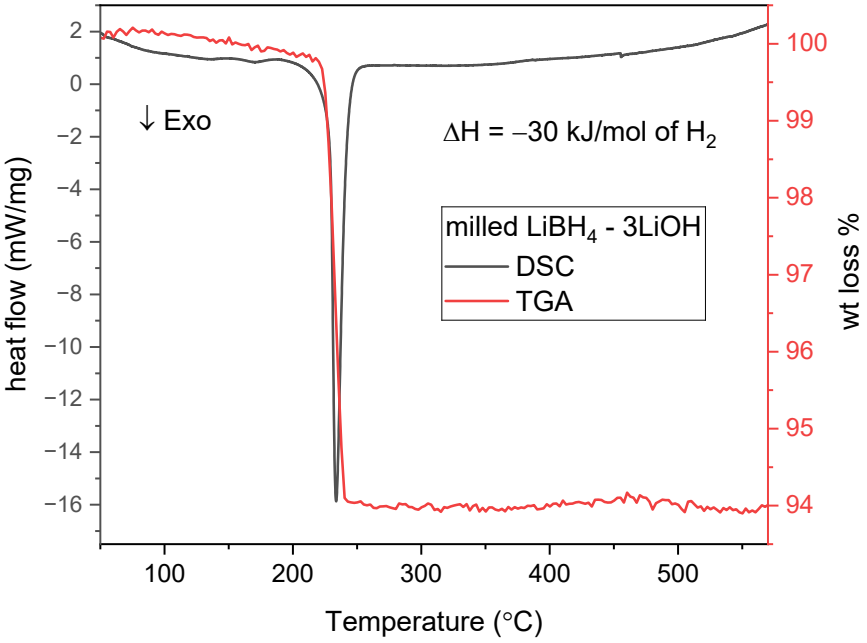
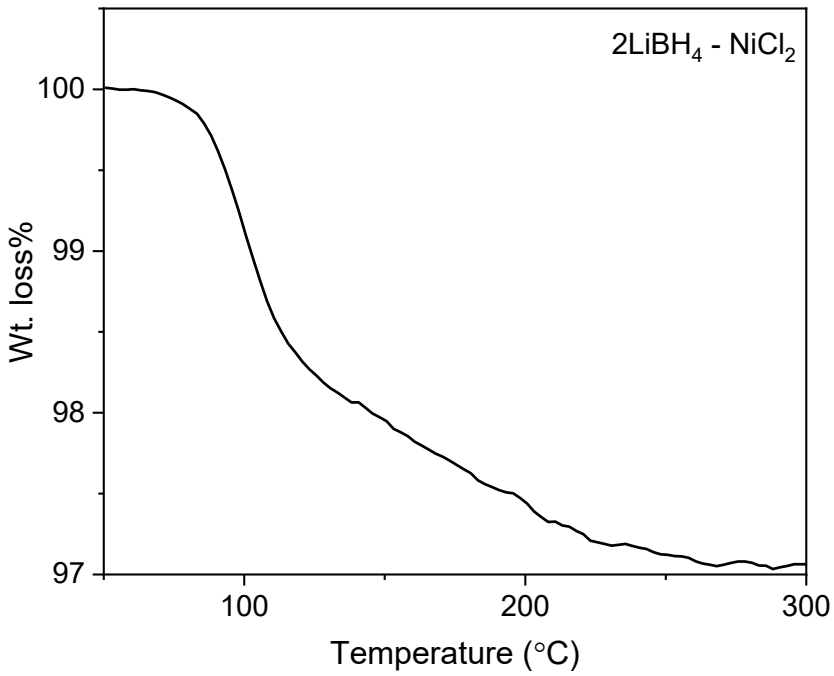
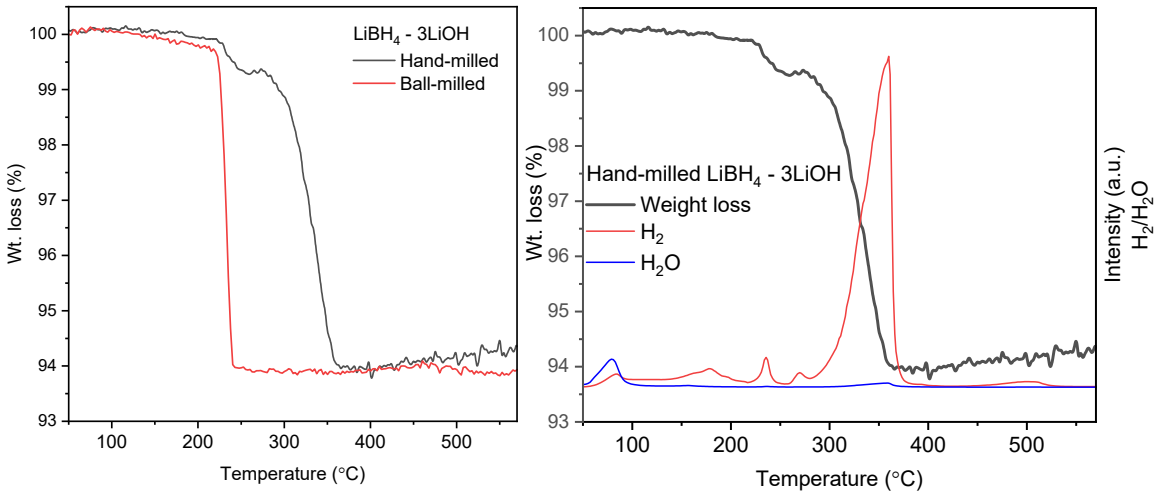
## Supporting material:




**ES 1** TGA and DSC data for ball-milled $LiBH_4$ – 3LiOH system on heating to 570 °C at 10 °C $min^{-1}$ under argon flow




**ES 2** TGA data for $2LiBH_4$ – $NiCl_2$ system upon heating to 300 °C at 10 °C $min^{-1}$ under argon

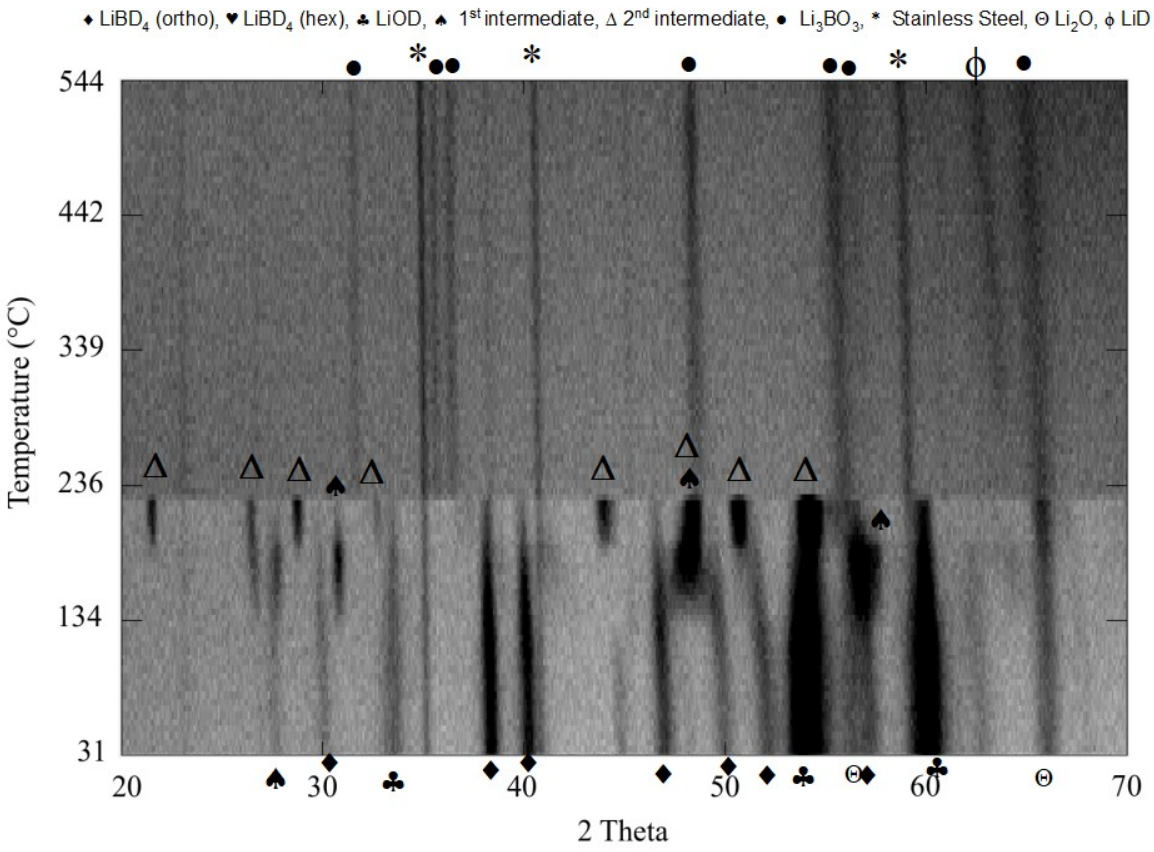



**ES 3** TGA and TPD-MS ($H_2$/$H_2O$) data for hand-milled $LiBH_4$ – 3LiOH on heating to 570 °C at 10 °C $min^{-1}$ under argon flow.

**Explanation of ES 3:**

This further study aimed to elucidate the effects of ball-milling conditions on the hydrogen desorption behaviour of the $LiBH_4$-3LiOH system. **ES 3** displays the TGA profile of the $LiBH_4$-3LiOH system when subjected to milling with milling balls 4 mm diameter vs hand-milling. While the onset decomposition temperature remained consistent at 220 °C, notable differences were observed in the hydrogen release curves. The ball-milled sample exhibited a single-step hydrogen release, whereas the hand-milled sample displayed a multi-step hydrogen release. Nevertheless, both cases demonstrated a total $H_2$ release of 6 wt.%. The TPD-MS curves of the hand-milled $LiBH_4$-3LiOH sample shows trace amount of $H_2$ release along with $H_2O$ below 100 °C due to moisture contamination in the sample. Throughout the entire heating process, no signals of $B_2H_6$ or $O_2$ were detected. Therefore, it can be inferred that the gas released from the $LiBH_4$-3LiOH system during heating is predominantly pure hydrogen, accompanied by a trace amount of $H_2O$. A small weight loss of 0.2 wt.% was observed below 200 °C, accompanied by a small $H_2$ peak appearing on TPD-MS profile at around 180 °C. Further heating above 220 °C, another weight loss was observed by 280 °C, loosing around 0.7 wt.%, matches with two small $H_2$ peaks appearing at same temperature range in TPD-MS data. After 270 °C, a significant mass loss step of approximately 5.3 wt.% was observed, with the majority of decomposition completed by 350 °C.

This weight loss corresponds to a prominent peak of $H_2$ detected in the TPD-MS profile within the same region, indicating it as the primary decomposition step.




**ES 4** PND heat map for $LiBD_4$–3LiOD under self-generated $D_2$ atmosphere.