

Experimental procedure:

LiBH₄ with 95 % purity was purchased from Acros. YH₃ was synthesized by the hydrogenation of yttrium (Acros, 99.9%, -40 mesh powder) at 350 °C and 9.0 MPa of hydrogen (99.9999 %) for 2 hours. The XRD pattern of the synthesized YH₃ powder shows that YH₃ is present as a main product together with a small amount of YH₂ and Y₂O₃ phase (Fig. S1). The yttrium oxide was formed due to the impurities of LiBH₄. 3 g of 4LiBH₄ + YH₃ composite was prepared using a planetary ball mill (Retsch PM200), sealed with a lid having a Viton O-ring at 650 rpm for 12 hours. Thirteen 12.7 mm diameter and twenty four 7.9 mm diameter Cr-steel balls were employed together with a 140 ml hardened steel bowl. The ball-to-powder weight ratio was 50:1. The whole process of sample mixing and loading was carried out inside an argon-filled glovebox (mBraun, UniLab), where oxygen and water vapor levels were kept below 1 ppm.

The dehydrogenation of the 4LiBH₄ + YH₃ composite under either hydrogen (99.9999 %) or argon (99.9999 %) back pressure was carried out using a Sievert-type volumetric apparatus. 0.3 g of the composite in a 110 ml reactor was dehydrogenated at 350 °C for 20 hours (heating rate = 30 °C/min), monitoring the pressure in the reactor.

High pressure differential scanning calorimetry (HP-DSC) measurements of the composite were performed in a Netzsch DSC 204 HP at 0.3, 0.4 and 0.5 MPa of 99.9999% hydrogen. 2 mg of the composite sample in an aluminum crucible was loaded into a chamber together with an empty reference aluminum crucible. The crucible was heated to 400 °C with a rate of 40 °C/min and then maintained at 400 °C for 200 minutes.

XRD measurements of the ball milled and dehydrogenated samples were performed using a Bruker D8 Advance X-ray diffractometer with Cu K α radiation. In order to prevent air exposure of the samples, borosilicate capillary tubes were used during the measurements.

Raman spectroscopy was performed at room temperature using a Horiba Jobin-Yvon LabRam ARAMIS with a 514 nm Ar-ion laser. The samples were prepared by using a Sievert-type apparatus as described above. 0.3 g of the composite was dehydrogenated at 400 °C for an hour (heating rate = 30 °C/min) under static vacuum and various hydrogen and argon back pressures. Subsequently, the samples were cooled down to room temperature within a few minutes. During the measurements, the samples were inevitably exposed to air.

Supporting results:

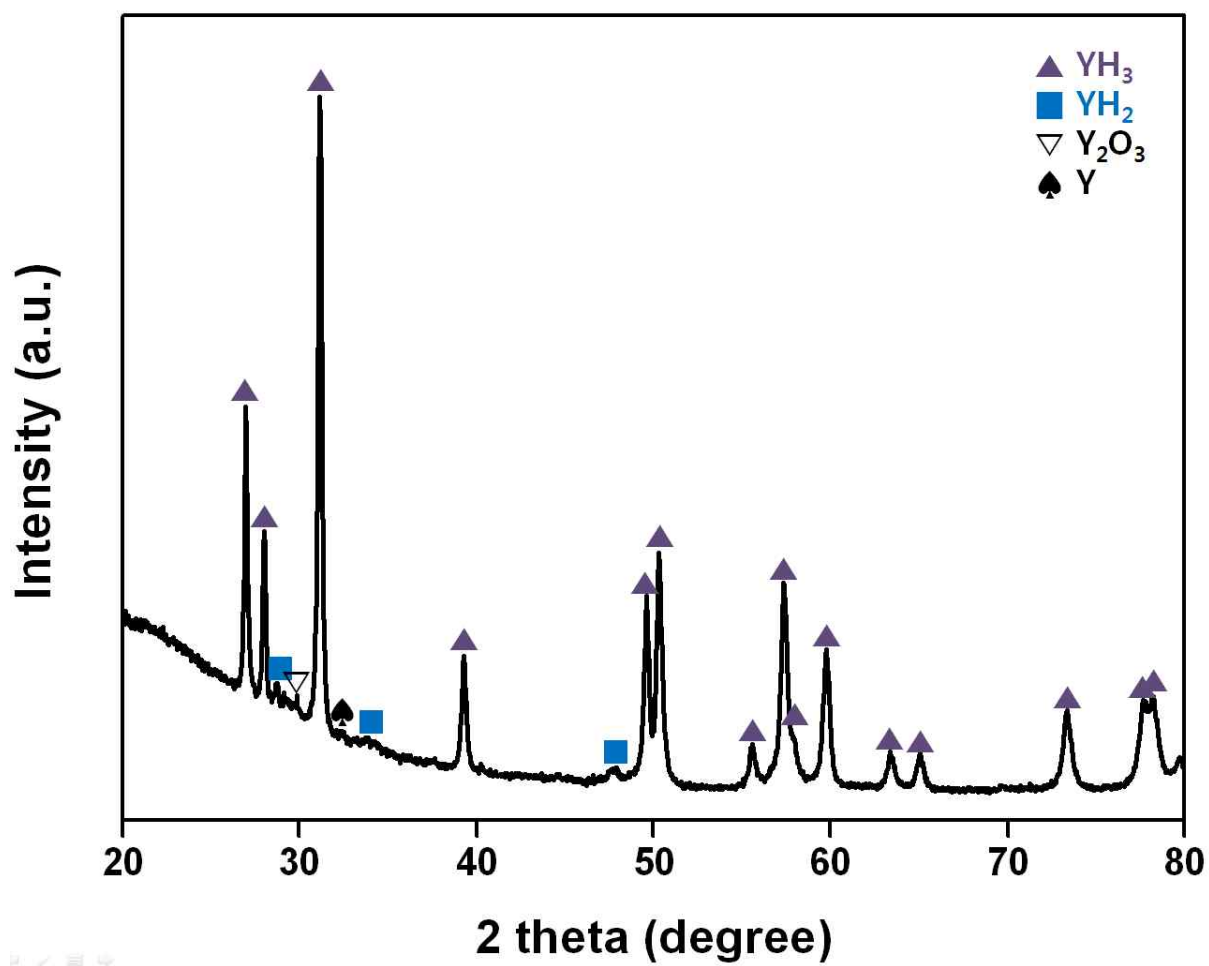


Fig. S1 XRD pattern of YH_3 synthesized at 350 °C for 2 hours under 9 MPa of hydrogen.

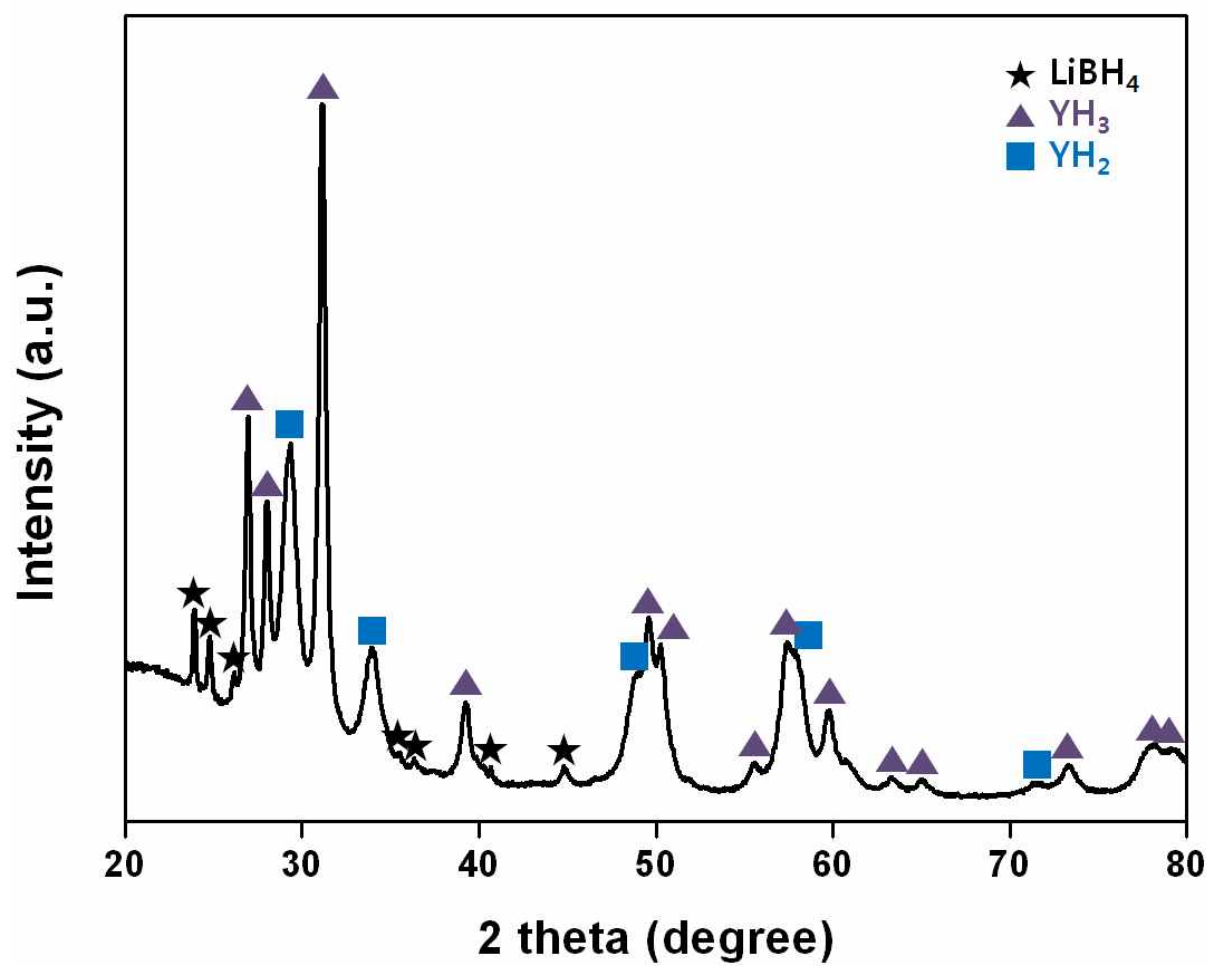


Fig. S2 XRD pattern of $4\text{LiBH}_4 + \text{YH}_3$ composite prepared by ball milling.

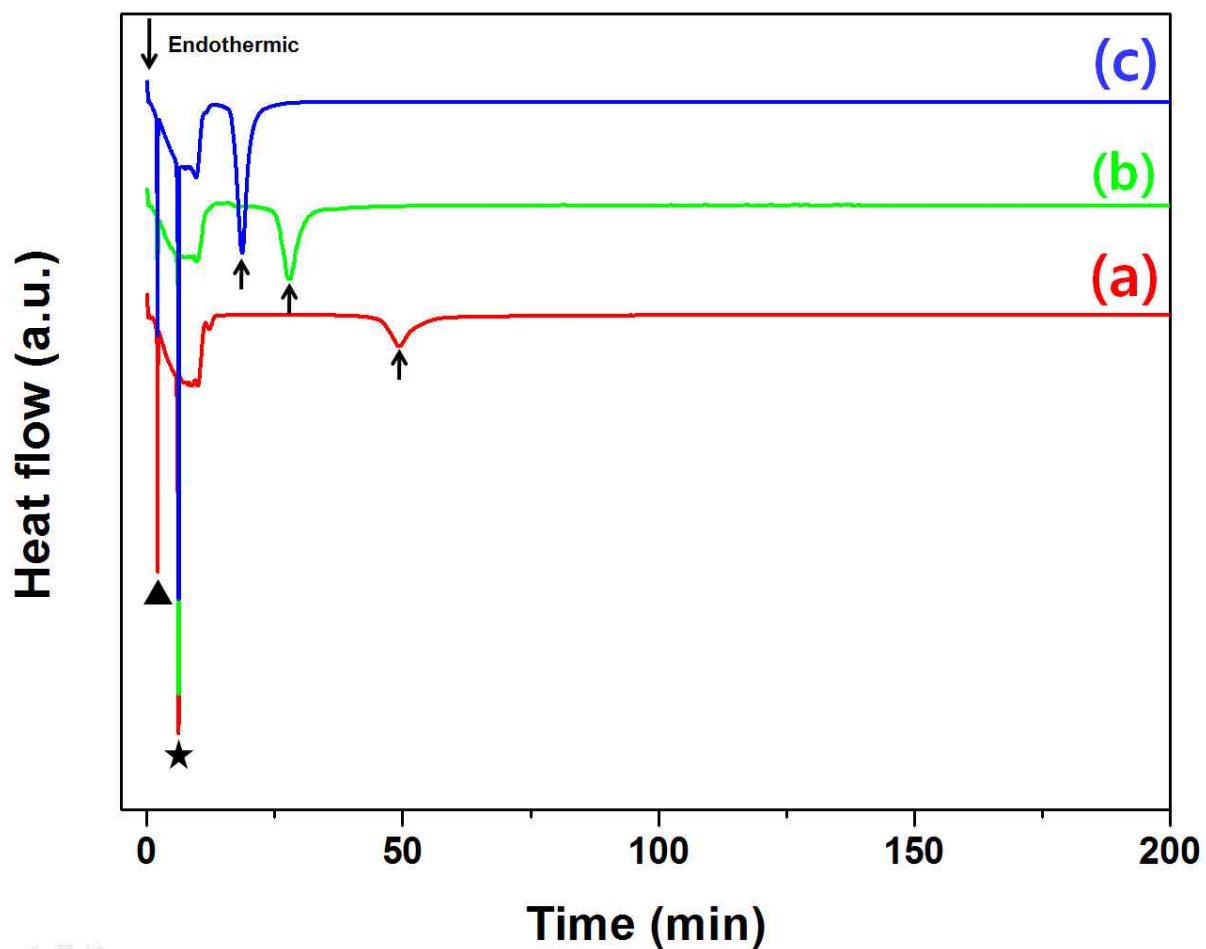


Fig. S3 HP-DSC curves of $4\text{LiBH}_4 + \text{YH}_3$ composite dehydrogenated under (a) 0.3, (b) 0.4 and (c) 0.5 MPa of hydrogen. The crucible was heated to $400\text{ }^\circ\text{C}$ with a rate of $40\text{ }^\circ\text{C}/\text{min}$ and then maintained at $400\text{ }^\circ\text{C}$ for 200 minutes. The symbol triangle, star and arrows indicate the phase transformation of LiBH_4 (orthorhombic to hexagonal), melting of LiBH_4 and the dehydrogenation of $\text{LiBH}_4 + \text{YH}_3$ composite, respectively.

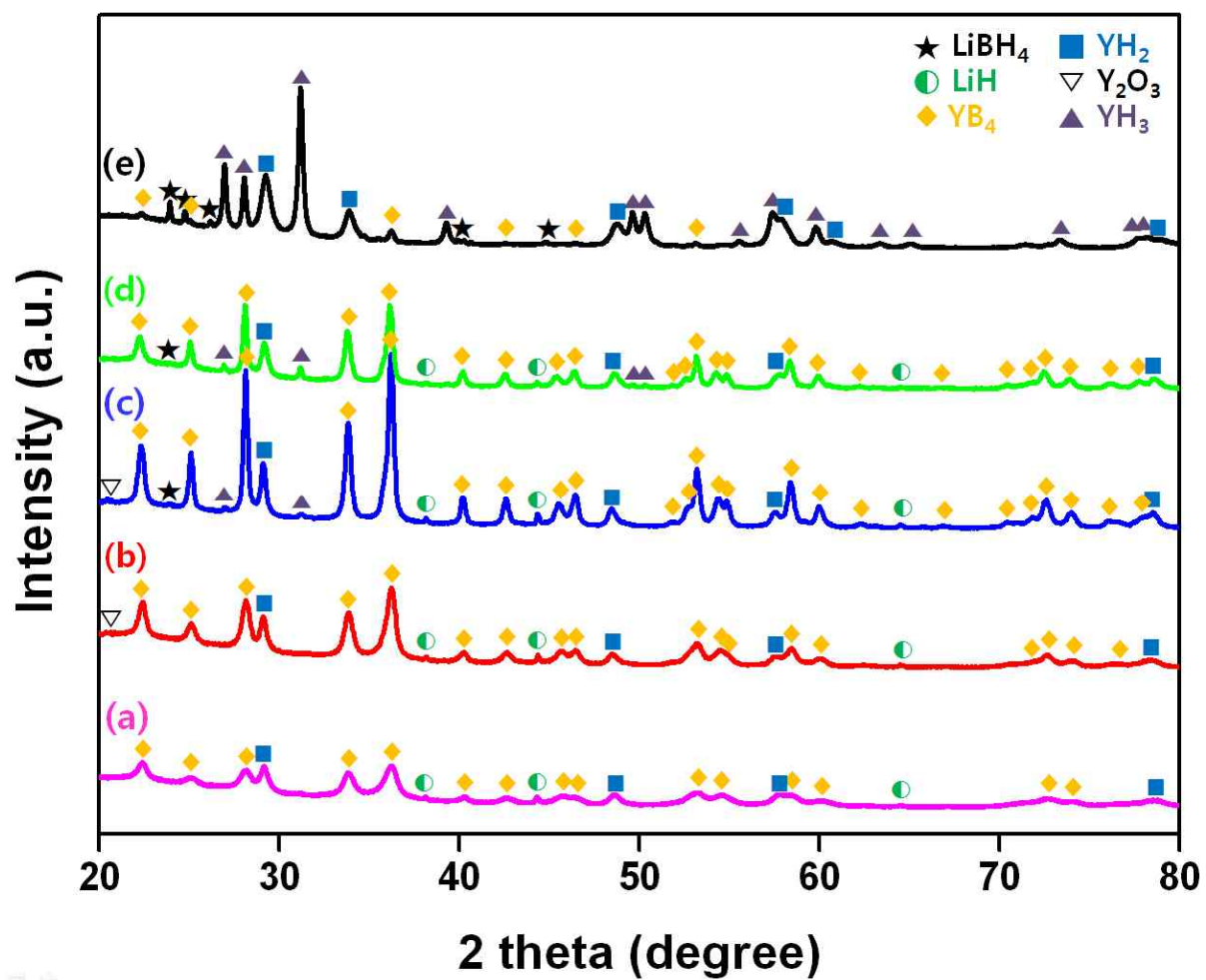


Fig. S4 XRD patterns of $4\text{LiBH}_4 + \text{YH}_3$ composite dehydrogenated under (a) 0.1, (b) 0.2, (c) 0.5, (d) 0.7 and (e) 1.0 MPa of hydrogen.

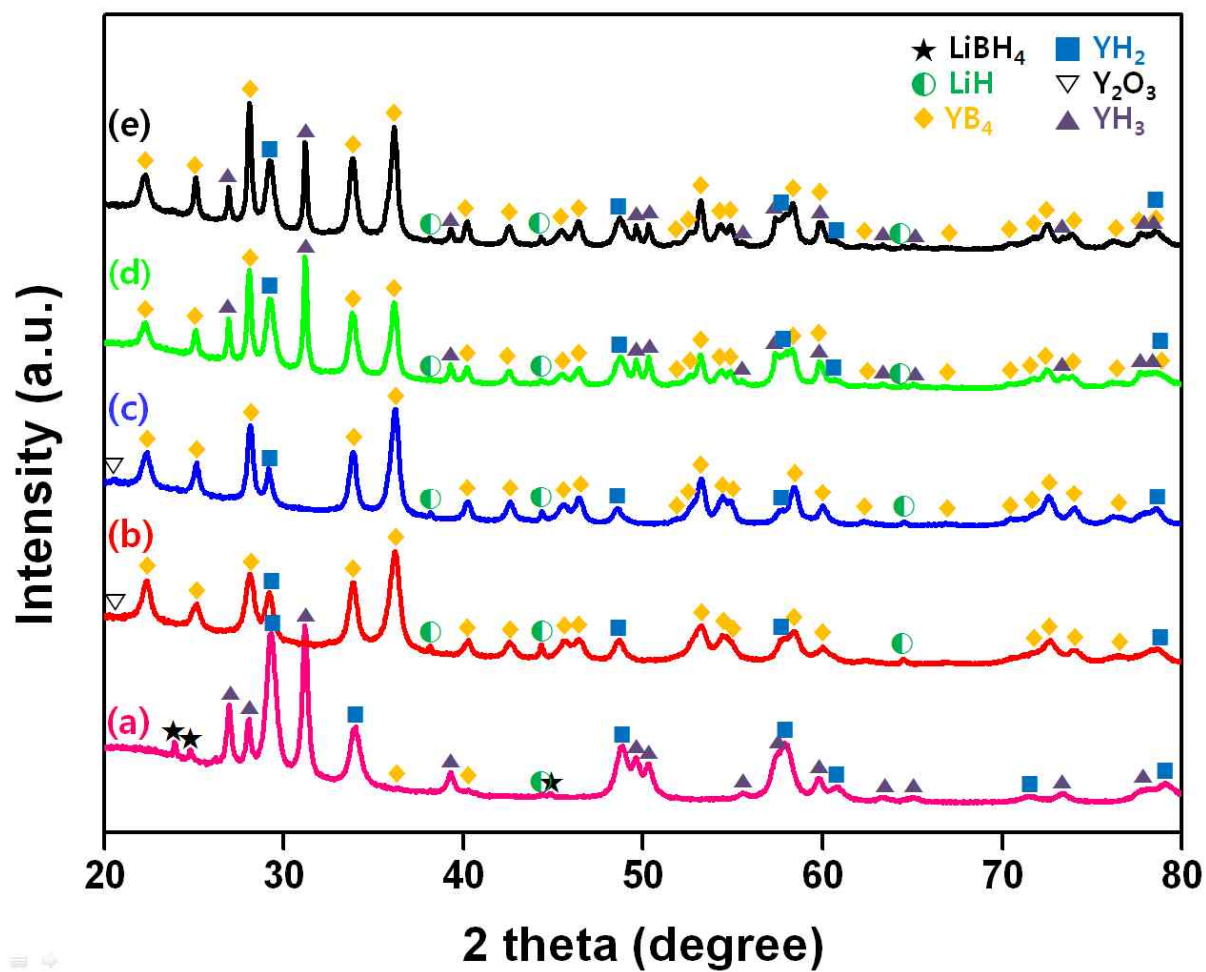


Fig. S5 XRD patterns of $4\text{LiBH}_4 + \text{YH}_3$ composite dehydrogenated under (a) 0.1, (b) 0.2, (c) 0.5, (d) 0.7 and (e) 1.0 MPa of argon.

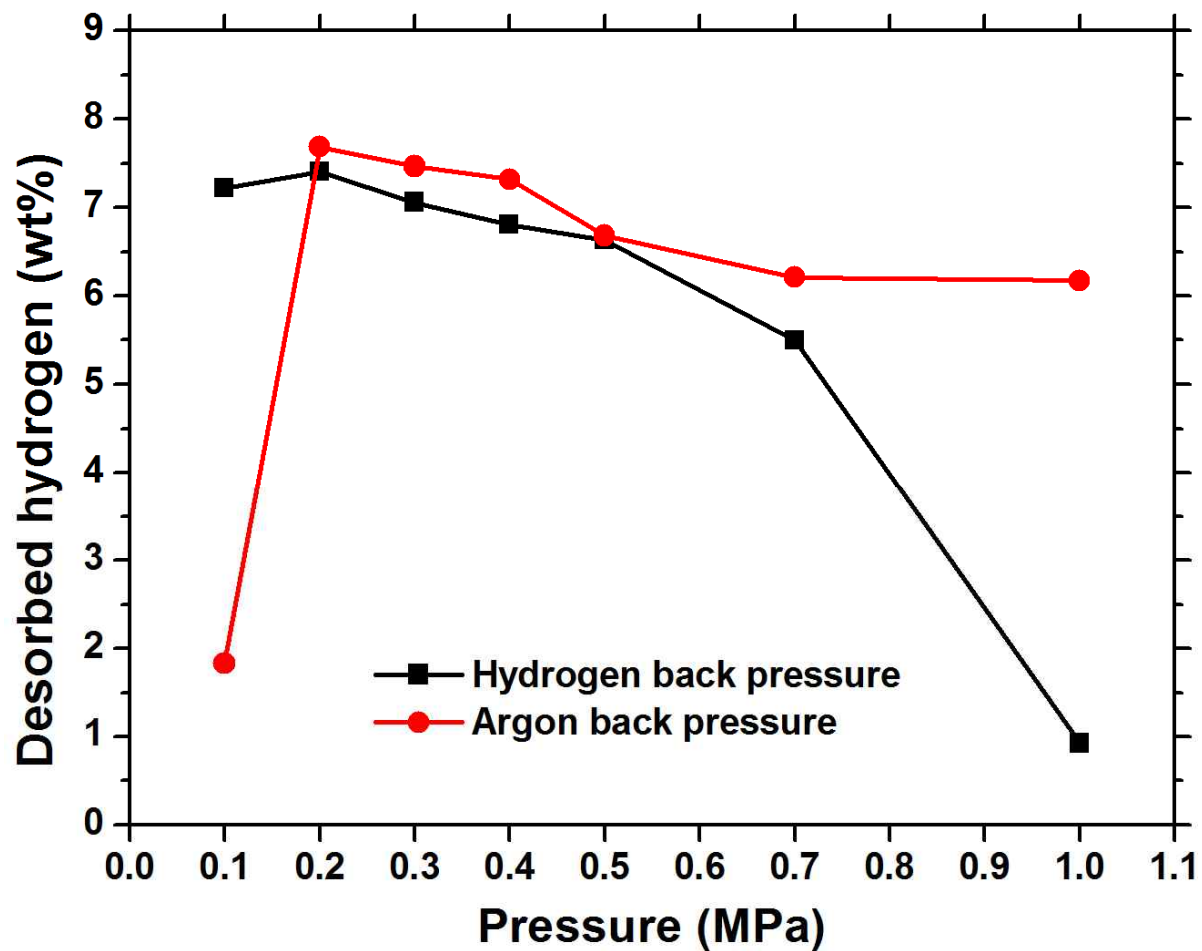


Fig. S6 The amount of desorbed hydrogen of $4\text{LiBH}_4+\text{YH}_3$ composite under (a) hydrogen and (b) argon back pressures.