiyMz)1-xO2 upon cycling.
Concerning the cationic deficient layered oxides Li(NiIIx;yMnIVx+3yCoIII1-2(x+2y))O2, the structure of the pristine materials has first to be determined before the study of its changes upon cycling: the goal is to obtain high resolution neutron powder diffraction patterns in order to determine the cationic distribution within these layered structures and to compare it with our other characterizations, and especially with the powder density measurements.

Report on D20's research proposal 5-25-256.

In the frame of the proposal we wanted to investigate thermal behavior of the perspective cathode material $LiNi_{0.5-x}Mn_{1.5+x}O_4$ by means of *in-situ* neutron powder diffraction (NPD) on the high-flux ILL-D20 diffractometer. We expected to gain information concerning Ni/Mn ordering within the crystal structure of the material.

During the experiment the industrial sample of LNMO (Umicore, Belgium) were heated up to 725°C under air atmosphere, NPD patterns were collected within 20 minutes during whole heat treatment. The obtained data shows that Ni/Mn ordering occurs (reduction of the symmetry and appearance of additional reflections) in the range of 600-680°C, at T ≥ 700°C the ordering process is disrupted probably due to oxygen release from the sample. Such information is vital for development and optimization of the synthesis conditions of the material.

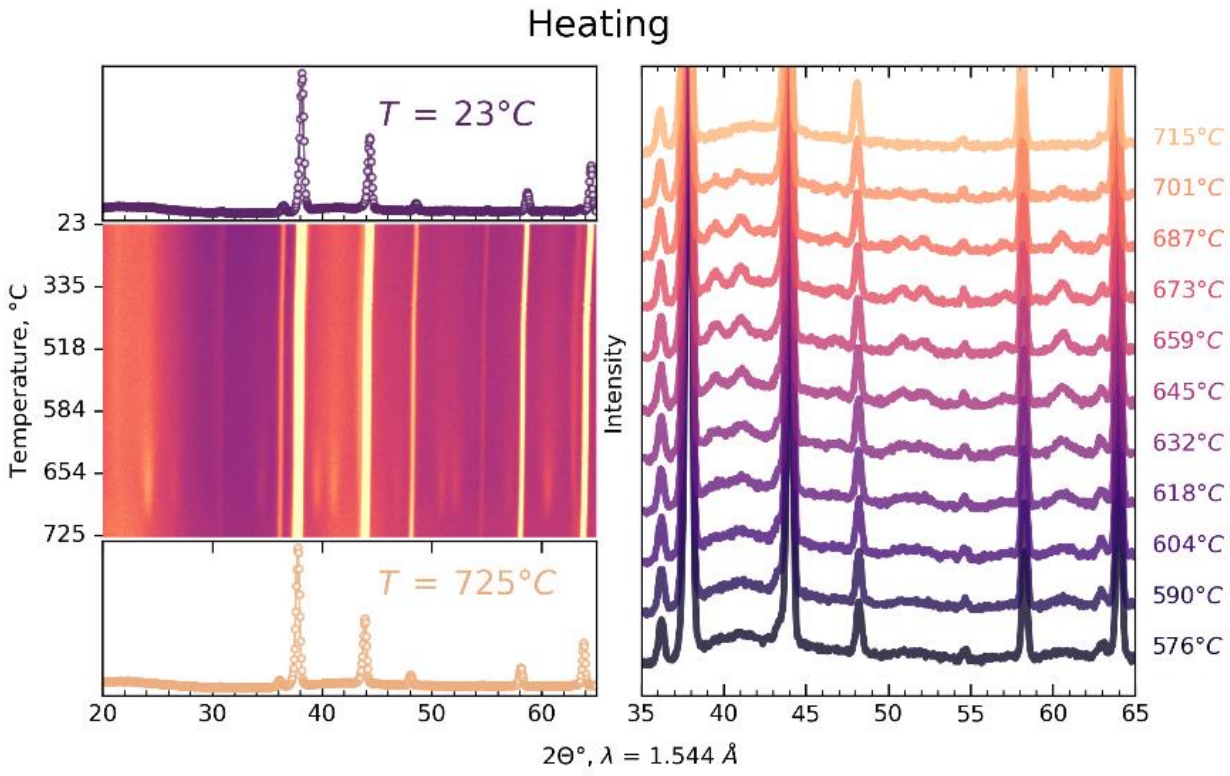

Figure 1. In-situ NPD data during the heating of LNMO sample under air atmosphere.