Supplemental Information

for

Electrolyte-Assisted Hydrogen Storage Reactions

John J. Vajo¹*, Hongjin Tan²**, Channing C. Ahn²-³, 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 H$_2$O and O$_2$ concentrations.

MgH$_2$ (98%) was obtained from Alfa Aesar. Sn (99.8%, -325 mesh), LiBH$_4$ (>95%), KBH$_4$ (99.9%), MgI$_2$ (98%), MgB$_2$ (>99%, -100 mesh), LiI (99.9%), KI (99.99%), CsI (99.99%), and Mg(BH$_4$)$_2$ (95%) were obtained from Sigma-Aldrich.

Mechanical milling was performed using a Fritsch Pulversette 6 planetary mill in an 80 cm$^3$ hardened steel vessel with 30 yttria stabilized zirconia milling balls 6.5 mm diameter from Inframat Advanced Materials. For MgH$_2$/Sn, a mixture of 1.228 g MgH$_2$ and 2.824 g Sn (2MgH$_2$/Sn molar ratio) was milled for 15 min at 400 rpm. For MgB$_2$, ~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 0.725LiBH$_4$/0.275KBH$_4$ eutectic was prepared in-situ during dehydrogenation by first hand grinding appropriate amounts of LiBH$_4$ and KBH$_4$ 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 0.725LiBH$_4$/0.275KBH$_4$ mixture at 110 °C to 120 °C and solidification at 90 °C (Figure S1). The 0.33LiI/0.33KI/0.33CsI eutectic was initially 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 MgB$_2$.

Dehydrogenation experiments were carried out in home-built Sieverts apparatus described previously (Ref 29, main text). Mixtures containing ~0.5 g of MgH$_2$/Sn and ~0.2 g of hydrogen treated MgB$_2$ were used. Samples were heated to desired isothermal temperatures at 2 °C/min. Dehydrogenation experiments with MgH$_2$/Sn or MgH$_2$/Sn with the 0.725LiBH$_4$/0.275KBH$_4$ eutectic were performed in an initial hydrogen pressure of 2 bar. This was done to prevent direct dehydrogenation of MgH$_2$ ($T_{eq}$(MgH$_2$, 2 bar) = 300 °C) and to suppress any possible decomposition of the 0.725LiBH$_4$/0.275KBH$_4$ eutectic. The amount of desorbed hydrogen is reported as wt%, with respect to the mass of the hydride (MgH$_2$+Sn or MgB$_2$) 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 Kα 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 ¹¹B 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 N₂ gas. Small tip angle (0.5 μs-π/12 rf pulse at operating frequency of 160.5 MHz for ¹¹B nucleus) was applied to record ¹¹B free induction signal with strong ¹H decoupling pulse. ¹¹B spectra were reported in ppm after external calibration to signal of BF₃(OCH₂CH₃) at 0 ppm.

**Other potential electrolytes investigated**

Preliminary experiments with milled MgH₂/Sn were conducted with several other potential electrolytes. The results of those measurements are briefly summarized:

1) 1-ethyl-1-methylpyridinium tetrafluoroborate (Tₘ ~60 °C): appeared to show some decomposition.

2) Sodium tetraethylborate (Tₘ ~141 °C): appeared to decompose.

3) Triethylphosphine oxide (Tₘ ~50 °C): appeared to decompose.

4) Hexamethylphosphoramide (Tₘ 7 °C): appeared to decompose.

5) Tetrabutylammonium bromide (Tₘ ~105 °C): appeared to decompose.

6) Tris(dimethylamino)phosphine + 0.04MgI₂: maybe some decomposition, however, similar dehydrogenation rate at 175 °C compared to no electrolyte.

7) 0.33Li/0.33K/0.33CsTFSI (TFSI = bis(trifluoromethanesulfonyl)imide) eutectic: little or no decomposition at 200 °C, however, appeared slower dehydrogenation rate.

8) 0.60LiTFSI/0.40KOTf (OTf = trifluoromethanesulfonate) eutectic: little or no decomposition at 200 °C, however, appeared slower dehydrogenation rate.

### Dehydrogenation rates for MgH₂/Sn from Figure 1 (wt% H₂/hr)

<table>
<thead>
<tr>
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<th>150 °C</th>
<th>175 °C</th>
<th>200 °C</th>
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<tbody>
<tr>
<td><strong>Control (no electrolyte)</strong></td>
<td>0.0008</td>
<td>0.01</td>
<td>0.07</td>
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<tr>
<td>0.510 g (MgH₂/Sn)</td>
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<tr>
<td><strong>With Li/KBH₄ eutectic</strong></td>
<td>0.01</td>
<td>0.05</td>
<td>0.23</td>
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<tr>
<td>0.499 g (MgH₂/Sn) + 0.486 g (Li/KBH₄)</td>
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<tr>
<td><strong>With Li/KBH₄ eutectic + MgI₂</strong></td>
<td>0.02</td>
<td>0.07</td>
<td></td>
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<tr>
<td>0.499 (MgH₂/Sn) + 0.498 g (Li/KBH₄) + 0.125 g MgI₂</td>
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Figure S1. DSC trace of the 0.725LiBH$_4$/0.275KBH$_4$ eutectic electrolyte. The heating rate is 5 °C/min. Three cycles are shown. The melting point is 110 °C to 120 °C. Solidification occurs at 100 °C to 90°C.
Figure S2. Dehydrogenation of 2MgH$_2$ + Si. (red) A mixture of 0.151 g milled (2MgH$_2$ + Si) with 0.770 g of 0.33LiI/0.33KI/0.33CsI eutectic electrolyte; (black) 0.165 g of (2MgH$_2$ + 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$_2$Sn hydrogenation with 0.725LiBH$_4$/0.275KBH$_4$ eutectic electrolyte. (blue) After dehydrogenation of MgH$_2$/Sn with 0.725LiBH$_4$/0.275KBH$_4$. The major peaks correspond to Mg$_2$Sn. (red) After dehydrogenation and high-pressure hydrogen treatment (Figure S3). Peaks for Mg$_2$Sn decrease or disappear while those for MgH$_2$ and Sn grow, showing for the first time reversible hydrogenation of Mg$_2$Sn, 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$_2$Sn. No peaks clearly from LiBH$_4$, KBH$_4$, or Mg(BH$_4$)$_2$ are seen.
Figure S5. Powder XRD patterns showing no hydrogenation of Mg$_2$Sn 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 Mg$_2$Sn 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 ~60 ° 2θ. Nevertheless, the result that the two patterns are nearly identical is unaffected. 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$_2$Sn.
Figure S6. High pressure hydrogen treatment of MgB$_2$. Samples with the 0.725LiBH$_4$/0.275KBH$_4$ and 0.33LiI/0.33KI/0.33CsI 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 MgB$_2$ hydrogenation results. Two samples were run. Sample #1 was 0.413 g milled MgB$_2$ + 0.911 g 0.33LiI/0.33KI/0.33CsI eutectic. This sample contained 31 wt% MgB$_2$. Sample #2 contained ~1/2 the amount of eutectic, thus 47 wt% MgB$_2$. It was 0.407 g milled MgB$_2$ + 0.461 g 0.33LiI/0.33KI/0.33CsI eutectic (47% MgB$_2$). (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).