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Supplementary Information for:

Studying Hydrogen Storage and Release Mechanisms in the Li-N-H system by *in situ* Powder Diffraction

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1 – Experimental Details

1.1 – Gas Cell Temperature Calibration

A sample of annealed platinum was heated from 50-400°C in steps of 50°C. The 'a' unit cell parameter extracted by Rietveld refinement of the diffraction data at each temperature was compared with literature values[1] and, using the known thermal expansion of platinum, a temperature calibration equation constructed. Based on these data, the calibration equation used to relate the temperature of the hot air blower to the actual sample temperature, where T is temperature (°C) was:

$$T_{sample} = 0.6928 * T_{blower}$$

The raw data for this calibration are shown below:

Literature Temperature (°C)	Literature a (Å)	Experiment Temperature (°C)	Experiment a (Å)
26.85	3.9238	50	3.92391
126.85	3.9274	100	3.92484
226.85	3.9311	150	3.92615
326.85	3.9349	200	3.92745
426.85	3.9387	250	3.92876
526.85	3.9427	300	3.93017
626.85	3.9468	350	3.93161
		400	3.93299

2 – Refinement Details

2.1 General Refinement Information

The majority of the refinements were performed using the batch facility in TOPAS. In this process, a refinement is carried out on an initial data set and a script is generated which uses this refinement as the starting point for the refinement of the next data set. The output from the second refinement is then used as the initial script for the third data set, and so on. Critical parameters in the refinement are output at the end of each refinement in the series, allowing for easy extraction of refined physical parameters such as weight percent, cell parameter etc.

It is worth noting that the batch approach works best when only small changes occur between the data sets. In order to prevent unrealistic features being accidentally incorporated into the batch refinement process, the physical parameters of each phase were carefully constrained. At a given temperature, the crystallite size and strain parameters and isotropic thermal parameters for each phase were held constant

In the Li-N-H region, $LiNH_2$ is modelled as a single phase, while the non-stoichiometric region was modelled as a series of 11 discrete phases, with a linear variation in stoichiometry between $LiNH_2$ and Li_2NH (ie $Li_{1+x}NH_{2-x}$, $0 \le x \le 1$, with increments of 0.1). The assumption has been made that the *a* lattice parameter of the cubic anti-fluorite lattice these species adopt varies linearly with stoichiometry, such that $a_x = a_{low} + 0.1x(a_{high}-a_{low})$. With such a large number of phases to fit the Li-N-H peak region, refined parameters are very carefully constrained. In addition to the constraints mentioned previously, the lattice constant range for the non-stoichiometric phases was kept constant at a given temperature. Thus, only the scale of each phase is allowed to vary.

2.2 Calculations from Refined Values

The molar amounts of phases through each reaction were calculated from the refined scale factors and unit cell parameters as extracted from TOPAS, according to the following formula:

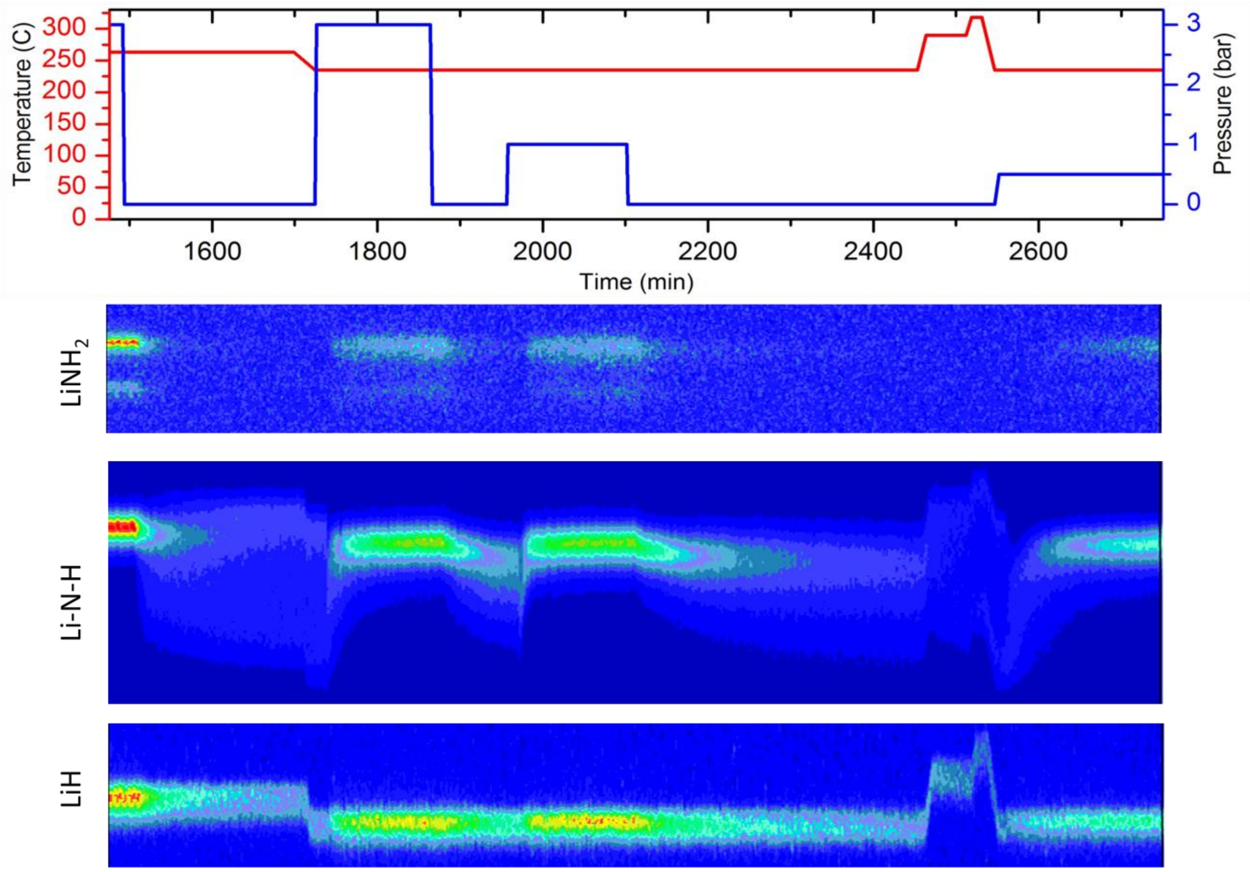
$n = Zvs$

where n = molar amount
Z = number of formula units in unit cell
v = unit cell volume
s = scale factor

Phase fractions, average stoichiometry values etc were calculated from these molar amounts.

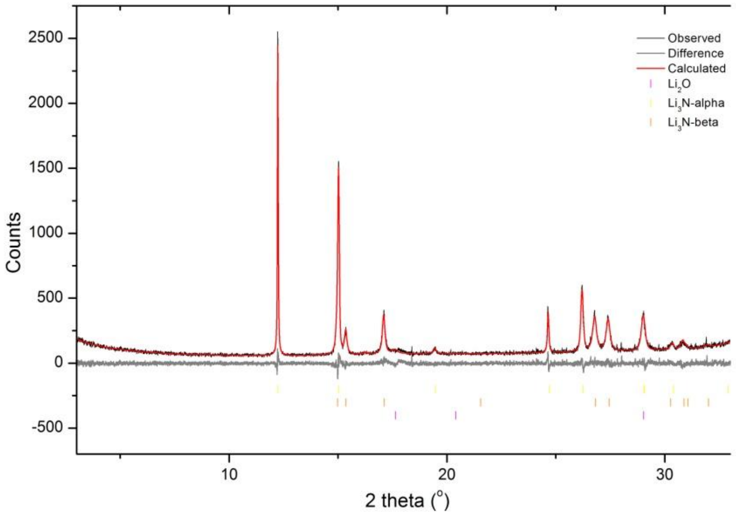
3 – Diffraction Data

Contour plots for the remaining diffraction data not included in the main body of the paper (processes 6-11) are shown below:

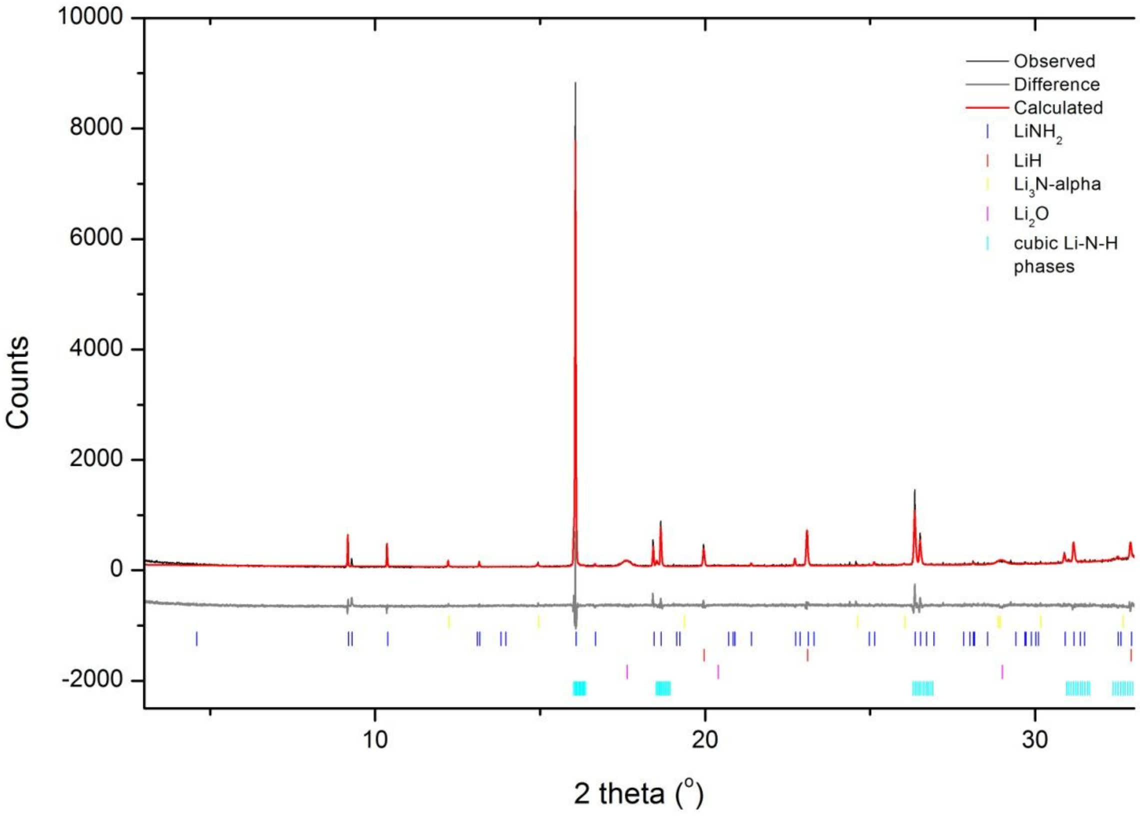


Individual patterns showing observed and refined results at the end of each reaction are given below, along with a refinement of the starting material.

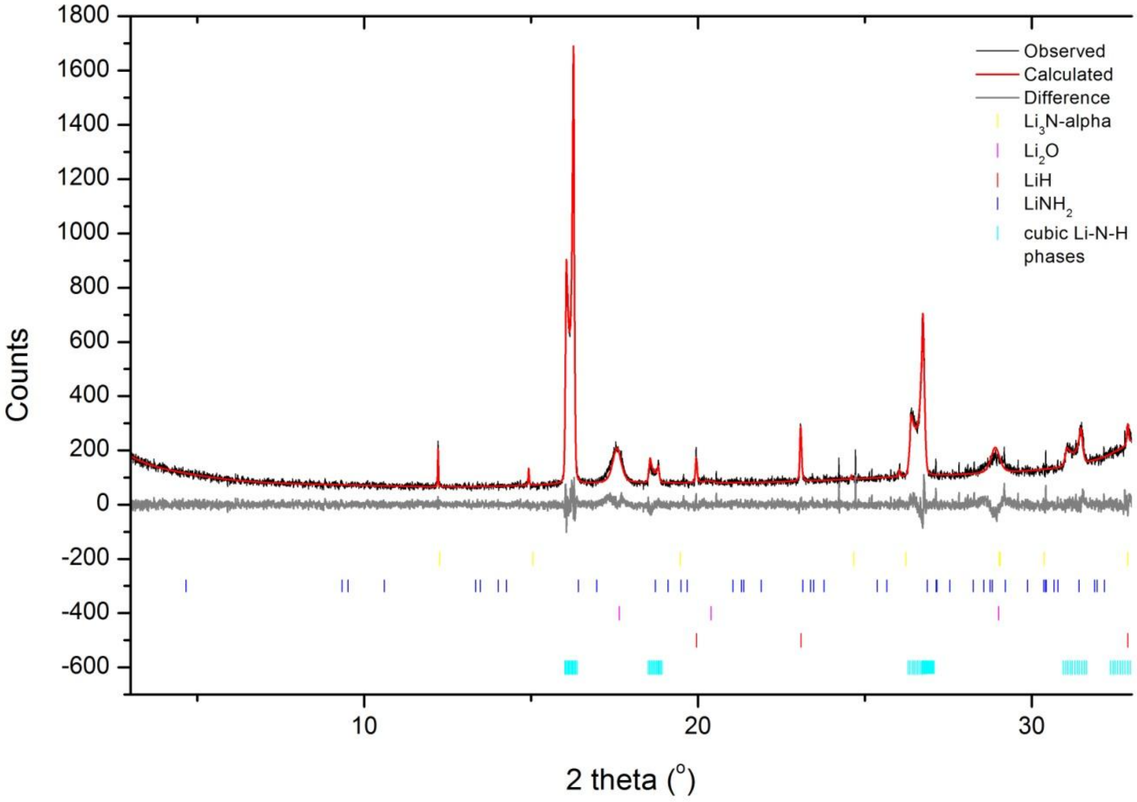
Starting material – Li_3N



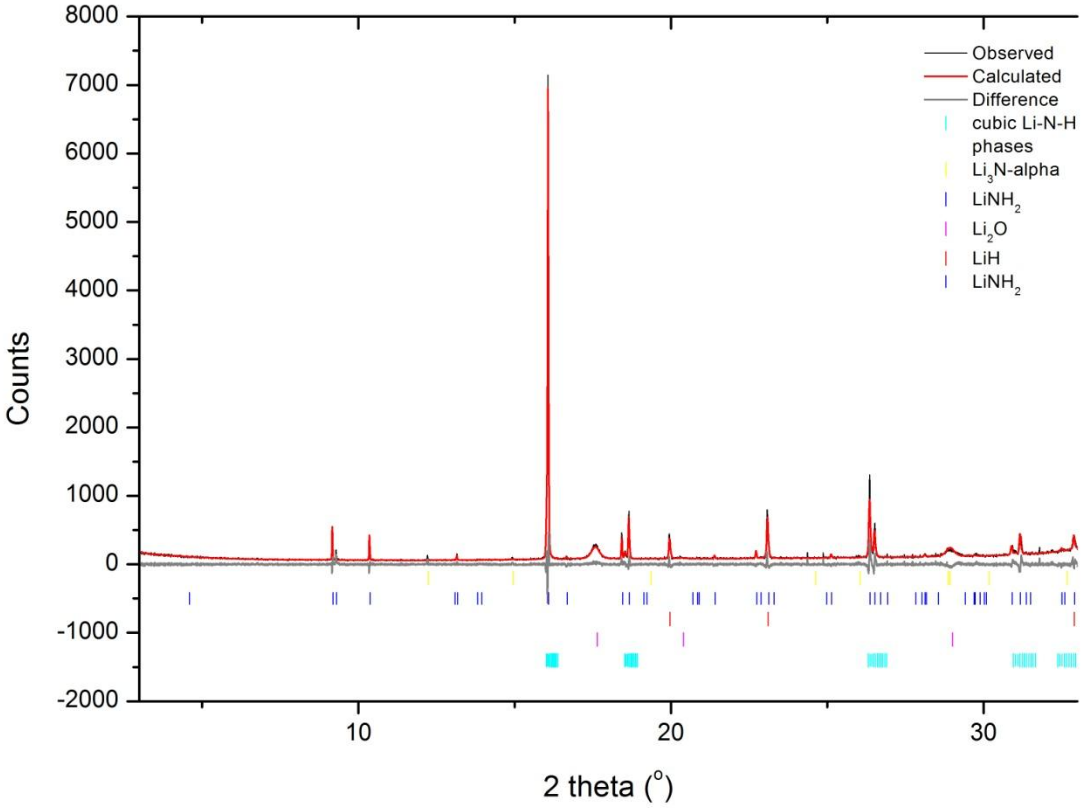
End of Process 1 – $Li_3N + H_2 \rightarrow LiNH_2 + 2LiH$ (290°C, 3 bar H_2)



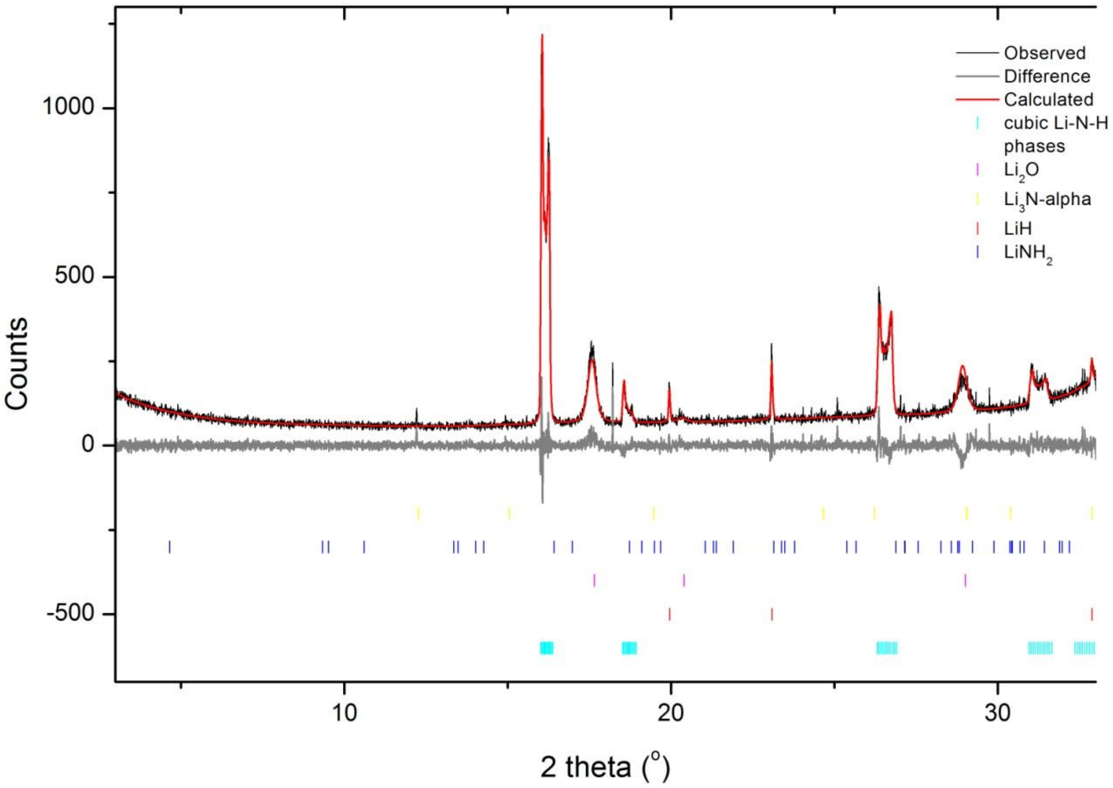
End of Process 2 – $LiNH_2 + 2LiH \rightarrow Li_2NH + LiH + H_2$ (290°C)



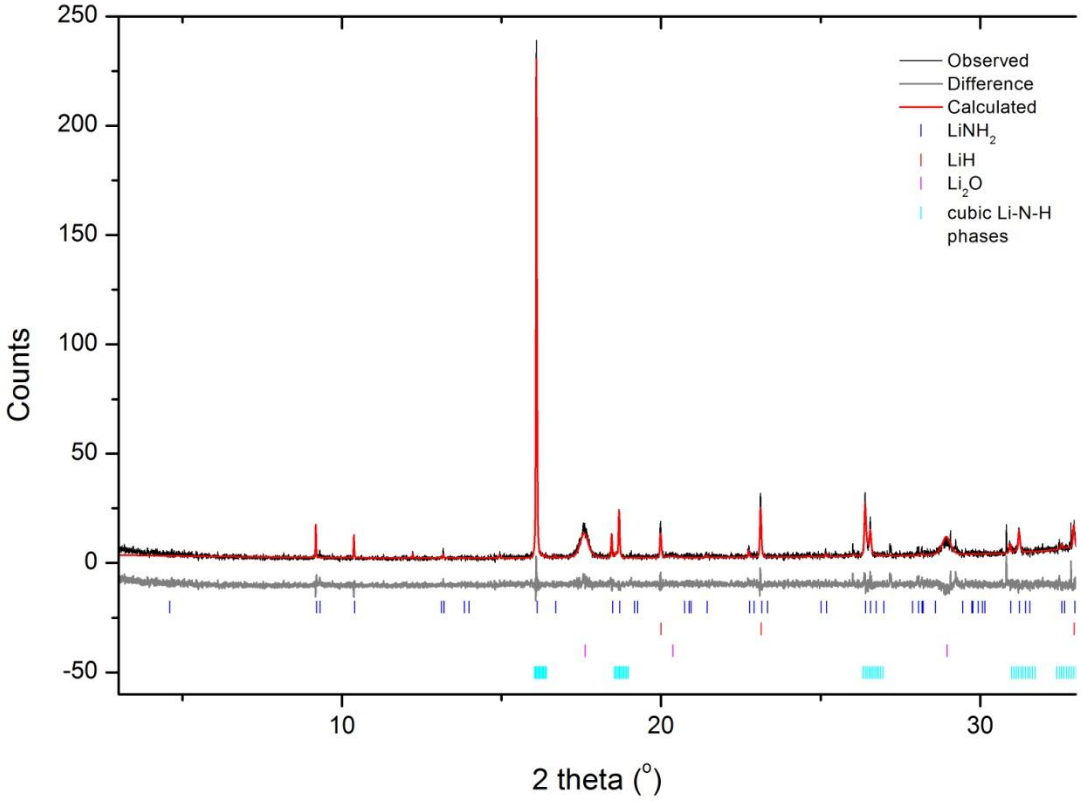
End of Process 3 – $Li_2NH + LiH + H_2 \rightarrow LiNH_2 + 2LiH$ (290°C, 3 bar H_2)



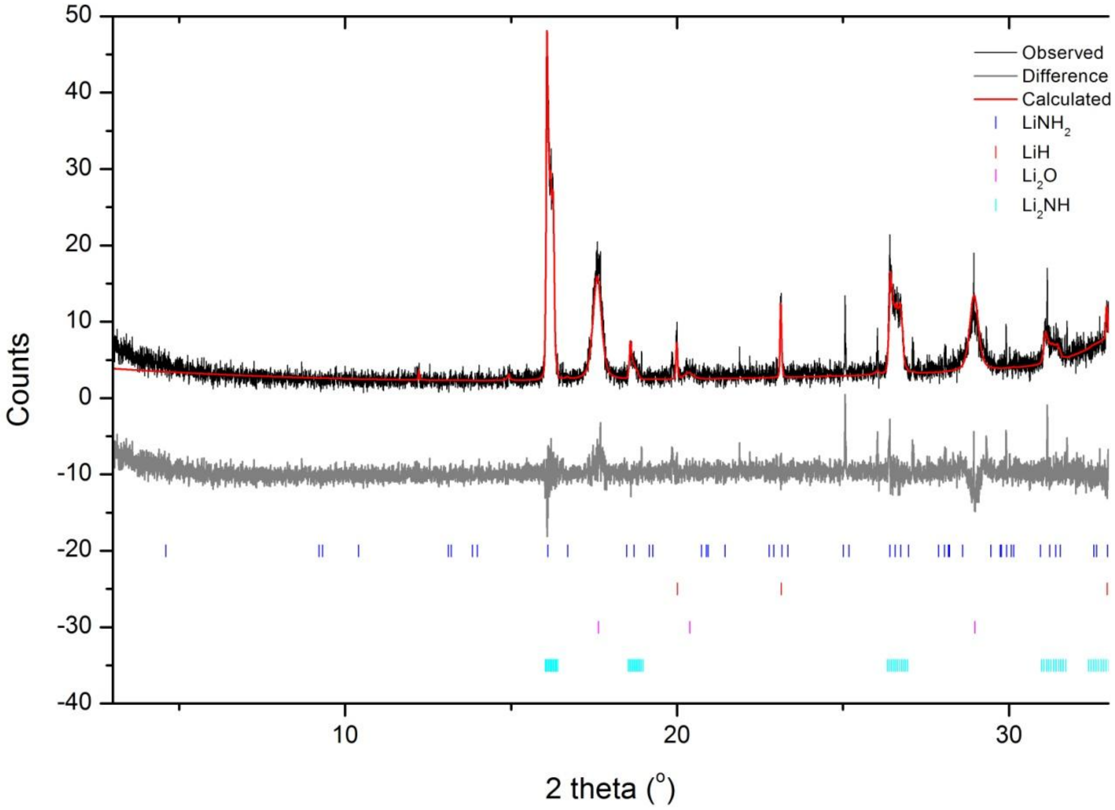
End of Process 4 – $LiNH_2 + 2LiH \rightarrow Li_2NH + LiH + H_2$ (290°C)



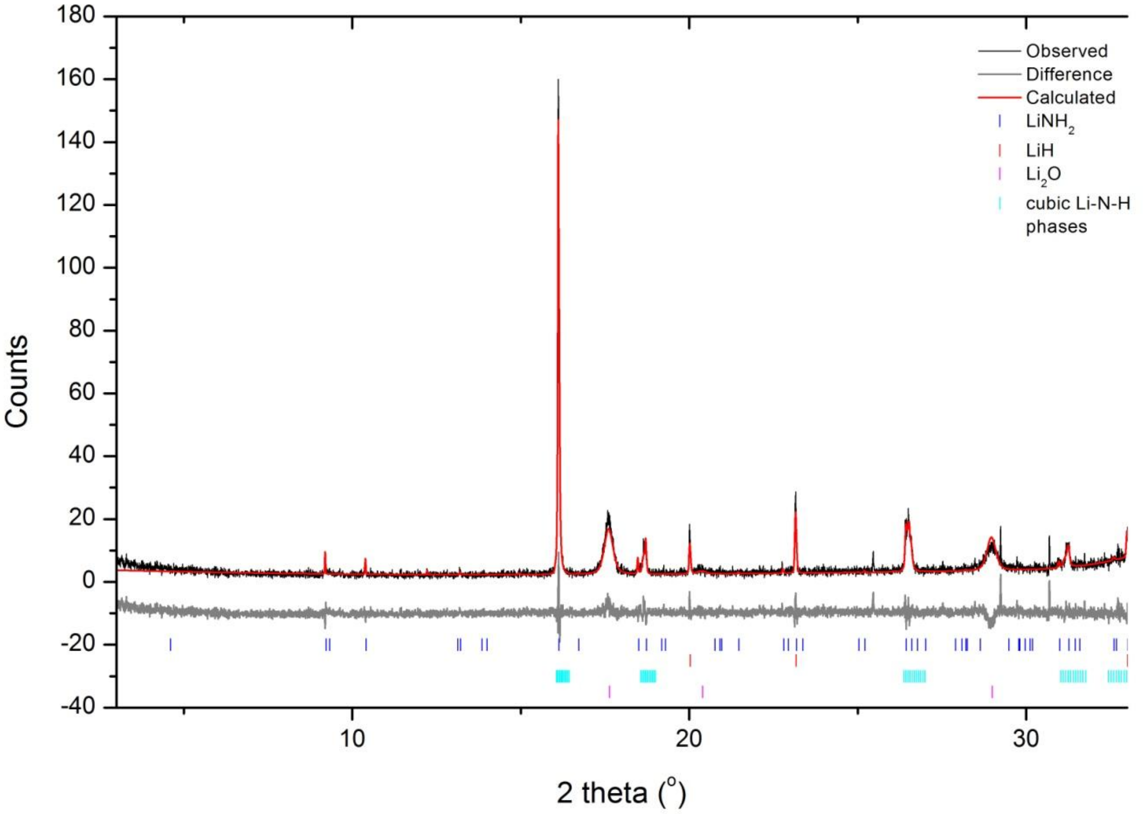
End of Process 5 – $Li_2NH + LiH + H_2 \rightarrow LiNH_2 + 2LiH$ (265°C, 3 bar H_2)



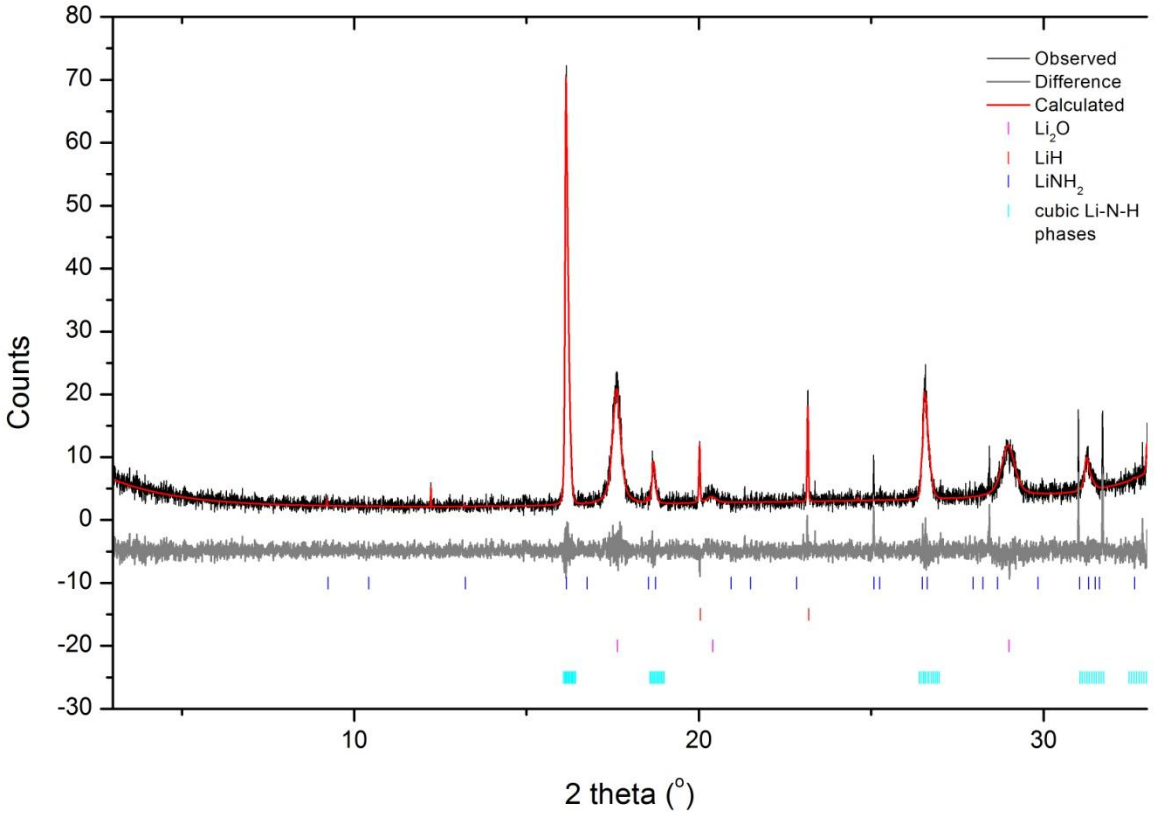
End of Process 6 – $LiNH_2 + 2LiH \rightarrow Li_2NH + LiH + H_2$ (265°C)



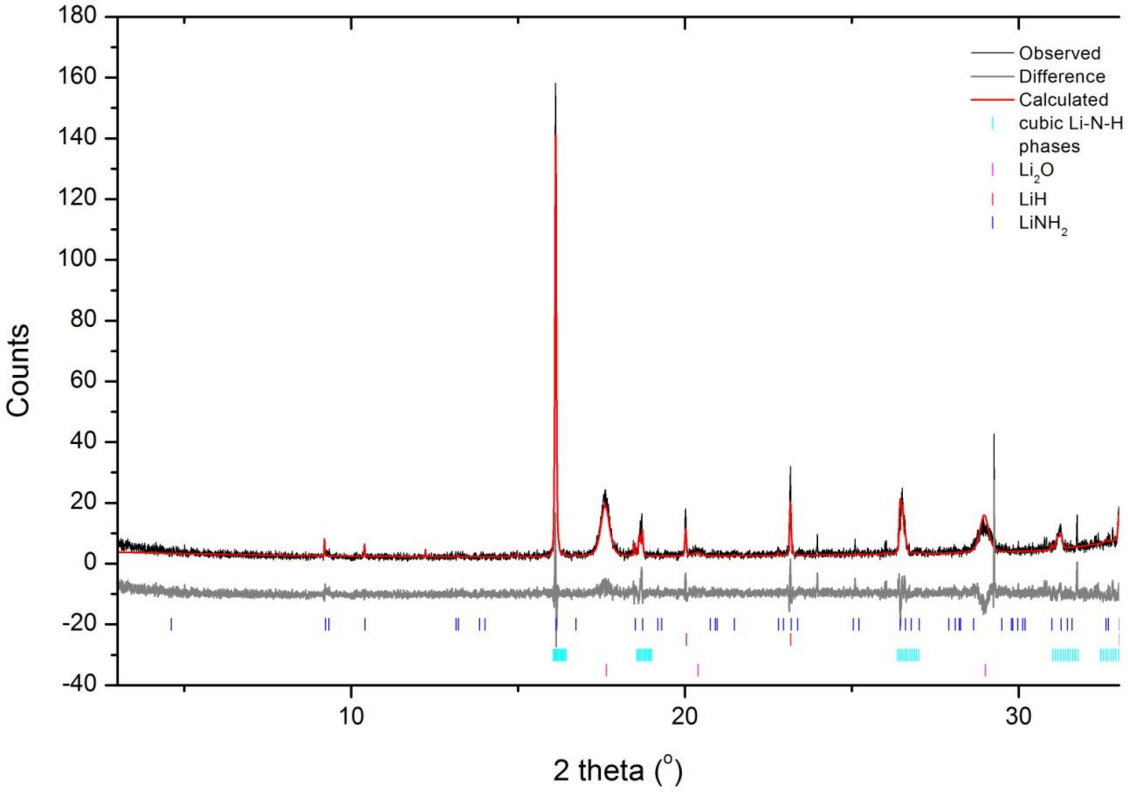
End of Process 7 – $Li_2NH + LiH + H_2 \rightarrow LiNH_2 + 2LiH$ (230°C, 3 bar H_2)



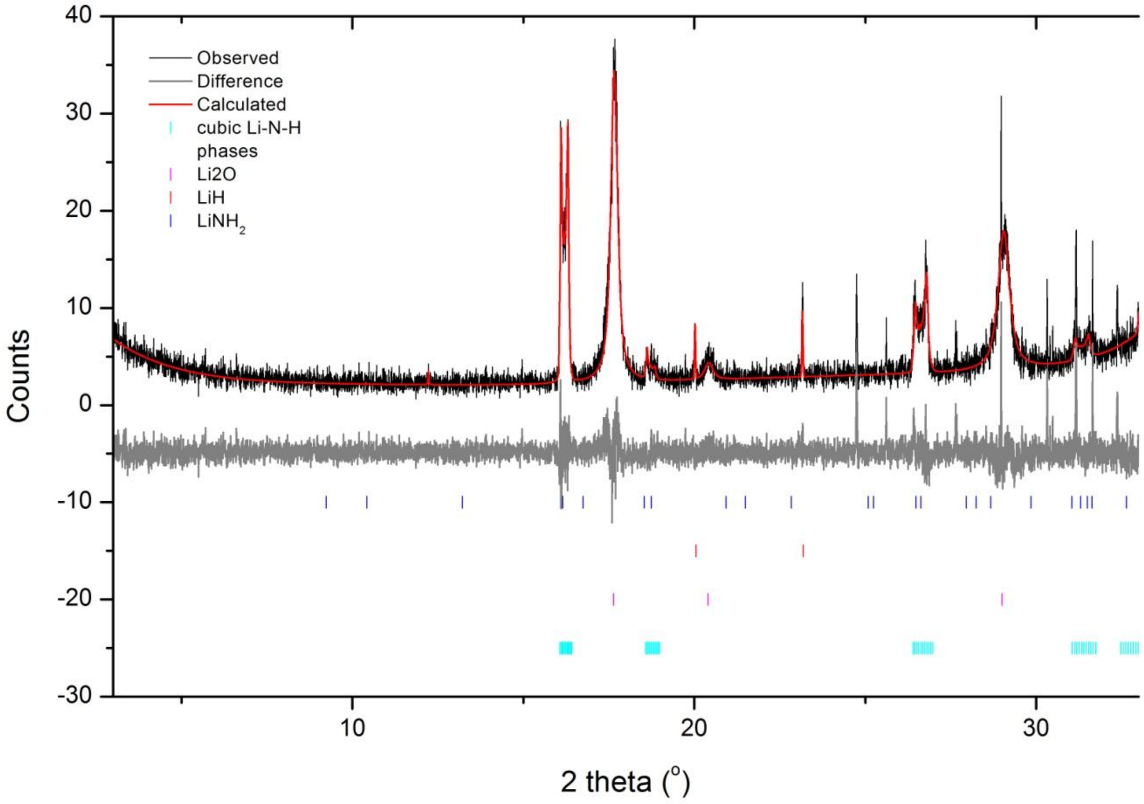
End of Process 8 – $LiNH_2 + 2LiH \rightarrow Li_2NH + LiH + H_2$ (230°C)



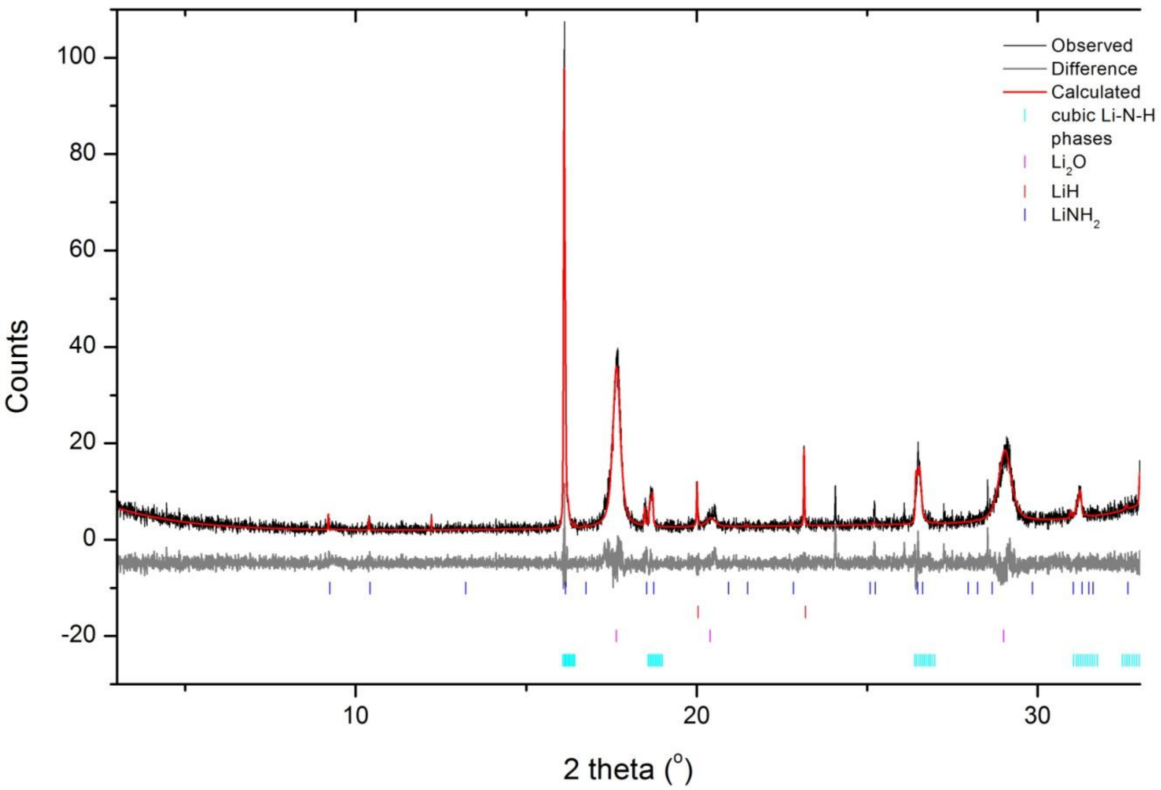
End of Process 9 – $Li_2NH + LiH + H_2 \rightarrow LiNH_2 + 2LiH$ (230°C, 1 bar H_2)



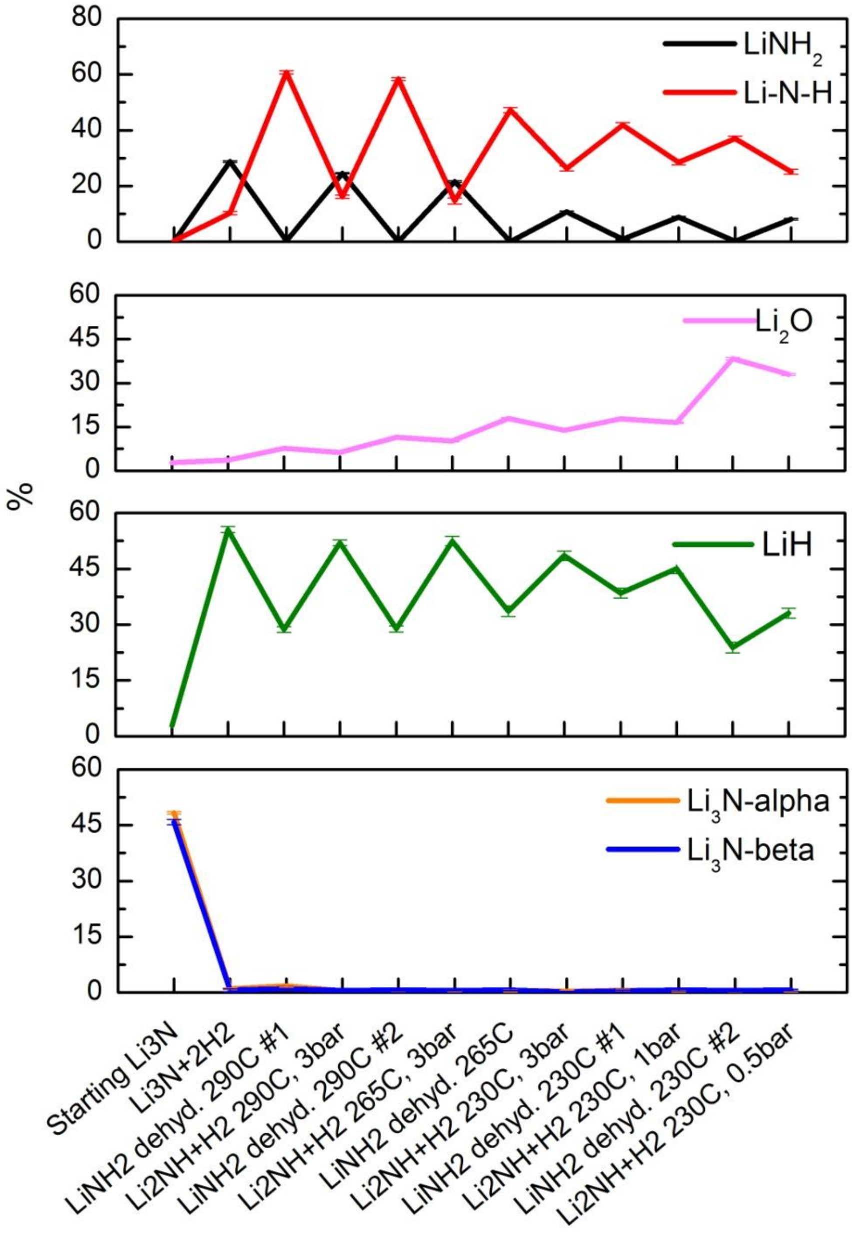
End of Process 10 – $LiNH_2 + 2LiH \rightarrow Li_2NH + LiH + H_2$ (230°C)



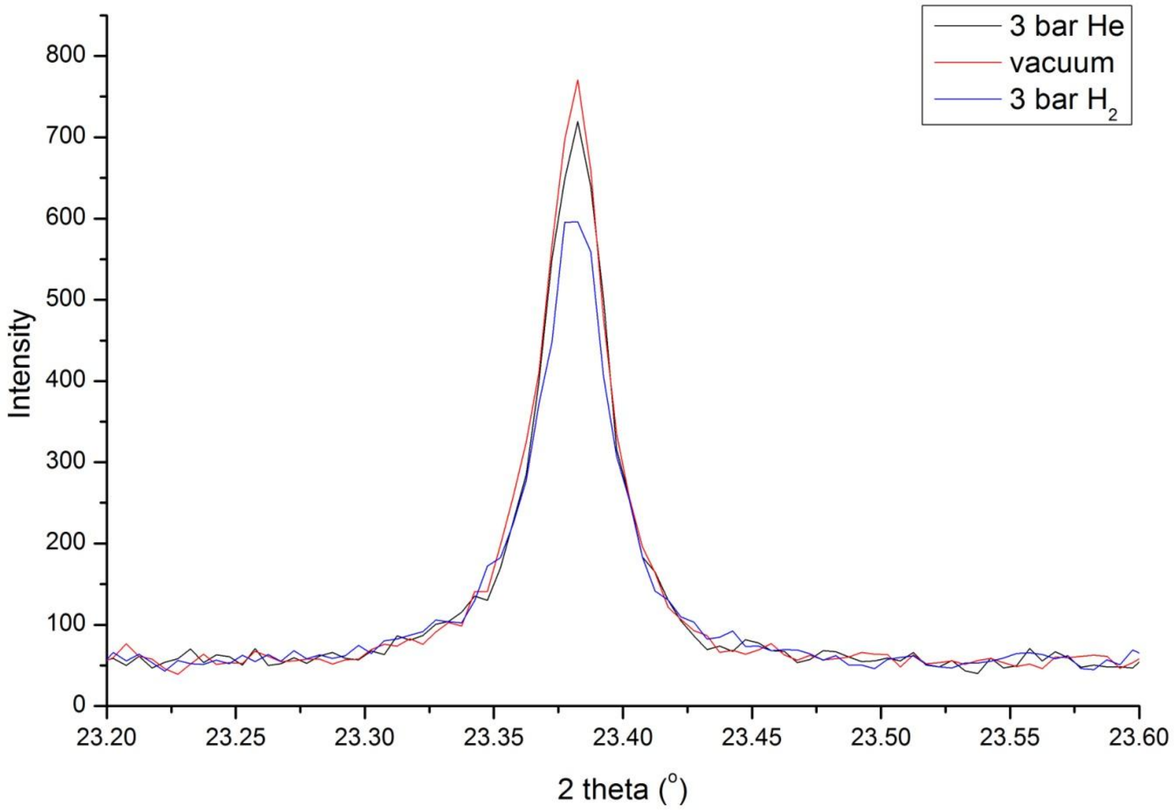
End of Process 11 – $Li_2NH + LiH + H_2 \rightarrow LiNH_2 + 2LiH$ (230°C, 0.5 bar H_2)



The relative amounts of each of the refined phases (taking all of the non-stoichiometric phases as Li_2NH) are shown below.



4 – Lithium hydride



This figure shows the (002) reflection of a sample of lithium hydride taken under (black line) 3 bar of helium, (red line) dynamic vaccum (c.a. 10mbar), and (blue line) 3 bar of hydrogen gas. These data show the negligible effect of the gas pressure on the lattice parameter of lithium hydride.

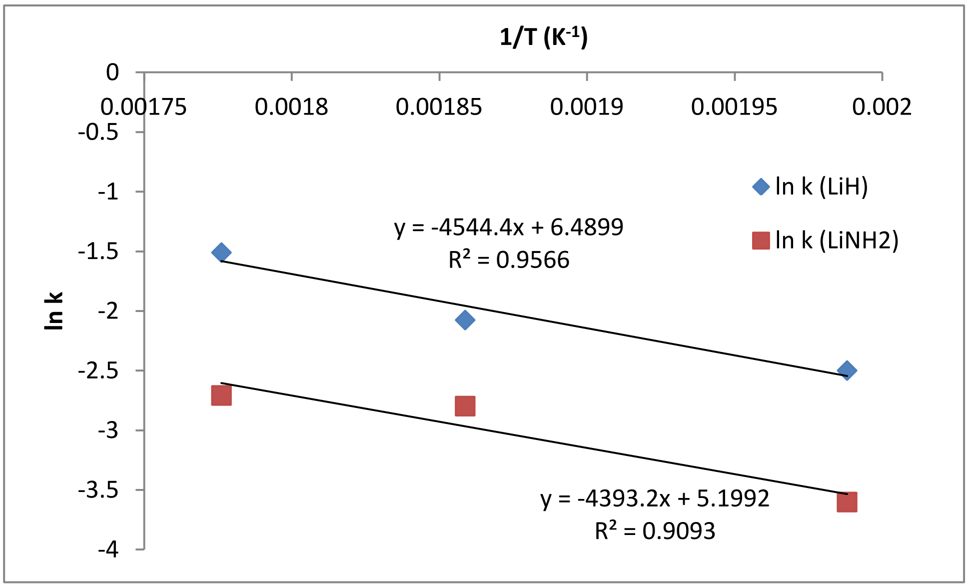
5 – Kinetic information

The kinetic data were extracted by fitting extracted molar amounts of the phases (from Rietveld refinement) to the following kinetic models:

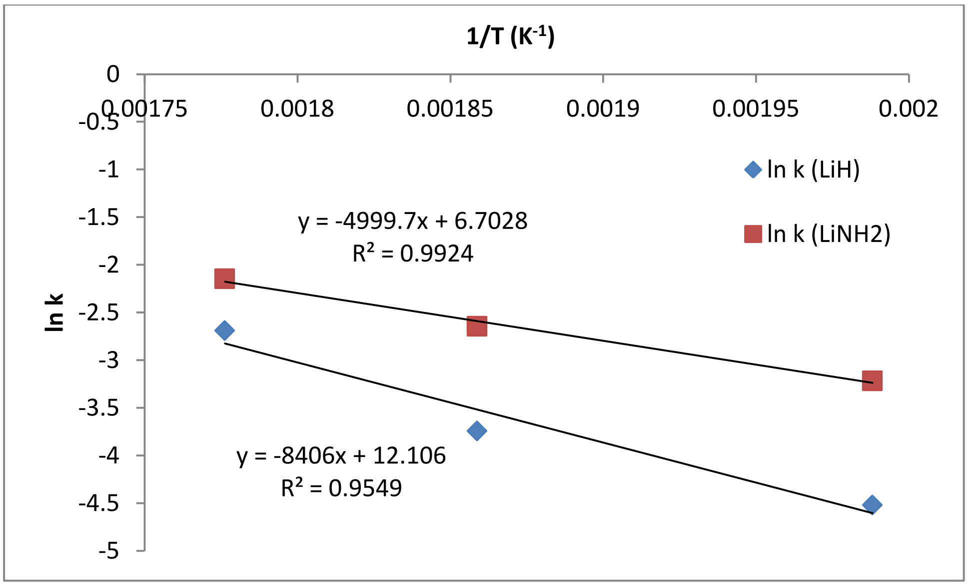
Hydrogenation : $n_t = n_{max} (1-e^{-kt})$

Dehydrogenation: $n_t = n_{initial}(e^{-kt})$

Where n = number of moles, k = rate constant, and t = time



This graph shows the Arrhenius type plot for the extracted k value against 1/T for the hydrogenation reactions. The slope of each line represents –Ea/R, where Ea is the activation energy, and R is the Universal Gas Constant.



This graph shows the equivalent plot for the dehydrogenation reactions.

References

1 - 'Crystallographic Properties of Platinum' J.W. Arblaster, Platinum Metals Rev., 1997, **41**, (1), 12-21