# Experimental Report

21/01/2014

**Proposal:** **6-06-452** **Council:** 10/2012

**Title:** Changes upon cycling in the short and long range ordering in Li1.20Mn0.54Co0.13Ni0.13O2, a promising positive electrode for Li-ion batteries

**This proposal is a new proposal**

**Researh Area:** Chemistry

**Main proposer:** **CROGUENNEC Laurence**

**Experimental Team:** ROUSSE Gwenaelle
BIANCHINI Matteo
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MASQUELIER Christian

**Local Contact:** SUARD Emmanuelle

**Samples:** Li1.20Mn0.54Co0.13Ni0.13O2

| Instrument | Req. Days | All. Days | From | To |
|---|---|---|---|---|
| D2B | 3 | 3 | 21/05/2013 | 24/05/2013 |
| D4 | 4 | 4 | 07/05/2013 | 11/05/2013 |

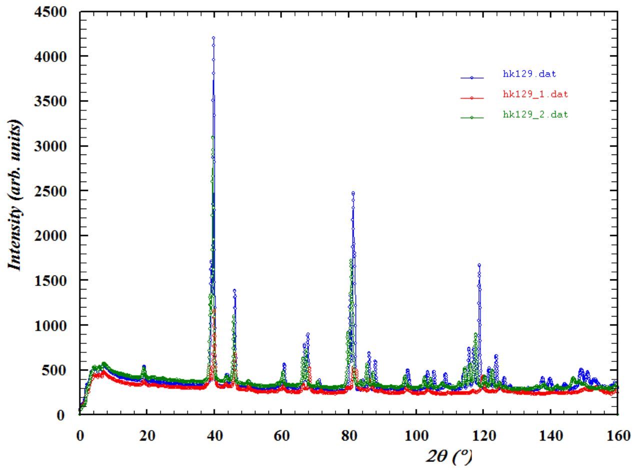
**Abstract:**

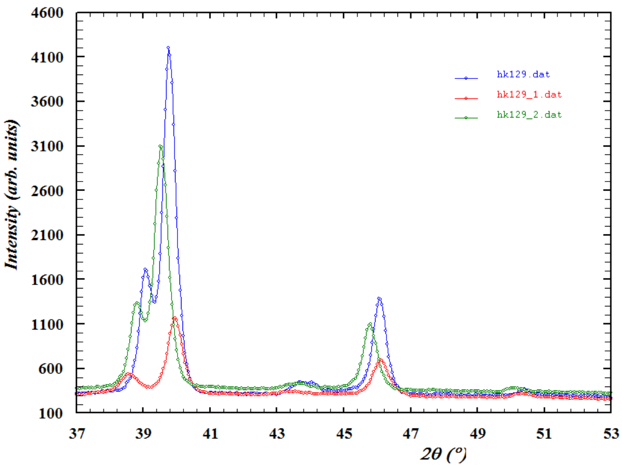
Rechargeable lithium-ion batteries still mainly use the layered oxide LiCoO2 as positive electrode and graphite as negative electrode for high capacity batteries developed for mobile devices. Nevertheless, LiCoO2 remains limited in energy density with a reversible capacity smaller than 160 mAh/g, expensive and with safety issues, to be maintained in large scale batteries for automotive applications. New systems such as Li[NixLi(1/3-2x/3)Mn(2/3-x/3)]O2 and (1-x )LiMO2.xLi2MnO3 (M = Ni, Co), rich in lithium and in manganese, were considered due an exceptionally high reversible capacity. The aim of the study is to get more insight into the atomic structure of the material Li1.20Mn0.54Co0.13Ni0.13O2 and especially into its changes upon cycling. Neutron PDF analysis will allow solving specific issues related with short range / long range disordering / ordering in the materials recovered at key compositions during the deintercalation and intercalation processes. The main goal is to determine changes in the anionic and cationic environment of each cation (Li, Ni, Mn and Co) upon cycling.

# Experimental report for the proposal 6-06-452:

# Changes upon cycling in the short and long range ordering in Li1.20Mn0.54Co0.13Ni0.13O2, a promising positive electrode for Li-ion batteries

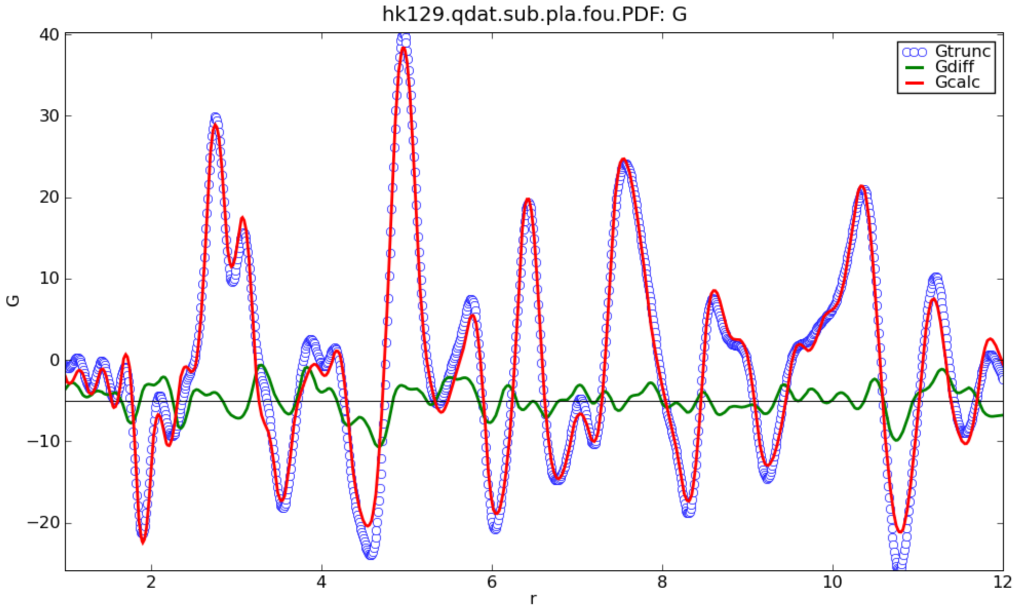
The proposal dealt with the study of different phases prepared thorough chemical extraction and re-insertion starting from the pristine material $Li_{1.20}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$. In particular, the first sample was the pristine material, the second one was prepared from it via chemical oxidation to extract all the lithium and a third one was prepared from the second one via chemical re-insertion of lithium in the structure. These three samples were the core of the two experiments on D2B and D4. In the first case, powder diffraction patterns were recorded on the powders at 1.59 A. The goal is to perform Rietveld refinement to determine the average structure. As expected, this is not banal. Indeed, the cations have an ordering in the pristine material that allows to describe it both in the R-3m space group and (better) in the monoclinic C2/m one. When lithium is extracted, not only this ordering is lost, but the material is also partially amorphized. Finally, lithium can be re-inserted, leading to a structure similar to the initial one but where the cations do not recover their ordering. In the figure below are reported the three pattern measured on D2B, showing a clear difference in their crystalline quality (blue = pristine (1), red = lithium extracted (2), green = lithium re-inserted (3)).





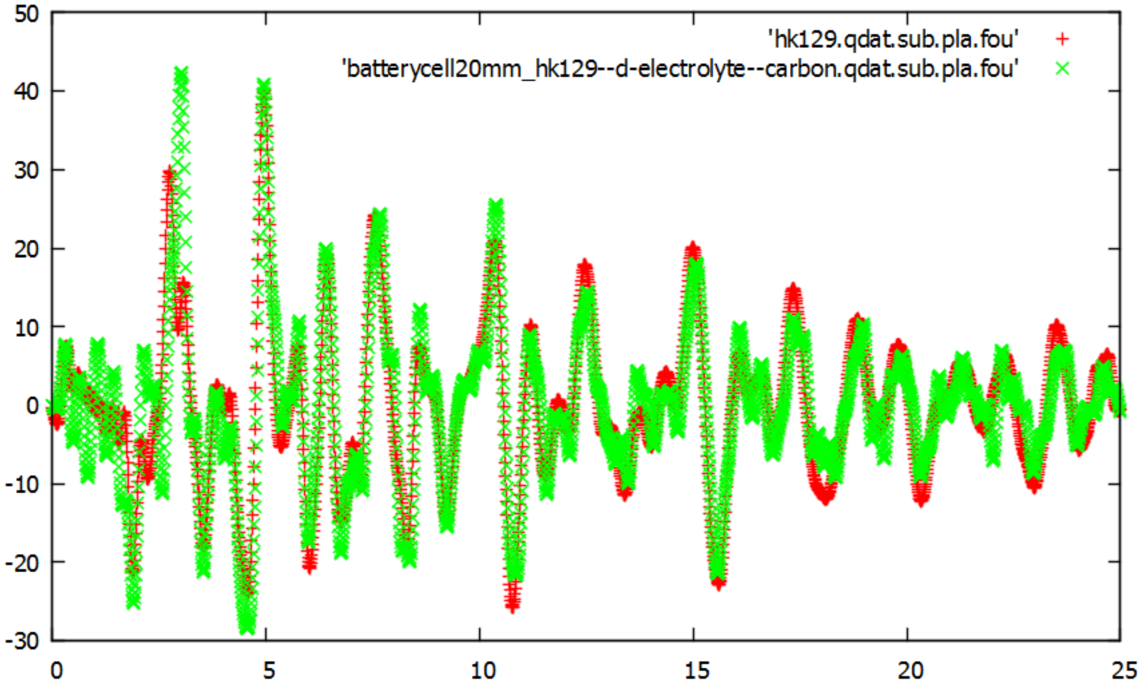
Rietveld refinements of the patterns have been done for patterns 1 and 3, while pattern 2 is still problematic because of the large and not intense Bragg peaks.

For this reason the experiment on D2B was complemented by one on the D4 diffractometer. Here we studied the same three samples at 0.5 A to analyze the Pair Distribution Function obtained from Fourier transformation of the powder patterns. This allows us to overcome the problem of the material's amorphisation and to study the short and medium range order in the material. Indeed, from preliminary data analysis we observe marked differences between the three samples, especially in the Li-O and Mn-O coordination shells. An example of the analysis of the data is shown below, where the pristine material's PDF is fitted in the C2/m space group, taking thus into account the cations ordering.



As soon as the analysis of the three samples will be completed the results will be published, together with other electrochemical measurements performed on them.

In the remaining time on D4 some important tests were conducted. These are correlated to the proposal 5-21-1076 and to the PhD topic of Matteo Bianchini. In particular, this involves the development of an electrochemical cell for in-situ and *operando* neutron diffraction studies of Li-ion batteries. As stated above, the cell was designed and tested for Rietveld refinements on the D20 diffractometer in the context of the proposal 5-21-1076. On D4 we conducted some tests to verify the possible use of this in-situ cell for PDF analysis. We did not conduct a complete *operando* experiment, since this would mean modify significantly the experimental setup. Hence we prepared a lithium battery within the cell using the same material $Li_{1.20}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$, we measured it on D4 in its pristine (discharged) state and then we charged the battery outside of the instrument until the composition $Li_{0.8}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ was reached, measured it again, and finally charged it to $Li_0Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ and we did a final measurement. To allow a correct data treatment, all the extra components of the battery had to be measured to be subsequently subtracted from the powder pattern (i.e. empty in-situ cell, deuterated electrolye, carbon). The data treatment is not straightforward and it has not been completed yet, but it can be seen from the figure below that the pristine material measured as a simple powder or measured inside the electrochemical in-situ cell in a full battery configuration are quite similar (the first 1.5 A are not because of experimental artifacts, but they don't have a physical meaning anyway).



These first tests on in-situ PDF analysis on electrochemical cells, performed for the first time, are very promising and we will submit new proposals in the next ILL rounds to try to complete a full *operando* experiment and to study different interesting materials.