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M.; Abetz, V.; Klassen, T.:

**Air-stable metal hydride-polymer composites of Mg(NH<sub>2</sub>)<sub>2</sub>-  
LiH and TPX™.**

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1 **Air-stable metal hydride-polymer composites of Mg(NH<sub>2</sub>)<sub>2</sub>-LiH and**  
2 **TPX<sup>TM</sup>**

3  
4 Hujun Cao,<sup>a\*</sup> Prokopios Georgopoulos,<sup>b\*</sup> Giovanni Capurso,<sup>a</sup> Claudio Pistidda,<sup>a</sup> Fynn Weigelt,<sup>b</sup>  
5 Anna-Lisa Chaudhary,<sup>a</sup> Volkan Filiz,<sup>b</sup> Jo-Chi Tseng,<sup>c</sup> Michael T. Wharmby,<sup>c</sup> Martin Dornheim<sup>a</sup>  
6 Volker Abetz,<sup>b, d</sup> and Thomas Klassen<sup>a, e</sup>

7  
8 a. Institute of Materials Research, Materials Technology, Helmholtz-Zentrum Geesthacht  
9 GmbH, Max-Planck-Straße 1, 21502, Geesthacht, Germany.

10 E-Mail: hujun.cao@hzg.de; Fax: + 49 4152 / 87-2625; Tel: +49 4152 / 87-2643

11 b. Institute of Polymer Research, Helmholtz-Zentrum Geesthacht GmbH, Max-Planck-Straße  
12 1, 21502, Geesthacht, Germany.

13 E-Mail: prokopios.georgopoulos@hzg.de; Fax: + 49 4152 / 87-2466; Tel: +49 4152 / 87-2420

14 c. Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg, Germany.

15 d. Institute of Physical Chemistry, University of Hamburg, Martin-Luther-King-Platz 6,  
16 20146 Hamburg, Germany.

17 e. Institute of Materials Technology, Helmut Schmidt University, Holstenhofweg 85, 22043  
18 Hamburg, Germany.

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20

## 1 **Abstract**

2 Light metal hydrides are prone to react with oxygen and/or water to produce oxides and/or  
3 hydroxides leading to reduction of hydrogen capacities, and deterioration of the hydrogen storage  
4 properties. It is therefore critical to address these issues when the materials are to be exposed to  
5 air or moisture. In this work, the combination of light metal hydrides,  $\text{Mg}(\text{NH}_2)_2\text{-nLiH}$  with  
6 polymethylpentene (TPX<sup>TM</sup>), an air/moisture protective barrier is presented. It was found that the  
7 fabricated composites exhibit significant improvement of the metal hydrides stability in air. No  
8 oxidation reactions in air can be proven even after air exposure for 90 minutes. Extending the air-  
9 exposure time to 12 hours, the reversible hydrogen capacities of these composites are much higher  
10 and more stable than they are in the case of the pure metal hydrides. In comparison to the pure  
11 metal hydrides, the composites retain the same hydrogen loading capacities and kinetic properties,  
12 with respect to the metal hydrides contents. Further, *in situ* synchrotron radiation powder X-ray  
13 radiation diffraction (SR-PXRD) experiments reveal that the thermal decomposition reaction  
14 pathways of the 90 minutes air-exposed composites are the same under air or  $\text{H}_2$  atmosphere.  
15 Moreover, morphology analysis confirms that the metal hydrides remain stable in the polymeric  
16 matrix and the three-dimensional integrity is retained, even after performing tens of de/re-  
17 hydrogenation cycles. The present study shows a promising way to fabricate air-stable metal  
18 hydride-polymer composite hydrogen storage materials that can be handled in ambient conditions.

19 **Keywords:** reactive hydride composite, air-stability, hydrogen storage, polymethylpentene

20

## 21 **Introduction**

22 The preparation of composite materials has been known for centuries with a variety of applications  
23 in everyday life.[1] Many composite materials derive from the combination of polymers, which

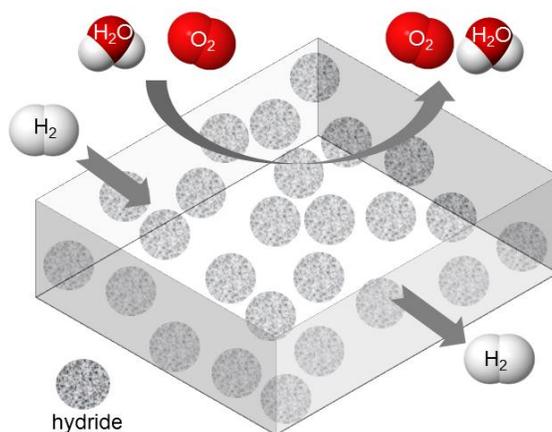
1 usually have the role of the matrix, and filler materials such as, *e.g.*, fibers, ceramics or metal  
2 oxides, etc..[2, 3] The combination of such materials leads to new materials usually with more  
3 advanced properties or even better performance for specific applications such as in membranes[4,  
4 5] or in energy applications.[6] Polymethylpentene under the trademark TPX™-RT18 of Mitsui  
5 Chemicals, INC., shortened to TPX hereafter, is a 4-methyl-1-pentene based polyolefin, similar to  
6 traditional polyolefin, with excellent gas permeability, heat and chemical resistance and strong  
7 hydrolysis resistance. Recently, polyolefines have been employed as matrices for composite  
8 materials due to their distinctive molecular structures, which display unique combinations of  
9 physical properties and characteristics.[7-9] The use of TPX as a matrix material for composite  
10 films is known in applications for gas separation, *e.g.*, in TPX/Al<sub>2</sub>O<sub>3</sub> mixed-matrix membranes for  
11 CO<sub>2</sub>/CH<sub>4</sub> separation. Nevertheless, until now, to the best of our knowledge, there are no references  
12 for the use of TPX polymers in composites used for hydrogen storage materials.

13 Composite materials have also received much attention in the hydrogen storage area recently, such  
14 as the approach of tailoring the thermodynamic properties by mixing two or more hydrogen-  
15 containing materials, denoted as Reactive Hydride Composites (RHC).[10-16] Amide-hydride  
16 composites are an example of such an approach. Such composites have been extensively  
17 investigated for hydrogen storage since 2002,[17-23][24] due to their advanced properties, such as  
18 thermodynamic stability, reversibility and high hydrogen capacity. Mg(NH<sub>2</sub>)<sub>2</sub>-xLiH, (x=2, 8/3, 4)  
19 systems were developed by different research groups in 2004.[25-28] The system where x = 2,  
20 namely, Mg(NH<sub>2</sub>)<sub>2</sub>-2LiH (hereafter labeled LMNH), has been considered as one of the most  
21 promising materials for on-board applications,[25] because of its suitable gravimetric hydrogen  
22 capacity (ca. 5.6 wt%) and dehydrogenation enthalpy ( $\Delta H$  ca. 40 kJ (mol-H<sub>2</sub>)<sup>-1</sup>).[29] A lot of  
23 studies[30-41] were devoted to optimizing the hydrogen storage properties of Mg(NH<sub>2</sub>)<sub>2</sub>-2LiH,

1 and these studies have shown that the best kinetic additives are KH and RbH. KH doped  
2  $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$  can reduce the peak temperature from ca. 190 °C to 130 °C. While its equilibrium  
3  $\text{H}_2$  pressure is roughly 2 bar at 107 °C.[42-45] In order to improve the reaction kinetics of  
4  $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$  composite even further, there is the need to modify the thermodynamics, allowing  
5 to release 1 bar  $\text{H}_2$  in equilibrium conditions at much lower temperatures. Following this target,  
6 the thermodynamically optimized system  $6\text{Mg}(\text{NH}_2)_2\text{-9LiH-LiBH}_4$  (hereafter labeled LMBNH)  
7 has been obtained by stabilizing the dehydrogenated product  $\text{LiNH}_2$ , which allows to release 1 bar  
8  $\text{H}_2$  at the equilibrium temperature of 64 °C.[46] In addition,  $6\text{Mg}(\text{NH}_2)_2\text{-9LiH-LiBH}_4$  shows an  
9 excellent reversibility, its complete absorption time is less than 10 min and full absorption can be  
10 achieved at 90 °C after adding  $\text{YCl}_3$  and  $\text{Li}_3\text{N}$ .[47] One drawback in the use of these amide-hydride  
11 systems is that after some de/re-hydrogenation cycles these systems lose their hydrogen storage  
12 capacities and reaction kinetics are reduced. One explanation for these changes is that amides and  
13 hydrides are prone to react with oxygen and/or water to produce oxides or hydroxides, thus  
14 contaminating the system. Another reason is that, during the de/re-hydrogenation cycles, the  
15 hydride microstructure coarsens, and the reactants phase separate over longer distances, increasing  
16 diffusion pathway lengths, thus slowing kinetics.[48] To overcome these drawbacks and reduce  
17 operating and manufacturing costs of the material systems, the production of air-stable hydrides  
18 would be a tremendous advantage. To date, only a few publications have been devoted to the  
19 investigation of the stability of amide-hydride composites in the presence of  $\text{O}_2$ ,  $\text{H}_2\text{O}$  or air.[49,  
20 50]

21 This work aims to solve this problem by deploying novel hydride-polymer composites. As already  
22 mentioned, the combination of metal hydride and polymer for hydrogen storage has not been  
23 addressed except for a few studies relating to poly(methyl methacrylate) - magnesium hydride

1 composites for hydrogen storage[51-53] or acrylonitrile-butadiene-styrene copolymer (ABS)-  
2  $\text{LaNi}_5$  type metal hydride,[54]  $\text{MnO}$  anchored to poly(ether-ether-ke-ton),[55] or ammonia borane  
3 in polystyrene.[56] Another energy storage application with a similar composite is the use of  
4 poly(acrylonitrile) in lithium batteries.[57] In this study, TPX has been selected as the host  
5 polymer, with the intention of protecting the metal hydrides from oxygen and water, whilst  
6 allowing the hydrogen to permeate through in order to enable hydrogen absorption or desorption.  
7 LMBNH and LMNH have been chosen as the active ingredients due to their low operating  
8 temperatures below  $250\text{ }^\circ\text{C}$ . Incorporating these materials into the TPX matrix (see Figure 1), the  
9 amide-hydride composites are enclosed in the polymer thus protecting the hydrides from  $\text{O}_2$  and  
10  $\text{H}_2\text{O}$  and contamination, leading to an almost air-stable hydrogen storage material. Additionally,  
11 owing to the confinement of hydrides within the TPX matrix, the amide-hydride composites  
12 remain in a stable position and do not coarsen to larger clusters and long-range phase separation  
13 is prevented. Detailed characterization regarding the hydrogen storage performance, the reaction  
14 mechanism as well as the air-stability and morphology are presented further on.



15  
16 **Figure 1.** Schematic of the metal hydride-TPX composite for hydrogen storage  
17

## 1 **Experimental Details**

### 2 *Materials synthesis and film preparation*

3 Magnesium amide,  $\text{Mg}(\text{NH}_2)_2$  (> 95 %), was synthesized by the reaction of  $\text{MgH}_2$  (Rockwood,  
4 Germany, 99%) with  $\text{NH}_3$  at 330 °C.  $\text{LiH}$  (97 %) and  $\text{LiBH}_4$  (95 %) were purchased from Alfa-  
5 Aesar and Sigma-Aldrich, Germany, respectively.  $6\text{Mg}(\text{NH}_2)_2\text{-}9\text{LiH-LiBH}_4$  (LMBNH) and  
6  $\text{Mg}(\text{NH}_2)_2\text{-}2\text{LiH}$  (LMNH) were ball milled for 36 h at 200 rpm using a Fritsch Pulverisette 6 classic  
7 line planetary mill under 50 bar of  $\text{H}_2$ , with a ball to powder ratio of 40:1. All the operations  
8 involving powder handling (including milling) were performed in a glovebox (MBraun, Germany)  
9 in argon atmosphere and the levels  $\text{H}_2\text{O}$  and  $\text{O}_2$  were kept below 10 ppm to prevent contamination.  
10 Commercially available pellets of polymethylpentene TPX, type RT18, were provided from Mitsui  
11 Chemicals, INC., (Düsseldorf, Germany), and used as a matrix material for the hydrides LMBNH  
12 and LMNH. Cyclohexane (99.9%, Merck, Darmstadt, Germany), was used as a solvent for the  
13 polymer and dispersant for the metal hydride powders LMBNH and LMNH. The solvent was  
14 degassed before use and kept under argon atmosphere.

15 The composite film was prepared in three steps. Initially, the polymer TPX was dissolved in  
16 cyclohexane at 75 °C under argon atmosphere. After that, the polymer pellets were dissolved in  
17 the liquid, resulting in a viscous solution and then transferred into a glovebox. The metal hydrides  
18 (LMBNH and LMNH) and the TPX solution were mixed under vigorous stirring around 5 min  
19 under an argon atmosphere and finally, the mixture was cast on a glass substrate with the use of a  
20 doctor-blade. The gap used for the casting was 2000  $\mu\text{m}$ . The cast film was dried in the glovebox  
21 and the solvent was trapped in a cooling trap system. The as-prepared films are labeled LMBNH-  
22 TPX and LMNH-TPX, respectively. The films produced were used for characterization without

1 further drying. The final film thickness achieved for the casting process was approximately 300  
2  $\mu\text{m}$ .

### 3 *Materials Characterization*

4 Differential thermal analysis (DTA), as well as temperature programmed desorption-mass  
5 spectrometry (TPD-MS) measurements were carried out using a Netzsch STA 409 C and a Hiden  
6 Isochema Analytical HAL 201 Mass-Spectrometer combined system, with  $50 \text{ mL min}^{-1}$  argon  
7 flow. The samples were heated from room temperature (RT) to 300 and 350  $^{\circ}\text{C}$  for DTA and TPD-  
8 MS, respectively, with a heating rate of  $2 \text{ }^{\circ}\text{C min}^{-1}$ .

9 High-pressure differential scanning calorimetry (HP-DSC) measurements were carried out using  
10 a Netzsch DSC 204 HP at hydrogen pressures of 1 bar and 80 bar, respectively. The samples were  
11 heated from RT to 200  $^{\circ}\text{C}$  for LMBNH and LMBNH-TPX, and 250  $^{\circ}\text{C}$  for LMNH and LMNH-  
12 TPX, with a heating rate of 5 and  $2 \text{ }^{\circ}\text{C min}^{-1}$  for dehydrogenation and re-hydrogenation,  
13 respectively. The samples including TPX underwent another treatment RT up to 200 and 250  $^{\circ}\text{C}$   
14 in two different ramps, with a heating rate of  $5 \text{ }^{\circ}\text{C min}^{-1}$ .

15 The reversibility experiments were investigated using an in-house developed Sieverts-type  
16 apparatus (Sonja II, HZG, Germany), keeping the samples in isothermal conditions at 180  $^{\circ}\text{C}$  for  
17 LMBNH-based samples and 200  $^{\circ}\text{C}$  for LMNH-based samples under a hydrogen pressure of 1 bar  
18 for desorption and 80 bar for absorption, respectively. In addition, it was estimated that 12 hours  
19 are enough for handling and packaging these composites from synthesis inside a glovebox to their  
20 insertion into a hydrogen storage tank, therefore, the air-exposure time was chosen for 12 hours  
21 for all those air-exposure samples before conducting the cycling experiments.

22 *In situ* synchrotron radiation powder X-ray radiation diffraction (SR-PXRD) experiments were  
23 performed at the diffraction beamline P.02.1 in the PETRA III storage ring of the synchrotron

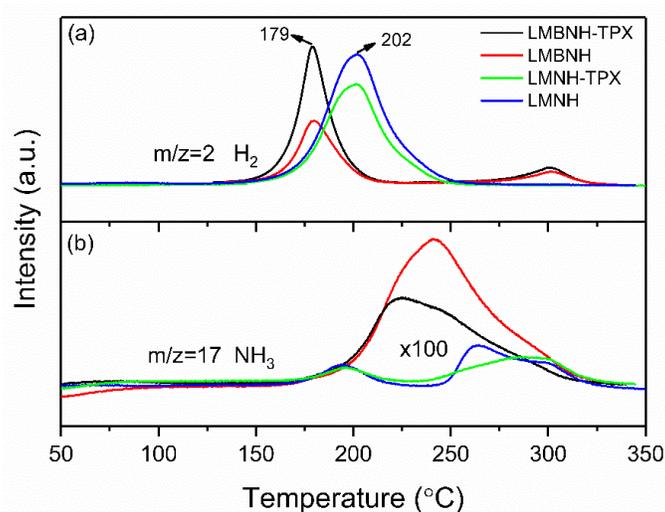
1 facility “DESY”, in Hamburg, Germany. The fixed wavelength ( $\lambda$ ) was 0.20716 Å and patterns  
2 were acquired with a PerkinElmer XRD1621 image detector (2048\*2048 pixel, each of size  
3 200\*200  $\mu\text{m}^2$ ) and the distance from the sample to the detector was ca. 1470 mm. The powder was  
4 loaded into a quartz capillary tube and then fixed on an in-house developed *in situ* measuring cell  
5 (HZG, Germany), which was able to control heating temperatures and operating pressures and  
6 atmospheres. Dehydrogenation experiments were performed from RT to 200 and 250 °C for  
7 LMBNH-TPX and LMNH-TPX, with a heating rate of 10 °C  $\text{min}^{-1}$  under 1 bar of  $\text{H}_2$ .  
8 Hydrogenation was done from RT to 200 and 250 °C for LMBNH-TPX and LMNH-TPX under  
9 80 bar of  $\text{H}_2$  with a heating ramp of 5 °C  $\text{min}^{-1}$ . For the oxidation experiments (Figure S1), samples  
10 were exposed to atmospheric air for 1 h before loading, and then the data were recorded by *in situ*  
11 SR-PXRD for 30 min at 40 °C before heating to a higher temperature. The 2D images were  
12 integrated with the software FIT2D.[58] Quantitative analyses were performed using MAUD  
13 software implementing the Rietveld approach.[59, 60]

14 XRD tests were carried out using a D8 discover X-ray diffractometer (Bruker, Germany) with Cu  
15  $\text{K}\alpha$  radiation ( $\lambda = 1.54184$  Å, 50 kV, 1000 mA) at a scanning rate of 1 degree  $\text{min}^{-1}$ . Air-tight  
16 sample holders were used (Bruker, Germany) to prevent contamination of the sample.

17 Scanning electron microscopy (SEM) was employed to investigate the morphological structure of  
18 the LMNH-TPX composites using a Helios Nanolab 200 DualBeam microscope (FEI, Co.,  
19 Netherlands). The samples for SEM experiments were mounted onto aluminum stubs with double-  
20 sided adhesive and coated with 8 nm platinum just prior to the measurements. The samples were  
21 exposed to air during this process for several minutes. In order to investigate the inner structure of  
22 the composites a fracture was induced on the surface of the LMNH-TPX composites.

1 The gas transport parameters were determined with the time-lag (variable pressure, constant  
 2 volume) method at 30 °C and 1000 mbar feed pressure for the gases H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and for H<sub>2</sub>O vapor  
 3 near the saturation pressure. Detailed information about the time-lag method can be found in  
 4 supporting information and Figure S2. In short, the method relies on maintaining a constant feed  
 5 pressure and measuring the permeate pressure changing as a function of time due to the diffusion  
 6 of gas molecules through the TPX film of known thickness as it is described elsewhere.[4, 61, 62].

## 7 Results and Discussion



8  
 9 **Figure 2.** H<sub>2</sub>-TPD-MS (a) and NH<sub>3</sub>-TPD-MS (b) curves of LMBNH-TPX, LMBNH, LMNH-TPX and LMNH, respectively.  
 10 Samples were heated from room temperature (RT) to 350 °C under 50 mL min<sup>-1</sup> of argon flow with a heating rate of 2 °C min<sup>-1</sup>.

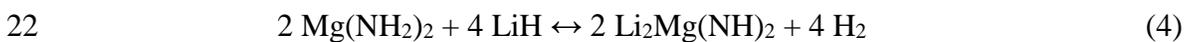
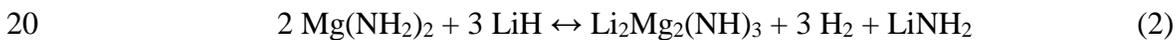
11 The evolution of hydrogen and ammonia upon heating was monitored by TPD-MS experiments  
 12 for all the investigated systems and the results are shown in Figure 2. As already reported in a  
 13 previous work,[46] the addition of LiBH<sub>4</sub> lowers the decomposition peak temperature for the  
 14 LMBNH composite to around 180 °C, which is more than 20 °C lower than that of the LMNH  
 15 system (Figure 2(a)). After incorporation within the TPX matrix, the dehydrogenation properties  
 16 of these metal hydride-TPX composites are completely relatable to those of the pure hydride  
 17 systems (Figure 2(a)). LMBNH-TPX and LMBNH composites display the same onset (~ 130 °C)

1 and peak temperatures (~ 179 °C). The onset and peak temperatures of LMNH-TPX and LMNH  
 2 are 140 and 202 °C, respectively. In addition, the end temperatures of LMBNH-based and LMNH-  
 3 based samples are ca. 200 and 250 °C, respectively. The NH<sub>3</sub>-TPD-MS analysis (Figure 2(b))  
 4 shows that the release of ammonia from these composites depends only on the properties of the  
 5 hydride systems. LMBNH and LMBNH-TPX have broad ammonia release peaks, which are likely  
 6 due to the thermal decomposition of Li<sub>4</sub>(BH<sub>4</sub>)(NH<sub>2</sub>)<sub>3</sub>, a product of LMBNH-based composites, as  
 7 shown in reaction (1).



9 In contrast to the LMBNH-based composites, the LMNH and LMNH-TPX systems exhibit two  
 10 separate events for ammonia release. The first one at around 200 °C can be attributed to the multi-  
 11 reaction mechanisms (solid-solid reaction mechanism and NH<sub>3</sub>-mediated mechanism[63]), typical  
 12 of amide-hydride systems. The second one is related to the decomposition of imides at high  
 13 temperatures.[28]

14 DTA traces acquired for the four samples are displayed in Figure S3. The endothermic events  
 15 below 200 °C match well with the release of H<sub>2</sub> observed in Figure 2(a). The LMBNH based  
 16 samples have lower decomposition temperatures as compared to LMNH-based samples, while the  
 17 LMNH based samples have both the main peak and the shoulder peak at ca. 186 and 197 °C,  
 18 respectively. These can be ascribed to the two-steps reaction of the LMNH system (reactions 2-  
 19 4).[42, 64]

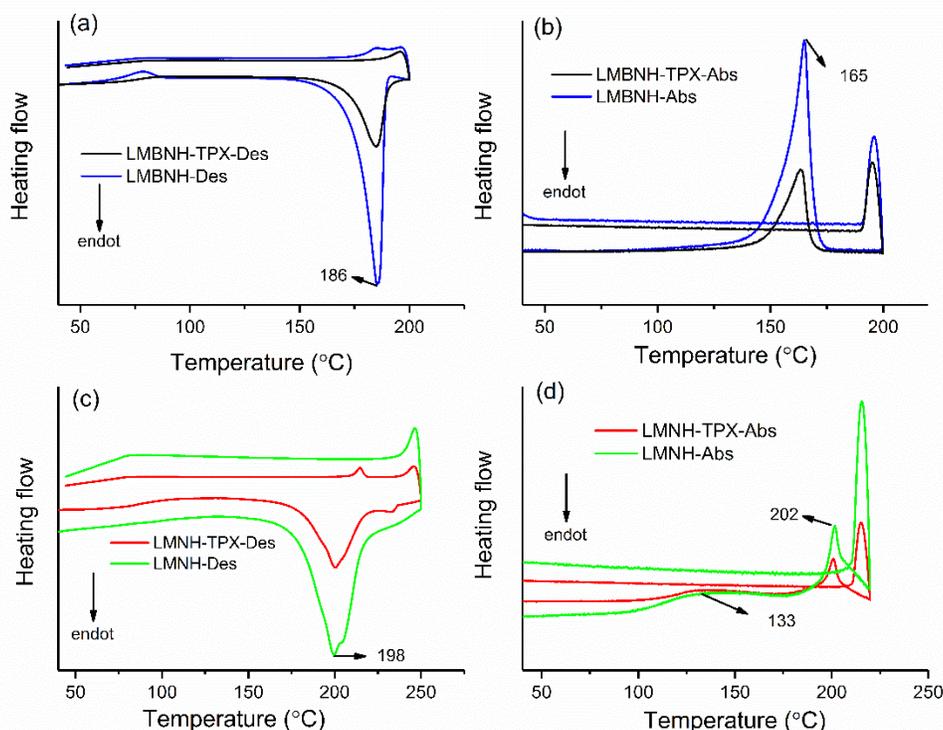


1 The small temperature differences between the thermal events and the observed gaseous species  
2 displayed in Figures S1 and 2 may originate from the distance (a 1.5 m heated capillary) that the  
3 gas released during the DTA analysis needs to pass before reaching the mass spectrometer.

4 There are two main DTA transitions above 200 °C for both the LMBNH and LMBNH-TPX  
5 composites; the first signal at about 210 °C and the second one at ca. 240 °C, as discussed in Figure  
6 2 (b), could be attributed to the decomposition reaction of  $\text{Li}_4(\text{BH}_4)(\text{NH}_2)_3$  and  $\text{Li}_2\text{Mg}_2(\text{NH})_3$ . The  
7 peak related to the melting of the polymer matrix is at around 240 °C (Figure S3); however, this  
8 signal is not clearly visible in the curves of LMBNH-TPX and LMNH-TPX composites, due to  
9 the superimposition with imide decomposition process. Upon cooling, the polymer  
10 recrystallization in TPX mixtures can be easily identified at 211 °C. Based on what was analyzed  
11 and discussed about TPD-MS and DTA in the Figures 2 and S3, it can be concluded that the by-  
12 reaction and by-product ( $\text{NH}_3$ ) occur at temperatures above 200 and 250 °C for LMBNH-based  
13 and LMNH-based samples, respectively. These results also show that, for the applied experimental  
14 conditions, the TPX matrix does not influence the dehydrogenation properties of LMBNH and  
15 LMNH composites.

16 To further investigate sorption properties of the composite materials, all the samples underwent  
17 one de/re-hydrogenation cycle. These measurements were carried out with a high-pressure DSC  
18 device and the results are summarized in Figure 3. The first cycle of LMBNH and LMBNH-TPX,  
19 shown in Figures 3(a) and (b), show highly comparable de/re-hydrogenation properties. Both  
20 materials exhibit a dehydrogenation peak temperature at 186 °C and an absorption peak at 165 °C.

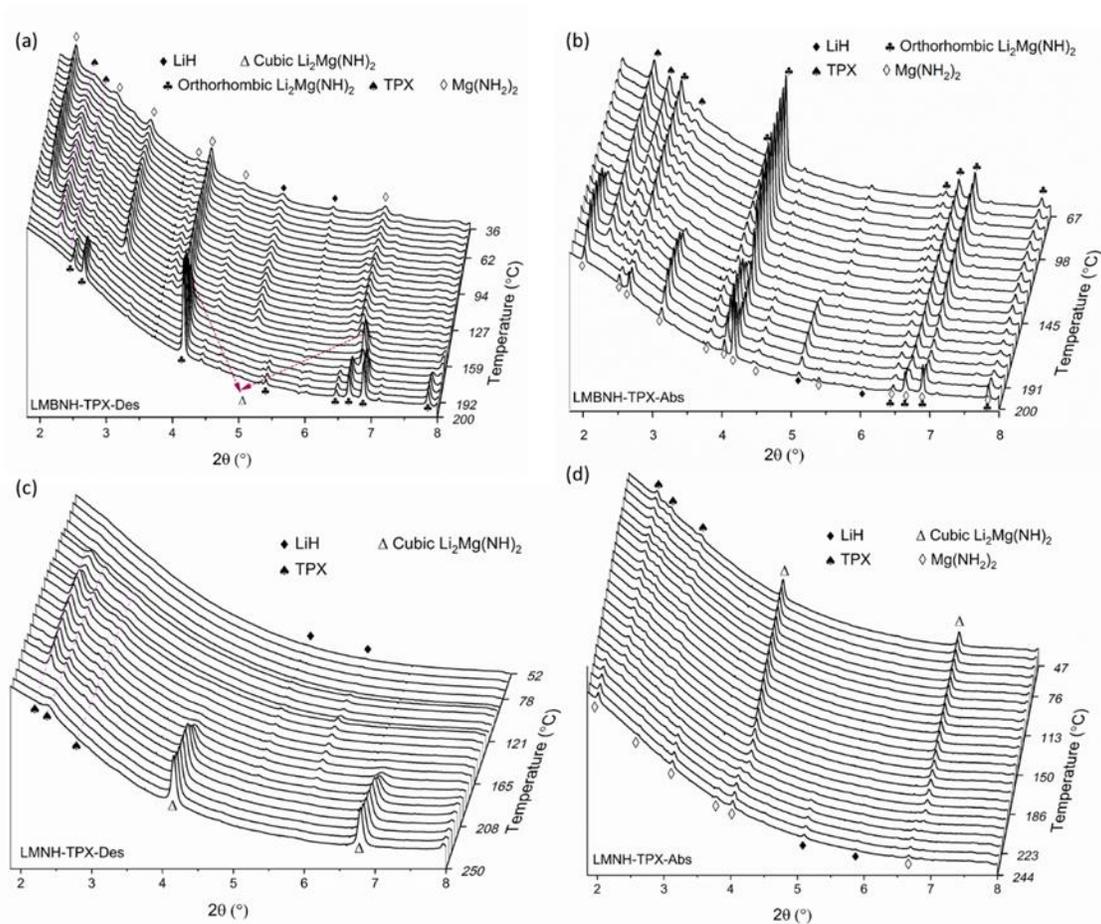
21 Apart from the melting and recrystallized temperatures of TPX, the thermal events shown in Figure  
22 3(c) are the same for the LMNH and LMNH-TPX composites. LMNH and LMNH-TPX show  
23 identical absorption properties too.



1  
2 **Figure 3.** HP-DSC desorption (Des) measurements of LMBNH-TPX and LMBNH (a); HP-DSC absorption (Abs) measurements  
3 of LMBNH-TPX and LMBNH (b); HP-DSC desorption measurements of LMNH-TPX and LMNH (c); HP-DSC absorption  
4 measurements of LMNH-TPX and LMNH (d). HP-DSC desorption measurements were heated from RT to 200 °C and 250 °C with  
5 a heating rate of 5 °C min<sup>-1</sup> under 1 bar of H<sub>2</sub>, respectively for (a) and (c). HP-DSC absorption measurements were conducted under  
6 80 bar of H<sub>2</sub> and heated from RT to 200 °C and 220 °C with a heating rate of 2 °C min<sup>-1</sup>, respectively for (b) and (d).

7 Although these calorimetric studies of the de/re-hydrogenation reactions provide essential  
8 information regarding the similarities between the investigated systems, they do not provide  
9 detailed information on the mechanistic aspects of the reactions. For this reason, the de/re-  
10 hydrogenation reaction pathways have been investigated by means of the *in-situ* SR-PXRD  
11 experiments and the results are plotted in Figure 4. The starting diffraction pattern for the  
12 dehydrogenation of the LMBNH-TPX composite indicates the presence of the three phases  
13 Mg(NH<sub>2</sub>)<sub>2</sub>, LiH and TPX (Figure 4(a)). Upon heating to ca. 150 °C, the diffraction peaks of  
14 Mg(NH<sub>2</sub>)<sub>2</sub> and LiH decrease, while simultaneously peaks of cubic Li<sub>2</sub>Mg(NH)<sub>2</sub> appear. With a  
15 further increase of temperature to 185 °C, the peaks of TPX disappear, meaning that the TPX  
16 semicrystalline structure begins to melt and Li<sub>2</sub>Mg(NH)<sub>2</sub> undergoes a polymorphic transition from

1 cubic to orthorhombic at the same temperature. The diffraction peaks which are still present at  
 2 200 °C belong exclusively to the orthorhombic phase of  $\text{Li}_2\text{Mg}(\text{NH}_2)_2$ .



3  
 4 **Figure 4.** *In situ* SR-PXRD desorption (a) and absorption (b) of LMBNH-TPX; desorption (c) and absorption (d) of LMNH-TPX.  
 5 In the desorption experiments (a) and (c), samples were heated from RT to 200 °C and 250 °C with a heating rate of 10 °C min<sup>-1</sup>  
 6 under 1 bar of H<sub>2</sub>. In the absorption experiments (b) and (d), samples were under 80 bar of H<sub>2</sub> and heated from RT to 200 °C and  
 7 250 °C with a heating rate of 5 °C min<sup>-1</sup>. All data were measured with  $\lambda = 0.20716 \text{ \AA}$ .

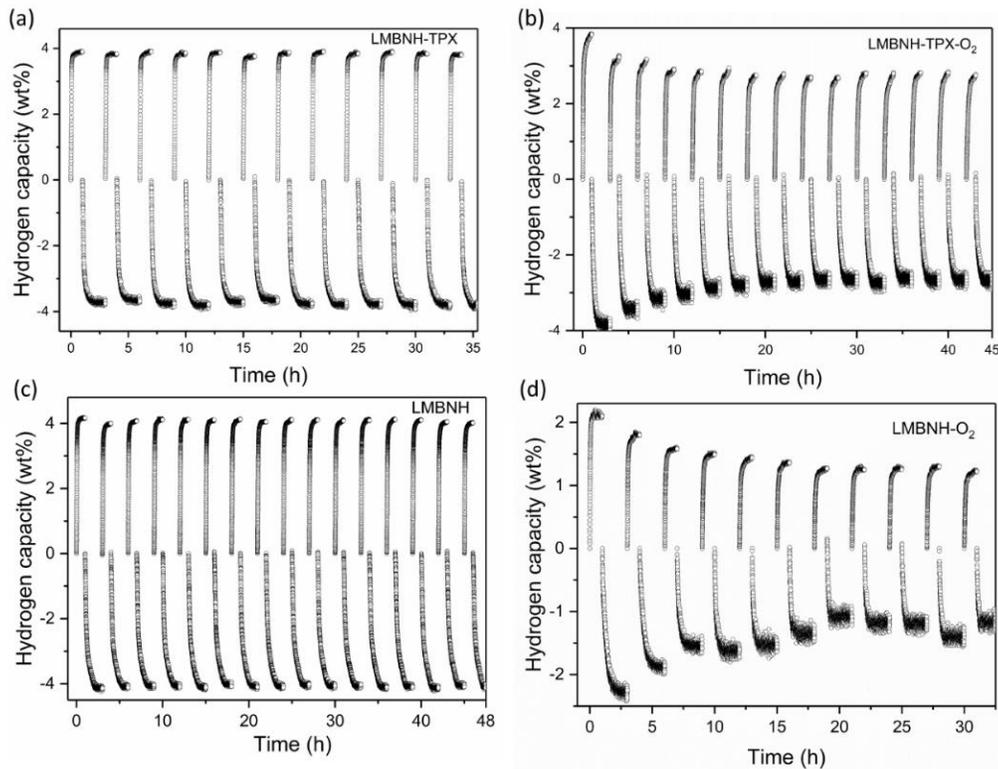
8 For the hydrogen absorption of LMBNH-TPX (Figure 4(b)), in the starting pattern and below  
 9 130 °C, the observed diffraction peaks can be assigned to TPX and orthorhombic  $\text{Li}_2\text{Mg}(\text{NH}_2)_2$ .  
 10 The characteristic patterns of  $\text{Mg}(\text{NH}_2)_2$  and LiH appear at ca. 140 °C and they can be seen until  
 11 the end of this process, together with a bit of unreacted  $\text{Li}_2\text{Mg}(\text{NH}_2)_2$ . This trace of  $\text{Li}_2\text{Mg}(\text{NH}_2)_2$

1 could be explained by taking into account that the reaction time for this *in situ* SR-PXD is not long  
2 enough to fully hydrogenate the material.

3 In contrast to the dehydrogenation pathway of LMBNH-TPX,  $\text{Mg}(\text{NH}_2)_2$  is hardly observed during  
4 the entire dehydrogenation process of LMNH-TPX (Figure 4(c)). However, after hydrogenation,  
5 the diffraction peaks of  $\text{Mg}(\text{NH}_2)_2$  can be identified as the primary phase along with LiH. The  
6 peaks of TPX disappear at the same temperature in the de/re-hydrogenation reactions of LMBNH-  
7 TPX and LMNH-TPX, while they appear again after those composites are cooled down after  
8 dehydrogenation (Figure 4(b) and (d)); DSC experiments show a similar behavior (Figure S4).  
9 This behavior of the polymer implies that, under the applied experimental and compositional  
10 conditions TPX is physically and chemically stable. The transformations of hydrides in the  
11 LMBNH-TPX and LMNH-TPX composites are the same as those in LMBNH and LMNH systems,  
12 which were reported in previous studies.[25, 27, 47, 65] One point to note is that  $\text{Li}_4(\text{NH}_2)_3(\text{BH}_4)$   
13 was not detected in the LMBNH-TPX system, possibly due to the use of cyclohexane. This may  
14 led to the formation of a thin layer of  $\text{LiBH}_4$ , which reacts with the *in situ* formed  $\text{LiNH}_2$ , producing  
15 a  $\text{Li}_4(\text{NH}_2)_3(\text{BH}_4)$  layer as well.

16 In an effective attempt to study the stability against oxygen and moisture contamination of the air-  
17 exposed hydride-polymer composites, their de/re-hydrogenation were investigated over a span of  
18 several cycles. Figure 5 summarizes the data acquired from the de/re-hydrogenation cycles of  
19 LMBNH-TPX, the air-exposed LMBNH-TPX (shortened as LMBNH-TPX- $\text{O}_2$  hereafter), the pure  
20 LMBNH, and the air-exposed LMBNH (shortened as LMBNH- $\text{O}_2$  hereafter). The as prepared  
21 samples show excellent reversibility, with both maintaining their hydrogen capacities of ca. 4.0  
22 wt% and 4.1 wt% for LMBNH-TPX and LMBNH, respectively. The hydrogen contents for these

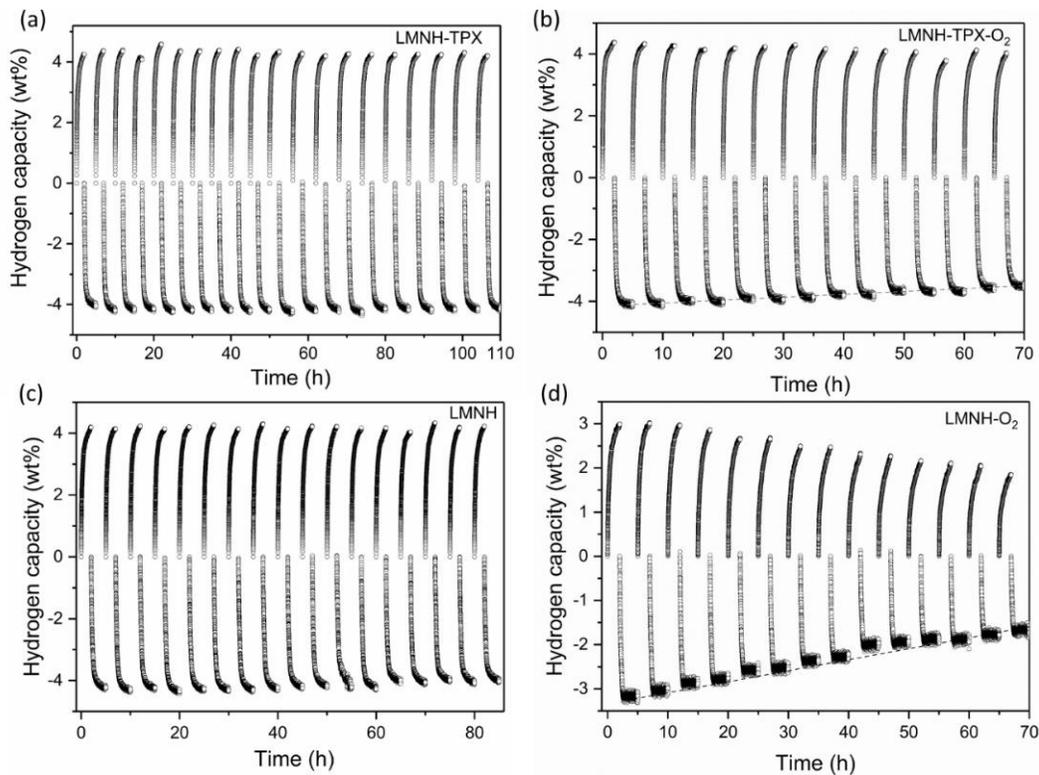
1 samples close to the previously reported value 4.2 wt%.[46] On the other hand, the air-exposed  
 2 composites show a decrease of the hydrogen capacities.



3  
 4 **Figure 5.** Reversibility of LMBNH-TPX (a); LMBNH-TPX-O<sub>2</sub> (air-exposed LMBNH-TPX) (b); LMBNH (c); and LMBNH-O<sub>2</sub>  
 5 (air-exposed LMBNH) (d). Isothermal de/ab-sorption cycling experiments were performed at 180 °C and 1 and 80 bar for  
 6 desorption and absorption, respectively. The hydrogen capacities of LMBNH-TPX and LMBNH-TPX-O<sub>2</sub> are just considered the  
 7 hydride fraction.

8 In detail, the LMBNH-TPX system is more stable than the pure LMBNH system. The hydrogen  
 9 capacity measured in the first cycle of the LMBNH-TPX-O<sub>2</sub> is the same as that of the as prepared  
 10 LMBNH-TPX, meaning that at room temperature O<sub>2</sub> and or H<sub>2</sub>O do not significantly affect the  
 11 integrity of the material. During cycling, the hydrogen storage capacity drops continuously from  
 12 the first to the fifth cycle; after the fifth cycle, the reversible H<sub>2</sub> content is stable at ca. 3.0 wt%.  
 13 The reason behind this phenomenon could be the physisorption or physical adhesion of O<sub>2</sub> and/or  
 14 H<sub>2</sub>O on the surface of LMBNH-TPX, which later reacts with the hydrides to form metal oxides  
 15 such as Li<sub>2</sub>O and MgO. In comparison, the first cycle of the LMBNH-O<sub>2</sub> system shows an

1 immediate drop in hydrogen capacity to ca. 2.0 wt%, which indicates that the material strongly  
 2 reacted with O<sub>2</sub> and/or H<sub>2</sub>O during air exposure. For this system, after 7 cycles, the hydrogen  
 3 capacity stabilizes to ca. 1.5 wt%. The stabilization of both LMNH-TPX-O<sub>2</sub> and LMNH-O<sub>2</sub>  
 4 observed from these cycling studies suggests that the polymer can effectively protect the hydrides  
 5 and thus increase the stability and reversibility of the hydrogen storage for the composites.



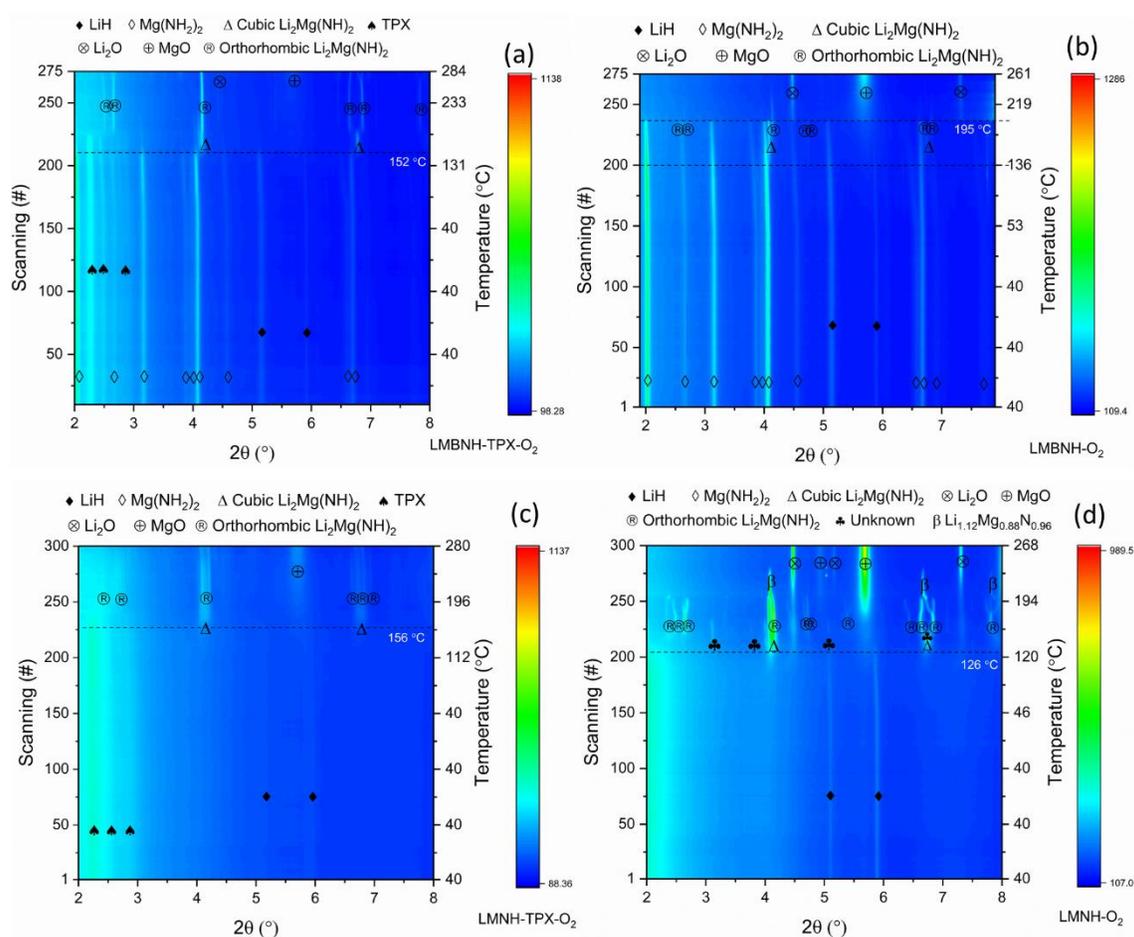
6  
 7 **Figure 6.** Reversibility of LMNH-TPX (a); LMNH-TPX-O<sub>2</sub> (air-exposed LMNH-TPX) (b); LMNH (c); and LMNH-O<sub>2</sub> (air-  
 8 exposed LMNH) (d). Isothermal de/ab-sorption cycles were performed at 200 °C and 1 and 80 bar for desorption and absorption,  
 9 respectively. The hydrogen capacities of LMNH-TPX and LMNH-TPX-O<sub>2</sub> are considered only the hydride fraction.

10 The reversibility of LMNH-TPX and LMNH after different treatments is summarized in Figure 6.  
 11 Not only the as prepared LMNH-TPX, but also the air-exposed LMNH-TPX show significantly  
 12 higher stability compared to the pristine LMNH systems. There is almost no H<sub>2</sub> content attenuation  
 13 during the first 20 cycles in the as prepared LMNH-TPX system; however, the LMNH system  
 14 starts to lose some capacity from the ninth cycle onwards. The higher material stability could be

1 attributed to a confinement effect of the metal hydride in the TPX polymer matrix, which does not  
2 allow the sintering of the LMNH particles and consequently does not lead to a drop of hydrogen  
3 capacity and kinetic properties. The hydrogen capacities of LMNH-TPX and LMNH are ca. 4.3  
4 wt%, considering the hydride fraction only. The cycled LMNH-TPX also underwent  
5 dehydrogenation at 250 °C and achieved a measured hydrogen capacity of 5.2 wt% which complies  
6 perfectly with previously reported results[27, 34] (Figure S5). The temperature, at 200 °C, is not  
7 high enough to release the hydrogen from the LMNH-based systems completely, which possibly  
8 explains the observed dehydrogenation values in Figures 6(a) and (c). Both samples exposed to air  
9 show a reduction in hydrogen capacity during cycling and the slope due to this decrease indicates  
10 that this effect is steeper for the LMNH-O<sub>2</sub> than that of LMNH-TPX-O<sub>2</sub>. The calculated rates of  
11 reduction are 0.021 wt% (Figure 6(b)) and 0.1 wt% (Figure 6(d)) per cycle, for LMNH-TPX-O<sub>2</sub>  
12 and LMNH-O<sub>2</sub>, respectively. The effect of atmospheric exposure in LMBNH-based and LMNH-  
13 based systems is slightly different. In this case, the H<sub>2</sub> content reduction subsides completely after  
14 several cycles in LMBNH-based systems; on the other hand, it continues with a rather constant  
15 rate during the cycles for LMNH-based systems. The reason behind this phenomenon could be the  
16 presence of the LiBH<sub>4</sub> film, which further limits O<sub>2</sub> and/or H<sub>2</sub>O contamination.

17 XRD patterns of the samples before and after hydrogenation (Figures 5 and 6) are shown in Figure  
18 S6. After 12 h exposure to air, the diffraction peaks of Li<sub>2</sub>O are observed in both LMBNH-TPX  
19 and LMBNH. Li<sub>2</sub>O along with some unreacted Li<sub>2</sub>Mg(NH)<sub>2</sub> is present in the hydrogenated  
20 samples. However, the peaks intensities of Li<sub>2</sub>O and Li<sub>2</sub>Mg(NH)<sub>2</sub> in the air-exposed LMBNH are  
21 much stronger than those in the air-exposed LMBNH-TPX system. Similar phenomena have also  
22 been observed in the LMNH-based system, where the Li<sub>2</sub>O and MgO are present in the air-exposed  
23 LMNH composite (Figure S6(d)), but not in the air-exposed LMNH-TPX system (Figure S6(c)).

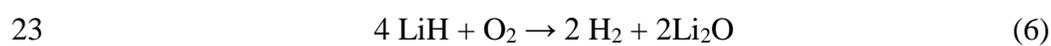
1 Unlike the other samples, all of the  $\text{Li}_2\text{Mg}(\text{NH})_2$  reacts with hydrogen to form  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$   
 2 in the system of LMNH-TPX (Figure S6(c)). It should be pointed out that traces of  $\text{Li}_2\text{O}$  found in  
 3 the hydrogenated LMBNH-TPX and LMNH-TPX composites could be due to contamination from  
 4 the reactor. The XRD results are in agreement with the hydrogen reversibility properties shown in  
 5 Figures 5 and 6.

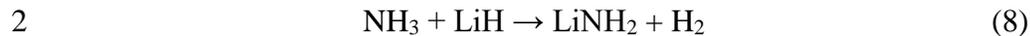
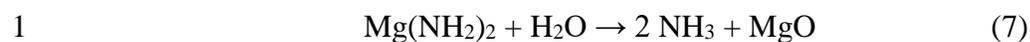


6  
 7 **Figure 7.** *In situ* SR-PXRD desorption of LMBNH-TPX (a); LMBNH (b); LMNH-TPX (c) and LMNH (d) under air. The samples  
 8 have been exposed to air for 1 h prior to the measurements. Samples were held isothermally at 40 °C for 30 min before being heated  
 9 to 300 °C with a heating rate of 10 °C min<sup>-1</sup>. All data were measured with  $\lambda = 0.20716 \text{ \AA}$ .

10 *In situ* SR-PXRD experiments were used to investigate the desorption reaction of the air-exposed  
 11 hydride-TPX composites (Figure 7). All of them have been exposed to air for 1 h before loading  
 12 them into the *in situ* cell (Figure S1), and then they were kept at 40 °C for 30 min before heating

1 to high temperatures. Figure 7 shows little evidence of oxidation before heating to high  
 2 temperatures. The results reported in Figure 7(a) are in very close agreement with the measurement  
 3 reported in Figure 4(a).  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$  are stable up to  $152\text{ }^\circ\text{C}$ , and then they react with each  
 4 other to form cubic  $\text{Li}_2\text{Mg}(\text{NH})_2$ , as shown in reaction 4. By increasing temperature, the diffraction  
 5 peaks of TPX disappear and  $\text{Li}_2\text{Mg}(\text{NH})_2$  changes from cubic to orthorhombic structure. Finally,  
 6 some weak peaks of  $\text{MgO}$  and  $\text{Li}_2\text{O}$  appear at about  $280\text{ }^\circ\text{C}$ . This is different to the LMBNH-TPX  
 7 composite where only traces of  $\text{Li}_2\text{Mg}(\text{NH})_2$  are observed at temperatures below  $190\text{ }^\circ\text{C}$  in the  
 8 LMBNH system (Figure 7(b)), and a small amount of  $\text{MgO}$  is visible at ca.  $140\text{ }^\circ\text{C}$ . As expected,  
 9 the peaks of  $\text{Li}_2\text{O}$  and  $\text{MgO}$  are visible at temperatures above  $195\text{ }^\circ\text{C}$ . This clearly indicates that  
 10 the thermal dehydrogenation reactions of LMBNH in air and  $\text{H}_2$  atmosphere are different. Figure  
 11 7(c) shows that  $\text{Mg}(\text{NH}_2)_2$  reacts with  $\text{LiH}$  to form cubic  $\text{Li}_2\text{Mg}(\text{NH})_2$  at ca.  $156\text{ }^\circ\text{C}$  in LMNH-  
 12 TPX, and  $\text{Li}_2\text{Mg}(\text{NH})_2$  undergoes its polymorphic change from cubic to orthorhombic structure at  
 13 around  $200\text{ }^\circ\text{C}$ . In addition,  $\text{MgO}$  starts to form at  $160\text{ }^\circ\text{C}$ . In Figure 7(d),  $\text{Mg}(\text{NH}_2)_2$  reacts with  
 14  $\text{LiH}$  to form cubic  $\text{Li}_2\text{Mg}(\text{NH})_2$  together with unknown phases at temperatures below  $126\text{ }^\circ\text{C}$  which  
 15 is  $30\text{ }^\circ\text{C}$  lower than in the experiments presented in Figures 7(a) and (c). At the same time, the  
 16 diffraction peaks of  $\text{Li}_2\text{O}$  and  $\text{MgO}$  appear. Upon increasing the temperature to ca.  $160\text{ }^\circ\text{C}$  the  
 17 polymorph of  $\text{Li}_2\text{Mg}(\text{NH})_2$  changes from the cubic to the orthorhombic. The formation of  $\text{Li}_2\text{O}$   
 18 and  $\text{MgO}$  affects the ratio of Li to Mg in the imide and nitride, and a non-equilibrium stoichiometry  
 19  $\text{Li}_{1.12}\text{Mg}_{0.88}\text{N}_{0.96}$  is formed at the temperature above  $200\text{ }^\circ\text{C}$ . Finally, all the Li and Mg change to  
 20 their oxides. This indicates that the reactions between  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$  are influenced by  
 21 exposure to air. As a result of studying these materials, the following reactions 5-8 are proposed:



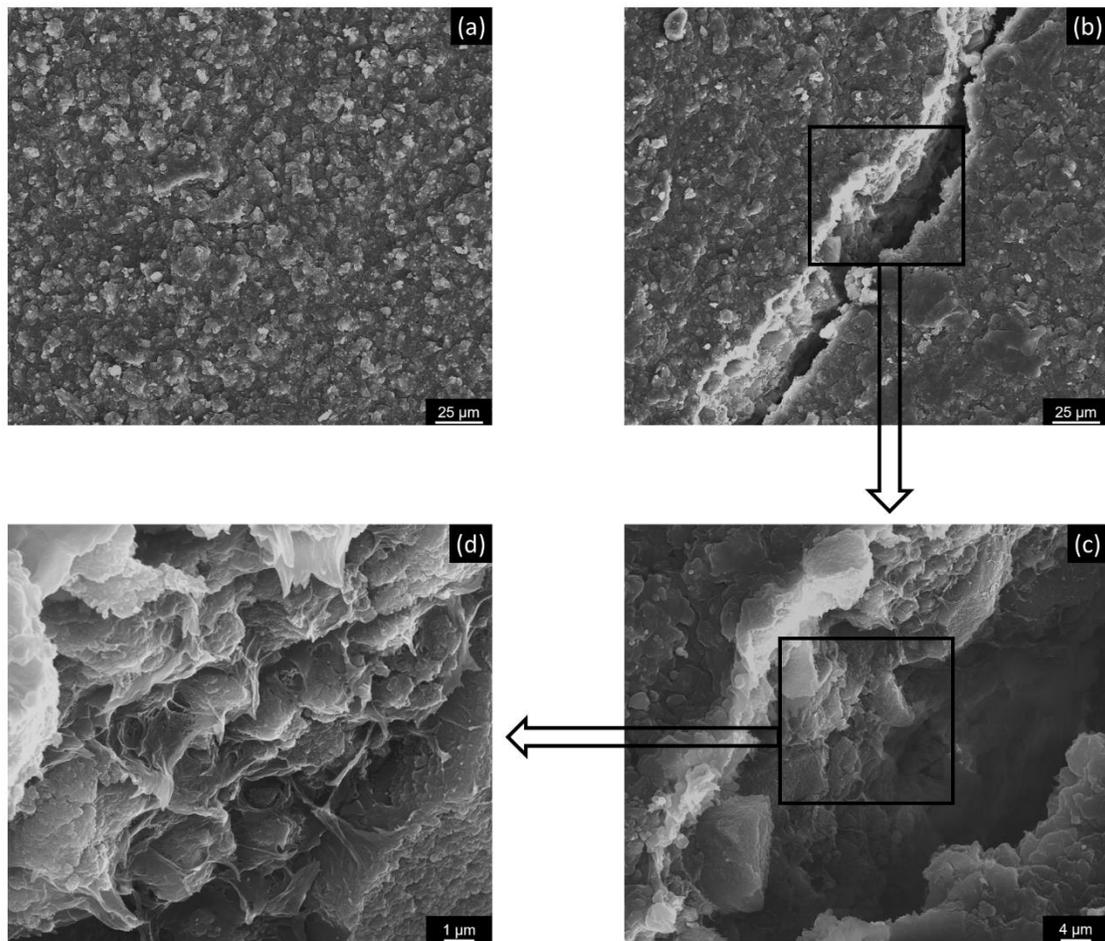


3 These results show that the hydride composites are more air sensitive than the hydride-TPX  
4 composites. O<sub>2</sub> and H<sub>2</sub>O from exposure to atmosphere affect the reactions between Mg(NH<sub>2</sub>)<sub>2</sub> and  
5 LiH leading to the observed reduction of hydrogen storage capacity (Figures 5 and 6). Irrespective  
6 of the atmosphere under which the reactions are carried out (*i.e.*, H<sub>2</sub> or air), the material exposed  
7 to air for ca. 90 min has similar reaction pathways for the hydride-TPX composites.

8 As a representative composite, the system LMNH-TPX after 20 cycles of de/re-hydrogenations  
9 (Figure 6) was studied by SEM to analyze the morphology of the hydride-TPX composites (Figure  
10 8). Figure 8(a) shows that the surface of the TPX polymer covers the whole surface of the LMNH  
11 and holds the particles stable after the cycling experiments. To investigate whether the same effect  
12 is visible in the bulk structure of the composites a fracture was induced on the surface of the  
13 LMNH-TPX (Figure 8b). The SEM images of the fracture (Figure 8b-d) indicate that the three-  
14 dimensional network structure of the cycled LMNH-TPX is the same as at the surface; the LMNH  
15 is uniformly distributed within the TPX.

16 To understand the stability of the metal hydride particles in the polymer matrix, it is necessary to  
17 comment on the gas transport properties of the polymer. The diffusion coefficient of O<sub>2</sub> and H<sub>2</sub>O  
18 in TPX are  $1.56 \times 10^{-10}$  [m<sup>2</sup>/s] and  $1.59 \times 10^{-12}$  [m<sup>2</sup>/s] at 30 °C (see Table S1), as determined by time-  
19 lag experiments with pure gases. The value of water solubility coefficient for TPX is indeed higher  
20 than that for other gases, but since the water vapour diffusion coefficient is very low the water is  
21 not passing through the polymer film rapidly, meaning that the process is controlled by the  
22 diffusion. In case of the hydrogen storage composites that means that water does not reach the  
23 particles as easily as it would have been if the particles were directly exposed to air. It is understood

1 from the low solubility values that during exposure in air atmosphere, the contact between hydrides  
2 and gases such as O<sub>2</sub> and H<sub>2</sub>O is hindered by the TPX matrix. That is the reason why the hydride-  
3 TPX composites exposed to air demonstrate initially and maintain both an excellent reaction  
4 stability (Figure 7) and reversibility (Figures 5 and 6). Also the high diffusion coefficient for  
5 hydrogen, which is equal to  $20.7 \times 10^{-10}$  [m<sup>2</sup>/s] at 30 °C, indicates that the polymer allows hydrogen  
6 to reach the metal hydrides fast.



7

8 **Figure 8.** SEM images of the 20-times cycled LMNH-TPX composite: (a) surface, (b) fracture induced on the surface and (c and  
9 d) higher magnifications of the fractured area.

## 1 **Conclusion**

2 LMBNH-TPX, LMNH-TPX composites have been prepared by casting the mixture of LMBNH  
3 and LMNH within the TPX matrix on a glass substrate using a doctor-blade technique. Hydrogen  
4 storage properties and reaction mechanisms of these composites under air and H<sub>2</sub> atmosphere are  
5 studied. *In situ* SR-PXRD reveals that both LMBNH-TPX and LMNH-TPX show significantly  
6 enhanced air-stabilities as compared to the pure LMBNH and LMNH. After exposing to air for 12  
7 hours, the reversible hydrogen capacities of LMBNH-TPX and LMNH-TPX in the tenth cycle are  
8 ca. 3.0 and 4.0 wt%, respectively, which are two-times higher than those of LMBNH (1.5 wt%)  
9 and LMNH (2.0 wt%) when exposed to the same conditions. The reduction rate of reversible  
10 hydrogen capacity of LMNH-TPX after exposing to air is 0.021 wt% per cycle. However, that  
11 value is 5 times larger (0.1 wt% per cycle) for pure LMNH. The hydrogen storage properties of  
12 these composites are dependent on the hydrides and not on the presence of the polymer matrix.  
13 Both LMBNH-TPX and LMNH-TPX retain the same loading capacities and kinetic properties,  
14 while the latter exhibits improved reversibility. SEM analysis confirms that the metal hydrides  
15 remain embedded in the polymeric matrix even after a number of cycles as proposed in Figure 1,  
16 and the three-dimensional integrity has been retained in both types of composites. The results  
17 detailed here show that the polymer provides an excellent barrier for the hydrides, avoiding direct  
18 contact with oxygen or water, therefore increasing the reversibility lifetime significantly and  
19 suppressing the sintering effects of the metal hydrides during hydrogenation and dehydrogenation  
20 reactions at this temperature. The present study therefore demonstrates a suitable way to fabricate  
21 air-stable metal hydride-polymer composite for hydrogen storage applications.

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13

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21

22

# 1 **Supporting information**

## 2 **Air-stable metal hydride-polymer composites of Mg(NH<sub>2</sub>)<sub>2</sub>-LiH and** 3 **TPX<sup>TM</sup>**

4  
5 Hujun Cao,<sup>a\*</sup> Prokopios Georgopoulos,<sup>b\*</sup> Giovanni Capurso,<sup>a</sup> Claudio Pistidda,<sup>a</sup> Fynn Weigelt,<sup>b</sup>  
6 Anna-Lisa Chaudhary,<sup>a</sup> Volkan Filiz,<sup>b</sup> Jo-Chi Tseng,<sup>c</sup> Michael T. Wharmby,<sup>c</sup> Martin Dornheim<sup>a</sup>  
7 Volker Abetz,<sup>b, d</sup> and Thomas Klassen<sup>a, e</sup>

8  
9 a. Institute of Materials Research, Materials Technology, Helmholtz-Zentrum Geesthacht  
10 GmbH, Max-Planck-Straße 1, 21502, Geesthacht, Germany.

11 E-Mail: hujun.cao@hzg.de; Fax: + 49 04152 / 87-2625; Tel: +49 04152 / 87-2643

12 b. Institute of Polymer Research, Helmholtz-Zentrum Geesthacht GmbH, Max-Planck-Straße  
13 1, 21502, Geesthacht, Germany.

14 E-Mail: prokopios.georgopoulos@hzg.de; Fax: + 49 04152 / 87-2466; Tel: +49 04152 / 87-2420

15 c. Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg, Germany

16 d. Institute of Physical Chemistry, University of Hamburg, Martin-Luther-King-Platz 6,  
17 20146 Hamburg, Germany.

18 e. Institute of Materials Technology, Helmut Schmidt University, Holstenhofweg 85, 22043  
19 Hamburg, Germany.

20

1 Time-lag method for the estimation of the gas transport properties:

2  
3 In short, the TPX film was placed into the measurement cell and sealed with a Viton<sup>®</sup> O-ring. The  
4 sealed membrane served as a barrier between the feed and permeate sides of the measurement  
5 instrumentation. Prior to the measurement, the apparatus was thoroughly evacuated. The pressure  
6 increase in the permeate chamber with known constant volume was monitored from the moment  
7 the gas was brought in contact with the membrane under a constant pressure. From the obtained  
8 curve, the time-lag,  $\theta$ , was determined by extrapolating the slope of the linear increase to its  
9 intersection with the time axis and the gas permeability coefficient of the membrane was calculated  
10 from the linear part of the curve.<sup>[S1]</sup> The schematic representation of the experimental result is

11 depicted in Figure S2. The diffusion coefficient of component  $i$  ( $D_{eff,i}$ ) was calculated by the  
12 following equation <sup>[S2]</sup>:  $\theta = \frac{l^2}{6 D_{eff,i}}$ , where  $l$  is the membrane film thickness and  $D_{eff}$  the effective

13 diffusion coefficient of the penetrant in the studied material. The permeability ( $P_{eff,i}$ ) is the function  
14 of: a) slope (i.e.  $dp/dt$ ) of the linear part of the curve (Figure S2); b) driving force, derived from  
15 the difference of the feed and permeate pressure at the moment the slope is determined; c)  
16 membrane area exposed to the gas and d) membrane thickness. Knowing the volume of the  
17 permeate side of the measurement instrumentation and assuming that in the pressure range 0-10  
18 mbar in which permeate pressure is acquired the gas in the permeate side can be considered as  
19 ideal, the ideal gas law helps to convert the pressure change into the gas volume change (i.e.  $dV/dt$ ).

20 Knowing all the aforementioned parameters the permeability coefficient can be determined. The  
21 solubility ( $S_{eff,i}$ ) coefficient can be calculated from the following equation

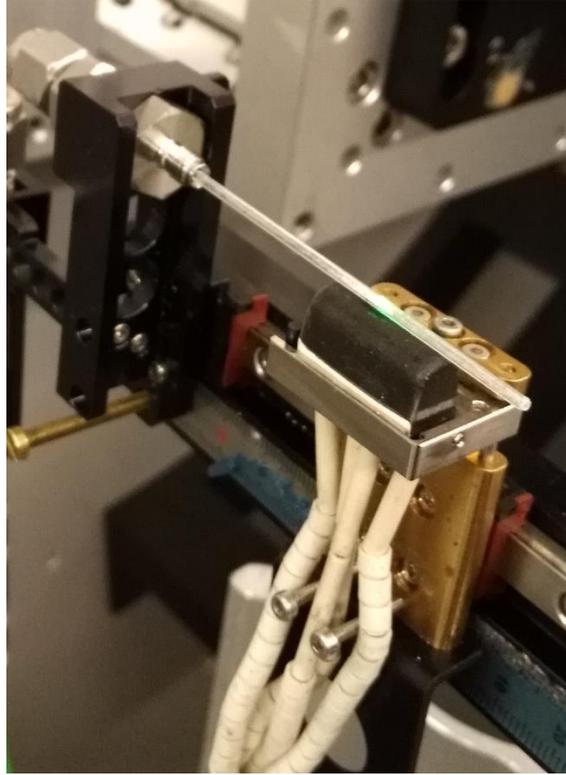
22  $P_{eff,i} = D_{eff,i} S_{eff,i}$ .

1 For the time-lag measurements, a custom-made machine was used. The gases used for the  
2 experiments (Linde AG, Munich, Germany) were of high purity, while a thermostat was used to  
3 maintain the temperature. The vacuum was generated by a turbomolecular pump (Pfeiffer GmbH,  
4 Asslar, Germany). A LabView (National Instruments, Austin, TX, USA) based custom software  
5 was used for the control of the time-lag experimental instrumentation as well as for the evaluation  
6 of the data. It should be noted that the placement of the Viton<sup>®</sup> O-ring involves relatively hard  
7 pressing of the O-ring onto the membrane. The O-ring has a 65 Shore hardness. The pressing  
8 ensures a good sealing of the membrane in the measurement cell. The accuracy of the method is  
9 based on the time measurement of the time-lag, which is measured with systematic error of  $35\pm 5$   
10 ms, rising from the speed of opening of the pneumatic KF16 vacuum valves. The precision of the  
11 permeability coefficient determination is ensured by: a) the thorough evacuation of the membrane  
12 before it is exposed to the gas under investigation; b) the careful calibration of the permeate volume  
13 ( $45.8\pm 0.1\text{ cm}^3$ ), and c) the use of highly accurate pressure sensors on the permeate side of the  
14 measurement instrumentation (Baratron 622 and 121 absolute capacitance manometers, 10 Torr  
15 range, MKS Inc., USA) For measurements of water as pure gas, the water used was Millipore  
16 deionized water ( $0.055\text{ }\mu\text{S/cm}$ ) thoroughly degassed before use by repeated flash evacuation. The  
17 water was poured into a special stainless steel reservoir inside the thermostated zone of the time-  
18 lag instrumentation, kept at the same temperature as for the whole instrumentation. The experiment  
19 with the water vapour started with thorough evacuation of the membrane and feed gas reservoir.  
20 After satisfactory evacuation the measurement cell was closed and the feed gas reservoir was  
21 connected to the liquid water containing reservoir by opening of vacuum valves. The liquid water  
22 was allowed to evaporate until stable pressure was reached. In case the pressure was exceeding the  
23 saturated vapour pressure at the temperature of the thermostated measurement instrumentation, the

1 measurement had to be aborted and liquid water was to be degassed again. Following this step, the  
2 feed gas and liquid water reservoirs were closed and the vacuum part evacuated to at least  $10^{-3}$   
3 mbar, the pressure in the permeate part was controlled to be not rising, and the measurement started  
4 by opening vacuum pneumatic valves, connecting feed gas reservoir and the feed side of the  
5 measurement cell. Obviously, at this time the pressure of the water vapour dropped due to the  
6 expansion into bigger volume. It means that the measurement of water vapour transport through  
7 the membrane cannot be done at water vapour activity close to unity which has double effect:  
8 disadvantage of not knowing behavior of the studied membrane at saturated water vapour  
9 conditions; and advantage of avoiding any possibility of water vapour condensation on the film  
10 surface by, e.g., Joule-Thomson effect. After experiments with the water vapour the vacuum  
11 system was flashed with nitrogen and evacuated repeatedly to avoid any gas contamination with  
12 water.

13

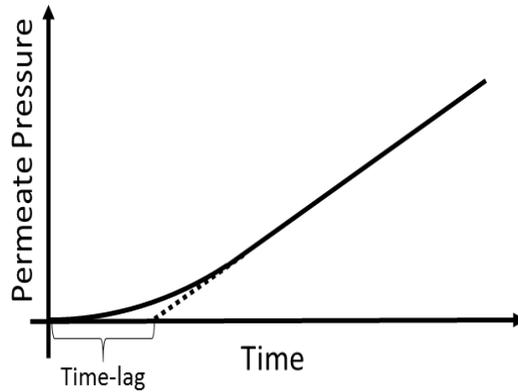
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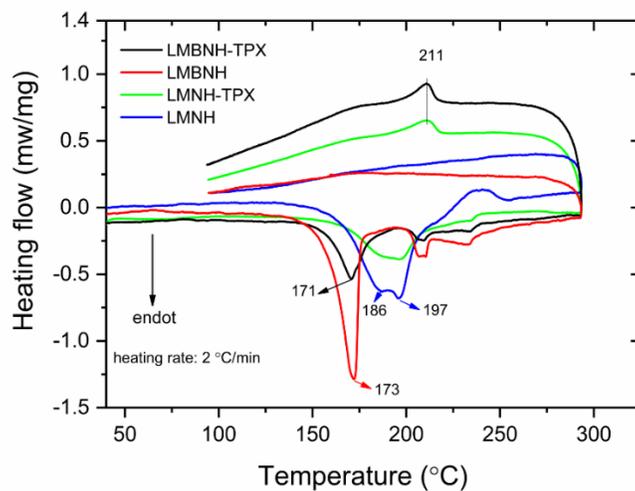
2 **Figure S1.** The digital photo of the setup for oxidation experiments, samples were loaded in the capillary, exposed to the air, and  
3 then heated to the high temperature.

4



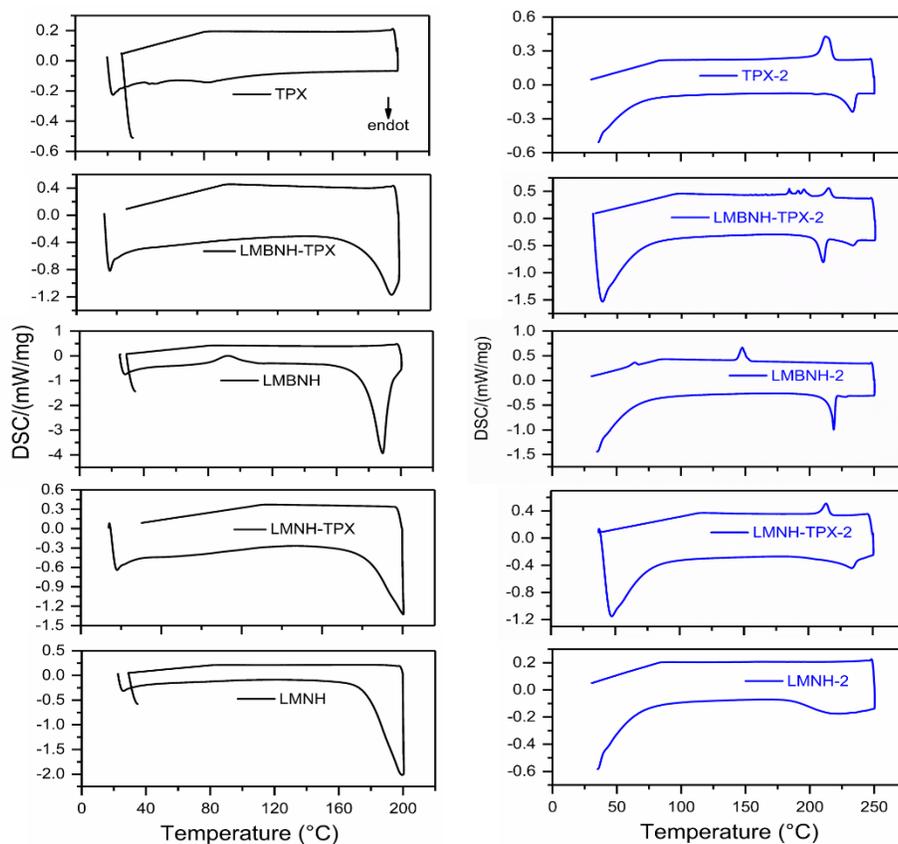
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6 **Figure S2.** Schematic representation of the experimental result of the time-lag method for the estimation of the gas transport  
7 properties of the polymer film.  
8



1  
2 **Figure S3.** DTA curves of LMBNH-TPX, LMBNH, LMNH-TPX and LMNH, respectively. All the samples have been heated  
3 from RT to 300 °C under 50 mL min<sup>-1</sup> of argon flow with a heating rate of 2 °C min<sup>-1</sup>.

4



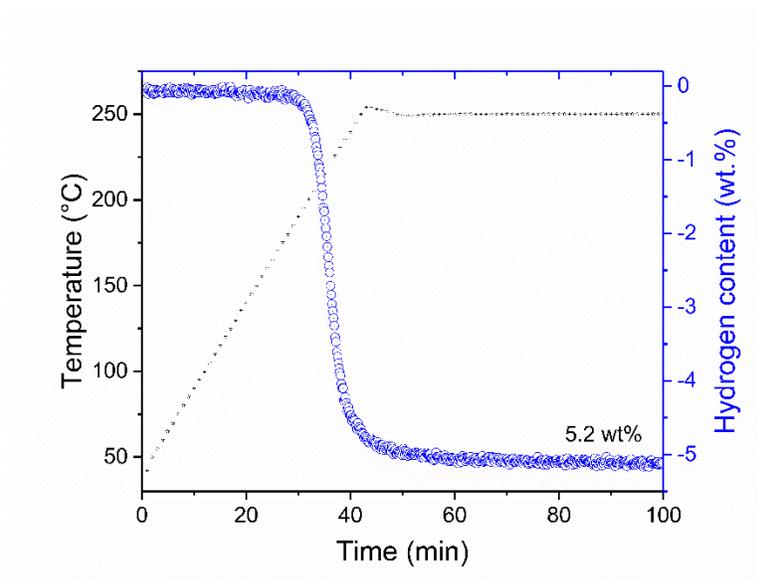
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 2 **Figure S4.** The first DSC thermal decompositions measurements of pure TPX, LMBNH-TPX, LMBNH, LMNH-TPX and LMNH  
 3 (left), samples were heated from RT to 200 °C with a heating rate of 5 °C min<sup>-1</sup> under 1 bar of H<sub>2</sub>. The second DSC thermal  
 4 decompositions measurements of pure TPX, LMBNH-TPX, LMBNH, LMNH-TPX and LMNH (right), samples were heated from  
 5 RT to 250 °C with a heating rate of 5 °C min<sup>-1</sup> under 1 bar of H<sub>2</sub>.

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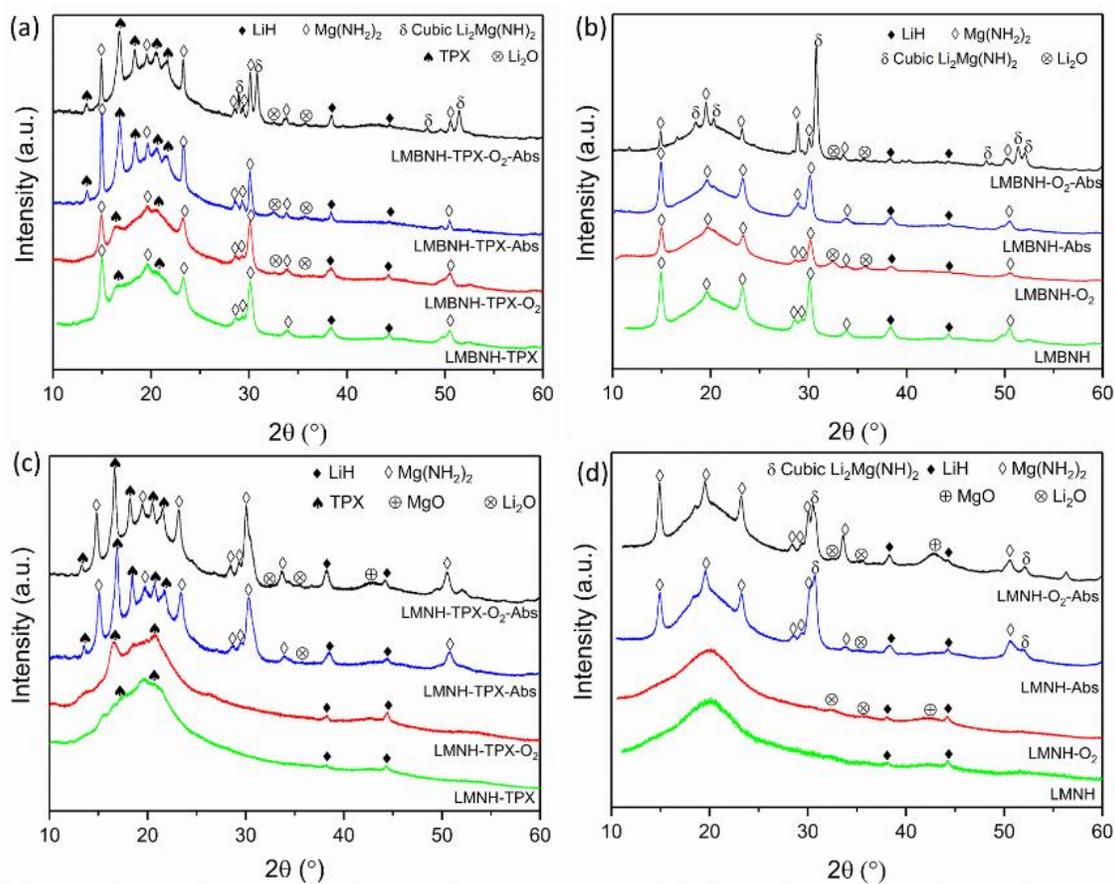


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3 **Figure S5.** Temperature programmed dehydrogenation of the post-cycled LMNH-TPX, sample has been heated from RT to 250  
4 °C with a heating rate of 5 °C min<sup>-1</sup> under 1 bar of H<sub>2</sub>.

5

1



2

3 **Figure S6.** XRD patterns of LMBNH-TPX, LMBNH, LMNH-TPX, and LMNH after preparing, exposing to air 12h (O<sub>2</sub>), and  
 4 absorption (Abs).

5

6

1  
2 Gas transport properties of TPX™

3  
4 **Table S1.** Permeability (P), diffusion coefficient (D) and solubility coefficient (S) of freestanding thick film TPX™ membranes  
5 measured at 30 °C with the time-lag method.

6

	P	D	S
	[Barrer]*	[10 <sup>-10</sup> m <sup>2</sup> /s]	[10 <sup>-3</sup> cm <sup>3</sup> <sub>STP</sub> /(cm <sup>3</sup> cmHg)]
H <sub>2</sub>	92.1	20.7	0.445
O <sub>2</sub>	24.4	1.56	1.56
N <sub>2</sub>	6.29	0.716	0.879
H <sub>2</sub> O	177	0.0159	1112

7 \* 1 Barrer = 10<sup>-10</sup> [cm<sup>3</sup><sub>STP</sub>/(cm s cmHg)]

8  
9 Reference:  
10 [S1] I. Blume, E. Smit, M. Wessling, C. Smolders, in: Macromolecular Symposia, Wiley Online  
11 Library, 1991, pp. 237-257.  
12 [S2] H.L. Frisch, The Journal of Physical Chemistry, 61 (1957) 93-95

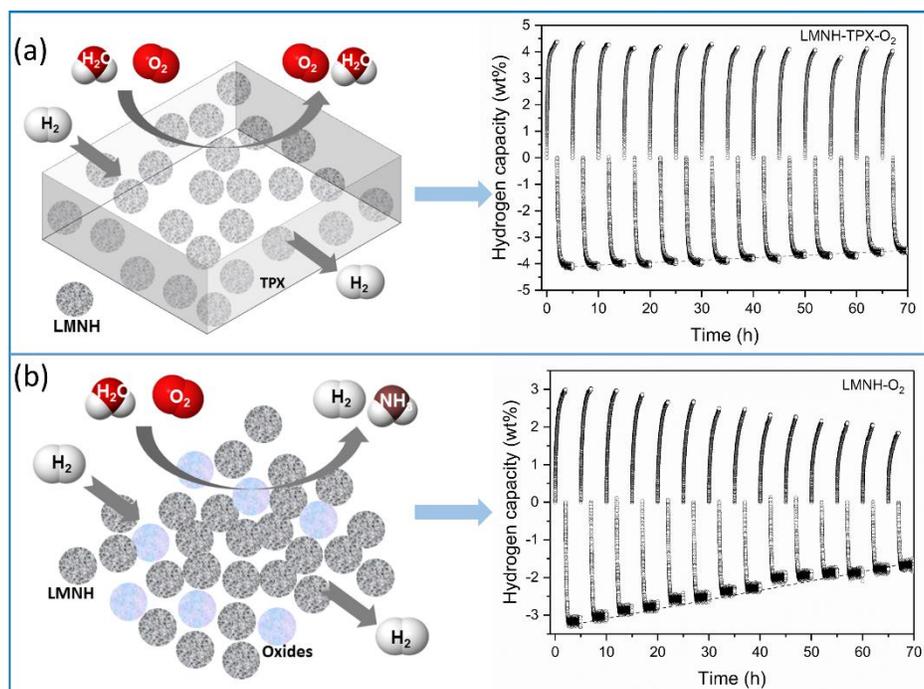
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TOC



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5 The amide-hydride systems remain stable in the polymeric matrix of polymethylpentene  
6 significantly improving the air stability of the metal hydrides. It shows a promising way to fabricate  
7 metal hydride-polymer composite energy storage materials that can be handled in ambient  
8 conditions.

9