THE JOURNAL OF PHYSICAL CHEMISTRY B LETTERS

**2005,** *109,* 3719−3722

# Reversible Storage of Hydrogen in Destabilized $LiBH_4$

**John J. Vajo* and Sky L. Skeith**

*HRL Laboratories, LLC, 3011 Malibu Canyon Road, Malibu, California 90265*

**Florian Mertens**

*General Motors Research and Development Center, 30500 Mound Road, Warren, Michigan 48090*

*Received: December 21, 2004*

Destabilization of $LiBH_4$ for reversible hydrogen storage has been studied using $MgH_2$ as a destabilizing additive. Mechanically milled mixtures of $LiBH_4 + {}^1/_2MgH_2$ or $LiH + {}^1/_2MgB_2$ including 2−3 mol % $TiCl_3$ are shown to reversibly store 8−10 wt % hydrogen. Variation of the equilibrium pressure obtained from isotherms measured at 315−400 °C indicate that addition of $MgH_2$ lowers the hydrogenation/dehydrogenation enthalpy by 25 kJ/(mol of $H_2$) compared with pure $LiBH_4$. Formation of $MgB_2$ upon dehydrogenation stabilizes the dehydrogenated state and, thereby, destabilizes the $LiBH_4$. Extrapolation of the isotherm data yields a predicted equilibrium pressure of 1 bar at approximately 225 °C. However, the kinetics were too slow for direct measurements at these temperatures.

Currently, reversible hydrogen storage materials are being sought that will yield gravimetric storage system capacities of >6−9 wt % hydrogen. These capacities have been deemed necessary for commercial development of vehicles powered by $H_2/O_2$ proton exchange membrane fuel cells. Because it is unlikely that capacities of >6 wt % can be obtained in transition metal-based materials, intense interest has developed in low-*Z* complex hydrides[1] such as alanates ($AlH_4^-$),[2−4] amides ($NH_2^-$),[5−10] and borohydrides ($BH_4^-$).[11−13] Use of complex hydrides for hydrogen storage is challenging because of both kinetic and thermodynamic limitations. Kinetically, the reversible formation of complex hydrides is slow, although, Bogdanović and Schwickardi showed that dramatic improvement in reaction rates are possible with appropriate catalysts.[2] Thermodynamically, the stability of a complex hydride must lie within a specific range for the hydrogenation/dehydrogenation phase boundary to occur at practical pressures and temperatures. For example, except for $NaAlH_4$, most low-*Z* alanates appear to be too unstable.[14] In contrast, the borohydrides $LiBH_4$ and $NaBH_4$ are too stable.[11] For $LiBH_4$, partial decomposition to $LiH + B + {}^3/_2H_2$ can yield 13.6 wt % hydrogen. However, the standard enthalpy for this reaction is ~67 kJ/(mol of $H_2$) and thus, if reversible, an equilibrium pressure of 1 bar would require a temperature of >400 °C.[15] Recently, we have pursued increasing the equilibrium pressure of strongly bound hydrides such as LiH and $MgH_2$ using additives that stabilize the dehydrogenated state.[16] Stabilizing the dehydrogenated state reduces the enthalpy for dehydrogenation, thereby increasing the equilibrium hydrogen pressure. Using this approach, the thermodynamic properties of reversible hydrogen storage material systems can potentially be tuned to an extent finer than would be possible with individual materials.

Here we show that $LiBH_4$ can be reversibly dehydrogenated and rehydrogenated with a reduced reaction enthalpy by the addition of $MgH_2$. Dehydrogenation of a $LiBH_4 + {}^1/_2MgH_2$ mixture reacts according to

$$LiBH_4 + {}^1/_2MgH_2 \leftrightarrow LiH + {}^1/_2MgB_2 + 2H_2 \qquad (1)$$

which has a maximum hydrogen capacity of 11.4 wt %. Formation of $MgB_2$ stabilizes the dehydrogenated state and effectively *destabilizes* the $LiBH_4$.

Details regarding sample preparation and the temperature ramp hydrogenation and dehydrogenation experiments have been described in detail elsewhere.[16] Briefly, all materials were obtained commercially, used without further purification, and handled under an inert atmosphere. Approximately 1.2 g mixtures of $LiBH_4 + {}^1/_2MgH_2$ or $LiH + {}^1/_2MgB_2$ were mechanically milled for 1 h as described previously.[16] Typically, 2 or 3 mol % $TiCl_3$ was included as a catalyst during milling. Isotherm measurements were performed manually in the same Sieverts apparatus used for the temperature ramp experiments. All hydrogen capacities are reported with respect to full hydrogenation, but not including the weight of the catalyst. X-ray analyses were conducted on samples sealed in glass capillary tubes using a Philips PW3040/60 X'Pert Pro diffractometer.

Hydrogenation and dehydrogenation of a $LiH + {}^1/_2MgB_2 + 0.03TiCl_3$ mixture are shown in Figure 1. During heating at 2 °C/min, hydrogen uptake from an initial hydrogen pressure of 100 bar begins at 230−250 °C. For the initial cycle, hydrogenation is relatively slow; uptake of only 2.5 wt % hydrogen occurs after 2 h at 300 °C. Upon heating to 350 °C additional hydrogen uptake occurs, reaching >9 wt %. On the second and third cycles, the uptake is faster and 9 wt % uptake occurs in approximately 2 h at 300 °C. Desorption, into an initially

---

* Corresponding author. E-mail: vajo@hrl.com.

10.1021/jp040769o CCC: $30.25

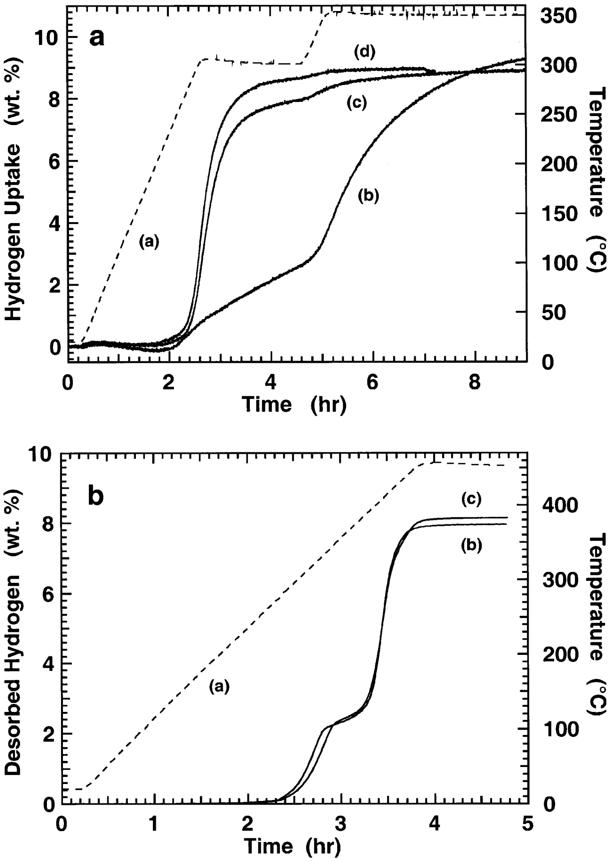

**Figure 1.** Hydrogenation and dehydrogenation of milled LiH + $^1/_2MgB_2$ with 3 mol % $TiCl_3$. (a) Hydrogen uptake during heating in 100 bar of hydrogen. Curve a shows the temperature profile. Curve b shows the initial uptake of hydrogen. Curves c and d show uptake during the second and third cycles, respectively. (b) Desorption following hydrogenation into a closed evacuated volume. Curve a shows the temperature profile. Curves b and c, respectively, show the wt % of desorbed hydrogen following the initial and second hydrogenation cycles that are shown in panel (a).

evacuated volume, begins at ~270 °C. Two desorption steps are evident at 270−340 and 380−440 °C, respectively. After heating to 450 °C, desorption of 8 wt % hydrogen was obtained. The desorption kinetics for the first two cycles are nearly identical. Final pressures were 5−6 bar and may be limited by equilibrium (see Figure 3 below). The increase in hydrogen pressure during desorption appears to be important for achieving dehydrogenation, according to reaction 1, and good reversibility. It was observed that dehydrogenation under dynamic vacuum resulted in formation of Mg metal, not $MgB_2$, and loss of capacity upon subsequent rehydrogenation. The effect of hydrogen pressure during desorption needs to be investigated further. Mass spectrometric analysis of the desorbed gas using a residual gas analyzer (RGA) attached to the Sieverts apparatus showed only hydrogen, although, low concentrations of species such as $B_2H_6$ or HCl cannot be ruled out.[17]

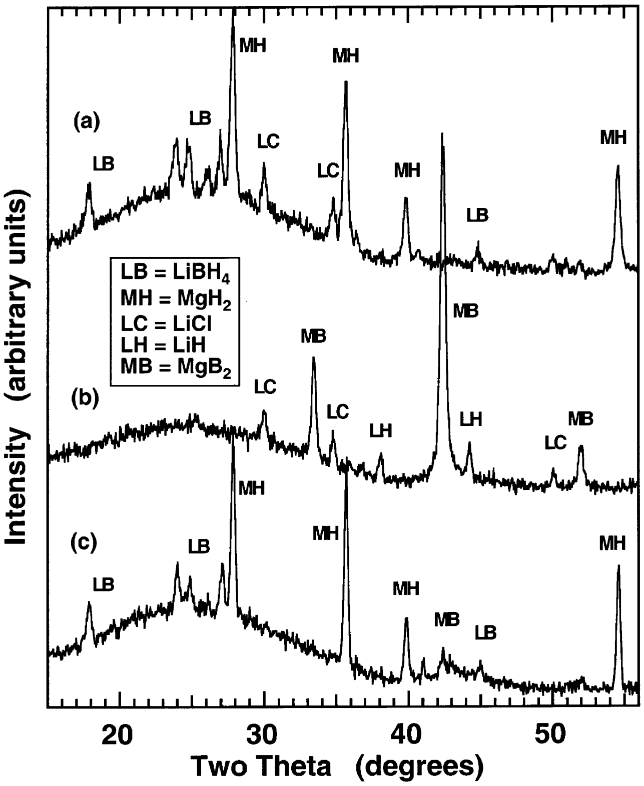

**Figure 2.** X-ray diffraction pattern from a mixture of $LiBH_4$ + $^1/_2MgH_2$ + $0.02TiCl_3$ after milling, dehydrogenation, and rehydrogenation. Curve a, after milling. Curve b, after dehydrogenation at 450 °C. Curve c, after rehydrogenation at 350 °C in 100 bar of hydrogen. The broad feature seen at 15−40° $2\theta$ originates from the glass wall of the capillary tubes. Peaks locations for $MgH_2$, LiCl, LiH, and $MgB_2$ were obtained from ICDD cards 00-012-0697, 01-074-1972, 00-009-0340, and 00-038-1369, respectively. Peak locations for $LiBH_4$ were obtained from ref 11.

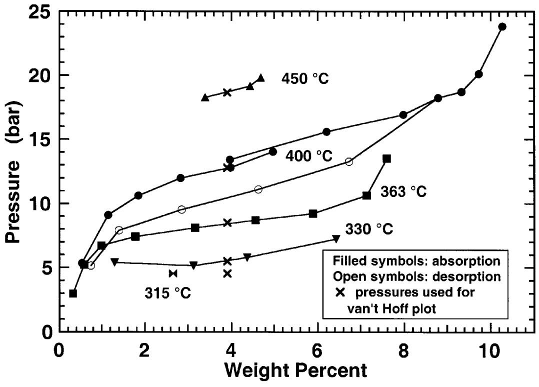

**Figure 3.** Absorption/desorption isotherms at 315−450 °C for the $LiBH_4$ + $^1/_2MgH_2$ system. Several samples starting with LiH + $^1/_2MgB_2$ + $0.02TiCl_3$ were used for these data. Each sample was hydrogenated and dehydrogenated through one cycle, as shown in Figure 1, before collecting the isotherm data. Filled symbols show absorption. Open symbols, at 400 °C only, show desorption. Pressures used for the van't Hoff plot in Figure 4 are indicated at 4 wt %.

Figure 2 shows X-ray diffraction patterns of a $LiBH_4$ + $^1/_2MgH_2$ + $0.02TiCl_3$ mixture after mechanical milling, and after dehydrogenation and rehydrogenation. Mechanical milling produces a physical mixture of $LiBH_4$ and $MgH_2$. However, at least a portion of the $TiCl_3$ reacts with the $LiBH_4$ to form LiCl. No diffraction from any species containing Ti was observed. After dehydrogenation at 450 °C, LiH and $MgB_2$ are formed. Upon rehydrogenation at 350 °C, $LiBH_4$ and $MgH_2$ re-form and the diffraction peaks from LiCl disappear.[18] The quartet of peaks around 25° $2\theta$ together with the peak at 18° distinctly identify $LiBH_4$ and demonstrate its reversible formation. However, some residual $MgB_2$ remains. Fourier transform IR spectra (data not shown) also confirmed the reversible formation of $LiBH_4$ with absorption at characteristic frequencies of 2385, 2289, 2223, and 1124 $cm^{-1}$.

Absorption and desorption isotherms for the $LiBH_4$ + $^1/_2MgH_2$ system at 315−450 °C are shown in Figure 3. The isotherms show sloping plateaus from 2 to 8 wt % with capacities of approximately 10 wt %. Equilibrium pressures

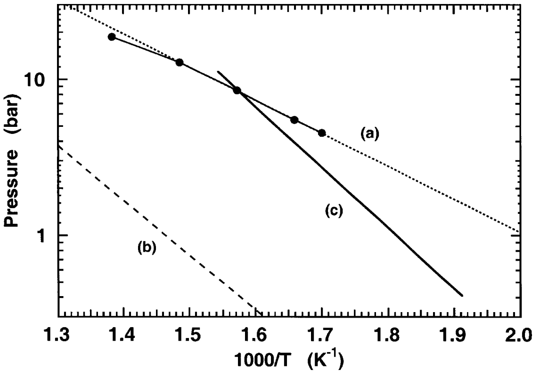

**Figure 4.** Van't Hoff plots for destabilized $LiBH_4$ + $^1/_2MgH_2$, pure $LiBH_4$, and $MgH_2$. Curve a shows equilibrium pressures obtained from the absorption isotherms at 4 wt %. A linear fit to the data at 315−400 °C indicates a dehydrogenation enthalpy of 40.5 kJ/(mol of $H_2$) and an equilibrium pressure of 1 bar at 225 °C. Curve b shows an estimate of the behavior for dehydrogenation of $LiBH_4$ to LiH + B.[15] Curve c shows the equilibrium pressure for $MgH_2$/Mg from ref 20. Addition of $MgH_2$ increases the equilibrium pressure by approximately 10 times while lowering the enthalpy by 25 kJ/(mol of $H_2$) compared with pure $LiBH_4$.

varied from 4.5 bar at 315 °C to 19 bar at 450 °C. Absorption and desorption isotherms obtained at 400 °C display a hysteresis of 2−3 bar. For all of these measurements, the kinetics were slow and times up to 100 h were necessary to attain equilibrium. Because of the slow kinetics, only a single point was obtained at 315 °C.

A preliminary van't Hoff plot (logarithm of the equilibrium pressure versus the inverse of the absolute temperature) using absorption equilibrium pressures at 4 wt % (see Figure 3) is shown in Figure 4.[19] From 315 to 400 °C the behavior is linear with an enthalpy of 40.5 kJ/(mol of $H_2$) and an entropy of 81.3 J/(K mol of $H_2$). At 450 °C ($1000/T = 1.38$) the equilibrium pressure is lower than the pressure predicted on the basis of an extrapolation of the linear behavior at lower temperatures (see discussion below). Also shown in Figure 3 are equilibrium pressures for $MgH_2$/Mg obtained from the IEA/DOE/SNL database[20] and an estimate of the equilibrium pressure for dehydrogenation of pure $LiBH_4$ to LiH + B.[15] The enthalpy for the $LiBH_4$/LiH + B system is estimated to be 67 kJ/(mol of $H_2$). Compared with pure $LiBH_4$, the hydrogenation/dehydrogenation enthalpy for the $LiBH_4$ + $^1/_2MgH_2$ system is lower by 25 kJ/(mol of $H_2$) and at 400 °C the equilibrium pressure is increased from approximately 1 to 12 bar. Alternatively, extrapolating the linear behavior gives a temperature of 225 °C for an equilibrium hydrogen pressure of 1 bar. Overall, the equilibrium pressure indicates that addition of $^1/_2MgH_2$ significantly destabilizes $LiBH_4$ for hydrogen storage.

Interestingly, the equilibrium pressure behavior for the $LiBH_4$ + $^1/_2MgH_2$ system crosses the curve for $MgH_2$/Mg at ~360 °C ($1000/T = 1.57$). At temperatures below 360 °C the equilibrium pressures are greater than those for pure $MgH_2$. Thus, in addition to $LiBH_4$, the $MgH_2$ is also destabilized. In this region the combined $LiBH_4$ + $^1/_2MgH_2$ system has equilibrium pressures higher than either individual component. Above 360 °C the equilibrium pressures, obtained from the isotherms at 4 wt %, are below the equilibrium pressures for $MgH_2$/Mg. Under these conditions, the system reacts according to

$$LiBH_4 + {}^1/_2Mg \leftrightarrow LiH + {}^1/_2MgB_2 + {}^3/_2H_2 \qquad (2)$$

Because hydrogenation of Mg is exothermic, the enthalpy for reaction 2 should be less than the enthalpy for reaction 1. Consequently, the variation of equilibrium pressure with temperature should display a lower enthalpy, i.e., a lower slope, above ~360 °C. The measured equilibrium pressure at 450 °C is indeed lower than the pressure extrapolated from lower temperatures.[21] These data points may indicate a transition from reaction 1 at temperatures below ~360 °C to reaction 2 at higher temperatures. However, additional data are necessary to clearly resolve this transition. At higher capacities, above approximately 8.5 wt %, a second plateau would be expected for the isotherms at 400 and 450 °C corresponding to hydrogenation/dehydrogenation equilibrium of Mg. Thus far, we have not detected a distinct second plateau. However, the slope of the isotherm at 400 °C gives an equilibrium pressure of ~19 bar at 9 wt %, which is close to the expected pressure for $MgH_2$/Mg. Although two plateaus have not been observed in the isotherm data, the temperature ramp desorption measurements (see Figure 1b) show two desorption steps that may correspond to dehydrogenation of $MgH_2$ followed by reaction of Mg with $LiBH_4$ to form $MgB_2$.[22] As mentioned above, dehydrogenation under vacuum results in formation of Mg, not $MgB_2$. Thus, it appears that a finite hydrogen pressure, approximately 2 bar after the first desorption step for the experiment shown in Figure 1b, is necessary for the subsequent reaction of Mg with $LiBH_4$ to yield $MgB_2$. Further work is underway to completely understand this behavior.

Extrapolation of the equilibrium pressures at 315−400 °C to lower temperatures gives a pressure of 1 bar at 225 °C. Direct measurements at this temperature have not been possible because the kinetics are currently too slow. Following work with $NaAlH_4$, 2−3 mol % $TiCl_3$ was added as a catalyst because initial experiments without added $TiCl_3$ displayed poor performance. However, the catalyst composition and system processing, i.e., milling conditions and particle and crystallite sizes, must still be optimized to obtain reasonable reaction rates at low temperatures and to realize the potential of this system for hydrogen storage. In addition, a temperature of 225 °C for an equilibrium pressure of 1 bar is higher than desired for most applications. Ideally, an equilibrium pressure of 1 bar would occur at ≤150 °C. Thus, further thermodynamic destabilization is also required.

In summary, we have shown that addition of $^1/_2MgH_2$ to $LiBH_4$ yields a destabilized, reversible hydrogen storage material system with a capacity of approximately 8−10 wt %. The hydrogenation/dehydrogenation enthalpy is reduced by 25 kJ/(mol of $H_2$) compared with pure $LiBH_4$, and the temperature for an equilibrium pressure of 1 bar is estimated to be 225 °C.

## References and Notes

(1) Grochala, W.; Edwards, P. P. *Chem Rev.* **2004**, *104*, 1283.

(2) Bogdanović, B.; Schwickardi, M. *J. Alloy Compd.* **1997**, *253−254*, 1.

(3) Sandrock, G.; Gross, K.; Thomas, G. *J. Alloy Compd.* **2002**, *339*, 299.

(4) Jensen, C. M.; Gross, K. *J. Appl Phys. A* **2001**, *72*, 213.

(5) Chen, P.; Xiong, Z.; Lou, J.; Lin, J.; Tan, K. L. *Nature* **2002**, *420*, 302.

(6) Chen, P.; Xiong, Z.; Lou, J.; Lin, J.; Tan, K. L. *J. Phys. Chem. B* **2003**, *107*, 10967.

(7) Ichikawa, T.; Isobe, S.; Hanada, N.; Fujii, H. *J. Alloy Compd.* **2004**, *365*, 271.

(8) Luo, W. *J. Alloy Compd.* **2004**, *381*, 284.

(9) Leng, H.; Ichikawa, T.; Hino, S.; Hanada, N.; Isobe, S.; Fujii, H. *J. Phys. Chem. B* **2004**, *108*, 8763.

(10) Orimo, S.; Nakamori, Y.; Kitahara, G.; Miwa, K.; Ohba, N.; Noritake, T.; Towata, S. *Appl. Phys. A* **2004**, *79*, 1765.

(11) Züttel, A.; Wenger, P.; Rentsch, S.; Sudan, P.; Mauron, Ph.; Emmenegger, Ch. *J. Power Sources* **2003**, *118*, 1.

(12) Nakamori, Y.; Orimo, S. *J. Alloy Compd*. **2004**, *370*, 271.

(13) Orimo, S.; Nakamori, Y.; Züttel, A. *Mater. Sci. Eng. B* **2004**, *108*, 51.

(14) Fichtner, M.; Engel, J.; Fuhr, O.; Kircher, O.; Rubner, O. *Mater. Sci. Eng. B* **2004**, *108*, 42.

(15) Estimates of thermodynamic parameters and equilibrium pressures were made using *Outokumpu HSC Chemistry* for Windows, version 4.0; ChemSW, Inc. 1999.

(16) Vajo, J. J.; Mertens, F.; Ahn, C. C. Bowman, R. C., Jr.; Fultz, B. *J. Phys. Chem. B* **2004**, *108*, 13977.

(17) Adsorption on the walls of the tubing and in the leak valve leading to the RGA could have prevented detection of reactive species at low concentrations.

(18) Loss of the diffraction features from LiCl is not fully understood. However, the LiCl may have dissolved into the $LiBH_4$, which is above its melting point of 275 °C when it is formed at 300−350 °C.

(19) We consider the data in Figure 4 preliminary because of the slow kinetics and, hence long times necessary to reach equilibrium. Optimizing the catalyst formulation, which has not been attempted here, could greatly increase the reaction rates and improve the equilibrium data.

(20) IEA/DOE/SNL Hydride databases available at Hydride Information Center, Sandia National Laboratories Home Page. http:/hypark.ca.sandi.gov/.

(21) We note that at temperatures above ∼400 °C sublimation of Mg can affect the system behavior and complicate the measurements. Thus at 450 °C, only a partial isotherm was collected.

(22) Interrupting the dehydrogenation after the first desorption should show Mg by X-ray diffraction. This measurement was not performed but is planned for future work.