Experimental report

02/02/2021

Proposal:	**5-25-272**	**Council:**	10/2018
Title:	Addressing the remaining questionson the ultimate Li-ion battery cathode: LiNiO2. Part I - Synthesis		
Research area:	Materials		

This proposal is a new proposal

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Samples: LiNiO2
Ni(OH)2
LiOH
Li2O2

Instrument	Requested days	Allocated days	From	To
D20	2	1	09/10/2019	10/10/2019

Abstract:

Li-ion batteries for automotive applications need cathode materials with high specific energy. LiNiO2 (LNO), was already investigated in the 90s but abandoned due to various forms of instability. From its doping, other cathodes were developed (NCM and NCA), now commercial because they sacrifice specific energy for stability. However the used of original LNO would bring great improvements in performance. We undertook a review project of the material and identified 2 main points where knowledge is lacking. This proposal deals with the observation in situ of the material s synthesis. LiNiO2 is always found off-stoichiometric as Li1-zNi1+zO2, with z = 0.01-0.02 in the best reports. This is due to the relationship between LNO with a layered structure, and its precursor rocksalt phase, both having a ccp oxygen lattice and only differing by the Li/Ni ordering in alternate layers. In combination with Li volatility issues, this makes the synthesis of true LNO challenging. We propose to observe the material s synthesis in real time, to observe the phases evolution and track lithium redistribution, to ultimately see whether any condition allow to make a true stoichiometric LNO.

In this beamtime, the goal was to observe the synthesis on $LiNiO_2$ (LNO) in real time with neutron powder diffraction. We planned to collect: first, ex situ NPD patterns on D2B for two different precursors mixtures, and for the LNO products prepared with them in our lab. Then, in situ NPD data measured in a quartz tube open to an O_2 flow, as available on D20. Data are to be measured upon annealing in a furnace, with typical reaction temperature of 700 °C. During these in situ experiments, diffraction patterns were collected for 10 minutes each and analyzed by the Rietveld method.

The two synthesis reactions investigated are:
$LiOH*H_2O + Ni(OH)_2 + \frac{1}{4} O_2 \rightarrow LiNiO_2 + 3/2\ H_2O$ (1)
$\frac{1}{2} Li_2O_2 + NiO \rightarrow LiNiO_2$ (2)

Reaction (1) is the most interesting from an industrial perspective; however due to the large amount of H, the precursors were pre-annealed in our lab at 350°C to evolve water from both hydroxide precursors, so that the reaction we actually studied on D20 was closer to:
(1b): $LiOH + NiO + \frac{1}{4} O_2 \rightarrow LiNiO_2 + 1/2\ H_2O$

The measurements on D2B of precursors and product materials in vanadium tubes succeeded as expected, without issues. The evolution of the in situ NPD reaction measured on D20 is depicted in Figure 1.

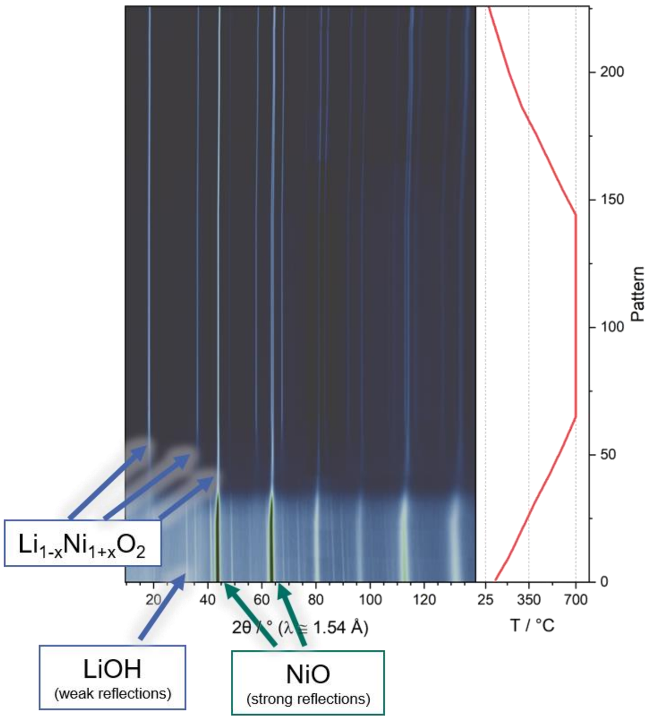


Figure 1

Since the quartz tube has a strong background, an empty tube has been measured as a function of temperature and the background has later been subtracted, as can be seen in Figure 2.

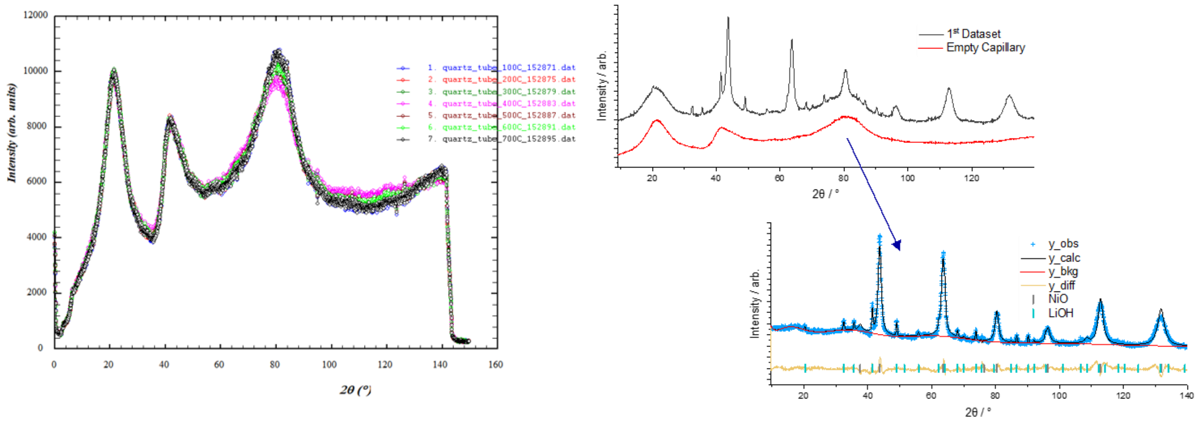


Figure 2

Initially, the S/N ratio is not excellent since a significant amount of H is still present in the form of LiOH. However, upon heating to 475 °C LiOH melts and very quickly reacts with the NiO, resulting in significantly improved data quality. The change in background can easily be noticed in Figure 3.

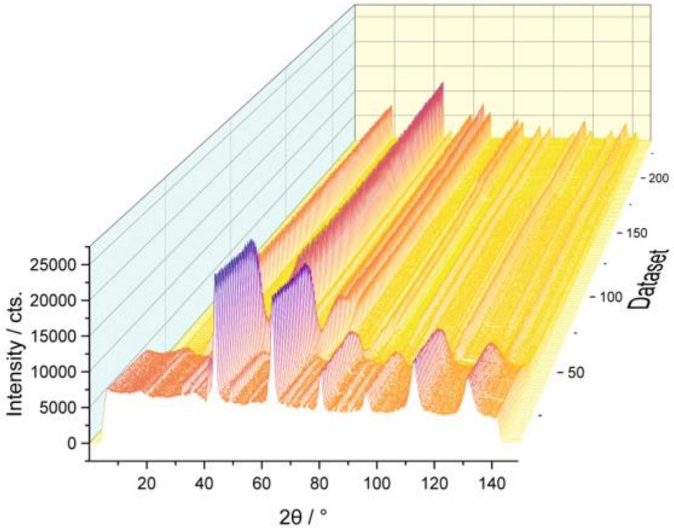


Figure 3

The quality of the data obtained during this in situ reaction was high and hence Rietveld refinement could be successfully performed. The structural parameters obtained from the fitting are gathered in Figure 4. The main features expected for this synthesis could be observed, ie the rhombohedral distortion of the cubic NiO rock salt lattice. The evolution of unit cell parameters of the phases was also in line with the expected results from a recent publication containing synchrotron data. [1]

This proves that neutron diffraction is a suitable tool to investigate solid state reactions in oxide materials. Of note, there are two advantages we found of NPD over synchrotron XRD:

- Much larger amount of powder in NPD (1 g vs 10 mg for sXRD), hence better representing real synthesis conditions in the lab.
- In sXRD, reactivity of Li precursors with the quartz tube was high due to the small amount of sample and large contact surface with the tube. Thus, Li4SiO4 impurities were observed,

undermining the right stoichiometry of the product. This was not observed with NPD; in fact, the final product was of high quality, comparable to one prepared in the lab (Figure 5).

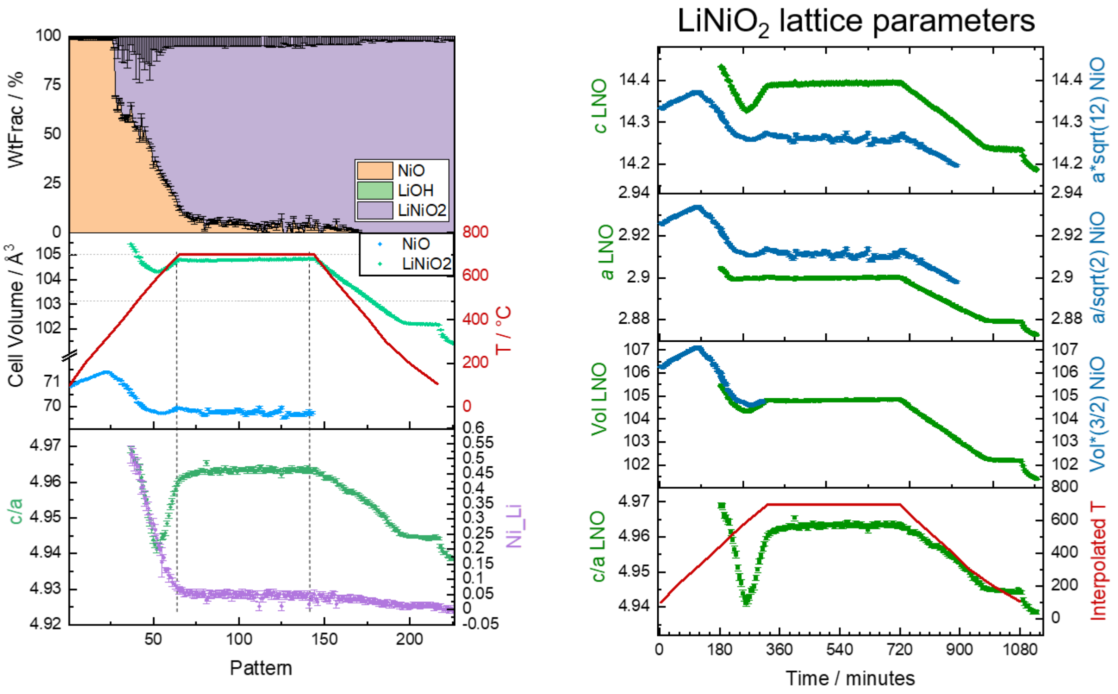
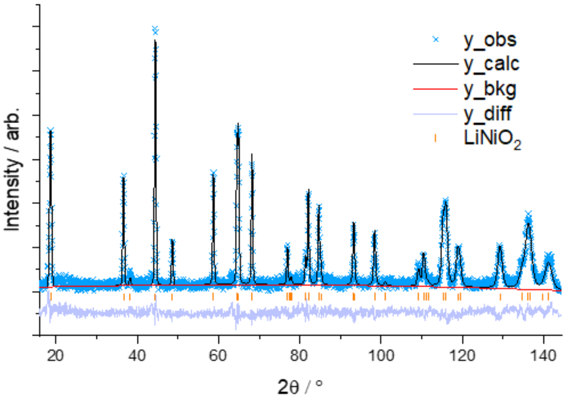


Figure 4



Last dataset:
a = 2.8759(4),
c = 14.1998(14),
Ni on Li site = 0.026(8)
R_w = 28.49 %

Figure 5

Regarding the second synthesis reaction (2) mentioned above, the results were not as positive; although the experiment itself worked, we believe that uneven mixing of the powders resulted in a low quality of the products. Regarding reaction (1), although some improvement to the data fitting is still required and ongoing, overall the experiment was successful and demonstrated the suitability of NPD to study the above-described reactions. We plan to request further beamtime in the future to complement our findings on the synthesis of LNO with further studies on closely related materials.

Bibliography

1. Bianchini, M.; Fauth, F.; Hartmann, P.; Brezesinski, T.; Janek, J., An in situ structural study on the synthesis and decomposition of LiNiO2. *Journal of Materials Chemistry A* **2020,** 8, (4), 1808-1820.