Reactive Hydride Composite Confined in a Polymer Matrix: New Insights into the Desorption and Absorption of Hydrogen in a Storage Material with High Cycling Stability

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1. Introduction

Climate change and scarce resources demand the development of sustainable technologies.[1] In particular, environmentally benign energy technologies are necessary for any future developments, as energy is required in all areas of our life: factories, cars, or airplanes consume a lot of energy, but also the production of potable water by desalination of seawater for a rapidly increasing world population requires a substantial amount of energy.

These challenges motivate efforts to generate electric power from renewable or sustainable sources such as hydro-, wind-, or solar power.[2] However, hydropower may not be available everywhere if there is insufficient rainfall and water reservoirs are depleted, and wind and sunshine intensity, though basically available everywhere, fluctuate within minutes or hours. Therefore, technologies are required for storing electricity in times of excess supply and releasing the energy to the grid when demand is higher than generation, so-called peak shaving to balance supply and demand. Excess electricity can be utilized for the generation of green hydrogen as an energy carrier by electrolysis of water. Green hydrogen may also be directly produced by photo-splitting of water (artificial photosynthesis). Hydrogen is a gas at ambient conditions and thus difficult to store. In order to achieve reasonable volumetric energy densities, hydrogen must be compressed to high pressures, typically 350 or even 700 bars, or cooled down to 20 K for liquefaction and cryogenic storage.[3] Both, pressurization or liquefaction require much energy, reducing overall efficiency. An alternative way to store hydrogen is chemical bonding in the form of energy-rich molecules or salts, such as synthetic carbohydrates (as green plants do by photosynthesis), ammonia (by Haber–Bosch synthesis), methane, methanol, ethanol (by power-to-X processes, where, e.g., hydrogen reacts with carbon dioxide).[4] While some of these molecules are easy to handle as a fuel, the challenge to really close the CO₂ cycle with acceptable efficiency remains unsolved. A promising alternative for solid storage are metal hydrides or so-called “reactive metal hydride composites” (RHC).[5] Several complex metal hydrides and reactive hydride composites have been intensively investigated as...
potential hydrogen storage materials for mobile and stationary applications during the last decades. In particular, amide-based RHCs (e.g., magnesium amide with lithium hydride (2Mg(NH2)_2 + 4LiH)) owing to low reaction enthalpies (i.e., <45 kJ mol\(^{-1}\)) and relatively high hydrogen storage capacities (i.e., up to 5.5 wt\%) attracted considerable attention.\(^6\) In 2014, a three-component RHC family based on Mg(NH2)_2–LiH–LiBH4 was developed.\(^7\) Compared to the parent system (i.e., 2Mg(NH2)_2+4LiH),\(^8\) this new RHC family allows tuning thermodynamic, kinetic and hydrogen storage properties by simply varying the content of lithium borohydride (LiBH4). For this system, the general reaction mechanism of unloading and reloading of hydrogen follows Equation (1):

\[
6\text{Mg(NH}_2)_2 + 9\text{LiH} + x\text{LiBH}_4 \rightleftharpoons 3\text{Li}_2\text{Mg}_4(\text{NH}_2)_4 + (\text{LiNH}_2)_4(\text{LiBH}_4)_x + 9\text{H}_2
\]

The thermodynamic tuning of the system is due to the formation of differently stable products, i.e., Li2Mg4(NH2)_4, MgNH2, LiNH2, Li4(BH4)(NH2)_3, Li2(BH4)(NH2)_2, and [(LiNH2–2LiBH4) + (LiNH2–2LiBH4)] depending on the components stoichiometric ratio.\(^9\) For example, the system 6Mg(NH2)_2 + 9LiH + LiBH4 possesses an overall endothermic reaction enthalpy upon unloading of nearly 36 kJ mol\(^{-1}\) H2, implying a theoretical operational temperature of only 50 °C. The presence of LiBH4 enhances the hydrogen sorption kinetics by forming highly Li\(^{+}\) conductive species (i.e., Li2(BH4)(NH2)_3) or/and Li2(BH4)(NH2)2 capable of supporting the mass transfer at the interface between the reactants.\(^10\)

Due to the presence of multiple reactants which are in different states (i.e., liquid and solid) under operating conditions, in the Mg(NH2)_2–LiH–LiBH4 RHCs upon dehydrogenation (unloading) and rehydrogenation (loading) cycling, spatial segregation phenomena inevitably lead to a sensible decrement of the hydrogen storage capacity and a deterioration of the kinetic properties. Therefore, the spatial separation between the reversibly forming products has to be kept as small as possible and coarsening phenomena resulting in larger phase aggregates have to be suppressed. In this regard, the fabrication of composite materials consisting of a polymer matrix and RHC particles appears to be a suitable approach to limit the mentioned detrimental phenomena occurring upon unloading and reloading cycling. The dispersion of micrometer-sized RHC particles (e.g., 2LiH + MgB2 and 2Mg(NH2)_2 + 4LiH) in a polymer matrix was already successfully proven by Le et al.\(^11\) and Cao et al.,\(^12\) respectively. Le et al. demonstrated that the presence of a polyolefin (TPX\(^\text{TM}\)) matrix sensibly enhances the cycling stability of Li-RHC particles (2LiH + MgB2) by reducing the segregation of the system components on a larger length scale. A similar effect with the same polymer matrix was reported for 2Mg(NH2)_2 + 4LiH RHC particles by Cao et al., who also found a substantial slowing down of oxidative processes when the composite was exposed to air.

Although these studies clearly demonstrated the beneficial effects of an inert and highly hydrogen-permeable polymer scaffold surrounding the RHC particles, the microstructural and chemical changes upon hydrogen loading and unloading were not investigated in detail yet.

The aim of this study is to reveal the chemical composition of an RHC polymer composite on the length scale of the RHC particles in the hydrogen-loaded and unloaded state. To facilitate this, several characterization techniques were applied to characterize these composite materials. First, results on macroscopic investigations of these materials are presented, which show the cycling stability of the hydrogen uptake and desorption of the material, and also give access to the chemical composition of the different components of the composite material and their thermal properties. These latter methods include X-ray diffraction (XRD), differential scanning calorimetry (DSC), and Fourier-transform infrared spectroscopy (FTIR). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) are used to visualize the microstructural and elemental features of the composite TPX\(^\text{TM}\)–6Mg(NH2)_2–9LiH–1LiBH4 in the as-prepared hydrogen-loaded state and after 21 hydrogen storage cycles in the unloaded and reloaded state. The obtained results are put in relation to the observed hydrogen storage properties. The decision of using TPX\(^\text{TM}\) as a matrix polymer is based on i) its excellent hydrogen permeability (>800 Barrer at 180 °C can be extrapolated from the temperature-dependent measurement shown in Figure S1 (Supporting Information)), ii) its thermal stability, and iii) its chemical resistance. These properties allow scaffolding of the RHC system without preventing the hydrogen exchange and at the same time without compromising its chemical integrity. Furthermore, TPX\(^\text{TM}\) (type RT18) is a fully saturated polyolefin that exhibits no reaction with the RHC system. The RHC system 6Mg(NH2)_2–9LiH–1LiBH4 was chosen because of its relatively high hydrogen storage capacity (i.e., 4.2 wt\%) and its low reaction enthalpy (i.e., 36 kJ mol\(^{-1}\)) that allows operating this material in a temperature range suitable for TPX\(^\text{TM}\), which remains in a semicrystalline state also at the cycling temperature, as shown by the HP-DSC analysis reported in Figure S4 (Supporting Information). It should be noted that the aim of this work is not to present a new alternative hydrogen storage material, but to reveal the microstructural changes occurring in the materials during hydrogen storage cycling.

2. Results and Discussion

Herein, first the hydrogen storage performance of the RHC–polymer composite will be presented, followed by analyzing the chemical composition and the thermal properties of the composite material. The information obtained from these macroscopic investigations allows the assignment of the local distribution of characteristic chemical elements to the different components within the RHC particles in the hydrogen-loaded and unloaded state, as given by Equation (1).

2.1. Gravimetric Analysis of the Cyclic Desorption and Absorption of Hydrogen

In order to evaluate the hydrogen storage properties of the RHC–polymer composite, a gravimetric characterization of the unloading/reloading processes over 21 cycles was carried out. As the as-prepared RHC powder is in the hydrogenated state (i.e., 6Mg(NH2)_2–9LiH–1LiBH4), the first gravimetric measurement of the composite monitors the unloading process. In this process, the RHC–polymer composite releases in a single step
an amount of hydrogen equal to about 2.3 wt%. This value corresponds to 54% of the theoretical value of a complete conversion, in good agreement with the fact that the ¼ of the mass of the composite is the polymer and that the real capacity of the system is ≈3.6 wt%.\cite{6b} The following reloading process led to the full recovery of the desorbed hydrogen capacity within 15 min. The subsequent 20 cycles were characterized by a slight decrement of the reaction rates. Although this phenomenon is visible in both the unloading and the reloading processes, it is more distinct for the reloading. In fact, the complete reloading of the material after 21 cycles occurred within 40 min. The overall hydrogen storage capacity loss after 21 cycles is equal to 0.15 wt% (Figure 1). The different kinetics in unloading and reloading also indicate that the hydrogen permeability in the polymer matrix is high enough not to affect the reaction kinetics of hydrogen sorption and desorption in the RHC particles, as permeability is independent of the transport direction. TPX\textsuperscript{TM} is known to have a hydrogen permeability of ≈100 Barrer and a diffusion coefficient of $20.7 \times 10^{-10}$ m$^2$ s$^{-1}$ at 30 °C, which are high values for a polymer.\cite{12} At 160 °C, a value of 770 Barrer was measured and since the permeability with the increase of the temperature follows an Arrhenius law, the permeability is expected to increase in the range of ≈900 Barrer near the cycling temperature (180 °C) (see Figure S1 in the Supporting Information). Thus, there is no retardation of the unloading/reloading processes by the hydrogen transport properties of the polymer matrix.

2.2. Chemical Composition and Thermal Properties of the Composite and Its Components

To investigate the evolution of the composites’ chemical composition upon cycling, the X-ray diffraction patterns (Figure 2) and FTIR spectra (Figure 3) of the composite cycled 21 times and of the as-prepared composite were measured (Figures 2a,b and 3a,b, respectively). As references, the diffraction pattern of the pristine TPX\textsuperscript{TM}, of the starting RHC, and of Li$_4$(BH$_4$)(NH$_2$)$_3$ were also measured (Figures 2c,d and 3c,d; Figure S2, Supporting Information, respectively).

In the diffraction pattern obtained for the as-prepared composite, the Bragg peaks corresponding to Mg(NH$_2$)$_2$, LiH and the semicrystalline polymer are visible. Interestingly, it was not possible to assign any diffraction peak to the presence of LiBH$_4$. This might be due to the low amount of LiBH$_4$ resulting in the low intensity of its peaks. Additionally, a signal at about 31° belonging to an unknown component is observed. Several possible phases were considered (Figure S3, Supporting Information). However, none of them convincingly matched the diffraction peak at 31°. It must be noted that this unknown phase appears to be present already in the as-synthesized Mg(NH$_2$)$_2$. The diffraction pattern of the material cycled 21 times in the loaded state, similarly to the pattern of the as-prepared material, shows the Bragg reflections of Mg(NH$_2$)$_2$, LiH, and TPX\textsuperscript{TM}. Besides, the cycled material offers some low-intensity
reflects, which might be attributed to the presence of Li₄(BH₄)(NH₂)₃ and traces of Li₄Mg₆(NH₃)₂, are also observed, which indicates an incomplete reloading with hydrogen. The Bragg signals caused by TPX™ indicate that the polymeric phase did not deteriorate during the cycling period despite of the relatively high temperature (i.e., 180 °C) and despite of the applied mechanical stresses arising from the volume changes induced by the unloading and reloading processes of the RHC. The increase in intensity and decrease in the half-width of the diffraction peaks after 21 hydrogen storage cycles occur due to the increasing average crystallite size of the material over the cycling.

The components undergoing thermal transitions within the relevant temperature scale, i.e., between room temperature and 250 °C, were further characterized by DSC. The semicrystalline structure of TPX™ was investigated by DSC under normal pressure conditions as well as HP-DSC under 50 bar hydrogen atmosphere, in order to observe any changes under the operation conditions of the RHC (Figure S4, Supporting Information). The DSC results show a fully reversible melting and recrystallization behavior. The melting temperature is ~230 °C (peak minima), while the range of the melting process is from 170 to 240 °C. Similarly, 210 °C is the peak maximum for the crystallization process, ranging from 225 to 170 °C. This may result from the size distribution of polymer crystals, where only smaller crystals melt within the temperature range of application. Thus, the polymer’s partial melting and recrystallization occurs in the temperature region of unloading and reloading, but overall it remains semicrystalline. This is advantageous, as it simultaneously gives mechanical and morphological stability as well as local flexibility toward the volume expansion and shrinkage of the RHC upon uptake or release of hydrogen. The second component showing a thermal transition in the relevant temperature range is Li₄(BH₄)(NH₂)₃, which shows a melting temperature at about 190 °C in the DSC analysis performed under 1 bar hydrogen pressure (Figure S5, Supporting Information). This transition temperature is slightly higher than the cycling temperature of the macroscopic sample (i.e., 180 °C). However, due to the exothermic nature of the hydrogenation reaction and in combination with the poor thermal conductivity of the material, temperatures higher than 190 °C can arise locally in the composite. The cooling trace displayed in Figure S5 (Supporting Information) suggests the possibility of Li₄(BH₄)(NH₂)₃ to form liquid Li₄(BH₄)(NH₂) at high-temperature which remains in the liquid state down to a temperature of even below 90 °C.[3]

FTIR spectra of the RHC–polymer composite after being cycled 21 times (in loaded state) and of the starting materials are shown in Figure 3a,b, respectively. For the spectra 3a, and 3b the range between 3100 and 3400 cm⁻¹ is displayed also in Figure 5a and 5b (Supporting Information). As references, the FTIR spectra of the starting RHC (in the loaded state) and of pure TPX™ are shown in Figure 3c,d. The FTIR spectrum of Li₄(BH₄)(NH₂)₃ is shown in Figure 5b (Supporting Information).

The spectrum of the pristine RHC–polymer composite clearly shows the absorptions typical of pure TPX™, i.e., at 2866 cm⁻¹, the symmetrical stretch of C–H bonds in –CH₃ and at 2840, 2911, and 2951 cm⁻¹ the asymmetric stretching of C–H bonds of the polymer backbone and methyl groups, respectively. Regarding the RHC system of the pristine composite, the absorption band centered at 2295 cm⁻¹ can be attributed to the stretching of the B–H bonds in the [BH₄]⁻ units of LiBH₄. Although barely visible under the utilized magnification of Figure 3, the presence of Mg(NH₂)₃ is confirmed by the stretching vibrations of N–H bonds in the [NH₂]⁺ units in the wavenumber region between 3250 and 3350 cm⁻¹ visible in Figure S6 (Supporting Information).

The FTIR spectrum of the composite cycled 21 times, similarly to the pristine material, shows the bands of the –CH₃ units of the TPX™ polymer and that of the [BH₄]⁻ units of LiBH₄ and possibly also of small amounts of Li₄(BH₄)(NH₂)₃. The stretching vibrations of N–H bonds of Mg(NH₂)₃ are not present anymore; instead, weak bands at 3242 and 3301 cm⁻¹ are present (Figure S7, Supporting Information). These bands can be related to the stretching of the N–H bonds in Li₄(BH₄)(NH₂)₃ (Figure S8, Supporting Information). Despite the fact that almost complete reloading was observed for the 21st cycle by the gravimetric measurements (Figure 1), the FTIR spectrum indicates the presence of very small amounts of the typical unloaded products, e.g., Li₄(BH₄)(NH₂)₃.

2.3. Local Chemical Composition and Morphological Properties of the Composite

The macroscopic characterization of the samples showed a large but incomplete degree of reversibility of the cycling reactions. Also, the kinetics of unloading and more pronounced reloading reactions slow down with the number of cycles. Therefore, it is essential to have a spatially resolved view into the RHC–polymer composite to observe their microscopic structures of the different charging states in detail. Spatially resolved information on the morphological and chemical state of the composite material on the micrometer and nanometer level can be extracted from scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). As mentioned in the experimental part, the samples were all prepared by argon ion milling and represent almost artifact-free cuts across the samples, i.e., the phases of the RHC–polymer composite were not deformed and exposed to reactive environmental gases like oxygen. In Figure 4, overview images are given for three sample conditions: the as-prepared untreated sample before cycling, a sample after 21 cycles in the unloaded state, and in the subsequent reloaded state. All samples show a very good and stable dispersion of the high-energy ball-milled RHC in the polymer matrix. A small increase on the size of the particles is observed; however, this is expected due to agglomeration phenomena after the initial loading cycles when the storage capacity has not yet attained the final value. This type of dispersion explains the still high degree of reversibility of the cycling reactions, as the polymer matrix effectively prevents larger scale segregation of the RHC components during cycling. Another observation is a smoothening of the edges of the RHC particles during cycling. While the as-prepared samples show rather sharp edges at the interface toward the polymer matrix, the sharp edges are no longer visible in the sample in the cycled samples, which may be a result of the liquid Li₄(BH₄)(NH₂)₃ formed in the reaction. To understand the very small but detectable reduction of the reversibility and also the slight reduction of the reaction...
kinetics, the inner structure of the RHC particles must be analyzed. Therefore, in the following, the X-ray elemental maps of magnesium, nitrogen, boron, and carbon are presented to demonstrate their location before and after the heterophase unloading and loading reactions according to Equation (1). Also, oxygen is presented, which is an impurity incorporated mainly by some oxidized debris of the initial components of the RHC. In Figures 5–7, respective SEM and EDX mapping images of the as-prepared composite in the hydrogen loaded state before cycling (Figure 5) and after 21 cycles in the unloaded state (Figure 6) and after 21 cycles in the finally reloaded state (Figure 7) are presented. The first two images (a, b) of Figures 5–7 are taken with secondary electrons (SE) and
energy-selective backscattered electrons (EsB). The morphological and material contrast of the examined sample sections show the shape, arrangement and phase domains of the RHC-particles. They also help to assign the elemental maps to the overall structures. Images f of Figures 5–7 presents an overlay of the individual elemental mappings shown in images c, d, e, g, and h.

From the elemental mapping for carbon (images g) and also the elemental mapping of oxygen in image c, it can be concluded that the polymer matrix stays unaffected during the loading-unloading cycles, i.e., it does not obviously change its morphology and also seems not to become chemically attacked by oxygen from the original impurities mentioned before.

The latter is to be expected as, after oxygen, carbon is the most electronegative element in the composite. An indication for oxidative debris is the absence or very low presence of nitrogen in the areas where magnesium and oxygen, or boron and oxygen, are dominant. As the oxidized impurities appear throughout the samples (mostly it seems to be oxidized magnesium from the originally prepared RHC), but do not influence drastically further to the reloading and unloading reactions, they will not be discussed further. The elemental mappings of boron, nitrogen and magnesium confirm a high degree of reversibility of the heterophase reactions of the RHC particles during the unloading and reloading reactions. For this, one has to look at the nitrogen (images e) and boron (images h) rich areas and check, according to Equation (1), if these two elements appear at the same locations, as to be expected for the unloaded state \((\text{LiNH}_2)_3(\text{LiBH}_4),\) right side of Equation (1)), or if these two elements are spatially more separated, as it would agree with the left side of Equation (1) \((\text{Mg(NH}_2)_2\) and \(\text{LiBH}_4).\)

Note that the discussion here is based on boron rather than lithium, as the Li K-peak overlays with the Mg L-peak in the EDX spectrum and therefore cannot be used for the analysis. Moreover, lithium is most likely distributed in both the magnesium and boron-rich domains. The appearance of boron in the magnesium-rich areas in the unloaded state is since, as discussed before, Li_4(BH_4)(NH_2)_3 is a liquid under the cycling conditions and can diffuse into the porous magnesium amide particles. Also, the magnesium mappings (images d) are in line with this interpretation.

In Figure 1, the gravimetric analysis of the cycling experiments showed a slowing down of both the reloading and unloading process with an increasing number of cycles. Still, almost the same final value of storage capacity was reached. The elemental mappings in Figures 5 and 7 may explain these slowed-down kinetics. It may be the consequence of an increasing distance between reactants. Exactly this feature is visible when comparing the sizes of the boron-containing phases in Figures 5h and 7h. The boron-containing phases in Figure 7h are larger than in the as prepared sample (Figure 5h), where boron is more finely dispersed in the magnesium-rich particles. As the reaction of loading and unloading occurs at the inter-phase between the boron and magnesium-containing phases, larger phases necessarily result in longer diffusion times for material from the center of the phases to their interface. This

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**Figure 6.** SEM Images of the polymer–RHC composite after 21 unloading/reloading cycles in the H₂-desorbed state. The hydrogen pressure applied for the unloading processes was 1 bar, whereas for the reloading processes, it was 50 bar. The temperature was kept constant at 180 °C during both de- and reloading. a) Secondary electron (SE) micrograph, b) energy selective backscattered electron (EsB) micrograph, c–i) elemental mappings obtained from energy dispersive X-ray analysis (EDX): c) oxygen (O), d) magnesium (Mg), e) nitrogen (N), g) carbon (C), and h) boron (B). f) Overlay of Mg, N, B, C, and O; i) overlay of Mg, N, B, and C. Scale bar: 10 µm.
is also shown in Figure 8, which summarizes results from Figures 5–7 for direct comparison. The components of Equation (1) are assigned to the different phases by accordingly mixed colors. The coarsening of the different phases can be seen clearly when comparing Figure 8a,c, which show the material in the hydrogen-loaded state. Although kinetics is slowed down slightly by this coarsening upon cycling, it should be pointed out that the composite of RHC particles embedded in TPX–polymer shows much better kinetics than the same RHC-mater-

3. Conclusions

Scanning electron microscopy in combination with energy-dispersive X-ray spectroscopy, X-ray diffraction and differential scanning calorimetry, new insights into the properties of these RHC–polymer composites could be obtained. The RHC particles remained well-dispersed in the polymer matrix throughout the hydrogen unloading and reloading reactions, despite the volume changes which the RHC experiences upon cycling. Gravimetric analysis showed that the overall hydrogen storage capacity remained stable upon cycling. However, the kinetics of unloading and reloading slowed down slightly during the course of cycling. This finding indicated morphological changes, namely a coarsening of the phases containing the different inorganic components within the well-dispersed RHC particles, which could be visualized by scanning electron microscopy for the first time. This study indicates that further stabilization of the fast initial kinetics may be achieved if the size of the RHC particles can be further reduced. To have a high storage capacity by volume and weight in the RHC–polymer composite, very high loadings of RHC in the polymer are desirable, which is still challenging and is subject to ongoing efforts. Although the developed
system does not fulfill the DOE targets for mobile and stationary hydrogen storage applications yet, this study demonstrates that a suitable matrix polymer can keep the particles apart from each other and thus can suppress the coarsening of particles during the hydrogen storage and release cycles successfully. The lower hydrogen storage capacity as compared to the storage material without polymer should not be considered too critical: this composite was designed to reveal the changes that the storage material undergoes during hydrogen cycling. In view of application, the knowledge gained here will serve as a basis for further optimization of microstructures, including reduced polymer fractions for maximized overall capacity. While this study demonstrated the powerful combination of different techniques for the characterization of a rather complex hybrid material and allowed the identification of local compositional changes, this strategy may very likely prove helpful for detailed analysis of other complex composite structures, including time-dependent phenomena such as, e.g., corrosion.

4. Experimental Section

**Materials**: Magnesium amide, Mg(NH₂)₂ (>95%), was synthesized by the reaction of magnesium hydride, MgH₂ (Rockwood, Germany, 99%) with ammonia (NH₃) at 330 °C. Lithium hydride, LiH (97%) and lithium borohydride, LiBH₄ (95%), were purchased from Alfa-Aesar/Thermo Fisher GmbH, Kandel, Germany and Sigma-Aldrich/Merck, Darmstadt, Germany. Impurities are oxidized debris. 6Mg(NH₂)₂–9LiH–LiBH₄ (LMBNH, in the following, simply called “reactive hydride composite,” RHC) was obtained from ball milling of the components in the given stoichiometric ratio for 36 h at 200 rpm using a Fritsch Pulverisette 6 classic line planetary mill under 50 bar of H₂, with a ball to powder ratio of 40:1. All operations involving powder handling (including milling) were performed in a glovebox (Unilab, M. BRAUN Inertgas-Systeme GmbH, Garching, Germany) under an argon atmosphere. The levels of H₂O and O₂ were kept below 1 ppm to prevent humidity or oxygen contamination.

Commercially available pellets of poly(4-methyl-1-pentene) (TPX™, type RT18), were provided by Mitsui & Co. Deutschland GmbH, Düsseldorf, Germany, and used as a matrix material for RHC. Cyclohexane (99.9%, Merck, Darmstadt, Germany) was used as a solvent for the polymer and dispersant for the metal hydride powders. Cyclohexane was briefly evacuated at room temperature, argon was inserted and shortly bubbled through two hollow needles and a septum. Specimen storage and solvent degassing were facilitated in a continuously purified argon atmosphere using filters with activated carbon as adsorbents for organic molecules, molecular sieve for adsorption of water and a copper catalyst closed column for removal of residual oxygen. Argon and hydrogen, both with a purity of 3.4 ppm, were provided by Linde AG, Pullach, Germany.

**Film Preparation**: The complete instrumentation was incorporated in a glovebox (GP-Concept, Jacomex SA, Dagneux, France) under a continuously purified argon flow (O₂ and H₂O levels lower than 1 ppm) for a period of at least five weeks before use in order for all the humidity that could be physically absorbed on the metal surfaces to be removed and trapped from the reactive cleaning system of the glovebox. The composite film was prepared in three steps. The polymer TPX™ (75 wt%) was dissolved in cyclohexane at 75 °C for at least 8 h under an argon atmosphere resulting in a viscous solution. RHC powder was then added to the polymer solution and dispersed under vigorous stirring for ≈24 h under an argon atmosphere at 75 °C. Finally, the suspension was cast on a stainless-steel metal support with a doctor blade (gap: 2000 µm) using a custom-made casting machine incorporated in the glovebox (Helmholtz-Zentrum Hereon, Geesthacht, Germany). The cast film was dried in the glovebox at 75 °C and the solvent was trapped in an adsorber filter system based on activated carbon. The as-prepared film was used for characterization without further drying. The final film thickness was ≈170 µm with a weight ratio of RHC to polymer of 3:1.
Characterization—Hydrogen Cycling Experiments: The unloading/loading experiments were carried out using an in-house developed Sieverts-type apparatus (Helmholtz-Zentrum Hereon, Geesthacht, Germany). The differential pressure between two calibrated volumes is measured. One volume is empty and the other contains the specimen. Any pressure difference is then attributed to hydrogen absorption or desorption of the specimen and converted into wt% using the previously determined specimen mass. During the unloading experiments, the samples were kept at 180 °C under a hydrogen pressure of 1 bar for 1 h. In contrast, during the rehydrogenation experiments, the samples were kept at 180 °C under an atmosphere of 50 bar of hydrogen for 2 h. This procedure was carried out 21 times. The as-prepared sample (H2-loaded) and samples after 21 cycles in the unloaded as well as in the reloaded state were used for detailed analysis. The number of cycles was selected based on the availability of the scientific instrumentation and thus complies with the fact that the storage capacity has already attained a stable state. For the same reason, it must be noticed that the desorption process was stopped when a nearly constant hydrogen capacity was achieved. The error of the measurement based on calibration using standard materials (commercial MgH2 and FeTi alloy) is about 5%. The parameters for the cycling experiments were defined according to previously published work.[6b]

X-Ray Diffraction (XRD): The X-ray diffraction experiments were carried out on a Bruker DB Discover diffractometer (Bruker AXS GmbH, Karlsruhe, Germany). This diffractometer is equipped with a copper X-ray source (Cu Kα radiation, λ = 1.54184 Å) and a VANTEC-500 area detector from Bruker. The diffraction patterns were acquired in nine steps in the 2θ range from 10° to 90° with an exposure time of 400 s per step and an angular resolution of about 0.001°. The 2D detector had 1024×1024 pixels. The specimens’ preparation to be analyzed via XRD was carried out in an MBraun Unilab glovebox under a continuously purified argon flow (O2 and H2O levels lower than 1 ppm). A small piece of the composite film or small amounts of powder were placed onto a sample holder and sealed with an airtight dome made of poly(methyl methacrylate) to avoid oxidation or hydrolysis of the samples during pattern acquisition.

Differential Scanning Calorimetry (DSC) and High-Pressure Differential Scanning Calorimetry (HP-DSC): Differential scanning calorimetry experiments were performed on a DSC 1 (NETZSCH Group, Selb, Germany) calorimeter under nitrogen atmosphere at a heating/cooling rate of 10 °C min−1. Several heating and cooling cycles were done in the range of 30 up to 250 °C with a heating/cooling rate of 10 °C min−1. High-pressure differential scanning calorimetry analysis of the as-prepared Li2(BH4)(NH3)3 as well as of the TPX™ was carried out on an HP-DSC Netzsch DSC 204 HP Phoenix and an HP-DSC 1 (NETZSCH Group, Selb, Germany) calorimeter. The HP-DSC measurement of the Li2(BH4)(NH3)3 was carried out under a constant hydrogen pressure of 1 bar using a heating/cooling rate of 3 °C min−1. The HP-DSC apparatus was placed in an MBrAun Unlab glovebox under a continuously purified argon atmosphere (O2 and H2O levels lower than 1 ppm). The HP-DSC measurement of the TPX™ was performed under pressures of 1 and 50 bar of hydrogen in order to investigate the effect of pressure on the thermal properties of TPX™ in the temperature range of 130–250 °C. The heating rate was 2 °C min−1.

Fourier-Transform Infrared Spectroscopy (FTIR): FTIR measurements were performed on a Cary 630 FTIR spectrometer from Agilent Technologies (Agilent Technologies, Santa Clara, California, United States of America) in transmission mode. In order to avoid detrimental alteration of the investigated material, the spectrometer was located in an argon-filled glovebox (Jacomex SAS, Daguex, France) keeping O2 and H2O levels lower than 1 ppm. For each analysis, a small amount of sample (as powder or film) was placed on the diamond ATR top-plate and the FTIR spectrum was acquired in a frequency range of 4000–400 cm−1 with a spectral resolution of 4 cm−1 for a total of 200 scans.

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDX): A scanning electron microscope (SEM) Merlin (Carl ZEISS, Oberkochen, Germany) was used to characterize the dispersion of the metal hydride particles in the polymer matrix. Images were taken with a secondary electron (SE) and an in-lens energy selective backscattered electron (EsB) detector using an accelerating voltage of 3 kV. Energy-dispersive X-ray spectroscopy (EDX) was done with an Extreme and an X-max 150 EDX detector (Oxford, Wiesbaden, Germany). Samples were prepared in a glovebox (Jacomex SAS) under a continuously purified argon atmosphere.

For SEM and EDX analyses, a precision etching and coating system PECs II (Gatan/AMETEK, München, Germany) was used to prepare cross-sections of the composite films and for coating of these samples. Argon ion beam milling was performed at −120 °C at 4 kV for several hours. The samples were then sputter-coated with ~4 nm carbon before analysis.

As the samples are sensitive to O2 and H2O, a specially adapted transfer unit (Gatan, München, Germany) was used to exchange the samples between the preparation area in the glovebox, the milling device, the SEM and vice versa without any exposure to air.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
C.A. and P.G. contributed equally to this work. V.A. and T.K. assisted in conceptualization; C.A., P.G., and C.P. contributed methodology, performed the experiments, and collected, analyzed and validated the data; V.A., T.K., and P.G. supervised the work; V.A. and T.K. contributed the resources; and all authors contributed to writing, reviewing, and editing of the manuscript.

Data Availability Statement
The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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