## Enhanced hydrogen uptake/release in 2LiH–MgB2 composite with titanium additives

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# Enhanced hydrogen uptake/release in 2LiHeMgB$_2$ composite with titanium additives

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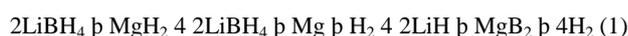
Abstract

The influence of different titanium additives on hydrogen sorption in LiHeMgB$_2$ system has been investigated. For all the composites LiHeMgB$_2$eX (X ¼ TiF$_4$, TiO$_2$, TiN, and TiC), prepared by ball-milling in molar ratios 2:1:0.1, Þve hydrogen uptake/release cycles were performed. In-situ synchrotron radiation powder X-ray diffraction (SR-PXD) and attenu-ated total reßection infrared spectroscopy (ATR-IR) have been used to characterize crystal phases developed during the hydrogen absorptionedesorption 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 w1.8 h for absorption and w2.7 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$_4$ addition the formation of new phases (TiB$_2$ and LiF) were observed. Characteristic diffraction peaks of TiO$_2$, TiN and TiC additives were always present during hydrogen absorptionedesorption. 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 applica-tion 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:

$$2LiBH_4 \text{ þ } MgH_2 \text{ 4 } 2LiBH_4 \text{ þ } Mg \text{ þ } H_2 \text{ 4 } 2LiH \text{ þ } MgB_2 \text{ þ } 4H_2 \quad (1)$$

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$_2$, was conÞrmed 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$_3$ [5]. The property enhancement arising upon this additive persists well in the subsequent hydrogen uptake/release cycles. Another prom-inent example of the additives effect was the composite LiBH$_4$eMgH$_2$eTi{OCH(CH$_3$)$_2$}$_4$ 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 reÞnement in LiBH$_4$eMgH$_2$ 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 reÞnement. Tita-nium diboride (TiB$_2$) has the same hexagonal lattice structure as MgB$_2$ with very small (1.85%) directional and interplanar misÞt. 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 efÞcient 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 deÞnes 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 inßuence of several titanium additives (TiF$_4$, TiO$_2$, TiN and TiC) on reversible hydrogen reactions in 2LiHeMgB$_2$ system during Þve 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 SievertÕs type apparatus (PCTpro 2000). The milled composites were hydrogenated under 50 bar of hydrogen pressure at 330 or 350 C in a special high pressuree 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 puriÞed argon atmosphere and oxygen and moisture values were less than 1 ppm.

ATR-IR (Attenuated total reßection infrared) spectra were taken with a Bru¬ker-ALPHA Platinum spectrometer with ATR diamond crystal accessory. The spectra were recorded in 4000e375 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 Þlled 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 LiHeMgB$_2$ 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 LiHeMgB$_2$ in molar ratio 2:1 are presented.

The reaction rate of hydrogen 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 absorptionedesorption cycle in the LiHeMgB$_2$eTiF$_4$ system (Fig. 2) showed similar hydrogen absorption time (w20 h) but lower gravimetric capacity (w7.5 wt% H$_2$) compared to that of the unmodiÞed LiHeMgB$_2$ (Fig. 1). Because of slower reactions at the 1-st cycle (1-st hydrogen absorption and 1-st desorption), an activation process could take place. It might be explained by grain reÞnement 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; w6.6 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 desorp-tion at various steps is increased because of the addition of TiF$_4$ to the LiHeMgB$_2$ system, though hydrogen storage capacity was lowered by 1.2 wt% H$_2$.

For the LiHeMgB$_2$eTiO$_2$ 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, LiHeMgB$_2$eTiO$_2$ showed the same value of hydrogen gravi-metric density as the unmodified LiHeMgB$_2$ but with faster kinetics.

The results of hydrogenation/dehydrogenation reactions in the LiHeMgB$_2$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 LiHeMgB$_2$eTiN system, indeed, showed 12 times faster desorption rate than the unmodified LiHeMgB$_2$, though hydrogen storage capacity was reduced by w0.7 wt% H$_2$.

For the LiHeMgB$_2$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 Þrst step (w2.0 wt % H$_2$ in w0.5 h; and further to be complete). We conclude that, among all presented system with titanium additives, the LiHeMgB$_2$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 unmodi-Þed LiHeMgB$_2$ system.

In conclusion, all titanium additives in the LiHeMgB$_2$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 hydroge-nation some amount of hydrogen could be absorbed when data acquisition had not been active yet.

### 3.2. In-situ SR-PXD for LiHeMgB$_2$eX (X ¼ TiF$_4$, TiO$_2$, TiN, TiC) systems

For all hydrogenated LiHeMgB$_2$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 first hydrogen desorption reaction, pure magnesium phase was clearly visible, con-firming the occurrence of a two-step reaction (1).

In the LiHeMgB$_2$eTiF$_4$ system (Fig. 6a), after the 1-st hydrogen absorption step, the expected products (LiBH$_4$ and MgH$_2$) were present as the main phases. In addition, new phases TiB$_2$ and LiF were detected in the sample, whereas there was no evidence of present TiF$_4$. Most probably, LiF formed during milling (similar to TiF$_3$ in [5]) by the following reaction:

$$4LiH þ TiF_4 / 4LiF þ TiH_2 þ H_2 \qquad\qquad (2)$$

And TiH$_2$ can easily react at higher temperatures with LiBH$_4$ to produce TiB$_2$ (estimated reaction enthalpy is w6.5 kJ/ mol H$_2$):

$$2LiBH_4 þ TiH_2 / 2LiH þ TiB_2 þ 4H_2 \qquad\qquad (3)$$
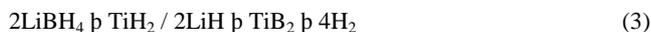
Upon heating the hydrogenated LiHeMgB$_2$eTiF$_4$ composite started hydrogen desorption through MgH$_2$ decomposition and Mg formation just before isothermal conditions. During the heat treatment two diffraction peaks characteristic of a cubic phase appeared. These peaks were quite broad, likely due to the superposition of reflections due to LiH and LiF phases. Upon cooling, the peaks of o-LiBH$_4$ reappeared. It should be denoted that, after the isothermal treatment of 2 h at 380 C, no diffraction peaks due to MgH$_2$ or Mg phases were detected, suggesting that after this period the first step of the reaction (1) was completed.

The SR-PXD pattern of the LiHeMgB$_2$eTiO$_2$ system (Fig. 6b) after 1-st hydrogen absorption showed diffraction peaks due to the products of the reversible reaction (1) (LiBH$_4$ and MgH$_2$), together with a small amount of residual MgB$_2$. Most of TiO$_2$ peaks were present during whole SR-PXD experiment. It means that this additive might be chemically inert toward the reagents. During heating of the hydrogenated mixture, hydrogen desorption started just before 380 C, as it was already observed for the previous composite, showing pure magnesium as intermediate. After cooling, no diffraction peaks related to Mg or MgH$_2$ phases were observed.

The pattern of the LiHeMgB$_2$eTiN system (Fig. 6c) showed diffraction peaks due to the products of reactions (1), similarly to the previous cases, together with evidence of the parent TiN phase. The additive was present during the whole SR-PXD measurement, confirming that no chemical reactions between the additive and the hydrides took place. Overall, the behavior of LiHeMgB$_2$eTiN sample under heating and cooling was similar to that observed for LiHeMgB$_2$eTiO$_2$ mixture.

The LiHeMgB$_2$eTiC system (Fig. 6d ) also showed the products of hydrogen absorptionedesorption and unreacted titanium-based additive, similarly to the case of LiHeMgB$_2$eTiO$_2$ and LiHeMgB$_2$eTiN mixtures. Four diffrac-tion peaks of TiC phase, indeed was observed SR-PXD patterns, confrming that the additive does not react with the hydrides.

Based on SR-PXD observations, it can be concluded that only TiF$_4$ additive was chemically reacting in the composite during ball-milling, so that the new LiF and TiB$_2$ phases were formed.

3.3. ATR-IR spectroscopy of milled and hydrogenated LiHeMgB$_2$eX (X ¼ TiF$_4$, TiO$_2$, TiN, TiC) systems

Infrared spectroscopy is a suitable tool for characterization of metal borohydrides since the molecular vibrations of [BH$_4$] group are readily distinguishable in the spectrum. Further-more, the normal modes of [BH$_4$] group are very sensitive to the surrounding so that the alterations in a borohydride chemical composition, lattice symmetry, and the bond type can be identified in the spectrum (see reference [12] and references therein).Free [BH$_4$] species belong to T$_d$ symmetry point group with four normal modes of vibration:, v2, v3, and v4, out of which the latter two triply degenerate modes are IR-active. The BeH stretching modes (v1 , v3) of [BH4] fall in the 2500e2100 cm region, HeBeH bending vibrations (v2 , v4) can be observed in the 1200e900 cm 1 region. In the Pnma space group of LiBH4, the site symmetry of [BH4] species is lowered till Cs, all modes become IR-active, and the degeneracy of normal modes is removed, giving rise to additional peaks in the spectra [13]. In this way, the IR spectrum of LiBH$_4$ is indeed a unique fingerprint of this solid.

The ball-milled LiHeMgB$_2$eX (X ¼ TiF$_4$, TiO$_2$, TiN, TiC) composites were tested by ATR before and after hydrogena-tion, in order to verify the formation of LiBH$_4$. ATR spectra for the as-prepared composites are shown in Fig. 7. The spectrum of LiH is also reported for comparison. The spectrumv$_1$ of LiH is characterized by a large absorption in the <1200 cm $^1$ region, due to the vibrations of the crystal lattice. It can be readily seen that this absorption is also present in all the LiHeMgB$_2$eX composites. It is also straightforward that LiBH$_4$ is not formed during ball-milling process, since no charac-teristic vibrations in 2500e2100 cm $^1$ and the 1200 - 900 cm $^1$ regions are present. All the composites have the baseline absorption steadily increasing at the lower frequencies, which is characteristic for MgB$_2$ (Fig. S1). No absorption peaks of TiF$_4$ at ca. 750 cm $^1$ (see Fig. S1 in Supporting Information) are observed in the composite with TiF$_4$ additive. The weak peaks at ca. 2800e3000 cm $^1$ and at ca. 1600e1400 cm $^1$ correspond to molecular vibrations of organic compounds (e.g. CeH stretching and bending of eCH$_3$ groups in aliphatic hydro-carbons; C]O groups, eCeOeCe groups, etc.). These carbon species were likely originated during ball-milling, where vials were cleaned with ethanol and a rubber O-ring was used as a gasket for sealing.

The IR-ATR spectra of ball-milled LiHeMgB$_2$eX (X ¼ TiF$_4$, TiO$_2$, TiN, TiC) composites after 1-st hydrogen absorption are presented in Fig. 8.

The characteristic [BH$_4$] vibrational profile of LiBH$_4$ is readily observable in the spectra of all hydrogenated composites. In general, the spectra of LiBH$_4$ formed in the
hydrogenation composites are similar to that one of the commercially available reference,  where  the  different components normal modes are clearly of v$_2$  v3 and v$_4$  distinguishable. The v$_1$ mode is very weak in the IR spectrum and falls in the region of the strong v$_3$ mode, such as it cannot be observed in the spectrum. In the spectrum of the composite doped with TiC, an additional peak at 1120 cm $^1$, marked with the asterisk on Fig. 9, appears. This peak, however, rather belongs to the impurities that to the modifications in LiBH$_4$, since all other principle modes remain almost unaffected. As the vibrational profile of [BH$_4$]  is almost the same in the As established by SR-PXD experiments, TiO$_2$, TiN and TiC   spectra of all the composites, we can conclude that pure LiBH4 did not react with the composites. Therefore they could only   is formed in these samples after hydrogenation. The strong catalyze hydrogen sorption kinetics. It should be mentioned   absorption due to LiH in the <1200 cm 1 region, as on the that transition metal oxides are more promising additives for   Fig. 7, is not present, which evidences the disappearance of hydrogen kinetics than pure transition metals though the   LiH phase from these samples after hydrogenation. latter have orders of magnitude higher activity to molecular The increase in baseline absorption (comparing to that of hydrogen dissociation [20e25].

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 Þt well with the vibrational proÞle 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 aluminaetitania solid (spectra 1e3 in Fig. 9) have very similar baseline proÞles 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 Þt with the making them useful in heterogeneous catalysts.

Probably, for vibrational proÞle of TiN (the ATR 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 surface activity toward the 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 Þnd 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 proÞle in the low region (Fig. S1), producing intermediates but finally cannot be recovered to the however, their presence cannot be excluded. Our conclusions parent reactants. 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 Òactive surface centersÓ, nLiBH4 þ MXn / nLiX þ M(BH4)n (4) where dissociation of molecular hydrogen under hydrogenation and association of atomic hydrogen under dehydrogenation can be accelerated. nLiX þ M(BH4)n / nLiX þ MBnþ 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 nLiX þ MBn þ 2nH2 / MXn þ nLiH þ nB þ 2nH2 (6) concluded that all these titanium additives effectively decrease the onset temperature of hydrogenation. Similar to This mechanism was observed in case of solid state reac- our present results, the TiH2, TiB2, TiCl3, and TiF3 additives tion between 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 participates in both hydrogenation and dehydroge- TiCl4: nation process [28]. This is again the conÞrmation of more pronounced role of anion (the more electronegative atom in 4LiBH4 þ TiCl4 / Ti(BH4)3 þ 4LiCl þ 1/2B2H6 þ 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 LiBH4eMgH2 composite Ti(BH4)3 was 298 K.

Thus, at room temperature and ambient catalyzed by TiCl3, ZrCl4 and HfCl4 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 signiÞcant 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 Þnd 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 absorptionedesorption properties of 2LiHeMgB$_2$ 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 LiHeMgB2eTiO2 system, during Þve 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 LiHeMgB2eTiO2 composite, magnesium phase was present during a short time and almost complete hydrogen sorption was conÞrmed after 2 h at 380 C.

IR analysis has shown the presence of peaks due to [BH4] , proving the LiBH4 formation after hydrogen absorption of the all composites. The spectrum of the ball-milled LiHeMgB2eTiF4 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 LiHeMgB2eX (X ¼ 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 detec-ted by SR-PXD measurements. For other LiHeMgB2eX systems (X ¼ 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.

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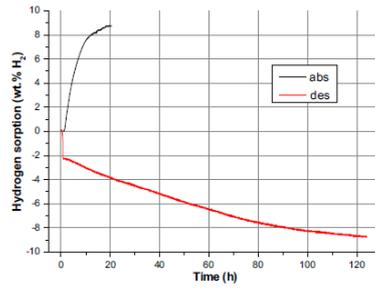
Fig. 1 e Hydrogen sorption for LiHeMgB$_2$ in molar ratio 2:1. Conditions for absorption and desorption were 350 C at 50 bar H$_2$ and 380 C at 5 bar H$_2$, respectively.
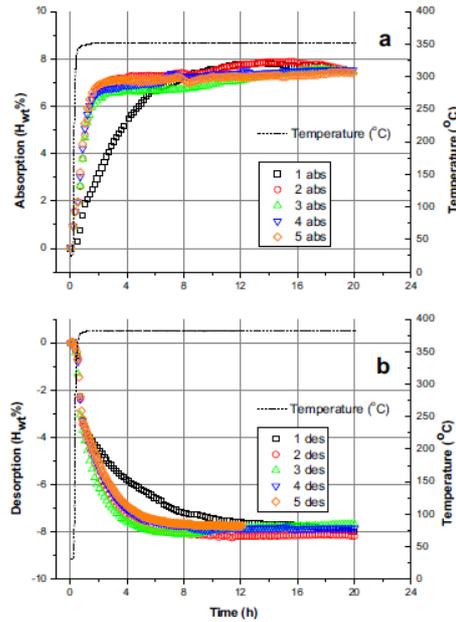


Fig. 2 e Hydrogen sorption for LiHeMgB$_2$eTiF$_4$ in molar ratio 2:1:0.1 during 5 cycles. Absorption (a) at 350 C and 50 bar H$_2$; desorption (b) at 380 C and 5 bar H$_2$.
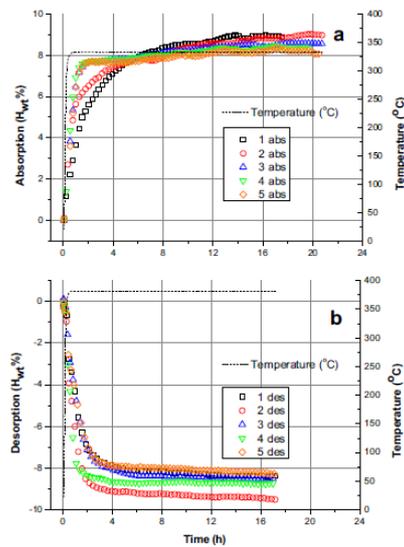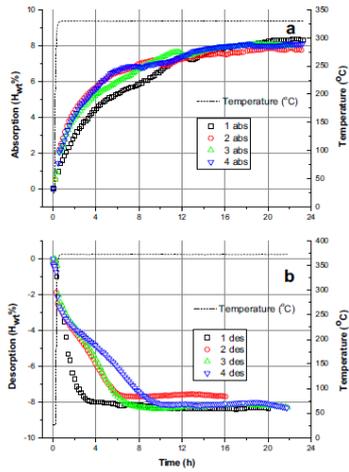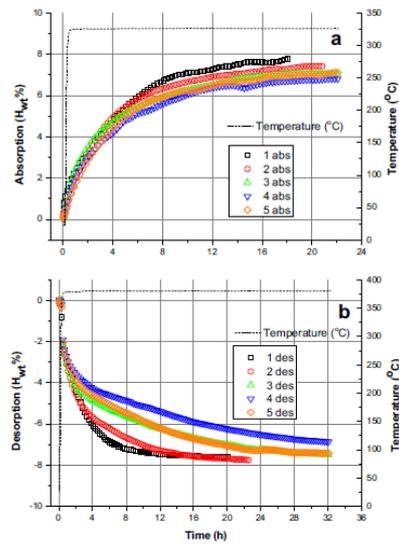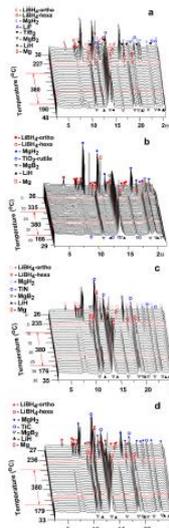


Fig. 3 e Hydrogen sorption for LiHeMgB$_2$eTiO$_2$(rutile) in molar ratio 2:1:0.1 during 5 cycles. Absorption (a) at 330 C and 50 bar H$_2$; desorption (b) at 380 C and 5 bar H$_2$

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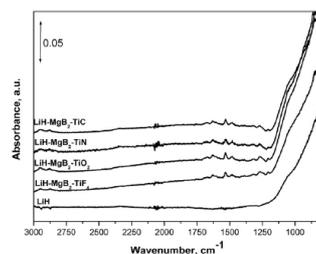
Fig. 7 e ATR-IR spectra of LiHeMgB$_2$eX (X [ TiF$_4$, TiO$_2$, TiN, TiC) systems after ball-milling. The reference spectrum of LiH is also shown. Spectra are translated along the Y axis for better representation.
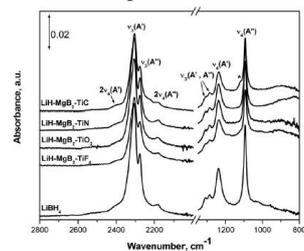


Fig. 8 e ATR-IR spectra of LiHeMgB$_2$eX (X [ TiF$_4$, TiO$_2$, TiN, TiC) systems after 1st hydrogen absorption. The reference spectrum of LiBH$_4$ is also shown. Spectra are translated along the Y axis for better representation.
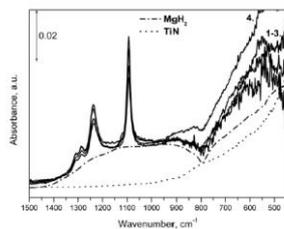


Fig. 9 e ATR-IR spectra in low region of LiHeMgB$_2$eX (X [ TiF$_4$, TiO$_2$, TiN, TiC) systems after 1st hydrogen absorption: Spectra 1e3 correspond to the composites with TiO$_2$, TiC, and TiF$_4$, respectively, spectrum 4 corresponds to the composite with TiN additive