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Letter

Reversible hydrogen storage in the lithium borohydride—calcium hydride coupled system

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Abstract

We report large reversible hydrogen storage in a new coupled system, LiBH₄/CaH₂, via the reaction $6\text{LiBH}_4 + \text{CaH}_2 \leftrightarrow 6\text{LiH} + \text{CaB}_6 + 10\text{H}_2$ having a theoretical hydrogen capacity of 11.7 wt% and an estimated reaction enthalpy of $\Delta H = 59 \text{ kJ/mol H}_2$. Samples that include 0.25 mol (18.2 wt%) TiCl₃ reproducibly store 9.1 wt% hydrogen, corresponding to 95% of the available hydrogen. H₂ is the only evolved gas detected by mass spectrometry. X-ray diffraction confirms that the sample cycles between LiBH₄ and CaH₂ in the hydrogenated state and LiH and CaB₆ in the dehydrogenated state.

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Development of practical on-board hydrogen storage systems based on solid hydride materials remains a significant technical and scientific challenge for fuel cell vehicles [1]. In the last few years, much of the focus in hydride research has been on light metal alanates [2–6] and borohydrides [7–10] because they offer relatively large gravimetric hydrogen densities. Built on earlier work of Reilly and Wiswall [11], Vajo and Olson [12] recently adopted a promising strategy for generating new hydride storage systems by coupling existing binary and complex hydrides that form mixed compounds or alloys upon dehydrogenation. Vajo et al. reported reversible hydrogen storage exceeding 9 wt% in the LiBH₄/MgH₂ system when catalyzed with TiCl₃ [13] according to the reaction:

$$2\text{LiBH}_4 + \text{MgH}_2 \leftrightarrow 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2 \tag{1}$$

The formation of MgB₂ as a reaction product of LiBH₄ and MgH₂ significantly changes the thermodynamic pathway and, most importantly, greatly improves rehydrogenation to form LiBH₄. Similar effects were observed in the MgH₂/Si system given by $2MgH_2 + Si \rightarrow Mg_2Si + 2H_2$, although rehydrogenation was proven much more difficult [14].

0925-8388/\$ – see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2007.09.125 Here we report synthesis and hydrogen cycling of the new, coupled complex hydride system LiBH₄/CaH₂, described by

$$6\text{LiBH}_4 + \text{CaH}_2 \leftrightarrow 6\text{LiH} + \text{CaB}_6 + 10\text{H}_2, \qquad (2)$$

with 11.7 wt% theoretical hydrogen capacity. The theoretical volumetric hydrogen density is also relatively large at 0.09 kg H₂/l (materials basis). Reversible hydrogen storage of 9.1 wt% has been achieved in samples that also incorporate 0.042 mol of TiCl₃ per LiBH₄; including the additional TiCl₃ weight, this represents 95% of the theoretically available hydrogen in the system. Our results are consistent with the enthalpy of reaction $\Delta H \sim 60$ kJ/mol H₂ recently predicted by Alapati et al. [15] for this system, and with thermodynamic estimates.

Samples of $6\text{LiBH}_4 + \text{CaH}_2 + 0.25\text{TiCl}_3$ were prepared by ball milling. TiCl₃ was included in the sample as a catalyst to increase the kinetics of hydrogen release and reabsorption, however it is not known at this time whether it actually had any effect on hydrogen cycling. All sample handling was done in an Ar inert gas glove box to prevent atmospheric exposure. Powders of LiBH₄ (Aldrich, 95% purity), CaH₂ (Aldrich, 95% purity), and TiCl₃ (Aldrich, 99.999% purity) were mixed in a 6:1:0.25 molar ratio having a total weight of 1 g, loaded into a hardened steel ball mill jar along with one large and two small steel balls, and ball-milled for 1 h in a SPEX 8000 Mixer/ Mill.

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X-ray diffraction (XRD) was performed using a Bruker AXS General Area Detector Diffractometer System (GADDS) using Cu K α radiation. The XRD samples were loaded under Ar into 1.0 mm diameter quartz capillary tubes and sealed with clay for transfer to the diffractometer.

Hydrogen cycling was carried out using a Cahn Model 2151 high pressure thermogravimetric analyzer (TGA). The as-milled powder (217 mg) was loaded into an open stainless steel sample bucket in the Ar glove box and protected during transfer to the TGA by covering the sample with anhydrous pentane. The TGA was purged with He gas while the pentane evaporated. The sample was cycled three times starting from the hydrogenated state (left side of reaction (2)). Samples were dehydrogenated in 0.13 MPa flowing He gas by heating to 450 °C at either 5 or 2°C/min, followed by soaking at 450°C until weight loss stopped. Rehydrogenation was accomplished in 8.3 MPa flowing H₂ gas by heating to 400 $^{\circ}$ C at 5 $^{\circ}$ C/min (first hydrogenation) or $25 \,^{\circ}$ C/min (second dehydrogenation) and soaking at 400 $^{\circ}$ C. For the third hydrogenation, the temperature was increased at 2°C/min through a series of constant temperature steps at 250, 275, 300, 350, and finally 400 °C. After the first desorption, the starting weight percent of each absorption or desorption scan was taken to be the ending weight percent from the previous scan. The sample was temporarily removed from the TGA under He gas and a small portion of the sample was extracted for XRD analysis after the first dehydrogenation, after the subsequent first rehydrogenation, and at the end of the third cycle. We monitored the composition of the TGA exhaust gas by residual gas analyzer (RGA) mass spectrometry to detect H₂ release during dehydrogenation, and to test for the presence of H₂O, CH₄, NH₃, B₂H₆, N_2/CO , O_2 , and CO_2 .

The XRD pattern of the as-milled powder, shown in Fig. 1(a), contains the expected LiBH₄ and CaH₂ phases, indicating that no reaction between the major phases occurred during milling. The TiCl₃, however, clearly reacted with a small portion of the LiBH₄ to form LiCl. No diffraction peaks corresponding to Ti-containing species were observed. A small quantity of oxide impurity was also present.

Dehydrogenation and rehydrogenation are shown in Figs. 2 and 3 for three hydrogen cycles of $6LiBH_4 + CaH_2 +$ 0.25TiCl₃. Starting from the as-milled state in Fig. 2(a), the sample began to lose significant weight in He at temperatures as low as 150 °C. Most of the weight loss, however, occurred after the sample reached 350 °C, and was complete after soaking at 450 $^{\circ}$ C for \sim 30 min. It should be noted that this is above the melting temperature of pure LiBH₄ (288 $^{\circ}$ C). Only H₂ was observed in the RGA of the evolved gas to within our detection limits. The total weight loss was 9.1 wt%. After correcting for the additional TiCl₃ content, the weight loss relative to the $LiBH_4/CaH_2$ content was 11.1 wt%, compared to the theoretical hydrogen capacity of 11.7 wt%, or 95% of the hydrogen predicted by reaction (2). After dehydrogenation, XRD confirms that the original LiBH₄ and CaH₂ phases have disappeared and in their place are diffraction peaks belonging to CaB₆ and LiH, as shown in Fig. 1(b) [16].

First cycle rehydrogenation is shown as the solid curve in Fig. 2(b). After several hundred minutes, the weight appears



Fig. 1. X-ray diffraction patterns from $6LiBH_4 + CaH_2 + 0.25TiCl_3$: (a) asmilled, (b) in the desorbed state, and (c) in the rehydrogenated state after three cycles.

to be asymptotically increasing toward its starting value. The absorption was terminated after 550 min with the weight at 99%. XRD obtained at this stage (not shown) showed only peaks that could be indexed as LiBH₄ and CaH₂, along with CaO and a small quantity of LiCl. The sample was replaced in the TGA and cycled again, as shown by the dash–dot lines in Fig. 2(a) and (b). The reabsorption kinetics were somewhat slower in the second cycle, and the experiment was terminated after 735 min.

A third desorption-reabsorption cycle is shown in Fig. 3. For this reabsorption experiment, a number of temperatures were tried between 250 and 400 °C. Some absorption did occur at the lower temperatures, but with poor kinetics. The sample was held at 400 °C until the total heating time reached 2700 min; its final weight was very close to the original value prior to cycling. A final XRD pattern obtained after this cycle, Fig. 1(c), clearly demonstrates that the sample returned to the original mixture of LiBH₄ and CaH₂. The CaO lines are somewhat stronger, most likely due to incidental exposure during sample extraction and reinsertion in the TGA and impurities in the flowing gas stream over the long time scale of the experiment. Although the sample weight gain due to the increased oxide is not known quantitatively, and probably accounts for the observation that the third rehydrogenation shown in Fig. 3(b) appears to be approaching a maximum value slightly greater than 100%, it is clear



Fig. 2. (a) H_2 desorption profiles and (b) subsequent absorption profiles for the first two cycles of $6LiBH_4 + CaH_2 + 0.25TiCl_3$. The sample started from the asmilled state at 100% weight in the upper panel. First cycle data is represented by solid lines, and the second cycle is shown as dash-dotted lines. The dashed curves show the corresponding temperature histories; the dash-double dot line in panel (b) is the temperature history of the second absorption.

that the third H₂ absorption is very close in magnitude to the original H₂ desorption of 9.1 wt%. Curiously, the LiCl lines are no longer observed in the hydrogenated state. A similar phenomenon was observed by Vajo et al. in the LiBH4/MgH2 system catalyzed with TiCl₃ [13]. We also note that Barkhordarian et al. [17] recently attempted to hydrogenate a ball-milled mixture of $6LiH + CaB_6$ (starting on the dehydrogenated side of reaction (2)) at 400 °C, but were unsuccessful in forming a hydride even by exposure to 35 MPa H₂ gas for 1440 min. In contrast, we have successfully cycled reaction (2) multiple times using 8.3 MPa H₂ pressure for hydrogenation. It is unclear why the Barkhordarian et al. sample did not hydrogenate, given that their experimental conditions appear similar to ours. One difference is that we began on the hydrogenated side of reaction (2) (6LiBH₄ + CaH₂) whereas Barkhordarian et al. started from the dehydrogenated state ($6LiH + CaB_6$). We also note that Barkhordarian et al. milled for 24 h, much longer than our 1 h milling



Fig. 3. (a) Third desorption and (b) reabsorption cycle for $6LiBH_4 + CaH_2 + 0.25TiCl_3$.

time. Another possibility is the presence of $TiCl_3$ in our sample, although we stress that the effect of Ti, if any, has not yet been assessed in the present work.

The thermodynamics of the LiBH₄/CaH₂ system were estimated from the enthalpy and entropy values for LiBH₄, CaH₂, LiH, and CaB₆ in the Outokumpu HSC chemistry thermodynamics database [18]. For reaction (2), HSC chemistry gives $\Delta H = 66.2 \text{ kJ/mol } H_2$ and $\Delta S = 100 \text{ J/K} \text{ mol } H_2$ at room temperature. These values, however, do not include the orthorhombic-to-hexagonal structural transformation of LiBH4 at 113 °C [19] or melting of the LiBH₄ component at 288 °C. Recently, Züttel et al. [20] have reported the enthalpies of the LiBH₄ structural phase transition ($\Delta H_s = 4.18 \text{ kJ/mol}$) and of melting ($\Delta H_{\rm m} = 7.56 \,\text{kJ/mol}$); when these values are combined with HSC chemistry the estimated enthalpy of reaction (2) at 400 °C is $\Delta H = 59.2 \text{ kJ/mol}$ H₂. Similar calculation of ΔS using entropies from HSC chemistry and including the entropy changes $\Delta S_{\rm s} = \Delta H_{\rm s}/T_{\rm s}$ and $\Delta S_{\rm m} = \Delta H_{\rm m}/T_{\rm m}$ for the structural transformation and melting, respectively, gives $\Delta S = 85.6 \text{ J/(K mol H}_2)$. The thermodynamic equilibrium temperature in 1 bar of H₂ gas is predicted to be $T(1 \text{ bar}) = 418 \,^{\circ}\text{C}$. Alapati et al. [15] obtained a similar estimate for the reaction enthalpy, $\Delta H \sim 60 \,\text{kJ/mol H}_2$, using ab initio density functional theory (DFT) calculations (neglecting the enthalpy of melting). The high temperatures required for dehydrogenation in the absence of H₂ gas, and rehydrogenation in an 8.3 MPa H₂ overpressure, are clear indications that the limited kinetics at lower temperatures dominates hydrogen cycling in these samples. Experimental determination of the reaction enthalpy and entropy would clearly be valuable, and such a study is planned for the near future.

Our results demonstrate that LiBH₄/CaH₂ forms a coupled complex hydride system according to reaction (2). By itself, CaH₂ is stable up to 600 °C. LiBH₄ in isolation can be decomposed to LiH + B + 3/2H₂ in the temperature regimes used here, but reversibility of this reaction has proven extremely challenging [7]. By coupling the two, we have succeeded in both destabilizing CaH₂ and promoting full reversibility of LiBH₄. The predicted *T*(1 bar) for this coupled reaction is too high for its use as an on-board hydrogen storage medium; this system nevertheless provides another excellent example of the power of coupled reactions in designing practical hydride-based storage systems.

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