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- (1)  $2LiNH_2 \rightarrow Li_2NH + NH_3$   
 (2)  $Li_2NH + H_2 \rightleftharpoons LiNH_2 + LiH$

In order to support CPMD results a solid-state NMR study on  $Li_2NH$  including its products upon hydrogenation has been carried out. The proton resonance of lithium imide was located at -4.7 ppm which is in good agreement with CPMD....

The  $^1H$  MAS NMR results are presented in fig. 1. A smaller peak at -1.6 ppm was initially assigned to remaining lithium amide, which was used as starting material according to eq. 1. The products of the hydrogenation reaction eq. 2 have also been investigated. Lithium imide and lithium hydride provide chemical shifts of -2.2 and 2.7 ppm, respectively. The first value, -2.2 ppm is similar to the chemical shift of the shoulder observed in the imide spectrum. It might therefore be attributed to the remains of lithium amide, but this assignment is controversial due to later observations upon hydrogenation (see below).

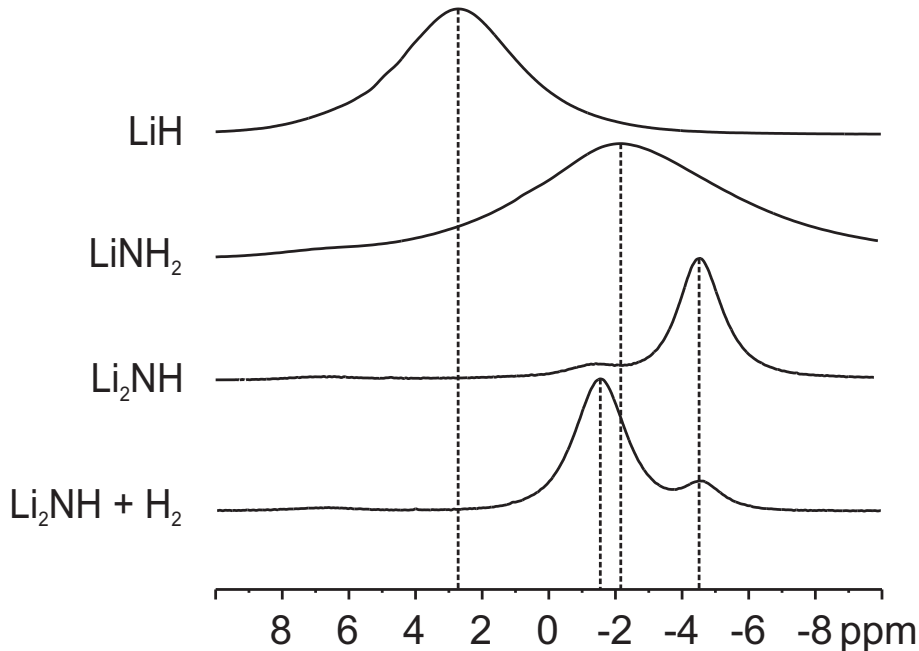


Figure 1:  $^1H$  MAS NMR spectra of all investigated compounds.

The greater line width of both resonances compared to the imide peak is striking and might generally be explained by two features as the morphology of the sample, i.e. grain boundary sites have different chemical shifts compared to bulk positions. This would lead, however, to rather Gaussian character of the signals, whereas the line shape predominately indicates Lorentzian shape, thus is mostly governed by spin interactions. Considering this, a more likely explanation is given by the strong heteronuclear dipolar couplings in case of  $LiH$  and homonuclear couplings in  $LiNH_2$ .  $LiH$  (FWHM: 2.5 kHz) is known as a cubic NaCl-type lattice, where lithium and hydride ions exhibit a distance of 2.04 Å[?]. The broad line width of lithium amide (FWHM: 4.9 kHz) can sufficiently be explained by dipolar couplings of close proton sites 1.32 Å[?]. In addition to the proton proximity within the amide group, the CPMD results are suggesting that a non-classical behaviour of the protons does not lead to a stabilisation of the known structure. A partial delocalisation as proposed for lithium imide is therefore not supposable, thus giving rise to the high homonuclear coupling

and a broad line in consequence.

Lithium imide in contrast possesses a comparatively small line width of 1.6 kHz at ambient conditions, which corresponds to a less dense packing of protons in the lattice (larger distance) and to a higher jump rate leading to less effective dipolar couplings. However, a higher uniformity due to the relatively slow ammonia release at 340 K, which may have led to a more uniform morphology and therefore a smaller dispersion. Moreover, it is to be said that the lithium imide possesses a literature known[?] phase transition at 83 °C. No abrupt phase transition could be observed with NMR on changing the temperature, however, a gradual, though remarkable broadening of both peaks was ascertained. The line width evolves from 0.76 kHz at 146 °C to 2.9 kHz at -24 °C.

Another feature demonstrating the differences between more classical compounds as lithium amide and lithium hydride and the system with a non-static proton, such as  $\text{Li}_2\text{NH}$ , is the shorter spin lattice relaxation time ( $T_1$ ) of lithium imide. The relaxation times of the two commercially obtained compounds lithium amide and lithium hydride, have been determined (not shown) as 3.7(4) m and 36(4) m, whereas that of lithium imide was found to be 2.03(7) s, that is, smaller by two orders of magnitude. The term non-static in this regard does not refer to the proton delocalisation in a flat potential because this dynamic could generally be traced on a fs-timescale and would not have a great impact on the NMR relaxation (ns-timescale). The shorter relaxation time of the imide rather indicates an exchange rate between different proton sites.

After hydrogenation at 230 °C (20 bar, 12 h) the peak at -4,7 ppm becomes less intense, hence a decrease of the lithium imide fraction is observed as it is expected. The reaction apparently did not complete since a remarkable peak remained after the process. At the same time the smaller peak increased considerably. The shift still resembles the amide peak, the width rather compares with the imide peak, though. According to the hydrogen storage mechanism given in eq. 2 the two possible products of the hydrogenation reaction are lithium amide and lithium hydride in equal amounts. Surprisingly, a third peak corresponding to the lithium hydride could, however, not be observed. This raises the question whether the storage mechanism is sufficiently described by formal reaction as given in eq. 2. At least a simple decomposition into two different spatially separated domains of lithium amide and lithium hydride can be excluded from the non-existing LiH resonance. It should be noted that the hydrogen uptake is not reversible since the compound was not mechanically activated by means of high energy ball milling which is required[?] for storage cycle in eq. 2.

Another interesting phenomenon with respect to the hydrogen uptake is the increase of  $T_1$  relaxation time of the formerly small side peak that gained intensity during the hydrogenation. Before the reaction this peak exhibited a  $T_1$  value close to that of the imide peak and even less 1.87(5) s, i.e. the pattern exhibited a rather uniform relaxation behaviour. After  $\text{H}_2$  uptake the value increased to about ~2 m which again matches the  $T_1$  time obtained for the lithium amide .

## Double Quantum – Single Quantum Correlation

Generally, 2D double quantum experiments might support the interpretation for two reasons. First, a high intensity as shown in fig. 2 implies a proton distance of less than 4 Å. Moreover, a high double quantum transfer efficiency means a certain constraint on the dynamic of the imide protons. The distance vector of two dipolar coupled protons is not averaged on the timescale of the experiment, i.e. ~100  $\mu\text{s}$  in case of the used recoupling sequence. The pattern consists of two autocorrelation peaks; a bulky peak is located at (-4.6 ppm; -9.2 ppm) and second much weaker peak at (-1.5 ppm; -3.0 ppm). The big diagonal peak means moderately strong dipolar coupling of like imide spins. Another more interesting feature is the cross correlation peak (-4.6 ppm, -1.4 ppm; 6.0 ppm) which relates to the distribution of the protons in the lattice. If the small signal at -1.6 ppm was due to a separated phase the cross coupling would only occur at the boundary layer between the imide phase and a second phase, hence it would be much weaker if seen at all. The observation is therefore in favour of a uniform distribution of "excess protons" within the material. This can be seen as another indication for a model that is based on the assumption of certain amide-like defect positions.

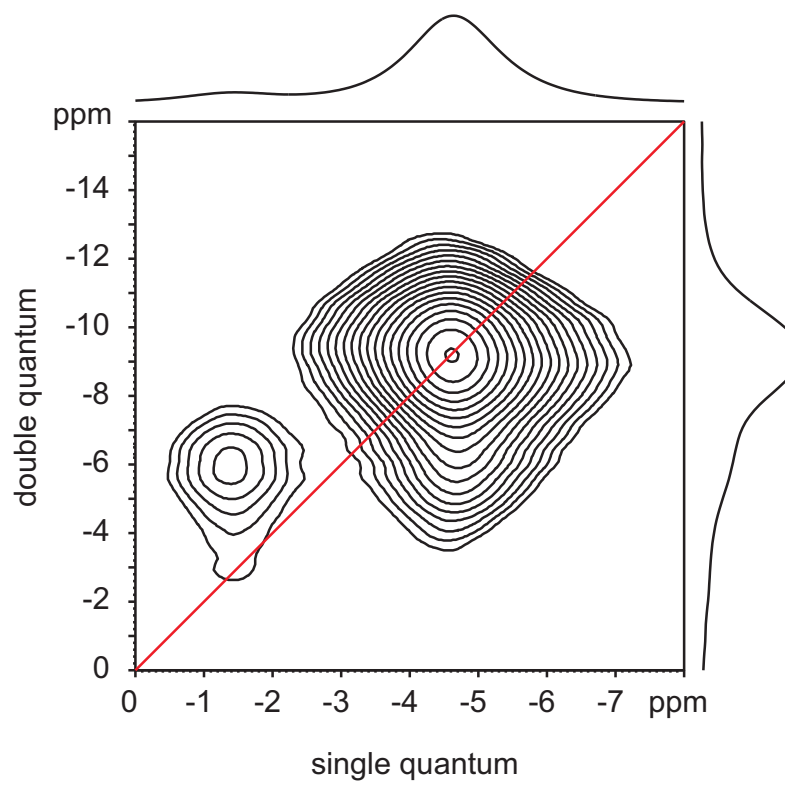


Figure 2: DQ-SQ correlation spectrum of lithium imide.