

LiBH₄ as a liquefying catalyst for hydrogen release/uptake from a storage material

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Hydrogen as energy carrier is one of the hot topics aimed at stopping global warming. Hydrogen storage is one of its challenges. The problems of storage in high-pressure vessels and liquefaction (physical methods) are, firstly, high energy requirements and, secondly, hydrogen leaks through vessel walls via diffusion. When stored chemically, H₂ is produced only on demand. This overcomes the escape threat and, provided there are moderate operation conditions, it is also an energy saving method. Lightweight complex hydrides are ionic compounds which consist of an anion complex, where hydrogen is covalently bonded to a central metal or non-metal atom, and one or several metal cations. They have high gravimetric hydrogen density and are capable of reversibly releasing and up-taking hydrogen. Due to their low weight, they are particularly advantageous for mobile applications. Amides (NH₂⁻), are one class of these light-weight complex hydrides. Obstacles preventing their use are high operation temperatures (energy cost) and the release of NH₃ under heating (due to fuel cell poisoning, which requires regeneration afterwards, and quantitative reduction of the desorbed hydrogen gas). However, when amides are mixed with hydrides (e.g. Mg(NH₂)₂ with LiH), NH₃ is caught by the latter, leading to hydrogen generation. A 6Mg(NH₂)₂–9LiH mixture is in principle a good storage candidate but the kinetics are sluggish and high operation temperatures are required. This is solved when using lithium borohydride LiBH₄ as an additive: it plays the role of a catalyst. Lithium amide LiNH₂, created in the first step of the hydrogen release reaction, forms a mixture with LiBH₄. Two known compounds, Li₂BH₄NH₂ (melting at 90°C) and Li₄BH₄(NH₂)₃ (melting at 190°C), form an ion-conducting liquid at working conditions. It is assumed that this accelerates the reaction. Varying the quantity of LiBH₄ changes the resulting mixture properties by forming different LiBH₄–LiNH₂ mixed phases. I will present the binary phase diagram (LiBH₄–LiNH₂), obtained from DSC and diffraction measurements, indicating LiBH₄ : LiNH₂ ratios with corresponding 6Mg(NH₂)₂ : 9LiH : xLiBH₄ compositions. Such juxtaposition is a prerequisite for understanding the reaction mechanisms in these hydrogen storage materials.

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