Electronic Supplementary Information:

Material preparing and measurement

The source materials were obtained commercially, namely $LiBH_4$ (95%, Fisher), MgH_2 (99%, Aldrich) and Mg (99%, Aldrich) and were used without further purification with all handling procedures conducted under an inert atmosphere. Approximately 0.5 g mixtures of $LiBH_4/MgH_2$ (or with Mg metal) with a mass ratio of 1 : 4 were mechanically milled for 1 h (EPX 800 Spex shaker ball mill) under an inert gas (N_2).

Hydrogen release property measurements were performed by differential thermal analysis / thermogravimetry (DTA-TG, TA-STD 600) connected to a mass-spectrometer (MS, Hiden) using a heating rate of 10 ˚C min^{-1} under 1 atm argon with a purge rate 200 cm^3min^{-1}. Typical sample quantities were 5-10 mg. The rehydrogenation of $LiBH_4/MgH_2$ sample was carried out on a Sievert's apparatus under 100 atm hydrogen pressure and 400 ˚C for 24 h. The powder X-ray diffraction (XRD, Bruker D8) measurements were conducted to confirm the phase structure. All the XRD for the dehydrogenated samples were measured after cooling down to room temperature. Powders were spread and measured on a Si single crystal. Amorphous polymer tape was used to cover the surface of the powder to avoid oxidation during the XRD measurement.

ESI 1

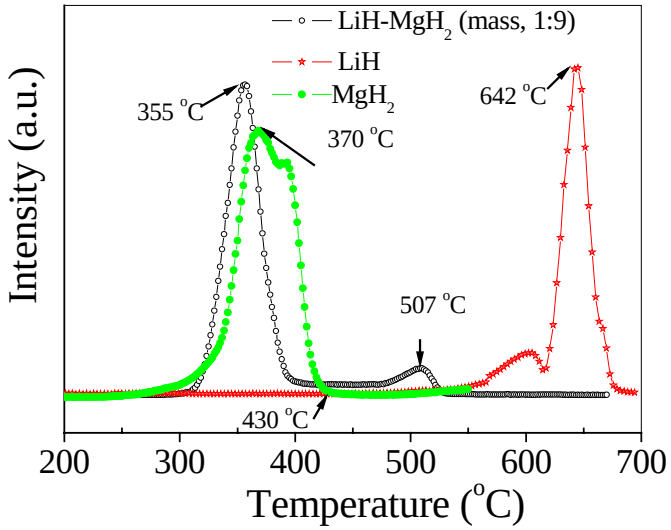


Figure 1. MS results for 1h milled MgH_2, LiH and LiH/MgH_2 (mass, 1:9) with a heating rate of 10 ^oC min^{-1}.

The dehydrogenation of LiH/MgH_2 mixture shows a large release of hydrogen below 400°C followed by a small constant evolution of hydrogen and a small peak just above 500°C. Considering that the terminal temperature for hydrogen release from ball milled MgH_2 is below 430 ^oC, the peak at 507 ^oC might result from dehydrogenation of LiH, which is much lower than that for ball milled LiH, which occurred around 650 ^oC. These results suggest that the MgH_2 destabilized the decomposition of LiH.

NB the hydrogen release from LiH/MgH_2 mixture does not stop during 400 ~470 ^oC, suggesting that there is a small amount LiH decomposed during this range of temperature.

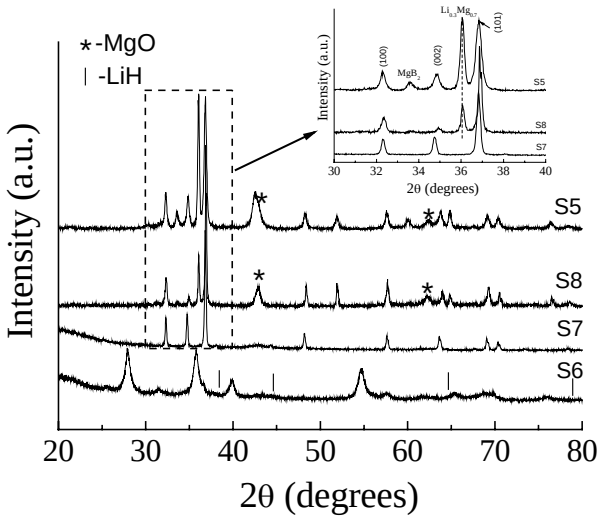


Figure 2. XRD patterns for $LiBH_4$+MgH_2 after dehydrogenated to 600 ^oC (S5) and LiH+MgH_2 (mass, 1:9) before (S6) and after dehydrogenated to 450 ^oC (S7) and 600 ^oC (S8). Peaks for $Li_{0.184}Mg_{0.816}$ were identified for S5 and S8, see inset an Table below.

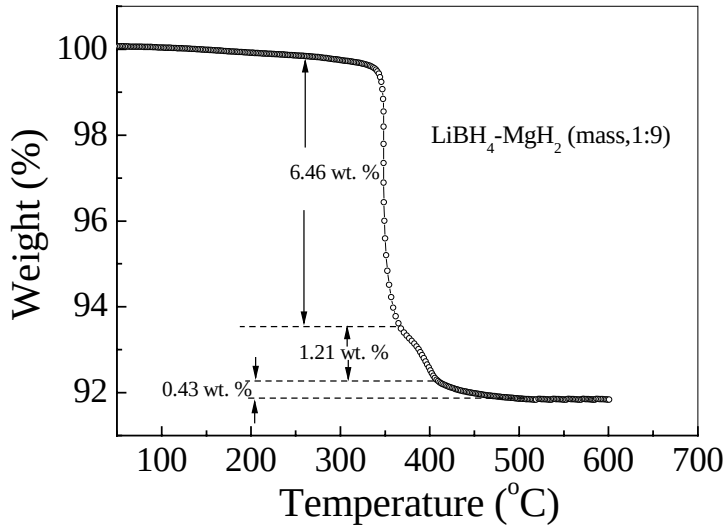
No LiH was observed for the as-prepared LiH/MgH_2 (mass, 1:9) sample due to a combination of low concentration and nanocrystallinity/disorder produced by the ball milling process.

In the case of LiH/MgH_2 heated to 450 ^oC (S7), 2θ values were between that of Mg metal and $Li_{0.184}Mg_{0.816}$. After heating to 600 ^oC, $Li_{0.184}Mg_{0.816}$ and $Li_{0.3}Mg_{0.7}$ were observed, which is similar to the results in $LiBH_4/MgH_2$ system.

Comparison of d-spacings for LiH/MgH_2 (mass ratio, 1: 9) heated to 450 ˚C (S7) and 600 ˚C (S8) with $Li_{0.184}Mg_{0.816}$ (ICSD: 104740).

Sample	D-spacings (Å)		
	(100)	(002)	(101)
$Li_{0.184}Mg_{0.816}$	2.764	2.566	2.434
S7	**2.768**	**2.580**	**2.439**
S8	**2.766**	**2.563**	**2.434**

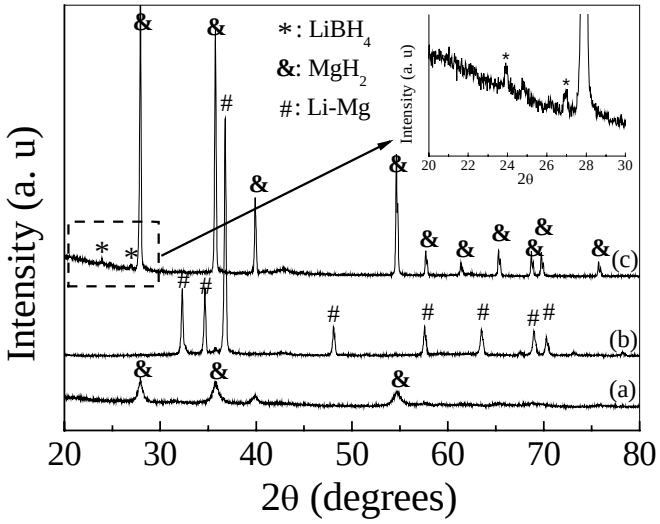
ESI 2



TG results for the 1h milled $LiBH_4/MgH_2$ (mass, 1:9) with a heating rate of 10 $^oC\ min^{-1}$.

The first weight loss of 6.46 wt. % correspounds to the dehydrogenation of MgH_2 from the $LiBH_4/MgH_2$ mixture. The ratio of the weight loss for the 2^{nd} and 3^{rd} dehydrogenation steps (1.21 wt. % and 0.43 wt. %, respectively) is about 3:1, which also indicates that the $LiBH_4$ dehydrogenated to LiH first and then the LiH decomposed at higher temperatures.

ESI 3



XRD patterns for the $LiBH_4/MgH_2$ mixture. (a) before dehydrogenating ; (b) after dehydrogenation at 400 ˚C for 2 h; (c) sample (b) rehydrogenated at 400 ˚C and 100 bar hydrogen pressure.

As explained in ESI 1, $LiBH_4$ could not be identified after ball milling (Figure (a)). The amount of dehydrogenation that will have occurred at 400°C (as demonstrated by TGA) can only have occurred with dehydrogenation of the $LiBH_4$ phase and the presence of a Li-Mg alloy (Figure (b)) could only have formed from the decomposition of $LiBH_4$. However, after rehydrogenation a very weak XRD pattern can be identified for $LiBH_4$ (Figure (c)) illustrating a successful reverse reaction.