Experimental report

27/07/2022

Proposal:	**1-04-232**	**Council:**	4/2021

Title: Resolving the relationship betweencomposition and structure in the synthesis of lithium rich nickel manganese oxides

Research area: Chemistry

This proposal is a continuation of 5-25-272

Main proposer: **Damian GOONETILLEKE**

Experimental team: Damian GOONETILLEKE
Marie DUFFIET

Local contacts: Thomas HANSEN
Emmanuelle SUARD

Samples: $LiNiO2$ (lithium nickel oxide)
LiOH (lithium hydroxide)
$Ni(OH)2$ nickel hydroxide
$Mn(OH)2$ Manganese(II) hydroxide

Instrument	Requested days	Allocated days	From	To
D2B	1	0		
D20	3	3	03/09/2021	06/09/2021

Abstract:

The rapid transition towards practical and accessible electromobility has been driven by improvements in lithium-ion batteries (LIBs). These batteries enable high energy and power densities with respect to both volume and weight compared to other secondary energy storage systems. The cathode material in these batteries is most commonly composed of layered transition metal oxide materials which reversibly intercalate lithium as the battery is charged and discharged. For high energy density applications, increasing the nickel content in these materials is desirable to improve the specific capacity, however this results in poor capacity retention after extended cycling. Having successfully studied the synthesis of the LiNiO2 end-member in real-time, using NPD at ILL (D20, proposal 5-25-272) we wish to continue exploring further regions of the Li-Ni-Mn-O phase diagram to better understand the synthesis of other Ni-rich layered oxides based on their Ni:Mn ratio and resolve the direct relation between material composition and structure as a function of temperature.

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In this proposal, *in situ* neutron diffraction was used to monitor the reaction mechanism during the high-temperature synthesis of the layered cathode materials $LiNi_{0.9}Mn_{0.1}O_2$ and $LiNi_{0.75}Mn_{0.25}O_2$., building on a previous investigation of the synthesis $LiNiO_2$ in a previous proposal (5-25-272). Rietveld refinement was further used to track the structural evolution of the hydroxide precursors to the final layered phases, and the three materials are qualitatively and quantitatively compared.

An example of the diffraction data collected during a typical synthesis reaction is shown in Figure 1, where a mixture of LiOH and NiO was heated to the desired annealing temperature to form $LiNiO_2$. Broad reflections from the cubic NiO phase can be observed at the beginning of the experiment, in addition to reflections from the LiOH precursor. The presence of hydrogen in the LiOH precursors creates a high background due to incoherent scattering, which persists until the phase reaches its melting point at 485 °C.

The reaction mechanism can be considered as taking part in three main regions: region I – the gradual lithiation of the cubic NiO phase (forming $Li_{1-y}Ni_yO$), where Li is distributed with Ni randomly within the octahedral sites in the structure; region II – the diffusion of Li ions within the cubic structure to formed a more ordered structure ('defective' layered phase – Li_xNiO_2); and finally the formation of the fully ordered layered structure $LiNiO_2$ towards the end of the synthesis. The reaction mechanism has been previously described in detail by Bianchini *et al.* as part of a synchrotron XRD study, however in this proposal we wished to validate the method using the unique properties of neutron diffraction to provide better sensitivity towards the lithiation process during synthesis, while the larger sample volume probed provides conditions more comparable to synthesising the materials in a laboratory environment. The onset of region II is observed to coincide roughly with the onset of LiOH melting. The melting is accompanied by the shift in the reflections of the cubic phase to higher angles, indicating a contraction of the lattice parameter. The melting of the LiOH significantly improves the kinetics of the reaction, which would result in a rapid uptake of Li into the now significantly lithiated $Li_{1-y}Ni_yO$ structure. In region II, the Li and Ni in the structure begin to form a more ordered crystal structure, resulting in the reduction of the unit cell volume. This process continues until the temperature of the sample environment approaches the annealing temperature of 700 °C, before which the initial formation of the layered structure can be identified by the characteristic splitting of particular reflections, such as the 220_c into the 108_R and 110_R reflections, beginning region III of the reaction mechanism.

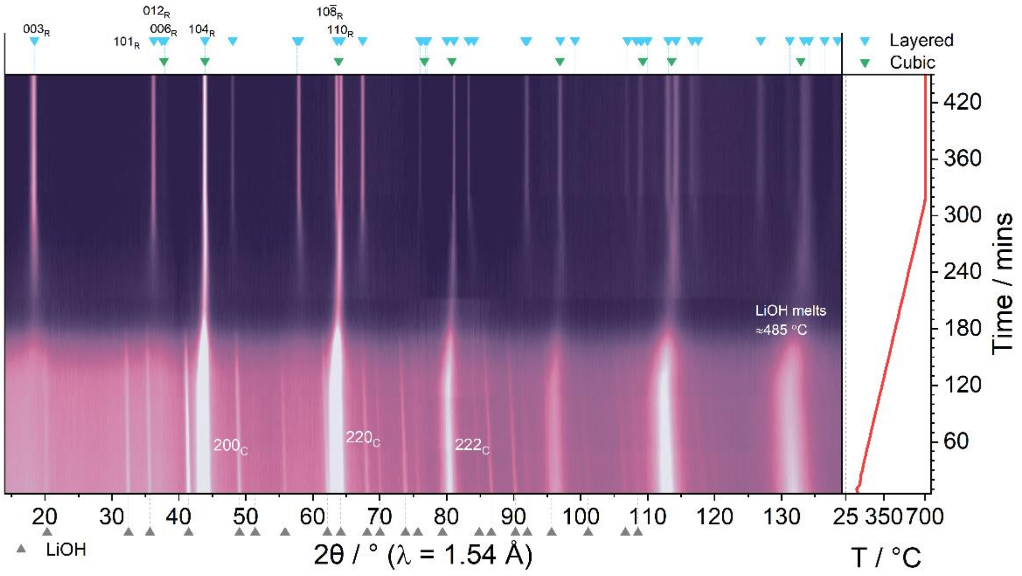

Figure 1 Contour plot of diffraction data collecting during the heating of the LiOH + NiO mixture.

To more precisely identify the phases present and their structural parameters during synthesis, Rietveld refinement was used to fit structural models to the data collected during the *in situ* experiment. Preliminary fitting results are presented in the figures below, and it is planned to use the data collected in this, and the previous proposal (5-25-272), to investigate the behaviour of these different layered cathode materials during synthesis. An example of the quality of fit and the structures identified at various temperatures is shown in Figure 2. Figure 3 shows refined structural parameters of the cubic and layered phases observed during the synthesis of $LiNiO_2$.

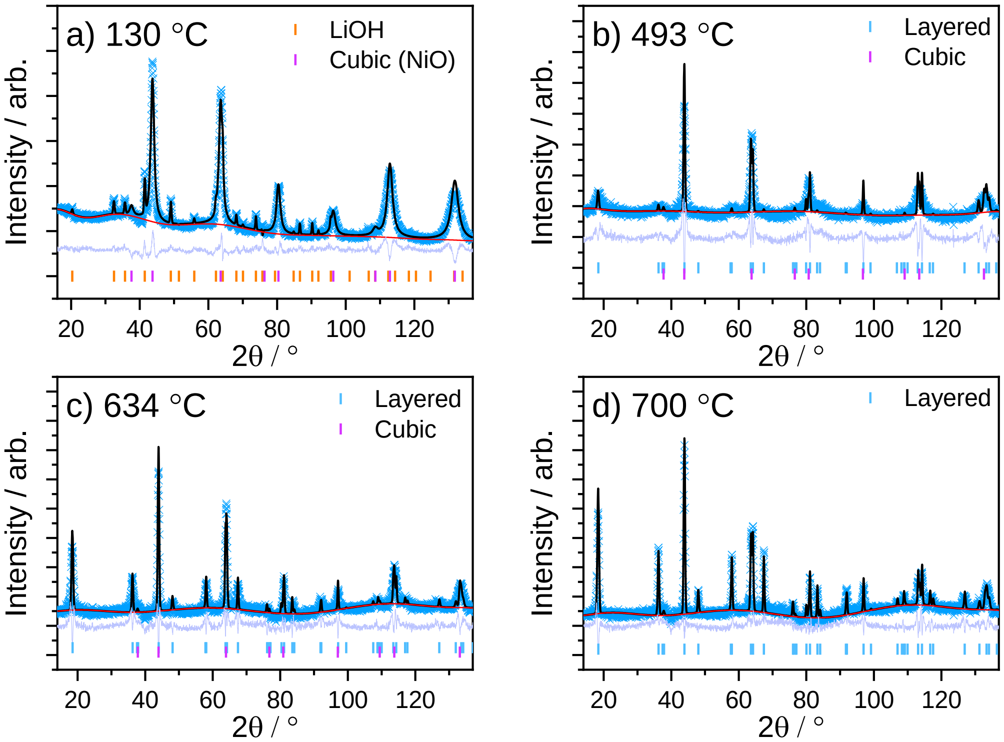

Figure 2 Rietveld refinement profiles and phases identified at various temperatures during the synthesis of $LiNiO_2$. a) 130 °C, b) 493 °C, c) 634 °C, d) 700 °C

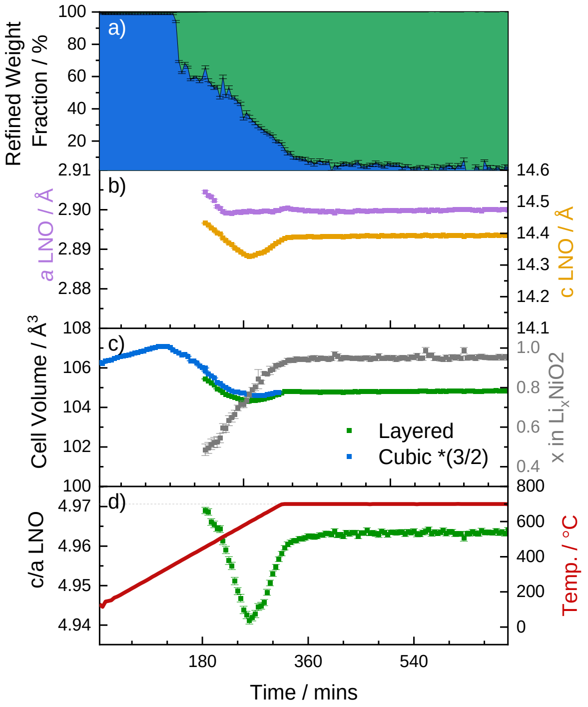

Figure 3 Refined parameters of the cubic and layered phases during the synthesis of $LiNiO_2$. a) Refined weight fractions of the cubic and layered phases. b) a and *c* lattice parameters of the layered phase c) Normalised cell volumes of the cubic and layered phases/ Refined lithium occupancy of the layered phase d) c/a ratio of the layered phase (green squares) and temperature evolution (red solid line).