

## Tetrahydroboranates the New Hydrogen Storage Materials

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Complex transition-metal hydrides provide new opportunities for hydrogen storage. Their hydrogen-to-metal ratios reach values of up to  $H/M = 4.5$  ( $BaReH_9$ ) and thus surpass the hydrogen-to-carbon ratios of hydrocarbons (methane:  $H/C = 4$ ); their hydrogen-volume efficiencies exceed that of liquid hydrogen by a factor of up to two ( $Mg_2FeH_6$ ), their weight efficiencies exceed 5% ( $Mg_3MnH_7$ ), and their hydrogen dissociation temperatures under 1 bar hydrogen pressure range from ca.  $100^\circ C$  ( $NaKReH_9$ ) to  $400^\circ C$  ( $CaMgNiH_4$ ). Their crystal chemistry is extremely rich and shows a large inventory of transition-metal hydrido complexes that often conform to the 18-electron rule. New synthetic methods are likely to yield further members of this class of materials. Concepts, to find new synthetic routes, and to understand the factors that govern hydride formation, hydrogen contents and thermal stability. In the review article by Klaus Yvon<sup>1</sup>, the basics of complex-transition-metal hydrides are outlined.

The group one two and three light elements (p-elements), e.g. Li, Mg, B, Al, build a large variety of metal-hydrogen complexes. They are especially interesting because of their light weight and the number of hydrogen atoms per metal atom which is in many cases 2. The hydrogen in the complex hydrides is often located in the corners of a tetrahedron with boron or aluminum in the center. The negative charge of the anion,  $[BH_4]^-$  and  $[AlH_4]^-$  is compensated by a cation e.g. Li or Na. The hydride complexes of borane, the tetra-hydro-borates  $M[BH_4]$ , and of alane the tetrahydroaluminate  $M[AlH_4]$  are interesting storage materials, however, they were known to be stable and decompose only at elevated temperatures and often above the melting point of the complex. The hydrogen desorption from a complex hydride is a decomposition reaction. Very little is known about the decomposition process. However, the compound does not decompose into a metal lattice and hydrogen, it decomposes often into an alkali hydride, a metal and hydrogen gas. In the bandstructure of the complex hydride often an almost complete transfer of the electron from the cation to the  $[BH_4]^-$  or  $[AlH_4]^-$  anion is found. Therefore, in the decomposition reaction<sup>2</sup> of a tetra-hydro-borate  $M(BH_4)$  an  $H^-$  is transferred from the  $[BH_4]^-$  to the  $M^+$  and 3 hydrogen can be desorbed as  $1.5 H_2$ . Borohydrides e.g.  $Li[BH_4]$ ,  $Na[BH_4]$ ,  $K[BH_4]$  and  $Mg[BH_4]_2$ ,  $Ca[BH_4]_2$  form at elevated

pressure and temperature from the elements<sup>3</sup>. The enthalpy of formation of the complex hydrides can be deduced from chemical reaction (indirect measurements of the stability)<sup>4</sup>. Due to the formation of the MH, the desorption reaction takes place at a lower temperature (lower energy) than the temperature deduced from the formation energy of M[BH<sub>4</sub>]. The mechanism of the hydrogen desorption and absorption as well as the hydrogen mobility in the lattice will be discussed in detail.

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<sup>1</sup> Klaus Yvon, "Complex transition-metal hydrides", *Chimia* 52:10 (OCT 1998), pp. 613-619

<sup>2</sup> Andreas Züttel, Andreas Borgschulte and Shin-Ichi Orimo, "Tetrahydroborates as new hydrogen storage materials", *Scripta Materialia* 56:10, (2007), pp. 823-828

<sup>3</sup> Goerrig D (1958), „Verfahren zur Herstellung von Boranaten“, Ger. Pat. 1,077,644, 1-4

<sup>4</sup> William D. Davis, L.S. Mason and G. Stegeman, "The heats of formation of Sodium borohydride, Lithium borohydride and Lithium Aluminium Hydride", *J. Am. chem. Soc.* 71 (1949), pp. 2775-2781