

Research Highlights

Probing Reaction Pathways Using *in situ* ¹H NMR Spectroscopy

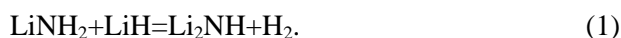
L Shaw,^(a) JZ Hu,^(b) JH Kwak,^(b) and Z Yang^(b)

(a) University of Connecticut, Storrs, Connecticut

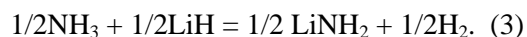
(b) Pacific Northwest National Laboratory, Richland, Washington

Real-time observation of the reaction mechanisms for the generation of H₂ will help researchers identify potential hydrogen storage materials.

In collaboration with Professor Leon Shaw's group from the University of Connecticut, Drs. Jian Zhi Hu, Ja Hun Kwak and Zhenguo Yang from PNNL used *in situ* variable temperature ¹H nuclear magnetic resonance (NMR) spectroscopy to observe the products produced during controlled conditions. The results gave direct evidence of the two-step reaction pathway for evolution of H₂ in the dehydrogenation reaction:



This Li-N-H system, first reported by Chen et al., has been extensively investigated as potential hydrogen storage material. It was shown that decomposition is rapid in the order of 25 milliseconds, and several studies have hinted that a two-step mechanism existed (see Equations 2 and 3).



Results from this *in-situ* experiment at EMSL resulted in definitive direct evidence for the two-step mechanism. The results were published online (<http://dx.doi.org/10.1016/j.jpowsour.2008.03.034>), and a paper is in press for publication in *Journal of Power Sources* (an ISI Top-5 journal in energy and fuels).

During the variable temperature *in-situ* NMR experiment performed on a powder sample of LiNH₂ that was prepared using high-energy ball milling, three separate peaks were identified in the subsequent ¹H spectra (Figure 1). These peaks verified the existence of bulk LiNH₂, surface LiNH₂, and gaseous NH₃. All assignments were assisted by understanding the connection of line width to molecular motion. In particular, fast motion on the NMR time scale leads to narrow lines and rigid slow motion to wide lines.

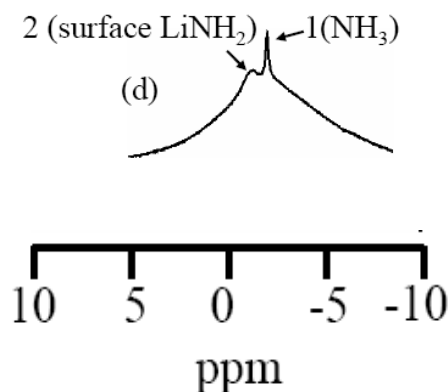


Figure 1. ¹H spectrum of LiNH₂ powder acquired at 30°C, which highlights the molecules attributed to surface LiNH₂ and the NH₃ released at 30°C.

Research Highlights

Changing the temperature conditions shows that NH_3 was released slowly at 30°C and the speed of ammonia release significantly increased at temperatures above 75°C .

The variable temperature *in-situ* NMR experiments (Figure 2) on a powder sample consisting of a mixture of $\text{LiNH}_2 + \text{LiH}$ that was mechanically activated via high-energy ball milling reveals the observation of NH_3 , indicating that reaction (3) is not very fast until temperatures above 150°C are reached and that the minimum temperature required activating (2) is lower than the temperature required to activate (3). The appearance of NH_3 peak in Figure 2(d) and the disappearance of the NH_3 peak in Figure 2(f) clearly confirm the two elementary reaction steps [i.e., NH_3 is generated first by LiNH_2 (see Equation (2)) and then NH_3 reacts with LiH to release H_2 (Equation (3))].

The *in-situ* techniques developed here serve to illustrate the potential application of a relatively simple approach that will enable the real-time observation of mechanistic data and performance evaluation in future hydrogen storage material studies.

Citation:

Chen P, Z Xiong, J Luo, J Lin, and KL Tan. 2002. "Interaction of Hydrogen with Metal Nitrides and Imides." *Nature* 420(6913): 302-304.

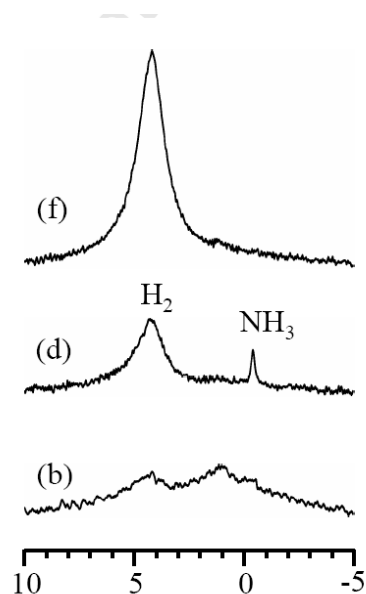


Figure 2. Representative *in situ* ^1H NMR spectra of the $\text{LiNH}_2 + \text{LiH}$ samples. Spectrum (f) was acquired when the temperature was ramped from 150°C to 180°C (no NH_3 peak observed). Trace Spectrum (d) was acquired when the temperature was ramped from approximately 40°C to 150°C . Both the NH_3 product from Equation 2 and the H_2 product from Equation 3 are observed. Spectrum (b) was acquired at room temperature.