

Supplemental Information

for

Electrolyte-Assisted Hydrogen Storage Reactions

John J. Vajo^{1}, Hongjin Tan^{2**}, Channing C. Ahn^{2,3}, Dan Addison², Son-Jong Hwang⁴,*

Vitalie Stavila⁵, James L. White⁵, Timothy C. Wang⁵, Jason Graetz¹

- 1) HRL Laboratories, LLC, 3011 Malibu Canyon Road, Malibu, CA 90265
- 2) Liox Power, Inc., 129 North Hill Ave., Suite 107, Pasadena, CA 91106
- 3) Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125
- 4) Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125
- 5) Sandia National Laboratories, P.O. Box 969, Livermore, CA, 94551

Experimental Methods

All sample handling was performed in argon-filled glove boxes with <1 ppm H₂O and O₂ concentrations.

MgH₂ (98%) was obtained from Alfa Aesar. Sn (99.8%, -325 mesh), LiBH₄ (>95%), KBH₄ (99.9%), MgI₂ (98%), MgB₂ (>99%, -100 mesh), LiI (99.9%), KI (99.99%), CsI (99.99%), and Mg(BH₄)₂ (95%) were obtained from Sigma-Aldrich.

Mechanical milling was performed using a Fritsch Pulversette 6 planetary mill in an 80 cm³ hardened steel vessel with 30 yttria stabilized zirconia milling balls 6.5 mm diameter from Inframat Advanced Materials. For MgH₂/Sn, a mixture of 1.228 g MgH₂ and 2.824 g Sn (2MgH₂/Sn molar ratio) was milled for 15 min at 400 rpm. For MgB₂, ~2.5 g was milled for 2 h at 400 rpm.

Eutectics were characterized by differential scanning calorimetry (DSC) using a TA Instruments Q2000 DSC. The ramp rate was 5 °C/min.

The 0.725LiBH₄/0.275KBH₄ eutectic was prepared in-situ during dehydrogenation by first hand grinding appropriate amounts of LiBH₄ and KBH₄ until a uniform consistency was obtained. Then the desired amount of this mixture (without first melting) was lightly mixed using a spatula with the hydride mixture. Thermal cycling up to 300 °C in the DSC confirmed reproducible melting of the 0.725LiBH₄/0.275KBH₄ mixture at 110 °C to 120 °C and solidification at 90 °C (Figure S1). The 0.33LiI/0.33KI/0.33CsI eutectic was initially fully formed by thermal cycling up to 300 °C before mixing with the hydrides. This initial cycling was done to remove any absorbed water from the iodide salts. This eutectic was seen to melt at ~210 °C and solidify at ~200 °C (Figure S7). Solidified chunks of the eutectic were crushed by hand grinding to a coarse powder before lightly mixing with the milled MgB₂.

Dehydrogenation experiments were carried out in home-built Sieverts apparatus described previously (Ref 29, main text). Mixtures containing ~0.5 g of MgH₂/Sn and ~0.2 g of hydrogen treated MgB₂ were used. Samples were heated to desired isothermal temperatures at 2 °C/min. Dehydrogenation experiments with MgH₂/Sn or MgH₂/Sn with the 0.725LiBH₄/0.275KBH₄ eutectic were performed in an initial hydrogen pressure of 2 bar. This was done to prevent direct dehydrogenation of MgH₂ (T_{eq}(MgH₂, 2 bar) = 300 °C) and to suppress any possible decomposition of the 0.725LiBH₄/0.275KBH₄ eutectic. The amount of desorbed hydrogen is reported as wt%, with respect to the mass of the hydride (MgH₂+Sn or MgB₂) only (i.e., not including the mass of any eutectic).

High pressure hydrogenation was conducted in a custom-built system utilizing Hi-Pressure and Autoclave components. Samples were loaded into individual holders which had porous frits held in place by retaining rings to allow gas transport; these were then sealed into a Hi-P pressure vessel inside a glovebox. Hydrogen was pressurized below 1000 bar initially so that the pressure would not exceed that level upon heating to the desired temperature. Occasional refills were necessary due to minor leaks in the pressure vessel.

Powder X-ray diffraction was performed using a Rigaku Oxford Diffraction SuperNova with Cu K α radiation. Samples were loaded into 0.7 mm quartz capillaries (Charles Supper) inside an argon-filled glovebox and sealed with wax before transfer to the instrument.

Magic angle spinning ^{11}B solid-state NMR was conducted using a Bruker DSX-500 MHz spectrometer and a 4 mm Bruker magic angle spinning (MAS) probe. Powder samples were packed into 4 mm zirconia rotors inside of an Ar filled glove box, and spun at 14-15 kHz using dry N_2 gas. Small tip angle ($0.5 \mu\text{s}-\pi/12$ rf pulse at operating frequency of 160.5 MHz for ^{11}B nucleus) was applied to record ^{11}B free induction signal with strong ^1H decoupling pulse. ^{11}B spectra were reported in ppm after external calibration to signal of $\text{BF}_3(\text{OCH}_2\text{CH}_3)$ at 0 ppm.

Other potential electrolytes investigated

Preliminary experiments with milled MgH_2/Sn were conducted with several other potential electrolytes. The results of those measurements are briefly summarized:

- 1) 1-ethyl-1-methylpyridinium tetrafluoroborate ($T_m \sim 60^\circ\text{C}$): appeared to show some decomposition.
- 2) Sodium tetraethylborate ($T_m \sim 141^\circ\text{C}$): appeared to decompose.
- 3) Triethylphosphine oxide ($T_m \sim 50^\circ\text{C}$): appeared to decompose.
- 4) Hexamethylphosphoramide ($T_m 7^\circ\text{C}$): appeared to decompose.
- 5) Tetrabutylammonium bromide ($T_m \sim 105^\circ\text{C}$): appeared to decompose.
- 6) Tris(dimethylamino)phosphine + 0.04MgI_2 : maybe some decomposition, however, similar dehydrogenation rate at 175°C compared to no electrolyte.
- 7) $0.33\text{Li}/0.33\text{K}/0.33\text{CsTFSI}$ (TFSI = bis(trifluoromethanesulfonyl)imide) eutectic: little or no decomposition at 200°C , however, appeared slower dehydrogenation rate.
- 8) $0.60\text{LiTFSI}/0.40\text{KOTf}$ (OTf = trifluoromethanesulfonate) eutectic: little or no decomposition at 200°C , however, appeared slower dehydrogenation rate.

Dehydrogenation rates for MgH_2/Sn from Figure 1 (wt% - H_2 /hr)

	150 $^\circ\text{C}$	175 $^\circ\text{C}$	200 $^\circ\text{C}$
Control (no electrolyte) 0.510 g (MgH_2/Sn)	0.0008	0.01	0.07
With Li/ KBH_4 eutectic 0.499 g (MgH_2/Sn) + 0.486 g (Li/ KBH_4)	0.01	0.05	0.23
With Li/ KBH_4 eutectic + MgI_2 0.499 (MgH_2/Sn) + 0.498 g (Li/ KBH_4) + 0.125 g MgI_2	0.02	0.07	

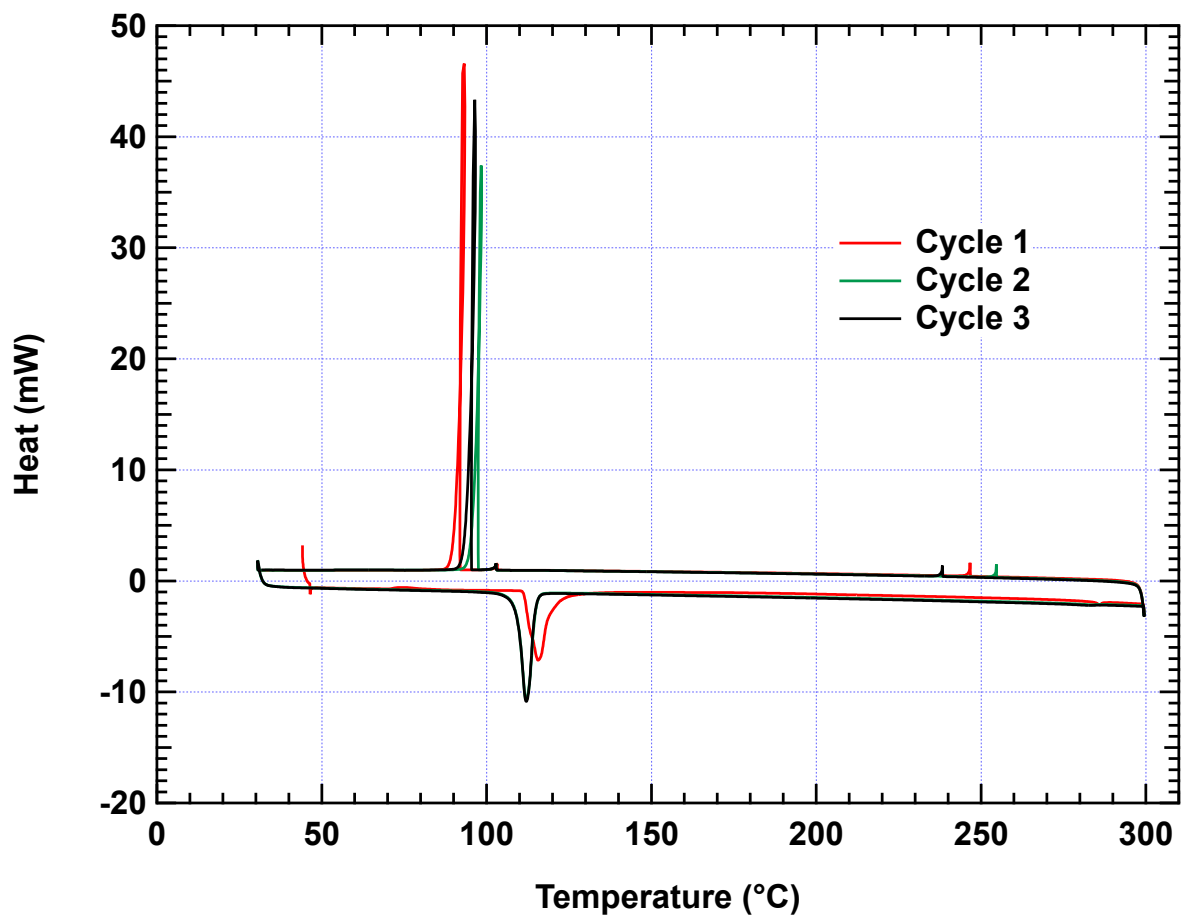


Figure S1. DSC trace of the $0.725\text{LiBH}_4/0.275\text{KBH}_4$ eutectic electrolyte. The heating rate is $5\text{ }^\circ\text{C}/\text{min}$. Three cycles are shown. The melting point is $110\text{ }^\circ\text{C}$ to $120\text{ }^\circ\text{C}$. Solidification occurs at $100\text{ }^\circ\text{C}$ to $90\text{ }^\circ\text{C}$.

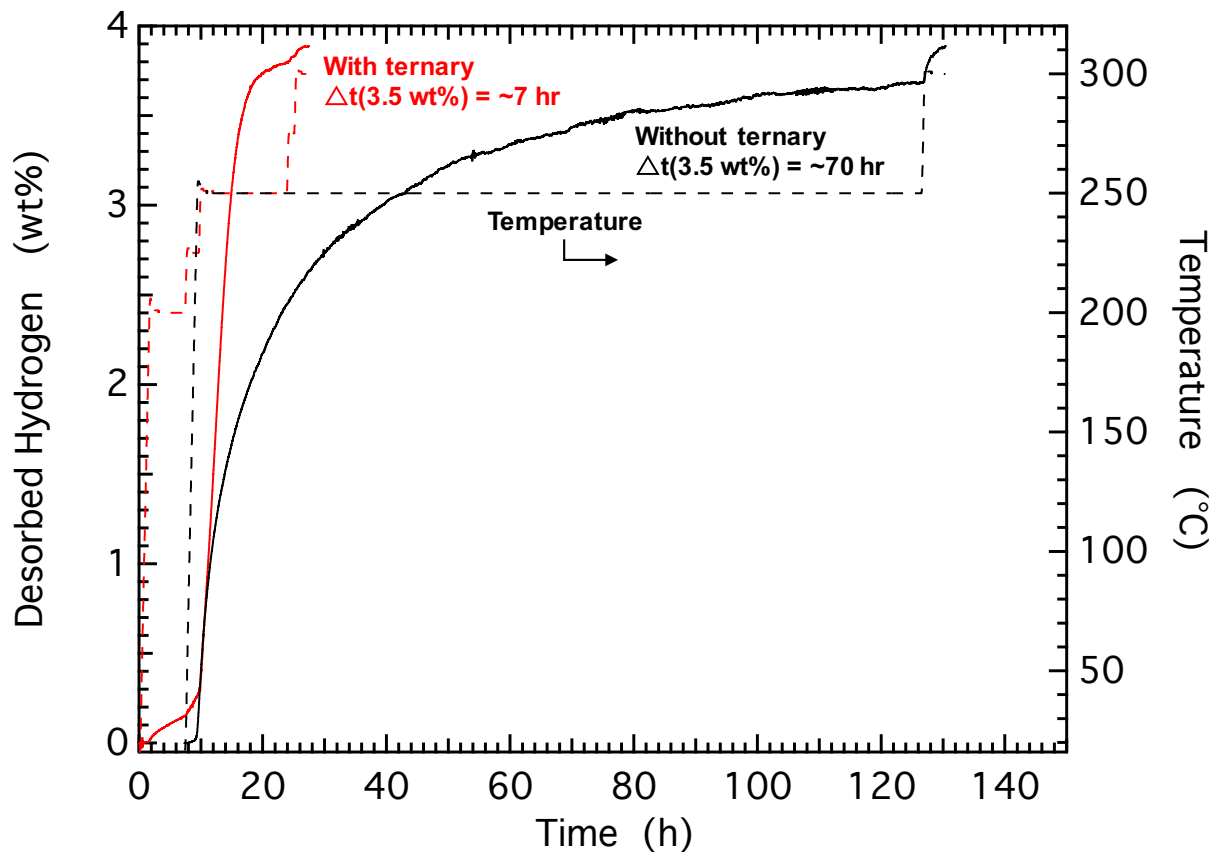


Figure S2. Dehydrogenation of $2\text{MgH}_2 + \text{Si}$. (red) A mixture of 0.151 g milled ($2\text{MgH}_2 + \text{Si}$) with 0.770 g of 0.33LiI/0.33KI/0.33CsI eutectic electrolyte; (black) 0.165 g of ($2\text{MgH}_2 + \text{Si}$) without added electrolyte. After heating to 250 °C, the initial rates of hydrogen evolution are similar (see similar slopes at 10 h). With electrolyte, the initial rate is sustained, while without electrolyte the rate continuously decreases. Without electrolyte, dehydrogenation to 3.5 wt% takes ~70 h compared to ~7 h with electrolyte.

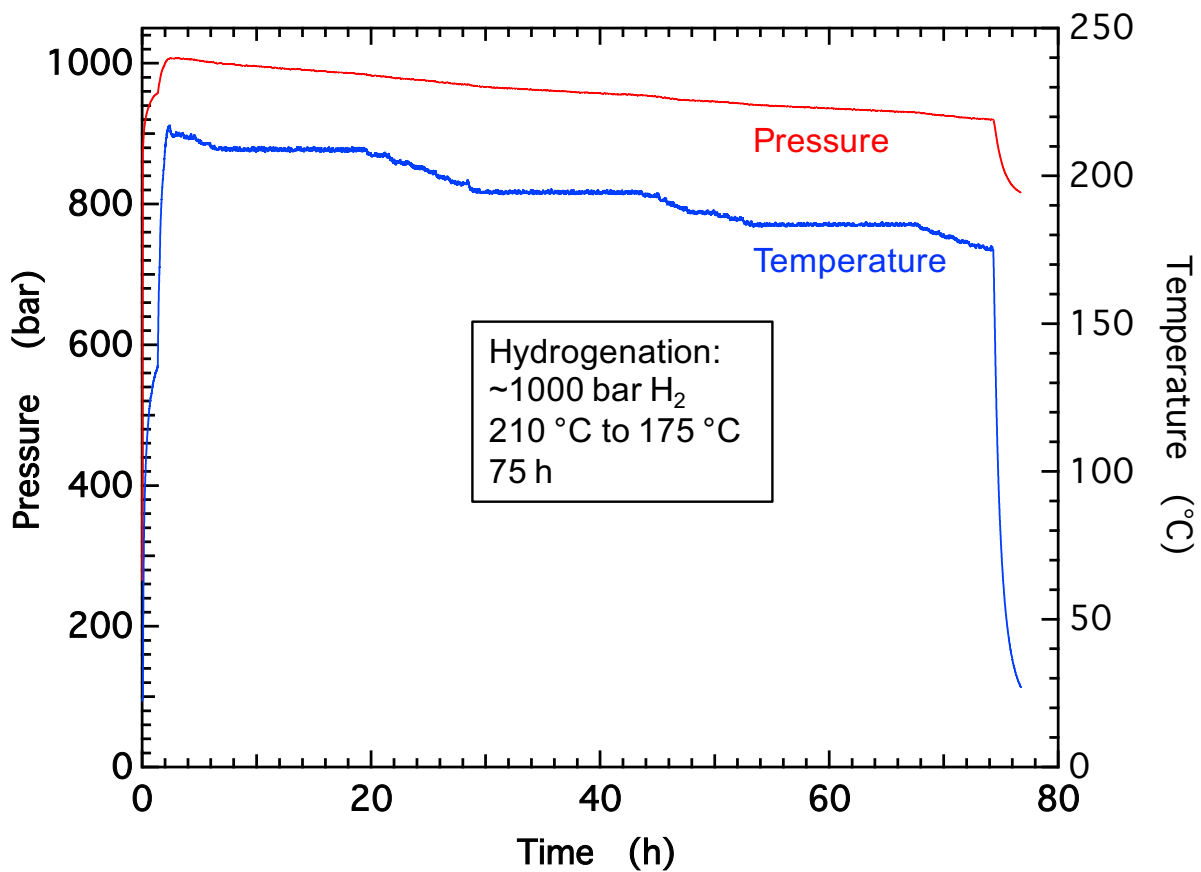


Figure S3. High pressure hydrogen treatment of MgH₂/Sn. Samples with and without the 0.725LiBH₄/0.275KBH₄ eutectic electrolyte (Figure S1) previously dehydrogenated were treated in hydrogen simultaneously. (blue, left axis) Pressure, (gray, right axis) temperature. The decreasing pressure is likely due to a leak, not hydrogen uptake. Nevertheless, a pressure about 900 bar was maintained while the temperature was cooled from 210 °C to 175 °C, over 75 h.

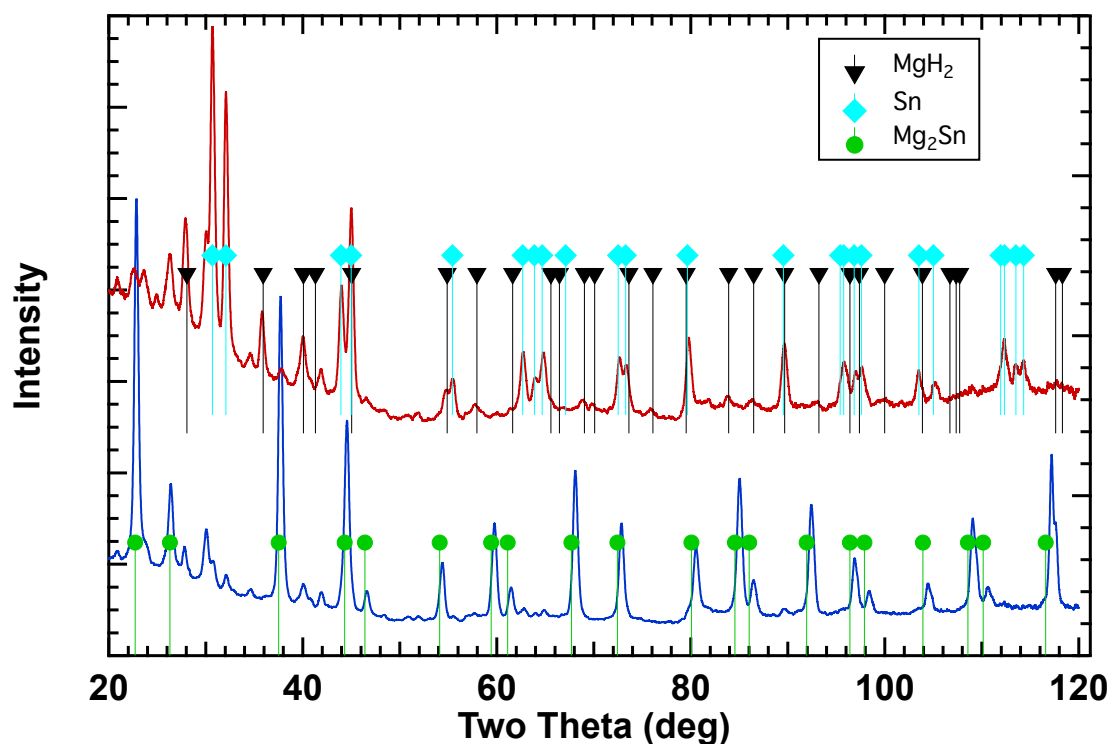


Figure S4. Powder XRD patterns showing Mg_2Sn hydrogenation with $0.725\text{LiBH}_4/0.275\text{KBH}_4$ eutectic electrolyte. (blue) After dehydrogenation of MgH_2/Sn with $0.725\text{LiBH}_4/0.275\text{KBH}_4$. The major peaks correspond to Mg_2Sn . (red) After dehydrogenation and high-pressure hydrogen treatment (Figure S3). Peaks for Mg_2Sn decrease or disappear while those for MgH_2 and Sn grow, showing for the first time reversible hydrogenation of Mg_2Sn , enabled by an electrolyte. Standard patterns shown correspond to pdf 01-078-4486 for MgH_2 , pdf 04-004-7744 for Sn, and pdf 01-073-2885 for Mg_2Sn . No peaks clearly from LiBH_4 , KBH_4 , or $\text{Mg}(\text{BH}_4)_2$ are seen.

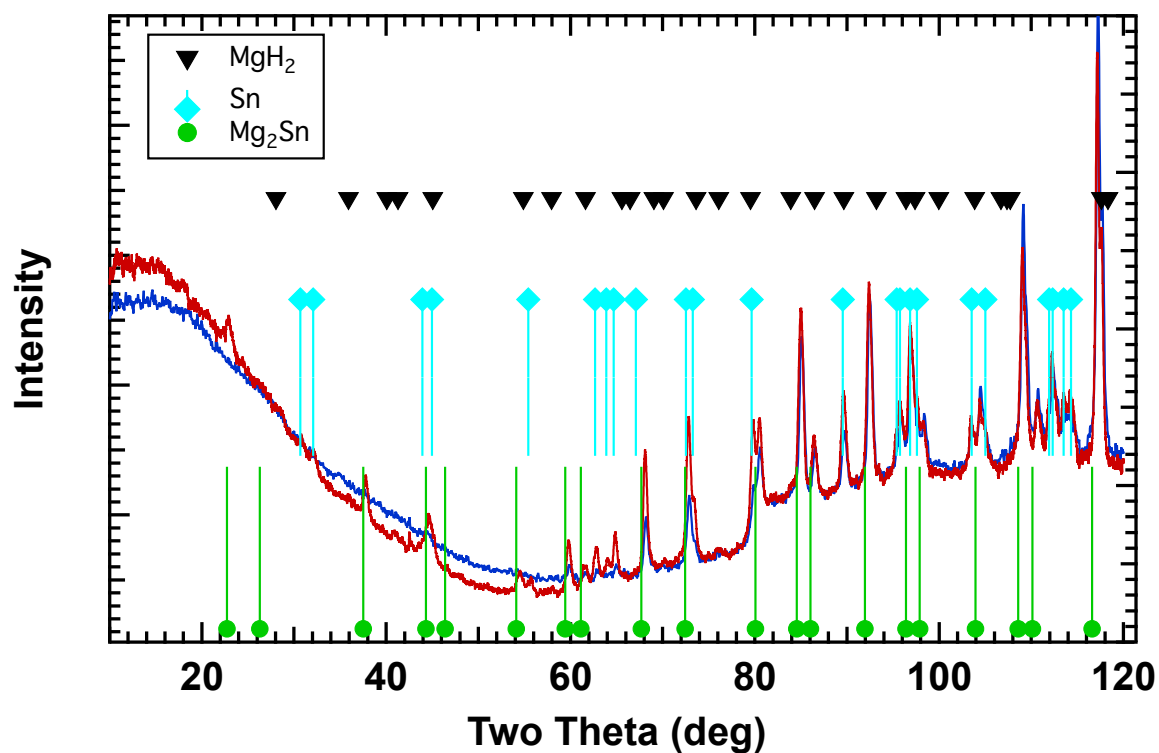


Figure S5. Powder XRD patterns showing no hydrogenation of Mg₂Sn without electrolyte. (blue) After dehydrogenation, (red) after subsequent hydrogen treatment (Figure S3) performed concurrently with the sample shown in Figure S4. After dehydrogenation, the diffraction pattern shows a mixture of Mg₂Sn together with unreacted Sn. Following hydrogen treatment, the pattern is nearly identical indicating little or no rehydrogenation. The patterns are nearly overlapped to highlight the close correspondence. Note: a misalignment during acquisition of these patterns “washed-out” peaks below $\sim 60^\circ 2\theta$. Nevertheless, the result that the two patterns are nearly identical is unaffected. Standard patterns shown correspond to pdf 01-078-4486 for MgH₂, pdf 04-004-7744 for Sn, and pdf 01-073-2885 for Mg₂Sn.

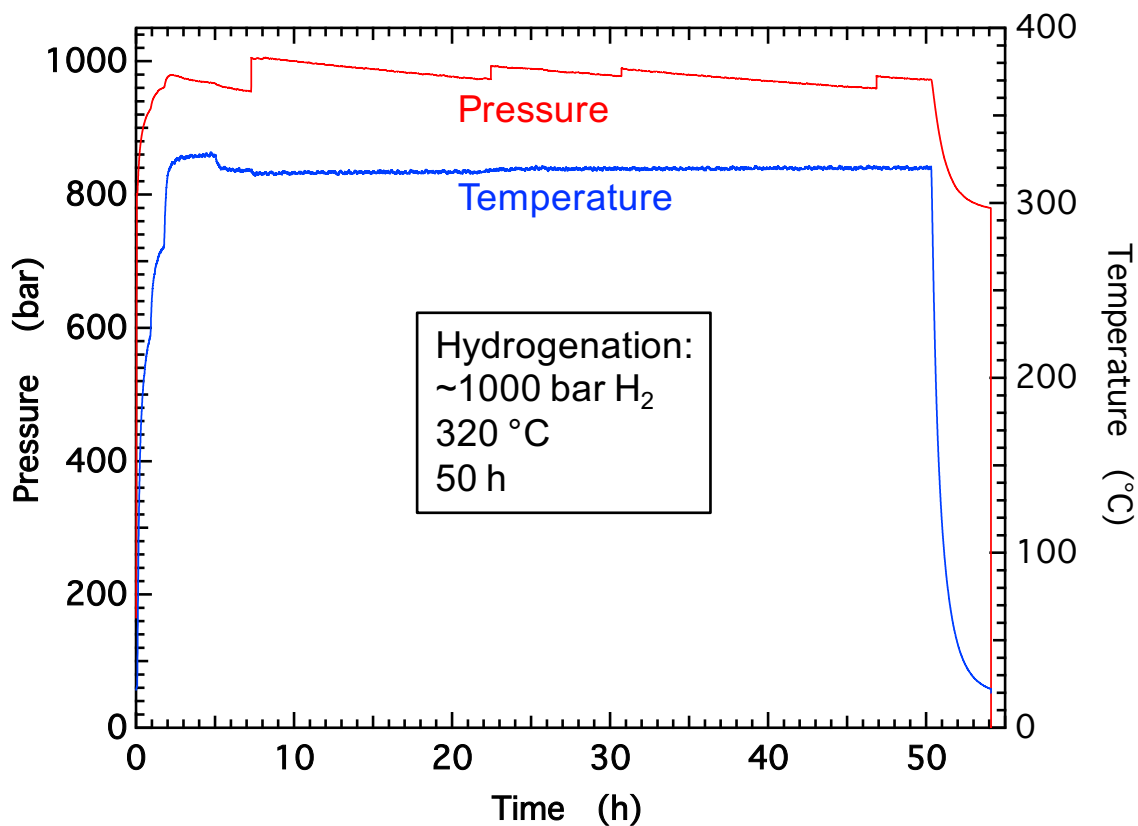


Figure S6. High pressure hydrogen treatment of MgB_2 . Samples with the $0.725\text{LiBH}_4/0.275\text{KBH}_4$ and $0.33\text{LiI}/0.33\text{KI}/0.33\text{CsI}$ eutectic electrolytes and without electrolyte were treated simultaneously in hydrogen. (red) Pressure, (blue) temperature. To compensate for leaks and maintain the pressure at ~ 1000 bar hydrogen was added at ~ 7 h, 22 h, 31 h and 47 h.

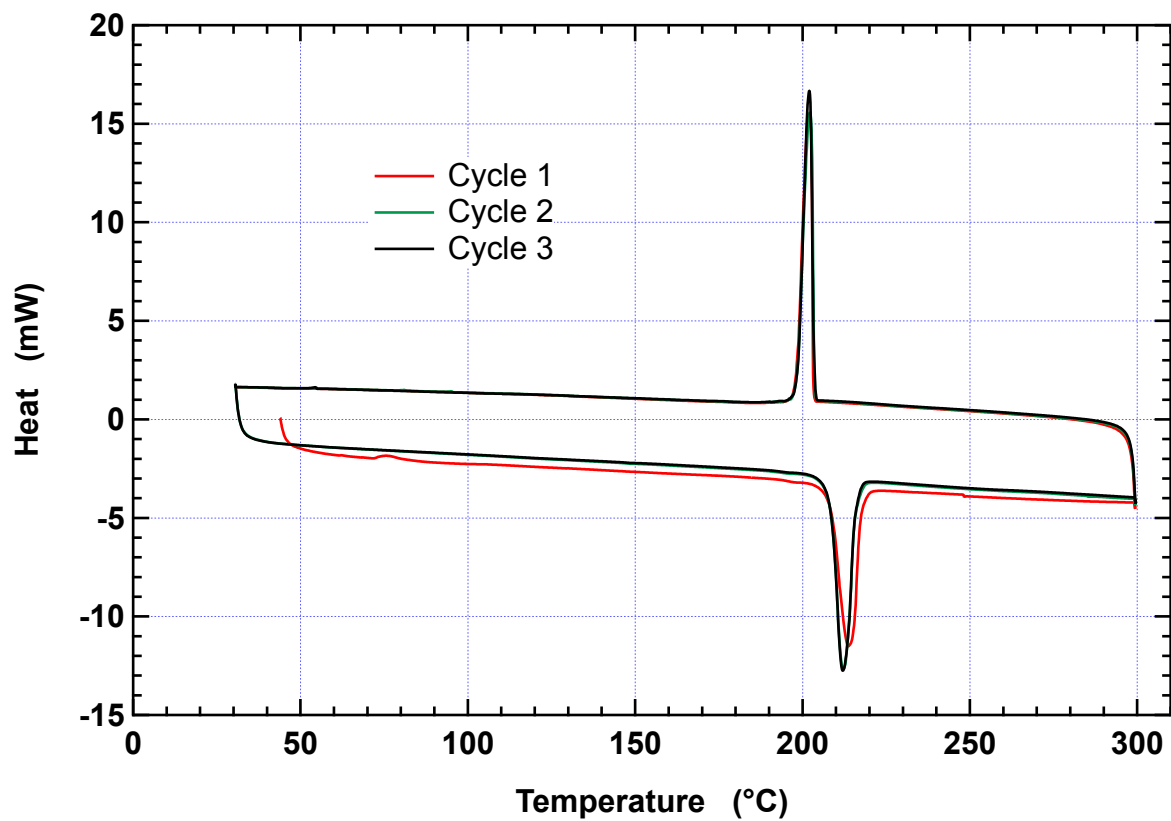


Figure S7. DSC trace of the 0.33LiI/0.33KI/0.33CsI eutectic electrolyte. LiI, KI, CsI were mixed and dried at 300 °C under vacuum for 20 h. Aluminum DSC pan was sealed in a glove box. The heating rate is 5 °C/min. Two cycles are shown. The melting point is ~210 °C. Solidification occurs at 200 °C.

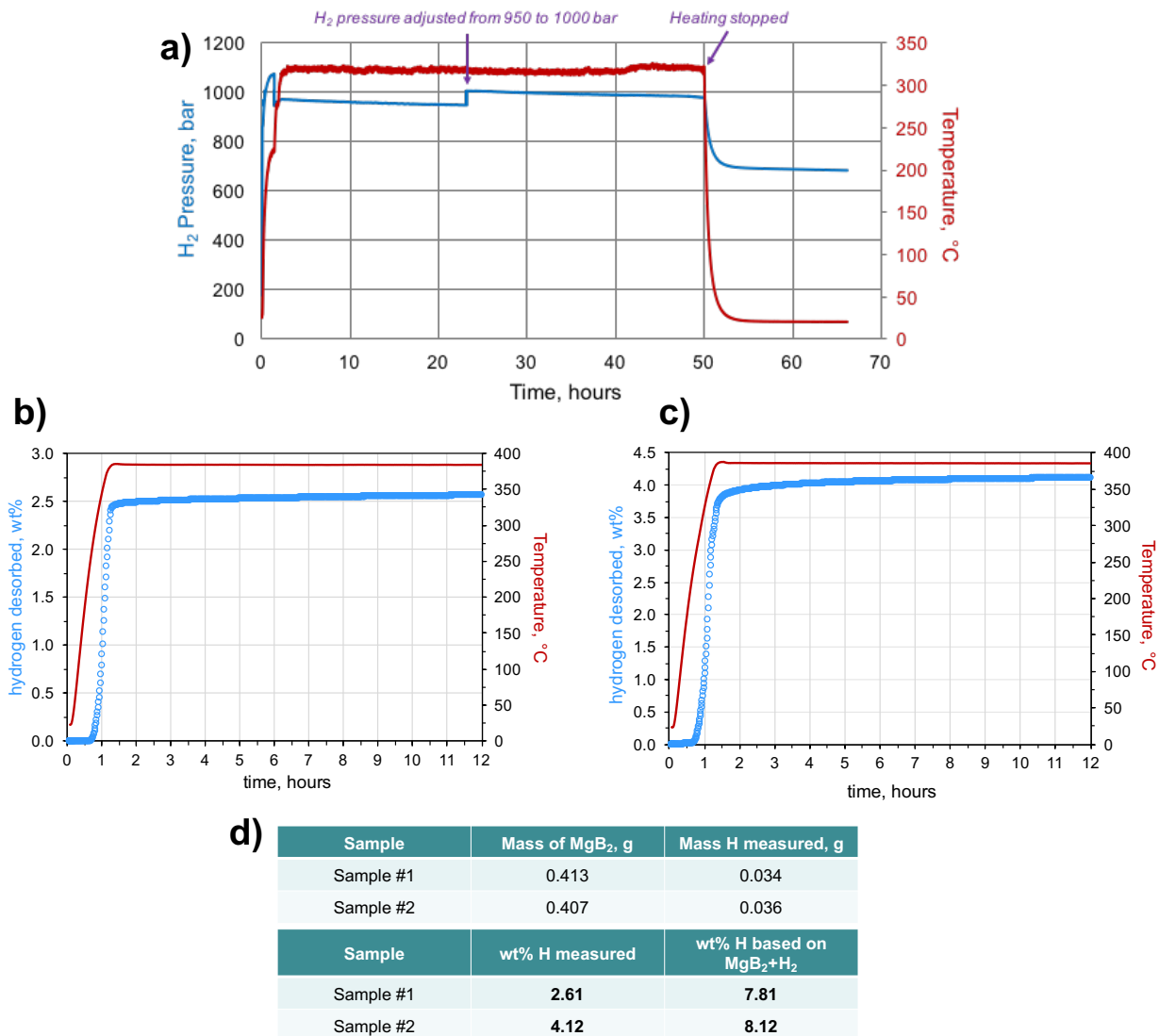


Figure S8. Additional MgB₂ hydrogenation results. Two samples were run. Sample #1 was 0.413 g milled MgB₂ + 0.911 g 0.33LiI/0.33KI/0.33CsI eutectic. This sample contained 31wt% MgB₂. Sample #2 contained ~1/2 the amount of eutectic, thus 47 wt% MgB₂. It was 0.407 g milled MgB₂ + 0.461 g 0.33LiI/0.33KI/0.33CsI eutectic (47% MgB₂). (a) High pressure hydrogen treatment showing pressure (blue) and temperature (red). (b) Dehydrogenation at 380 °C of sample #1 following hydrogen treatment; (blue) hydrogen desorbed with respect to the full sample mass; (red) temperature. (c) Dehydrogenation at 380 °C of sample #2 following hydrogen treatment; (blue) hydrogen desorbed with respect to the full sample mass; (red) temperature. (d) Summary of results indicating ~ 8 wt% hydrogen for both samples (ignoring the weight of the eutectic).