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New Insights into the Thermodynamic Behavior of $2LiBH_4$-MgH_2 Composite for Hydrogen Storage

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ABSTRACT

The composite $2LiBH_4$:MgH_2 has been studied as a potential hydrogen storage material due to its high storage capacity. The present work is aimed at clarifying the thermodynamic behavior of the system, especially within the temperature region above 400°C. Different reaction paths which have important implication for storage applications during hydrogen absorption and desorption at various

temperatures were revealed. At temperatures over 413°C, two different absorption pressure plateaus are observed. This indicates that two different reactions occur: Mg hydrogenation at higher pressures, and the reformation of $LiBH_4$ from H_2, LiH and MgB_2 at lower pressures. On the other hand, at temperatures below 413°C only one plateau is present in the system. During desorption, the double plateau can be observed at temperatures as low as 375°C. This effect restricts the applicability of this composite as a hydrogen storage material.

1. INTRODUCTION

$LiBH_4$ is a lightweight complex hydride with a very high hydrogen content (18.3 wt. %). Due to these characteristics, it has been thoroughly studied for hydrogen storage. However, the hydrogen can only be completely utilized at temperatures above 900°C.[1] At lower temperatures (~ 400°C), a partial dehydrogenation reaction could be obtained with a hydrogen release of 13.6 wt. % and the formation of solid products such as LiH and B. Although this partial dehydrogenation temperature remains high for practical applications of hydrogen storage with PEM fuel cells, the major drawback of the $LiBH_4$ is that even at 400°C, long desorption times are required to complete the reaction. Various solutions to lower desorption temperature and to enhance kinetics have been proposed. A promising strategy is to destabilize the system by incorporating various additives, in particular MgH_2. Destabilization is a term used to refer to the process of lowering the enthalpy of hydrogen desorption reaction. That is, lowering the enthalpy of the product phases, and hence, lowering the stability of the original compound. The $2LiBH_4{:}1MgH_2$ system was initially studied by Vajo et al. who showed the destabilizing effect due to the formation of the $LiBH_4{:}MgH_2$ composite.[2] The presence of Mg during the dehydrogenation of $LiBH_4$ leads to the formation of MgB_2 as a product instead of B. This decreases the enthalpy of the reaction. The enthalpy of the destabilized reaction (40.5 kJ/molH_2) becomes 1.6 times lower than the one of the original reaction (66.7 kJ/molH_2), and facilitates the absorption and desorption of hydrogen at lower temperatures.[2]

The study of this system has been mainly focused on the determination of the conditions, i.e. pressure and temperature, for which the hydrogen release from the $LiBH_4$ occurs reversibly. Nakagawa et al. studied the reactions of the $LiBH_4$-MgH_2 system under hydrogen and inert gas pressure of several bar at temperatures up to 450°C and found that the MgB_2formation only occurred in a hydrogen atmosphere during desorption.[3] The formation of MgB_2 is assumed to reduce the system enthalpy and, therefore, facilitates reversibility of the reaction.[3–6] Several authors have reported required pressure and temperature ranges to ensure the reversibility of the system under different conditions.[5,7]

In this work the thermodynamic of the reactions between hydrogen and Ni catalyzed $2LiBH_4$:MgH_2 composite material has been studied. To complement the previous studies by other authors we attempt to clarify the behavior of the system at high temperatures and the different reaction paths that occur during the hydrogen absorption and desorption.[2,8,9] Walker predicted the presence of two different pressure plateaus at high temperatures indicating that two different reactions should occur at temperatures over this point.[8] The $2LiBH_4$:MgH_2 system has been thoroughly studied and the reaction pathways for the hydrogen absorption have also been analyzed by several authors. However, none of them reported the presence of this double plateau.[2,5,7–9] The only experimental reference is a recent work published by Catti et al.[10] In the article mentioned, the authors presented a study of the system $2LiBH_4$:Mg_2FeH_6 which decomposes into the system $LiBH_4$:$2MgH_2$ through an irreversible reaction. Whereas this system has four times the necessary amount of MgH_2 for the stoichiometric reaction, the $LiBH_4$ and part of the MgH_2 can be dehydrogenated following the same pathway as the $2LiBH_4$:MgH_2. This fraction of the system presents a double plateau in a wider range of temperatures than the predicted by Walker.[8] In a recent article, Shao et al.[11] reported the presence of a triple plateau in the $2LiBH_4$:nanoMgH_2 system. However, the associated pressures and the enthalpies obtained do not correspond to the predicted by Walker[8] and in the article they are ascribed to reactions occurring in the presence of nano MgH_2.The relevant hysteresis between absorption and desorption pressures in this system and its potentiality as a hydrogen storage system has been also analyzed.

2. EXPERIMENTAL

2.1 Synthesis of the composites

The samples used in this work were synthesized from the following starting materials: MgH_2 (Sigma Aldrich, hydrogen storage grade), Ni (Sigma Aldrich, purity 99%) and $LiBH_4$ (Sigma Aldrich, purity >90%). The purchased materials are referred to in this work as M, N and LB, respectively. Due to the high reactivity of MgH_2, $LiBH_4$ and LiH with moisture and oxygen, the samples were prepared and manipulated in an MBraun Unilab argon-filled glove box, with oxygen and moisture levels < 1 ppm.

The sample preparation was performed by mechanical grinding in a medium-energy planetary type mill (Fritsch Pulverisette 6) under 0.1 MPa of argon atmosphere. All samples were ball-milled for 10 h at 400 rpm with a ball mass/sample mass ratio of 40:1. Due to the slow reaction kinetics of the $2LiBH_4$-MgH_2 system, Ni was added as a catalyst. The selection of Ni was based on previous experiences with this element in MgH_2.[12] The chosen composition for the synthesized samples was 2LiBH4-MgH_2 + 5 wt. % Ni. This material will be referred as LBMN.

2.2 Characterization

Microstructural, structural, thermal and hydrogen storage properties of the composites were studied using powder X-ray diffraction (PXRD, Bruker Advance D8), Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum 400), differential scanning calorimetry (DSC, TA 2910 calorimeter), solid state neutron magnetic resonance (NMR) and a Sieverts type volumetric equipment.

Structural information of the samples was obtained by PXRD (CuKα radiation), NMR and FTIR analyses. During PXRD data collection, a tight sealed sample holder was used to completely prevent any reaction between samples and air. For IR spectroscopy measurements, the selected samples were ground with dry KBr and pressed into pellets using an airtight sample cell. Solid-state IR spectra were obtained in the range of 800-4000 cm^{-1} in transmission mode.

Two samples of $2LiBH_4$:MgH_2 were investigated by ^{11}B MAS-NMR: 1) as-milled, 2) as partially desorbed at 425°C. The NMR samples were packed into boron-free zirconia rotors under inert atmosphere. The sample was referenced to $NaBH_4$ (-41 ppm) and experiments were performed at 7.1 T, 300 MHz, ^{1}H frequency.

The thermal behavior of the samples was analyzed by DSC at a heating rate of 5°C.min^{-1} under a 122 ml.min^{-1} argon flow to avoid oxidation during desorption. About 5 mg of sample was loaded into aluminum capsules hermetically closed in a glove box under a purified argon atmosphere.

The kinetics of hydrogenation and dehydrogenation of the samples were measured using a modified Sieverts type device, coupled with a mass flow controller. During the hydrogen desorption, the mass flow controller kept an almost constant backpressure during the whole experiment (0.6 MPa). The samples were desorbed at 425°C and 0.6 MPa before performing the pressure-composition isotherm absorption measurements. For PCI measurements, a programmed hydrogen amount was extracted (introduced) from (into) the system using the mass flow controller. The hydrogen was extracted (introduced) in batches of 0.45 mg (equivalent to 0.3 wt. %). Consequently the pressure decreased (increased) around 30 kPa. To determine whether the system reached the equilibrium condition, two different criteria were used. One, by verifying if the temporal variation of the pressure was lower than a fixed value (1.10^{-2}). The second, waiting for a selected time (1000 seconds). When any of these criteria is met, the system is considered to be in equilibrium and a data point in the PCI curve is saved. The hydrogen absorption process was studied at 375-475°C.

3. RESULTS AND DISCUSSION

Although the objective of this work is to study the thermodynamic behavior of the $2LiBH_4$:MgH_2 + 5 wt. % Ni (LBNM) system, a characterization of the raw materials is of great importance in order to establish a reference point. The as-milled LBMN samples were studied by PXRD to ensure that no reaction occurred among the initial materials during the milling process. Figure 1 A shows that only the materials introduced in the vial for milling are present. Figure 1 B shows the DSC study of the LBMN sample, and the measurements done on samples milled during 10 hours with a composition of $50MgH_2$:1Ni (MN). A milled mixture of $2LiBH_4$-MgH_2 and milled $LiBH_4$ were prepared as a reference and are also presented in Figure 1 B. The onset at 115°C is due to the transition from orthorhombic to hexagonal phases (O → H).[1,6,13] The next onset at 275°C has been reported as the melting of pure $LiBH_4$.[1,6,13] In the LBMN sample it is observed that there is a broadening of this peak, compared to the pure $LiBH_4$ and the milled mixture $2LiBH_4$-MgH_2. This broadening is attributed to the overlapping of two peaks, the first one corresponding to the melting of the $LiBH_4$ and the second one associated with the desorption of the catalyzed MgH_2. The higher temperature onset corresponds to the desorption of a part of the MgH_2 which is not catalyzed.[14] However, it can be noted that there is a slight displacement to lower temperatures of the LBNM peak, indicating that MgH_2 may still have a minor catalytic effect. The ratio of the area between the MgH_2 peak and the LBMN peak indicates that the Ni introduced into the sample is not fulfilling its catalytic role for most of MgH_2. Due to limitations in the calorimetry equipment it was not possible to clearly observe the desorption peak of $LiBH_4$ as it is only present at temperatures above 450°C. This can be deduced from the reference curve, seeing that at 400°C an increase in the heat flow is not observed for the $LiBH_4$ or the milled mixture $2LiBH_4$-MgH_2. However, the onset temperature for the hydrogen desorption of the LBMN sample is observed at 400°C. This may suggest that Ni has a slight catalytic effect on the system. This effect is not as significant as the one observed in the MgH_2-Ni system.

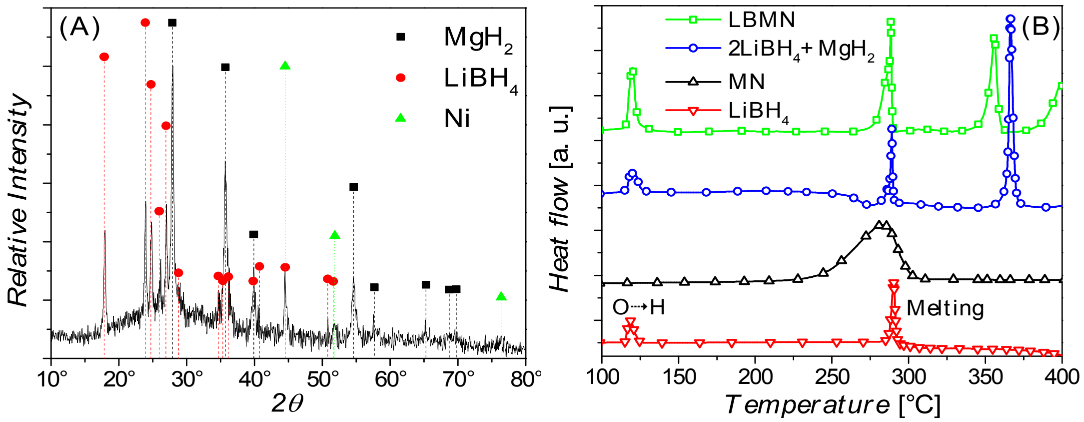

Figure 1: PXRD (A) and DSC (B) analyses of the LBMN sample. Reference curves are also added to the DSC.

FTIR measurements of the as-milled LBMN sample were performed (see results in the supplementary material). The bands corresponding to the bending vibration mode of the B-H bond of $LiBH_4$ mounted on the band assigned to the MgH_2 were observed in the region around 1100 cm^{-1}. The stretching vibration modes of the B-H bond were also present in the region around to 2300 cm^{-1}. As the grinding during ball-milling can generate internal stresses in the material which modify the environment of B-H bonds, the peaks were not well defined. As expected the results agree with the PXRD analysis shown in Figure 1 A.

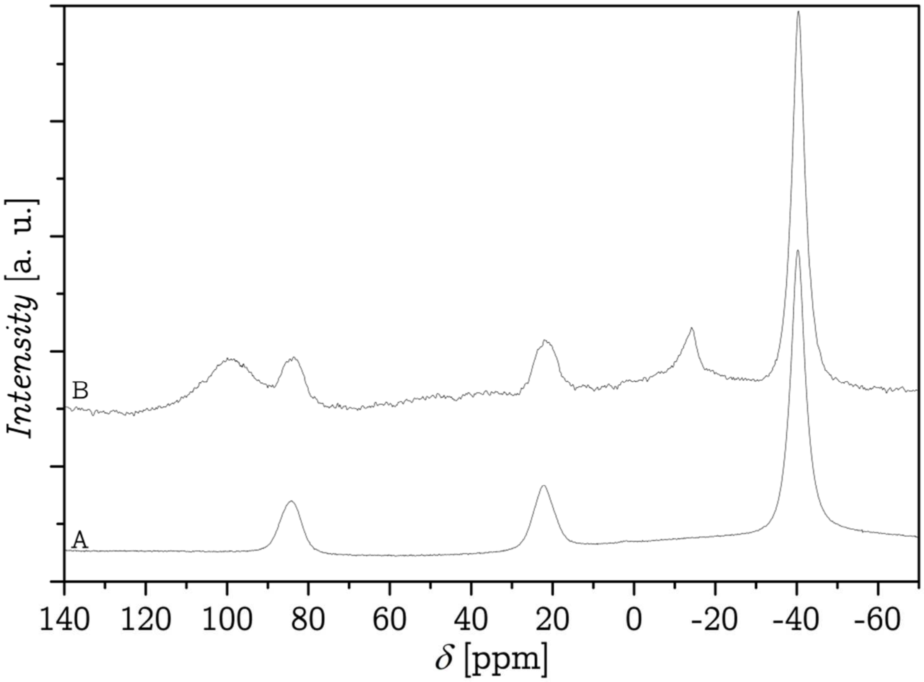

Figure 2: NMR spectra of the as-milled LBMN sample (A) and partially desorbed sample at 425°C (B).

^{11}B NMR measurements were performed to identify formation of desorption products after partial desorption. The results obtained are shown in Figure 2. Spectrum A corresponds to the as-milled sample. The peak at -40 ppm corresponds to the main peak of the $LiBH_4$.[15] The other two peaks can be attributed to the spinning sidebands.[16] Spectrum B shows the formation of MgB_2 and $Li_2B_{12}H_{12}$ after partial desorption and will be further discussed.[15]

Due to the hysteresis in the material systems that hindered the systematic study of the desorption isotherms at temperatures below 400°C, initially this work was mainly focused on absorption PCI measurements rather than desorption ones. However, in an attempt to clarify the behavior during desorption, dehydrogenation measurements were performed and the results are presented further on in this article. In Figure 3, two PCI curves at 425°C (absorption and desorption) are shown. These curves demonstrate the significant hysteresis that exist between the absorption and the desorption plateau, especially for the one at low pressure (ln(Pabs/Pdes)=1.26).

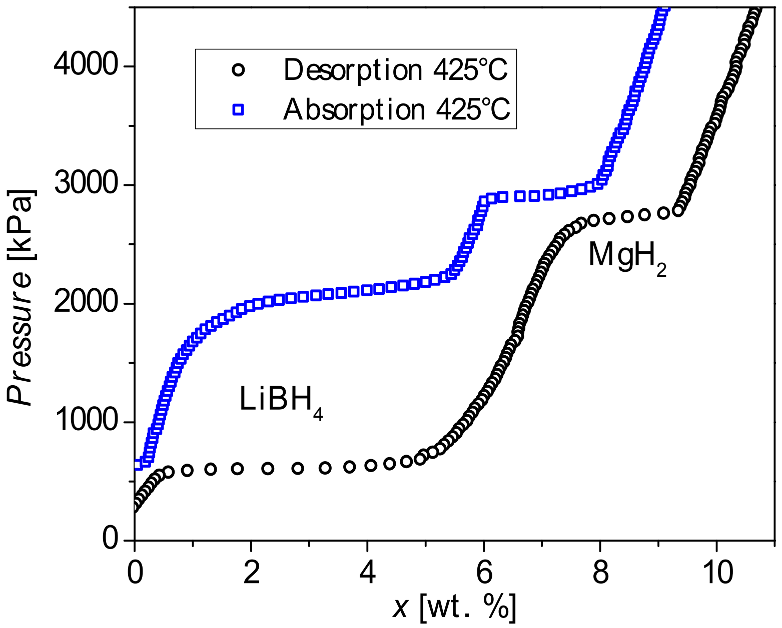

Figure 3: Absorption (blue squares) and desorption (black circles) PCI measurements at 425°C of the LBMN sample.

Since the composite was synthesized from raw materials in their hydrogenated states, i.e. $LiBH_4$ and MgH_2, it was necessary to desorb the samples before performing the absorption PCI measurements. Each PCI was measured in a new sample to ensure the same thermal record. All these samples were obtained from a single batch of the LBMN material. As it was previously mentioned, the selected conditions for the hydrogen desorption measurements were 425°C with 0.6 MPa of hydrogen backpressure. These conditions ensured a reaction pathway which forms MgB_2, LiH and H_2 as products and therefore guarantees the reversibility of the system.[5,7] From the desorption measurements it was observed that different samples obtained from the same batch did not show a reproducible behavior during the first desorption. Several measurements showed different times required for the reaction completion and also different amounts of hydrogen desorbed. However, further studies of the desorbed samples showed no disparities structure-wise according to PXRD, which indicates that this phenomenon could be attributed to an uneven distribution or proximity between $LiBH_4$ and MgH_2 particles in the powder, which affects the mechanism of MgB_2 nucleation.[6] Desorption kinetics are shown in Figure 4. After 2 cycles of absorption/desorption it can be seen that the material stabilizes and shows similar desorption curves for different samples.

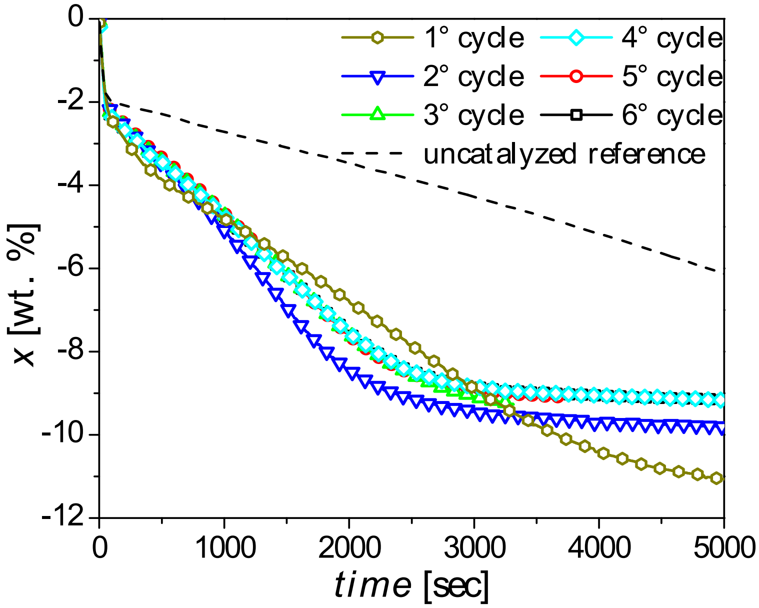

Figure 4: Successive desorption kinetics of the LBMN sample at 425°C. Uncatalyzed sample presented as reference.

This material showed a significant reversible hydrogen storage capacity of 9 wt. %, which not many hydrogen storage materials can obtain. Almost complete hydrogen absorption was achieved after 3500 seconds. Previous experiments performed in the same materials at the same temperature without adding Ni as a catalyst required a desorption time of 7000 seconds (presented as reference in Figure 4). It is concluded that a factor two improvement can be obtained by using Ni as a catalyst.

As seen in Figure 4, the hydrogen storage capacity is reduced after the first desorption, which can be partially related to the formation of $Li_2B_{12}H_{12}$ which appears after that initial desorption. This compound is very stable and, therefore, hinders hydrogen absorption reversibility under the studied experimental conditions.[15] The formation of $Li_2B_{12}H_{12}$ is supported by the NMR spectra from the partially desorbed sample (Figure 2 B). The peak near -10 ppm corresponds to the main peak of $Li_2B_{12}H_{12}$ and was not observed in the milled sample. In Figure 2 B, the peak at 100 ppm can be associated with MgB_2, indicating that it was formed during the desorption process.[15]

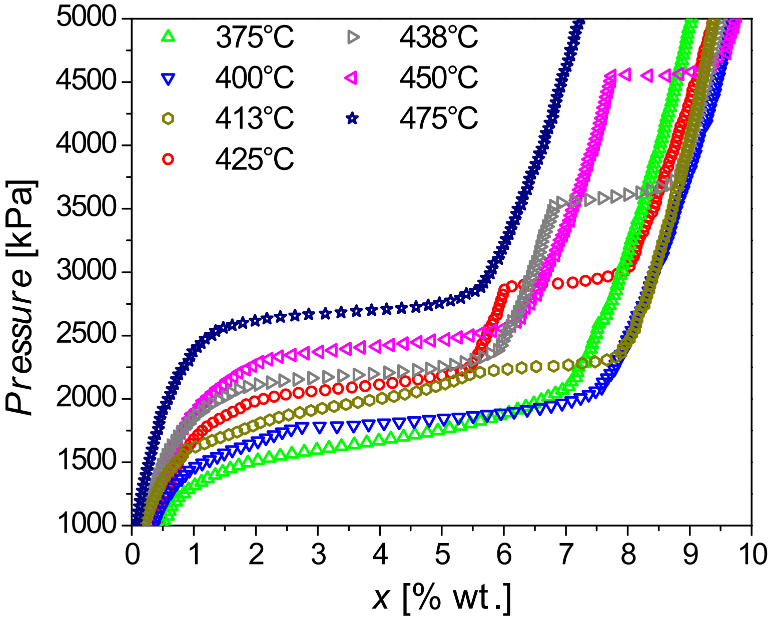

Figure 5: Absorption PCI measurements of the LBMN sample at various temperatures.

Absorption PCI measurements were done in a range of temperatures from 375°C to 475°C. At lower temperatures a single plateau was observed, whereas at temperatures over 413°C two plateaus were observed. These results are shown in Figure 5. Note that in the isotherm at 475°C, the upper plateau cannot be observed because the equilibrium pressure is higher than the maximum pressure allowed by the available measuring device. The plateaus presented in this figure exhibit a steeper slope compared to those measured in other systems with this equipment (see measurements of hydrogen absorption of Mg in supplementary material). This may be ascribed to a combination of much slower reaction kinetics and a larger number of steps involved in the absorption.

Using the measured pressure in the middle of the hydrogenated fraction of each plateau (for temperatures above 413°C the upper and the lower plateau were considered separately), a van't Hoff graph was constructed in order to obtain a value for the enthalpy of the reaction in this range. This plot is presented in Figure 6, and it can be observed that values for temperatures between 375°C and 413°C can be fitted into a straight line. The ΔH obtained from the slope of this line is 41±4 kJ/molH_2 K, which is similar to what has been previously reported for this composite.[2]

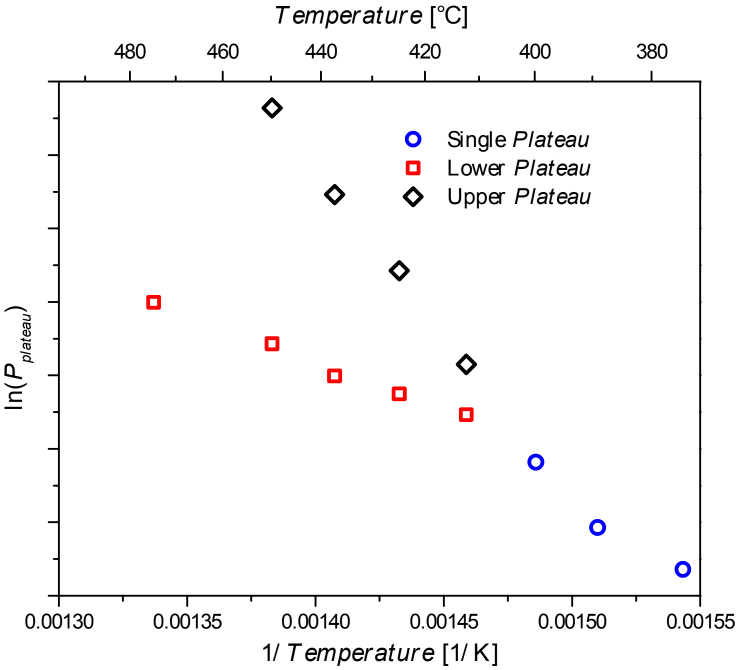

Figure 6: van´t Hoff plot for the LBMN sample obtained from hydrogen absorption PCI measurements.

The experimental data points above 413°C can also be fitted within two linear functions: for the lower plateaus and the upper plateaus. This indicates that the five data points obtained from the lower plateau at temperatures above 413°C belong to the same equilibrium reaction. The value obtained for the reaction enthalpy of the composite is 21±4 kJ/molH_2 K. The two plateaus correspond to different desorption reactions. Based on the enthalpy obtained in the van´t Hoff plot for each plateau, it can be assumed that the lower one is associated with the following reaction: $MgB_2 + 2LiH + 3H_2 \rightarrow 2LiBH_4 + Mg$. The second one could be attributed to the hydrogenation of Mg ($Mg + H_2 \rightarrow MgH_2$). This is supported by the relative width of the two plateaus, as the one at higher pressure represents 23% of the total absorbed hydrogen (theoretical percentage of MgH_2 = 21%) while the lower plateau corresponds to the remaining 77% (theoretical percentage of $LiBH_4$ = 79%). The fit of the points corresponding to the higher pressure plateau gives a reaction enthalpy of 76±6 kJ/molH_2 K. This value is within the range reported for the Mg hydrogenation reaction.[17]

In the previously mentioned article by Catti et al.[10], the excess of Mg in the system causes the presence of the double plateau at temperatures below the intersection of the van´t Hoff plots corresponding to the reactions MgB_2+2LiH+3H_2→2$LiBH_4$+Mg and Mg+H_2→MgH_2. Moreover, Catti et al. did not report a change in the slope for the absorption after the intersection, indicating that both reformations of $LiBH_4$ (one resulting in the production of Mg and the other one, of MgH_2), have the same reaction enthalpy.[10]

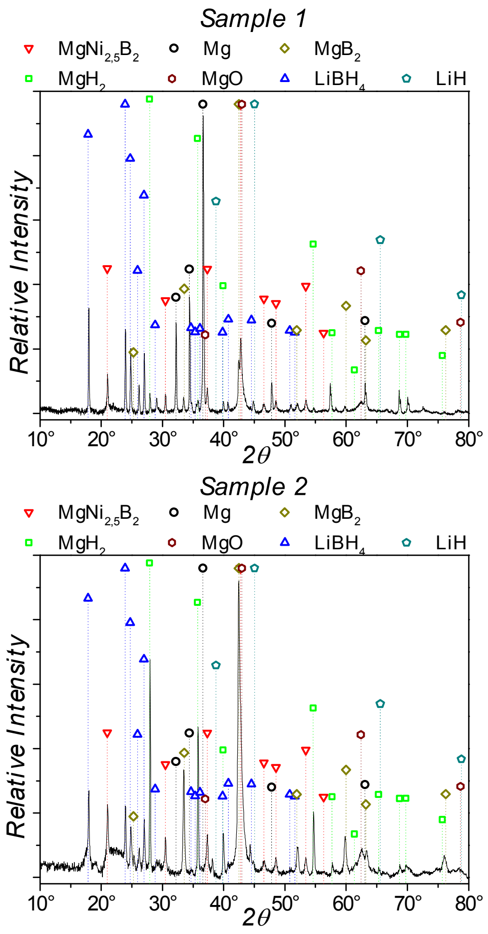

Figure 7: PXRD of the partially desorbed sample at two different temperatures: 425°C (Sample 1) and 375°C (Sample 2).

In order to confirm the assumptions about the reactions corresponding to each plateau, two experiments were designed. The first one corresponds to an absorption PCI measurement at 425°C. The sample was removed from the Sieverts device when the pressure reached 2500 kPa. It can be seen in Figure 5 that at this pressure the sample is between the two plateaus indicating that only the reaction corresponding to the first plateau has occurred. The sample in the second experiment was removed from an absorption PCI at 375°C when the hydrogen absorbed weight percent reached the same value at which the first sample was removed (5.5 wt. %). PXRD analyses of both samples were performed and the results are shown in Figure 7. The diffractograms presented in this figure confirm the assumptions about the reaction corresponding to each plateau. After the experiment, the first sample was composed by $LiBH_4$ and Mg with small amounts of MgB_2, $MgNi_{2.5}B_2$, LiH and MgH_2 while the second sample presented a composition of $LiBH_4$, and roughly the same quantity of MgB_2 and MgH_2, indicating that the formation of MgH_2 and $LiBH_4$ happens simultaneously. The formation of $MgNi_{2.5}B_2$ occurs during the first desorption and is not reversible as it has been previously reported.[12]

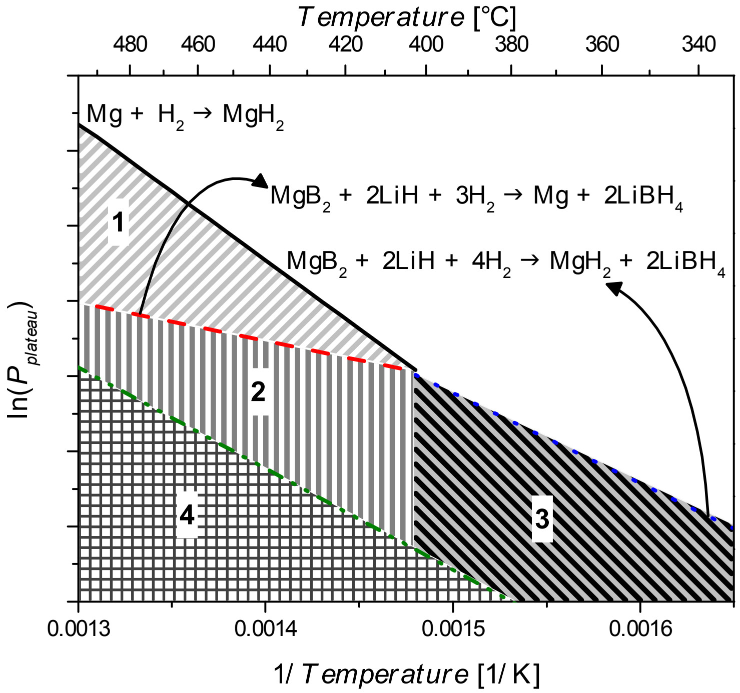

Figure 8: Absorption van´t Hoff plot of the composite 2LiBH4:MgH2:5wt%Ni (LBMN).

A map of the system reactions can be designed with the reaction enthalpy and entropy values for the different reactions obtained from the linear fit of each of the data sets presented in Figure 6 and the theoretical values calculated by Ohba et al.[18] In this map (Figure 8), the van´t Hoff straight lines correspond to each reaction which delimits four regions.

In region 1, Mg is more stable than MgH_2. However, the decomposition of $LiBH_4$ is not thermodynamically favorable. In this zone, the destabilizing effect of Mg on $LiBH_4$ is not strong enough to cause $LiBH_4$ to release its hydrogen content to form MgB_2. Therefore, in region 1 conditions, a coexistence of Mg and $LiBH_4$ occurs.

Region 2 in Figure 8 is the zone in which Mg destabilizes $LiBH_4$. Consequently, hydrogen is released at higher pressures than expected, based on the thermodynamics for pure $LiBH_4$. Under these conditions the system is in its desorbed state MgB_2+2LiH.

In region 3 both compounds (MgH_2 and $LiBH_4$) destabilize each other. This allows both to release hydrogen at higher pressures than required when found in pure state. This double destabilization causes the system to change from its hydrogenated state to its dehydrogenated state. It is important to notice that full dehydrogenation of the system only occurs at temperatures over 900°C.[1]

Region 4 is the zone in which $LiBH_4$ decomposes through the reaction $LiBH_4 \leftrightarrow 1/12\, Li_2B_{12}H_{12} + 5/6\, LiH + 13/12\, H_2$ as predicted by Ohba.[18] This reaction is not expected under these hydrogen desorption conditions. However, other authors[19,20] have reported the existence of $Li_2B_{12}H_{12}$ after cycling similar materials. The NMR analysis revealed the formation of $Li_2B_{12}H_{12}$ after partial desorption (Figure 2 B). Although this seems to be thermodynamically impossible, the formation of this compound could be attributed to either kinetic reasons or to local inhomogeneities which prevented the contact between $LiBH_4$ and Mg in some regions of the sample.

Region 3 is the most suitable for the composite to be applied as a hydrogen storage system. In this region the composite shows a single plateau and higher storage capacity. Although it is possible to use the composite between regions 2 and 1, the double plateau causes a loss in the amount of hydrogen stored. To overcome this inconvenient, much higher pressures would be required.

Figure 3 showed a hysteresis between absorption and desorption equilibrium pressures. It was also noticed that the lower pressure plateau presented a difference in absorption and desorption pressure which was much more significant than the one presented by the upper plateau. This leads to a noticeable discrepancy in the hydrogen desorption van´t Hoff plot compared to the absorption plot. The small hysteresis observed in the upper plateau causes a slight displacement of the line corresponding to the reaction $Mg + H_2 \rightarrow MgH_2$. This line delimits region 1, and the small displacement can be noticed by comparing the black full lines in Figure 9. As it was previously mentioned, the lower plateau presented a much greater hysteresis. The absorption pressures of the reaction $MgB_2 + 2LiH + 3H_2 \rightarrow 2LiBH_4 + Mg$ were larger than the desorption pressures. This difference causes the line that corresponds to the reaction $MgB_2 + 2LiH + 3H_2 \rightarrow 2LiBH_4 + Mg$ to shift significantly to lower pressures. This line separates region 1 from region 2 and its displacement effect can be observed in Figure 9 by comparing the red dashed lines. These two combined phenomena cause an expansion of region 1 to lower pressures and temperatures (illustrated in Figure 9). It can also be noticed that the uneven displacement observed between the red and black lines causes the intersection of both to occur at lower temperature and pressure. Another important effect of the expansion observed in region 1 is that it will cause the displacement of regions 2 and 3 to lower pressures and temperatures. This displacement is crucial because, as it has been mentioned, region 3 is the ideal zone for the composite and its shift may limit the range of applicability or the hydrogen storage capacity of the composite.

Figure 9, shows an overlapping of absorption and desorption van´t Hoff plots. The marks represents the experimental pressure obtained from absorption and desorption isotherm measurements at 450°C, 425°C, 400°C and 340°C.

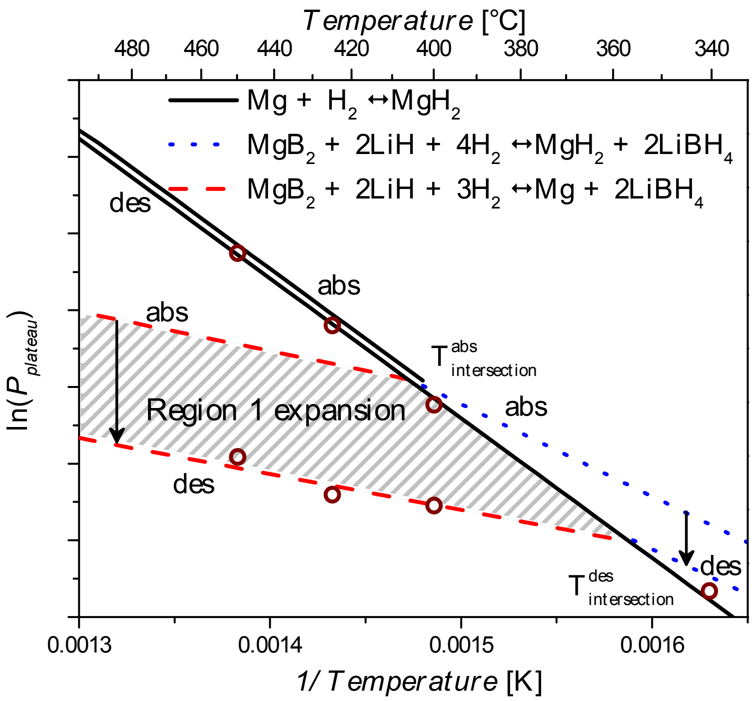

Figure 9: Absorption and desorption van´t Hoff plot for the sample LBMN. The marked points represent the measured desorption data.

It is important to highlight that between 360°C and 413°C the system presents different pathways for dehydrogenation and hydrogenation. This phenomenon has not been previously studied in the literature. During desorption, MgH_2 first releases hydrogen, obtaining the mixture $2LiBH_4$:Mg. Then, at a lower pressure, $LiBH_4$ decomposes to form MgB_2 and LiH. Unlike desorption, during the absorption process, complete hydrogenation occurs through a single reaction, in which the MgB_2:2LiH mixture reacts with hydrogen to form MgH_2 and $LiBH_4$. The line in Figure 8 corresponding to the reaction $MgH_2 + 2LiBH_4 \rightarrow MgB_2 + 2LiH + 4H_2$ was estimated considering that this reaction becomes thermodynamically more favorable when the equilibrium pressure of the MgH_2 is lower than the pressure corresponding to the $Mg + 2LiBH_4 \rightarrow MgB_2 + 2LiH + 3H_2$ reaction. It is worth noting to notice that the latter reaction cannot occur due to the absence of Mg in those conditions. At 340°C the estimated line in Figure 8 predicts the simultaneous decomposition of MgH_2 and $LiBH_4$. However, the pressure-composition isotherm measurements performed at this temperature showed that only the desorption of MgH_2 occurs and $LiBH_4$ does not decompose. This could be attributed to slow desorption kinetics of $LiBH_4$ at lower temperatures.

The results obtained from the isotherm measurements indicate that the hysteresis between absorption and desorption is to be highly considered when analyzing the viability of this composite for real applications. The difference in the reaction pathways between absorption and desorption in the temperature range bounded by 360°C and 413°C establishes a practical limitation in the applicability of the material as a hydrogen storage system.

4. CONCLUSIONS

The thermodynamic of the Ni catalyzed $2LiBH_4$:MgH_2 composite's reaction with hydrogen was investigated. The lower limit temperature was found to be 413°C at which the reaction $MgB_2 + 2LiH + 3H_2 \leftrightarrow 2LiBH_4 + Mg$ occurs instead of the $MgB_2 + 2LiH + 4H_2 \leftrightarrow 2LiBH_4 + MgH_2$ reaction as had been previously proposed. Above 413°C, two pressure plateaus were observed; the first corresponding to the formation of $LiBH_4$ and the second to formation of MgH_2.

The presence of the double plateau and the temperature at which the split occurs were predicted by Walker.[8] In our experiments this double plateau was observed only for temperatures over 413°C. Catti et al.[10] recently showed the presence of this double plateau in a system with an excess of MgH_2. In that work, a threshold temperature of around 370°C can be observed. This threshold is the temperature where the intersection of the lines corresponding to the two hydrogenation reactions occurs. Due to the additional Mg, the presence of the double plateau is observed at a temperature significantly lower (below 340°C) than the threshold temperature predicted by Walker[8] (near 426°C) and Catti[10] (near 370°C). Whereas these double plateaus observed at temperatures below the intersection may not correspond to the same reactions than the ones observed at higher temperatures, the enthalpies obtained from their calculations showed no difference between the reactions on both ends of this threshold. In the present work we have found a limit temperature that is much closer to the one predicted by Walker[8] and a significant change in the slope after the intersection. This change clearly indicates that a different reaction is occurring when the threshold temperatures is surpassed.

The hysteresis between the absorption and desorption plateau pressures of the composite was studied. The construction of the van't Hoff plot for the hydrogen absorption and desorption reactions allowed identifying the hysteresis as a limiting factor in the applicability of the system. Therefore, efforts should be mainly focused towards the viability of the system i.e. the addition of catalysts that increased the reaction rate. Based on the results presented in this article it is clearly necessary that hysteresis should be taken into account. Moreover, thorough work will be required to decrease the equilibrium pressure drop that occurs in desorption compared to absorption. This is of great importance because a composite may be following different reaction paths in absorption and desorption, even when both reaction occur at the same temperature. This difference in reaction paths should be considered for the design of a storage system based on $2LiBH_4$:MgH_2.

Supporting Information

S1. FTIR spectra of $2LiBH_2$:MgH_2 composite (LBMN).

S2. PCI measurements of $50MgH_2$:1Ni samples.

"This material is available free of charge via the Internet at http://pubs.acs.org."

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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GRAPHICAL ABSTRACT