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(Article begins on next page)
Enhanced hydrogen uptake/release in 2LiHeMgB$_2$ composite with titanium additives

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Abstract

The influence of different titanium additives on hydrogen sorption in LiHeMgB$_2$ system has been investigated. For all the composites LiHeMgB$_2$eX (X = TiF$_4$, TiO$_2$, TiN, and TiC), prepared by ball-milling in molar ratios 2:1:0.1, the hydrogen uptake/release cycles were performed. In-situ synchrotron radiation powder X-ray diffraction (SR-PXD) and attenuated total reflection infrared spectroscopy (ATR-IR) have been used to characterize crystal phases developed during the hydrogen absorption/desorption cycles.

All the composites with the titanium additives displayed an improvement of reaction kinetics, especially during hydrogen desorption. The LiHeMgB$_2$eTiO$_2$ system reached a storage of about 7.6 wt % H$_2$ in 1.8 h for absorption and 2.7 h for desorption. Using in-situ SR-PXD measurements, magnesium was detected as an intermediate phase during hydrogen desorption for all composites. In the composite with TiF$_4$, the formation of new phases (TiB$_2$ and LiF) were observed. Characteristic XRD peaks of TiO$_2$, TiN, and TiC additives were always present during hydrogen absorption/desorption. For all as-milled composites, ATR-IR spectra did not show any signals for borohydrides, while for all hydrogenated composites BeH stretching ($2450e2150$ cm$^{-1}$) and BeH bending ($1350e1000$ cm$^{-1}$) bands were exactly the same as for commercial LiBH$_4$.

1. Introduction

Hydrogen can be one of the alternative energy carriers, which should replace the traditional fossil fuels in the near future. One of the promising materials for hydrogen mobile application which has been studied approximately for 10 years is LiBH$_4$ [1]. Having high gravimetric and volumetric hydrogen density, this material, though, exhibits unfavorable kinetics and thermodynamics for real application in fuel cells. Recently, it was found that LiBH$_4$ can be destabilized by the addition of MgH$_2$, showing better decomposition kinetics with respect to the pure compound [2]. A detailed analysis of the reversible interaction between LiBH$_4$ and MgH$_2$ was made in [3] and can be summarized as follow:

$$\text{2LiBH}_4 + \text{MgH}_2 \Rightarrow 4 \text{LiH} + \text{Mg} + 4 \text{H}_2$$ (1)

The direct reactions (1) take place at w400 C. Opposite reactions, with simultaneous formation of LiBH$_4$ and MgH$_2$ under 50 bar of H$_2$, were conformed at the temperatures 250e300 C [3]. It was observed that suitable additives might decrease reaction temperatures and improve kinetics of Eq. (1). Experimental evidence of kinetic improvement for reversible middle-temperature Na, Li and Al based complex hydrides doped by titanium additives appeared in 1997 [4]. It has also been reported that the kinetic improvement of the reaction (1) was reached by addition of 1 mol% of TiF$_4$ [5]. The property enhancement arising upon this additive persists well in the subsequent hydrogen uptake/release cycles. Another prominent example of the additives effect was the composite LiBH$_4$eMgH$_2$eTi[OCH(CH$_2$)$_2$]$_4$ mixed in molar ratio 2:1:0.1 [6]. After ball-milling TiO$_2$ anatase was found and during 1-st hydrogen desorption Ti$_2$O$_3$ and TiB$_2$ appeared to be stable after cycling. XPS analysis showed that the reduction of Ti(IV) to Ti(III) was coupled with the migration of titanium species from the surface into the bulk of the composite. The role of additives and microstructure repnentm in LiBH$_4$eMgB$_2$ system were studied in [7,8], revealing that two main factors, proposed as potential driving force for kinetic improvement, were related to (i) favoring heterogeneous nucleation of MgB$_2$ and (ii) increasing of interfacial area trough grain repnentm. Tita-nium diboride (TiB$_2$) has the same hexagonal lattice structure as MgB$_2$ with very small (1.85%) directional and interplanar misPt. This fact is a necessary condition for heterogeneous nucleation of MgB$_2$ because of the interfacial energy lowering. The appropriate concentration of the additive and its homo-geneous distribution were found to be the main conditions for the efficient heterogeneous nucleation of MgB$_2$. However because of no change of the limiting rate neither for hydrogen absorption (contracting volume model) nor for desorption (interfaced-controlled one-dimensional growth) [8], induced by the additives, the latter do not show catalytic behavior. The theoretical work [9] has shown that thermodynamic stability of point defects in complex hydrides dePnes the ground or inter-mediate states or the driving force for atomic motion. Incor-poration of Ti cations in LiBH$_4$ is energetically unfavorable suggesting that only surface effect takes place.

In order to understand thoroughly the effect of titanium additives, where metallic part is Ti and non-metal is the element of 2-nd period of the Periodic Table from F to C, we have started a systematic investigation. In this work the study on the influence of several titanium additives (TiF$_4$, TiO$_2$, TiN and TiC) on reversible hydrogen reactions in 2LiHeMgB$_2$ system during the hydrogen uptake/release cycles is presented.

2. Experimental details
Commercial LiH (95%, Sigma Aldrich) and MgB\(_2\) (>96%, Alfa Aesar) powders were used to prepare composite with titanium additives in molar ratios 2:1:0.1, respectively. TiF\(_4\) (98%, Alfa Aesar), TiO\(_2\) (rutile, 99.7%, Sigma Aldrich), TiN (97.7%, Alfa Aesar) and TiC (99.5%, Alfa Aesar) were chosen as additives. The composites of powders were high-energy milled for 5 h using Spex 8000 M Mixer Mill in argon atmosphere. Stainless steel balls 10 mm in size with 10:1 ratio balls to powders were used.

Hydrogen sorption measurements were carried out in a commercial Sievert\(\text{Os}\) type apparatus (PCTPro 2000). The milled composites were hydrogenated under 50 bar of hydrogen pressure at 330 or 350 C in a special high pressure temperature sample holder. Hydrogen desorption was per-formed under 5 bar back pressure of hydrogen at 380 C, after previous absorption. Five complete hydrogen uptake/release cycles were performed.

In-situ SR-PXD was performed in D3 beamline at DESY Hamburg (Germany). The samples were airtight encapsulated in sapphire capillaries to be installed in a special in-situ SR-PXD cell; further details are described in [10]. Samples after complete 1-st hydrogen absorption were heated at 5 C/min from room temperature up to 380 C and kept in isothermal conditions for 2 h and then cooled down to room temperature. All handling and preparation of materials took place in a glove-box with continuously purified argon atmosphere and oxygen and moisture values were less than 1 ppm.

ATR-IR (Attenuated total reflection infrared) spectra were taken with a Bruker-ALPHA Platinum spectrometer with ATR diamond crystal accessory. The spectra were recorded in 4000-6575 cm\(^{-1}\) range with 2 cm\(^{-1}\) resolution. Sixty four scans were averaged for background and sample spectra. All the measurements were carried out in the nitrogen purged glove-box with oxygen and moisture levels less that 0.1 ppm.

3. Results and discussion

3.1. Hydrogen uptake/release cycling

As a reference, a complete hydrogen uptake/release cycle for the LiH-MgB\(_2\) system without any additive has been per-formed. In Fig. 1, the results of volumetric analysis of hydrogen absorption at 350 C and 50 bar H\(_2\) and desorption at 380 C and 5 bar H\(_2\) for LiH-MgB\(_2\) in molar ratio 2:1 are presented.

The reaction rate of volumetric absorption and desorption is approximately six times different: w20 h are required for hydrogenation (w8.7 wt% H\(_2\)) and more than 120 h for complete dehydrogenation. A two-step hydrogen release was observed, displaying: approximately w2.3 wt% H\(_2\) from MgH\(_2\) and w6.4 wt% H\(_2\) from LiBH\(_4\) decomposition. Absorption curve is very similar to that obtained in [11] at the same conditions. Probably, due to a slightly smaller desorption temperature (400 C in [11] and 380 C in present work) the process in our case was much slower although it showed the same two-step reaction.

The 1-st hydrogen absorption/desorption cycle in the LiH-MgB\(_2\)-TiF\(_4\) system (Fig. 2) showed similar hydrogen absorption time (w20 h) but lower gravimetric capacity (w7.5 wt% H\(_2\)) compared to that of the unmodified LiH-MgB\(_2\) (Fig. 1). Because of slower reactions by grain re-attrition in solid material under repeating of hydrogen sorption reactions. After that, the system displays three-step reversible reaction (w2.3 wt% H\(_2\) in w0.7 h; w6.0 wt% H\(_2\) in w2.2 h; and further to be complete) and (w2.3 wt% H\(_2\); in w0.6 h; w7.4 wt% H\(_2\) in w5.4 h; and further to be complete) on hydrogen absorption and desorption, respectively. It can be concluded that the rate of hydrogen absorption and desorption at various steps is increased because of the addition of TiF\(_4\) to the LiH-MgB\(_2\) system, though hydrogen storage capacity was lowered by 1.2 wt% H\(_2\).

For the LiH-MgB\(_2\)-TiO\(_2\) system, at least two cycles were necessary to stabilize hydrogen absorption/desorption properties (Fig. 3). After the 2-nd cycle, the system showed w8.1 wt% H\(_2\) hydrogen storage capacity after w10 h of hydrogenation. Beginning from 3-rd cycle two reaction steps were very well distinguished and resulted to w7.6 wt% H\(_2\) in w1.8 h and 2.7 h for hydrogen absorption and desorption, respectively. In this case, rates for hydrogen absorption and desorption are rather similar.

During the 1-st cycle, LiH-MgB\(_2\)-eTiO\(_2\) showed the same value of hydrogen gravi-metric density as the unmodified LiH-MgB\(_2\), but with faster kinetics.

The results of hydrogenation/dehydrogenation reactions in the LiH-MgB\(_2\)-eTiN system are shown in Fig. 4. After the 1-st cycle, the process is stable and requires w20 h to reach the maximum gravimetric capacity of w8.0 wt% H\(_2\). The hydrogenation curve does not show distinctive steps, however during the hydrogen desorption three separate steps are clearly visible. The 4-th desorption cycle displays only two steps (w2.6 wt% H\(_2\) in w0.5 h; w7.9 wt% H\(_2\) in w9.2 h) and the process is not completed. The LiH-MgB\(_2\)-eTiN system, indeed, showed 12 times faster desorption rate than the unmodified LiH-MgB\(_2\), though hydrogen storage capacity was reduced by w0.7 wt% H\(_2\).

For the LiH-MgB\(_2\)-eTiC system at least four cycles were needed in order to have a stable hydrogen uptake/release reaction. Hydrogen storage capacity of w7.0 wt% H\(_2\) within w20 h was achieved at the 5-th cycle (Fig. 5). Only for hydrogen desorption it was possible to distinguish the 1-st step (w2.0 wt% H\(_2\) in w0.5 h; and further to be complete). We conclude that, among all presented systems with titanium additives, the LiH-MgB\(_2\)-eTiC one showed the major reduction in hydrogen storage capacity (w1.7 wt% H\(_2\)) though much higher hydrogen desorption rates were observed with respect to the unmodified LiH-MgB\(_2\) system.

In conclusion, all titanium additives in the LiH-MgB\(_2\)-eX systems (X ¼ TiF\(_4\), TiO\(_2\), TiN and TiC) demonstrated kinetic improvement, especially during hydrogen desorption. The system with the TiO\(_2\) additive showed faster rates for both hydrogen uptake and release, together with the lowest decrease in hydrogen storage capacity (w0.6 wt% H\(_2\)). One important note that should be mentioned in this subtitle is the value of hydrogen absorption and desorption capacity. Theo-retically, during hydrogen uptake/release cycling the value of hydrogen storage capacity must be exactly the same as under complete absorption or desorption, of course if the system is stable. In present results (Figs. 1e5) quite often small uncer-tainties were present where hydrogen capacity under desorption was higher than that under absorption. It might be explained by a shorter incubation period before the system start to react, especially in the next cycles. It is suggested that during manual switching from dehydrogenation to hydride-nation some amount of hydrogen could be absorbed when data acquisition had not been active yet.

3.2. In-situ SR-PXD for LiH-MgB\(_2\)-eX (X ¼ TiF\(_4\), TiO\(_2\), TiN, TiC) systems

For all hydrogenated LiH-MgB\(_2\)-eX (X ¼ TiF\(_4\), TiO\(_2\), TiN, TiC) systems in-situ SR-PXD analysis was performed (Fig. 6). Traces of MgB\(_2\) were found in all the samples after 1-st hydrogen absorption, suggesting that the hydrogenation process was not completed. At
the beginning of 1st hydrogen desorption reaction, pure magnesium phase was clearly visible, con-""
Obviously, the explanation of the pure LiBH₄ in the spectra of the hydrogenated composites catalytic effect by metal oxides should be found by tools of evidences the presence of some binary compounds. As it can surface science. Indeed, the interaction of high surface area be clearly seen on Fig. 9, the baselines of all the hydrogenation oxides (alumina, titania or their mixtures) with gas has been composites Pt well with the vibrational profile of MgH₂, widely studied in heterogeneous catalysis. With respect to Among the four composites, those with TiF₄, TiO₂, and TiC alumina or titania, the single phase alumina-titania solid (spectrum 1e3 in Fig. 9) have very similar baseline profiles in the acids [26] have stronger acid sites and higher acid site density. low energy region of the ATR-IR spectra, whereas the These facts, coupled with their high surface area produce the composite with the TiN additive (spectrum 4) obviously has materials with an even larger number of acid sites per gram, some additional absorption, which has the best Pt with the making them useful in heterogeneous catalysts. Probably, for vibrational profile of TiN (the latter) spectra of other reference TiN and TiC catalytic effects also can be explained by their compounds can be found in the Fig. S1 of the Supporting information toward the surface molecular hydrogen since no Information).

Even after hydrogenation, no absorption peaks chemical reactions with these additives were found. due to TiF₄ at ca. 750 cm -1 are observed in the composite with Because of high reactivity of LiBH₄, it is not easy to find an TiF₄ additive. It is not possible to identify the presence of other additive which is not consumed by chemical reaction. In most phases, (LiF, TiB₂, TiO₂, TiC, Ti) from these spectra, since they cases, proposed in literature additives behave as reagents all have rather similar profile in the low region (Fig. S1), producing intermediates but finally cannot be recovered to the however, their presence cannot be excluded. Our conclusions parent reagents. For TiF₄, TiO₂, TiN and TiC, depending on the are supported by the SR-PXD results. non-metal, the standard enthalpy of formation are 1649.3; 3.4.

General discussion 944.0; 338.1 and 184.5 kJ/mol, respectively [27]. Depending on the free energy for the possible interactions between the additives and LiH or LiBH₄, their behavior can be different: Theoretically a general catalytic mechanism for reaction chemical, physical etc. However, the kinetics of hydrogen between LiBH₄ and MxN additive (where M is metal with n sorption is related to the surface properties of the additives. valence; X is halogen) would be presented as follows: We suppose that chemically unreacted titanium additives (TiO₂, TiN and TiC) could be the Oxidative surface centers. nLiBH₄ + MxN / nLiX + MBₙ (4) where dissociation of molecular hydrogen under hydrogenation and association of atomic hydrogen under dehydrogenation can be accelerated. nLiX + M(BH₄)n / nLiX + MBn + 2nH₂ (5) In recent work [28] the investigation of the effect of Ti, TiH₂, TiB₂, TiCl₃, and TiF₃ additives on the hydrogen sorption kinetics in LiH/MgB₂ mixture has been done. There it was

\[ \text{nLiX} + \text{MBₙ} \rightarrow \text{nH}_2 + \text{M} \]

(7)

This mechanism was observed in case of solid state react - our present results, the TiH₂, TiB₂, TiCl₃, and TiF₃ additives to LiBH₄ and TiCl₃ [14,15]. The reaction occurs at were mostly responsible for faster hydrogen desorption room temperature with the formation of LiCl. Similar result kinetics and only metallic titanium in LiHeMgB₂ composite was observed in [16] for the interaction between LiBH₄ and actively participate in both hydrogenation and dehydroge- TiCl₄; nation process [28]. This is again the transformation of more pronounced role of anion (the more electronegative anion in 4LiBH₄ / TiCl₄ / Ti(BH₄)₃ + 4LiCl / Ti(BOH)₃ / 1/2BH₂ / Ti₅Cl₄ / 1/2H₂ (7) (titanium additives) at association of atomic hydrogen than dissociation of molecular hydrogen. From another hand, It was concluded that the dehydrogenation temperatures of based on the measurements for LiBH₄/MgH₂ composite Ti/(BH₄)₃ was 298 K.

Thus, at room temperature and ambient catalyzed by TiCl₃, ZrCl₄ and HCl₄ additives in [29], we pressure Ti/(BH₄)₃ decomposes releasing hydrogen and suggest that regards to hydrogen desorption Ti cation might possibly trace amounts of gaseous B₂H₆. Similar ion-exchange be the most significant element among all of IVB group in interactions (4) could take place in case of LiBH₄ with MgCl₂ Periodic Table. In conclusion of the discussion, it would be [17], MnCl₂ [18] or ZnF₂ [19], and as in the present paper, with reasonable to proceed the studying about the effects of tita- TiF₄. In case of RHCs, based on lithium borohydride, the nium additives on hydrogen sorption of LiHeMgB₂ composite additives likely react with LiBH₄ in similar way. However, in order to find suitable chemical structure and optimal MgH₂ plays an additional role in the kinetic improvement [9], amount of the proposed dopant. In addition to that, the In our experiment, because of the higher temperature of LiBH₄ comparison with another type of additives (e.g. Sc- or Ce- crystallization, Ti/(BH₄)₃ was not found as a product of reaction based [30] additives) will be important for general under- (4) but the formation of LiF was confirmed. standing of their behavior.

Conclusions

It can be noted that the combination of the volumetric, SR-PXD and spectroscopic techniques gives a comprehensive description of reactive hydride composites. In present work, we studied the effects of titanium-based additives on hydrogen absorption/desorption properties of 2LiHeMgB₂ composite. We found that:

- All the systems with additives showed an improvement of reaction rate, especially for hydrogen desorption. In case of TiO₂, the composite demonstrated the best kinetics for both hydrogen absorption and desorption (w7.6 wt% H₂ in w1.8 h and 2.7 h, respectively). Moreover, hydrogen storage capacity of LiHeMgB₂/TiO₂ system, during 3ve sorption cycles, was only slightly reduced by w0.6 wt% H₂ with respect to that of the unmodified LiHeMgB₂.

For all composites, hydrogen desorption was observed through intermediate step of reaction (1) with the formation of pure magnesium. For LiHeMgB₂/TiO₂ composite, magnesium phase was present during a short time and almost complete hydrogen sorption was confirmed after 2 h at 380°C.

IR analysis has shown the presence of peaks due to [BH₄]²⁻, proving the LiBH₄ formation after hydrogen absorption of the all composites. The spectrum of the ball-milled LiHeMgB₂/TiF₄ did not exhibit any peaks due to TiF₄, neither after ball-milling nor after 1-st hydrogen absorption. The baselines of the spectra of hydrogenated LiHeMgB₂X (X = TiF₄, TiO₂, TiN and TiC) systems indicate the presence of MgH₂. Only TiF₄ additive was chemically active in the composite and consequently new phases (LiF and TiB₂) were detected by SR-PXD measurements. For other LiHeMgB₂X systems (X = TiO₂, TiN and TiC) titanium-based additives were chemically inert during the entire experiment. It means that TiO₂, TiN and TiC did not react during hydrogen sorption and apparently they could be respon-sible for kinetic effect as catalysts.
Acknowledgments

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References


Fig. 1 Hydrogen sorption for LiHeMgB$_2$ in molar ratio 2:1. Conditions for absorption and desorption were 350 °C at 50 bar H$_2$ and 380 °C at 5 bar H$_2$, respectively.

Fig. 2 Hydrogen sorption for LiHeMgB$_2$eTiF$_4$ in molar ratio 2:1:0.1 during 5 cycles. Absorption (a) at 350 °C and 50 bar H$_2$; desorption (b) at 380 °C and 5 bar H$_2$.

Fig. 3 Hydrogen sorption for LiHeMgB$_2$eTiO$_2$ (rutile) in molar ratio 2:1:0.1 during 5 cycles. Absorption (a) at 330 °C and 50 bar H$_2$; desorption (b) at 380 °C and 5 bar H$_2$. 
Fig. 4. Hydrogen sorption for LiHeMgB\textsubscript{2}cTiN in molar ratio 2:1:0.1 during 5 cycles. Absorption (a) at 330 C and 50 bar H\textsubscript{2}; desorption (b) at 380 C and 5 bar H\textsubscript{2}.

Fig. 5. Hydrogen sorption for LiHeMgB\textsubscript{2}cTiC in molar ratio 2:1:0.1 during 5 cycles. Absorption (a) at 330 C and 50 bar H\textsubscript{2}; desorption (b) at 380 C and 5 bar H\textsubscript{2}.

Fig. 6. In-situ SR-PXD under 5 bar H\textsubscript{2} for LiHeMgB\textsubscript{2}cTiX (X \textsubscript{[TiF\textsubscript{4}} (a); TiO\textsubscript{2} (b); TiN (c); TiC (d))] in molar ratio 2:1:0.1 composites after complete 1-st hydrogen absorption.
Fig. 7 e ATR-IR spectra of \( \text{LiHeMgB}_{2}\text{eX} \) (\( X = \text{TiF}_4, \text{TiO}_2, \text{TiN}, \text{TiC} \)) systems after ball-milling. The reference spectrum of LiH is also shown. Spectra are translated along the Y axis for better representation.

Fig. 8 e ATR-IR spectra of \( \text{LiHeMgB}_{2}\text{eX} \) (\( X = \text{TiF}_4, \text{TiO}_2, \text{TiN}, \text{TiC} \)) systems after 1st hydrogen absorption. The reference spectrum of \( \text{LiBH}_4 \) is also shown. Spectra are translated along the Y axis for better representation.

Fig. 9 e ATR-IR spectra in low region of \( \text{LiHeMgB}_{2}\text{eX} \) (\( X = \text{TiF}_4, \text{TiO}_2, \text{TiN}, \text{TiC} \)) systems after 1st hydrogen absorption: Spectra 1e3 correspond to the composites with \( \text{TiO}_2 \), \( \text{TiC} \), and \( \text{TiF}_4 \), respectively, spectrum 4 corresponds to the composite with \( \text{TiN} \) additive.