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Hydrogen-Deuterium Exchange experiments to probe the decomposition reaction of Complex hydrides.

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Hydrogen storage in complex metal hydrides offers a safe alternative for transportation and storage of hydrogen. Among those storage materials, LiBH_4 is a promising candidate, as it can store up to 18.4 mass% hydrogen. Storage capacity, thermodynamic stability and sorption rate are the most important properties of hydrogen storage materials and are intensively studied, but in particular the slow sorption kinetics of complex hydrides is controversial [1]. Diffusion of hydrogen is one of the main mechanisms in hydrogen sorption. Insight into the specific diffusion processes could help to improve sorption kinetics. While the diffusion of H in metals is relatively well understood, only rudimentary knowledge exists for the dynamics of hydrogen in complex hydrides. The reason for this originates from the different electronic structures of the hydrides. Hydrogen in most transition metals occupies interstitials [2]. The covalent contribution to the hydrogen-metal bond is small and thus hydrogen can easily jump from interstitial to interstitial. Accordingly, the diffusion of hydrogen in transition metals is fast with small activation energies [3]. Hydrogen in complex hydrides, on the contrary, is covalently bound and arranged in subunits ('complexes'). It is not known, whether hydrogen can be removed from such a subunit without degradation of the whole compound, i.e. diffusion of hydrogen would then require the movement of the whole subunit and/or degradation of it. Indeed, first quasi-inelastic neutron scattering measurements indicated a very slow diffusion of hydrogen in NaAlH_4 [4]. Nuclear magnetic resonance measurements failed in determining the hopping rate of hydrogen, as most relaxation processes are associated with the molecular reorientation of the complex anion. An alternative method to shed light onto the specific diffusion process is to label the diffusing atoms. This is experimentally realized by hydrogen-deuterium exchange either by exposing deuterium to hydrides or by solid-solid exchange.

The first method allows the investigation of the decomposition of NaAlH_4 [5] and LiBH_4 [6] by thermogravimetry, mass spectrometry and Raman spectroscopy. By these experiments we are able to obtain specific information on the surface processes, diffusing species and formation of intermediates.

The second method is realized by the investigation of hydride/deuteride diffusion multiples (see Figure 1). We demonstrate the use of spatially resolved Raman spectroscopy to derive the tracer diffusion parameters and mechanism of hydrogen containing species in complex hydrides, exemplarily on LiBH_4 [7]. The measurements confirm recent NMR and Raman experiments and thereby clarify the mechanism of hydrogen diffusion in LiBH_4 . Hydrogen is directly exchanged between BH_4 units at an extremely low rate and then transported through the ionic crystal by intact BH_4 units at diffusion rates similar to rates in isoelectronic ionic compounds. This results in an effectively fast diffusion of hydrogen. We compare the

diffusion of various species in LiBH_4 to similar materials and discuss possible diffusion mechanisms (Figure 2).

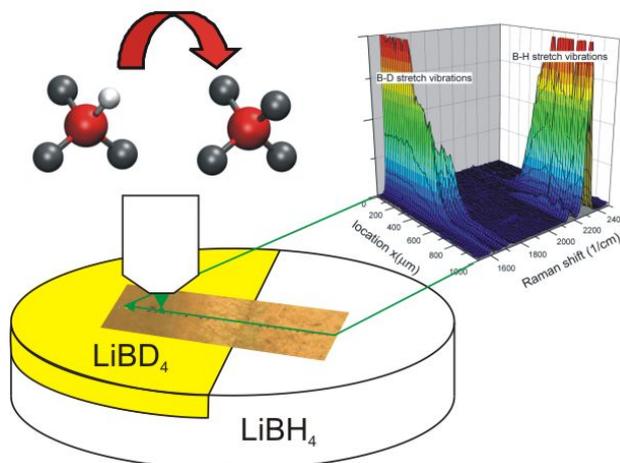


Figure 1: Raman spectroscopy on hydride/deuteride diffusion multiples.

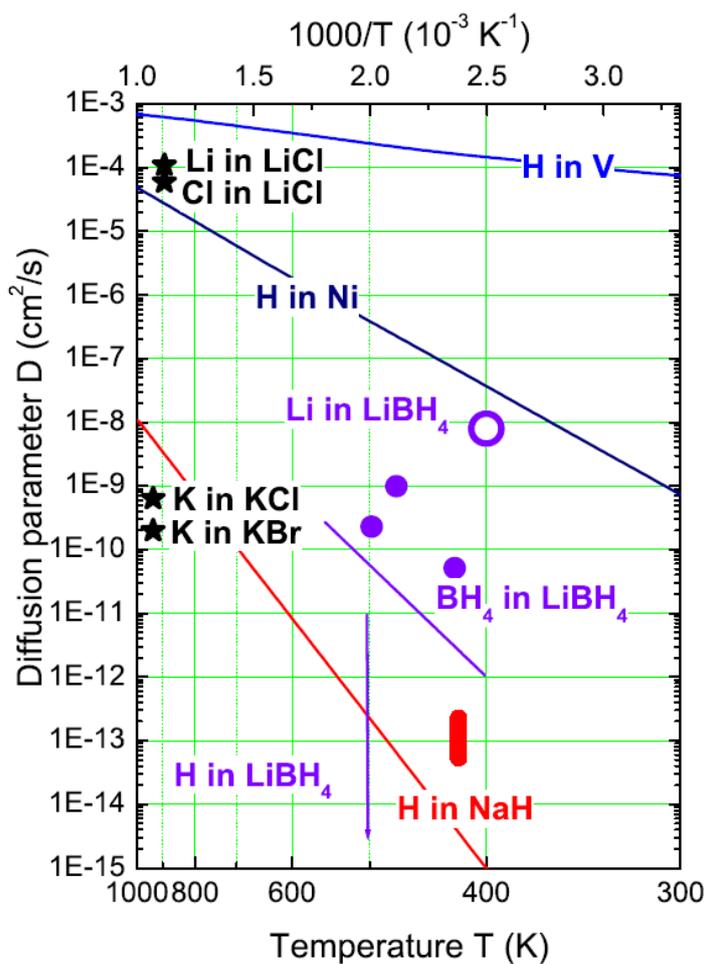


Figure 2: Diffusion of hydrogen in various metal hydrides.

The measurement of ion motilities is a generally important subject in research on complex hydrides [8]. The here presented method is not restricted to hydrogen, but can be applied to all possible ions in the compound. By interdiffusion of different hydrides, samples with locally different compositions are obtained. Spatially resolved Raman spectroscopy allows the determination of possibly formed new phases in one single sample, and with further characterization the corresponding pseudo-binary phase diagram is obtained. Thus the method is suitable as a novel high-throughput method (hydrogenography [9]) using spatially resolved Raman spectroscopy. As an example of technologically high relevance, we apply the method on $\text{LiBH}_4 - \text{LiI}$ and $\text{LiBH}_4 - \text{LiNH}_2$, being superionic Li-ion conductors [8].

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Background Histidine Hydrogen-Deuterium Exchange Mass Spectrometry (His-HDX-MS) determines the HDX rates at the imidazole C2-hydrogen of histidine residues. This method provides not only the HDX rates but also the pKa values of histidine imidazole rings. His-HDX-MS was used to probe the microenvironment of histidine residues of *E. coli* dihydrofolate reductase (DHFR), an enzyme proposed to undergo multiple conformational changes during catalysis.