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Supporting Information

Changing the dehydrogenation pathway of $LiBH_4$-MgH_2 by adding nanosized lithiated TiO_2

J. A. Puszkiel*[a], M. V. Castro Riglos[b], F. Karimi[c], A. Santoru[c], C. Pistidda[c], T. Klassen[c], J.M. Bellosta von Colbe[c] and M. Dornheim[c]

1. Experimental details

1.1 Additive and material preparation

1.1.1 Additive preparation

As starting materials LiH (Alfa Aesar, powder, purity 99.4 %) and TiO_2 (Aldrich, 99.99%, 21 nm, weight fraction: 0.85 of anatase and 0.15 of rutile determined via a method described in[1]) were used. In Fig. S1 A the XRD of the starting TiO_2 is shown. A stoichiometric mixture of $0.5LiH+TiO_2$ was milled during 2 h in Ar atmosphere using a P6 Pulverissette planetary device, an 80 cm^3 milling chamber and ball to powder ratio of 40:1. As seen, the $0.5LiH+TiO_2$ after milling is composed of Li_xTiO_2 (x = 0.07 and 0.5) in agreement with previous works as rutile-TiO_2 forms Li-poor polymorphs and anatase-TiO_2 forms Li-rich polymorphs[2,3], Fig. S1 B. Additionally, after the preparation process the presence of H_2 gas in the milling chamber atmosphere was verified with a Bacharach combustible gas leak detector. This confirms the interaction between LiH and TiO_2.

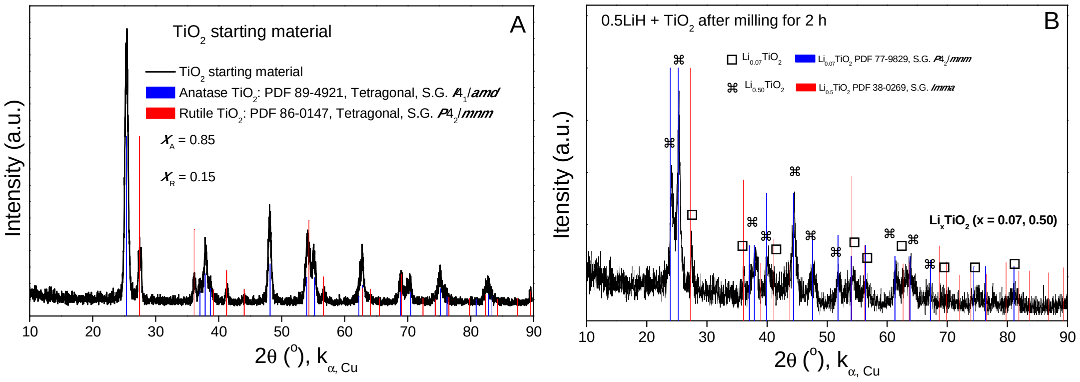

Fig. S1 XRD for **A** TiO_2 and **B** $0.5LiH+TiO_2$ after milling.

1.1.2 Materials preparation

$2LiBH_4+MgH_2$ stoichiometric mixture was milled for 2 h in Ar atmosphere using a P6 Pulverissette planetary device, an 80 cm^3 milling chamber and ball to powder ratio of 40:1. 5 mol % of Li_xTiO_2 (x = 0.07 and 0.5) was added to $2LiBH_4+MgH_2$ mixture and milled in the above described conditions for 2 h. The mixture, as decribed in the work resulted in $2LiBH_4+MgH_2$ plus further lithiated TiO_2 (LixTiO2 with x = 0.59 and 1) which is also in agreement with previously reported works[4,5]. As starting materilas $LiBH_4$ (Sigma aldrich, powder, purity ≥ 90 %) and MgH_2 pre-milled for 10 h (Alfa Aesar, powder, purity 98 %).

1.2 Materials characterization

1.2.1 Powder X–ray diffraction (PXD)

Ex-situ Lab PXD experiments (Device: PANanalytical Empyrean, CuKa radiation, λ = 1.5405 Å, graphite monochromator, 30 mA and 40 kV) were carried out for crystalline phase identification for the materials after milling, different stages of the dehydrogenation and hydrogenation-dehydrogenation during cycling. A specially sealed chamber was used to avoid the hydrolysis/oxidation during the experiment.

1.2.2 Titration measurements

The dehydrogen and hydrogenation kinetic the pure $2LiBH_4+MgH_2$ and $2LiBH_4+MgH_2+0.05Li_xTiO_2$ materials were assessed in a Sieverts kind device with mass flow controllers. Non-isothermal measurements wer performed from room temperature to 425 °C and 450 °C under 3 bar of hydrogen overpressure. Isothermal hydrogenation and dehydrogenation measurements were carriesd out for the $2LiBH_4+MgH_2+0.05Li_xTiO_2$ at 400 °C and 425 °C under 50 bar and 3.0 bar of hydrogen pressure, respectively.

1.2.3 High resolution transmission electron microscopy (HR-TEM)

HR-TEM images were obtained on a Tecnai G^2 microscope with a point resolution of 0.12 nm and gun emission field operating at 200 keV. $2LiBH_4+MgH_2$ and $2LiBH_4+MgH_2+0.05Li_xTiO_2$ samples were observed at different conditions: after milling, different steps of the first dehydrogenation process and after re-hydrogenation. It is important to point out that each sample was observed at least 4 times and the statistics were done from an average of 50 HR images to assure the nanocrystalline structure, nanosize and morphology of the Ti containing and MgB_2 phases. Samples for TEM were prepared by dispersing a small amount of powder in hexane and then ultrasonicated 10 minutes before depositing a drop of the resulting suspension on a commercial copper grid with an amorphous Formvar film and carbon coating. The sample was exposed a short time to the air. In order to identify the Ti species rich zone, point elemental analysis via energy dispersive X-ray spectroscopy (EDS) was performed – not shown. TEM images processing were done with the following programs: Digital Micrograph (License № 90294175), iTEM (License № A2382500) and JEMs (License № IEb59yBDflUMh).

1.2.4 Raman spectroscopy (RS)

Raman spectroscopy measurements were carried out on a Confocal Jobin Yvon Micro-Raman T64000 NIR-UV with 20×LWD objective. Spectra of the $2LiBH_4+MgH_2$ and $2LiBH_4+MgH_2+0.05Li_xTiO_2$ samples after differnent stages of the first dehydrogenation were collected at room temperature with a 514 nm excitation laser and 15 mW of laser power on the sample. The spectra were taken as an average of 10 iterations of 15 seconds. To prevent the samples from air exposure during the RS measurements, the samples (5–10 mg) were loaded into 7 mm diameter aluminium pans and sealed with optical quality glass window inside glove box. For RS analysis, reference peak positions of $LiBH_4$[6,7], $Li_2B_{12}H_{12}$[8–10], B[9–13] and MgB_2[10,13] were taken from the literature. Additionally, spectra for as-purchased MgB_2 (Alfa Aesar, powder, 325 mesh) and $LiBH_4$ (Sigma-Aldrich, purity ≥ 90%) were collected.

1.2.5 Thermogravimetry (TG)

TG measurements were performed in a TG device TGA-HP50F – TA Instruments with $2LiBH_4+MgH_2$ and $2LiBH_4+MgH_2+0.05Li_xTiO_2$ samples after MM and differnent stages of the first dehydrogenation from room temperature to 450 °C at a heating rate of 5 °C/min and under 3 bar of H_2 maintained at a flow of 50 cm^3/min. All samples were put into aluminium capsules in order to minimize the exposure to the air. Then the aluminium capsules were introduced into the TG device in a quarz crucible.

1.2.6 High Pressure-Differential Scanning Calorimetry (HP-DSC)

HP-DSC measurements were performed in a TA 2910 calorimeter with $2LiBH_4+MgH_2$ and $2LiBH_4+MgH_2+0.05Li_xTiO_2$ samples after MM and differnent stages of the first dehydrogenation from room temperature to 390 – 400 °C. For HP-DSC a heating rate of 5 °C/min and hydrogen overpressure pressure of about 3 bar were utilized. All samples were put into aluminium capsules, pressed and carried to the DSC/HP-DSC device in a sealed vessel. Then, the aluminium capsules were introduced into the DSC device exposing them to air for a short time.

1.3 Material handling

All material handling was carried out in MBraun Unilab glove boxes with oxygen and moisture controlled atmosphere (level of O_2 and H_2O were below 5 ppm, respectively), so as to prevent the oxidation of the samples.

2. Additional results

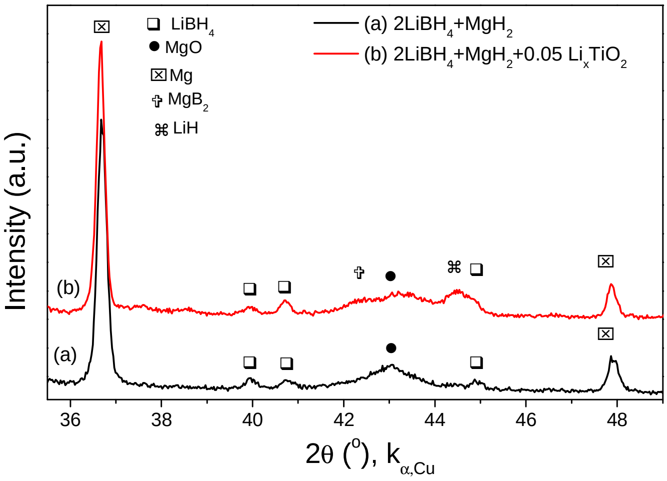

Fig. S2 XRD patterns from 35° to 50° of 2θ at Point 1 od the first dehydrogenation for $2LiBH_4+MgH_2$ and $2LiBH_4+MgH_2+0.05Li_xTiO_2$.

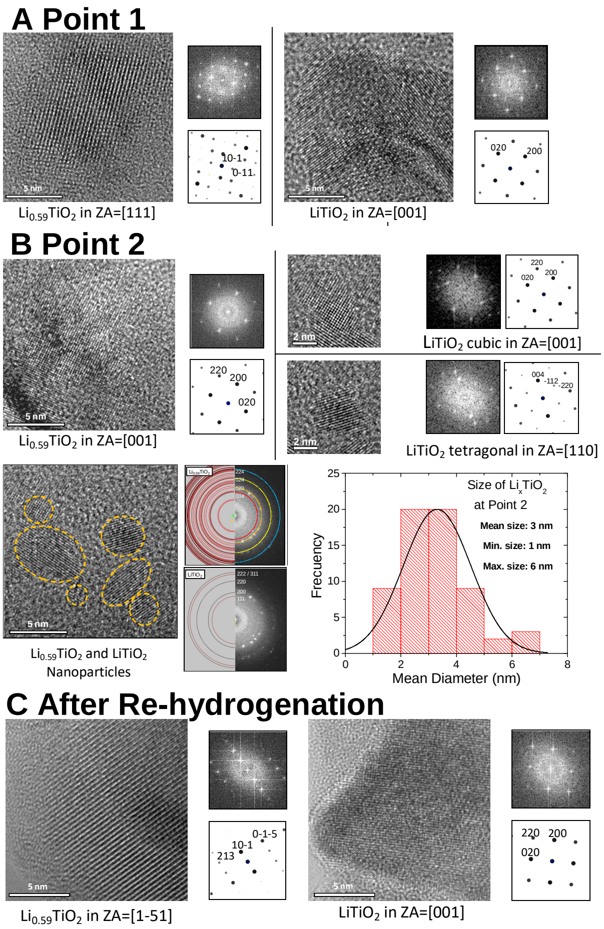

Fig. S3 HR-TEM, FFT, DP, structure simulations and size distribution of Li_xTiO_2 nanoparticles at different points of the 1st dehydrogenation from room temperature to 425 °C and 3 bar of hydrogen overpressure: **A** Point 1 and **B** Point 2, and **C** after re-hydrogenation at 425 °C and 50 bar of H_2.

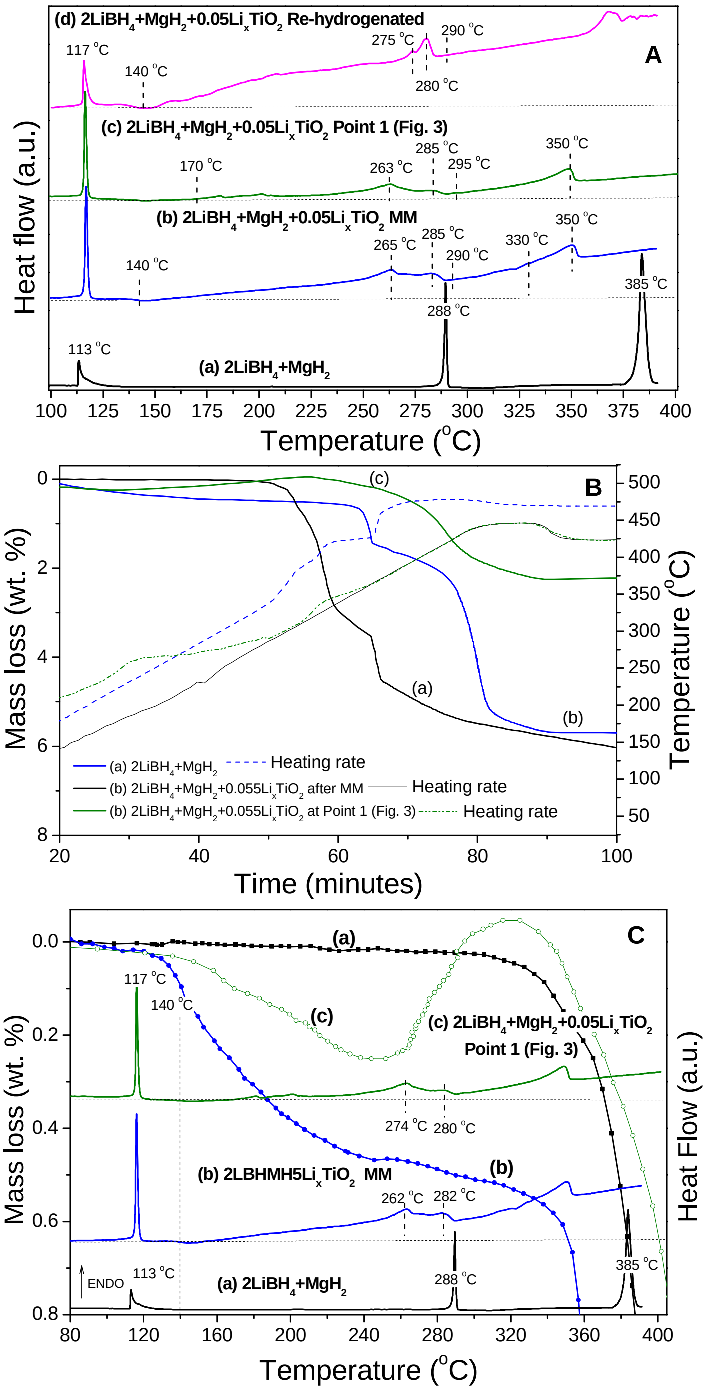

Fig. S4 **A** HP-DSC curves, **B** TG curves and **C** HPDSC and TG measurements for (a) $2LiBH_4$ + MgH_2, (b) $2LiBH_4$ + MgH_2+$0.05Li_xTiO_2$ after milling, (c) $2LiBH_4$ + MgH_2+$0.05Li_xTiO_2$ during the first dehydrogenation (point 1, Fig. 3) and (d) $2LiBH_4$ + MgH_2+$0.05Li_xTiO_2$ after re-hydrogenation at 425 °C and 50 bar of H_2. **Comments:** 1 - The TG curve (C) presents a mass gain owing to the re-hydrogenation of free Mg since the dehydrogenation was performed at 3 bar of hydrogen overpressure and at about 300 °C the equilibrium pressure for hydrogenation is about 2 bar. Then as the temperature increases, the formed MgH_2 decomposes. This observation is supported by the XRD shown in Fig. 5S (d) where is possible to noticed the most intense reflection of MgH_2 at about $2\theta = 27^{\circ}$. 2 – The fact that the small mass loss from about 140 °C to 300 °C associated to hydrogen release is noticed by the TG technique, but it is not evident in the titration curves (Fig. 2) is related to the sensitivity of the titration device.

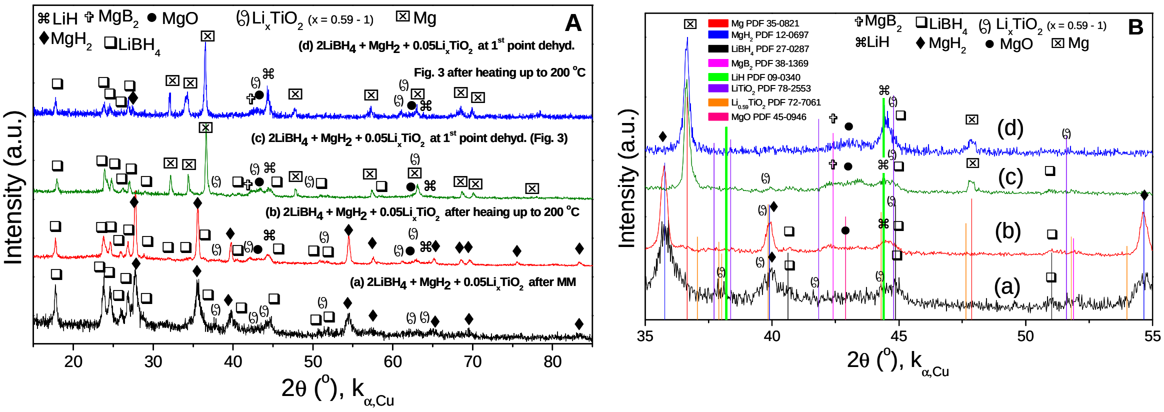

Fig. S5 A XDR for $2LiBH_4$+MgH_2+$0.05Li_xTiO_2$ after (a) milling, (b) milling and then heated up to 200 °C, (c) dehydrogenation at first point (Fig. 3) and (d) dehydrogenation at first point (Fig. 3) and then heated up to 200 °C. **B** Zoom from 2θ = 35° – 55°.

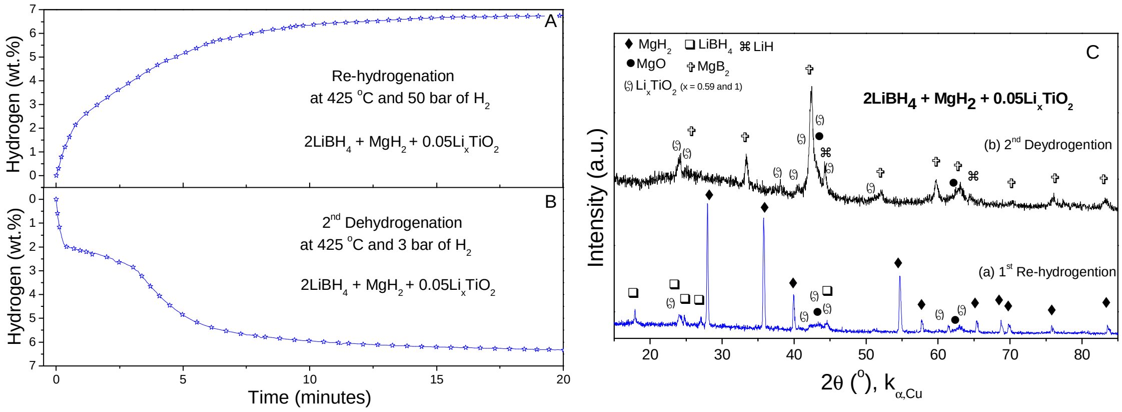

Fig. S6 A Kinetic behaviour for $2LiBH_4$ + MgH_2+$0.05Li_xTiO_2$ at 425 °C under 50 – 3 bar of H_2 and **B** XDR after (a) re hydrogenation and (b) 2nd dehydrogenation.

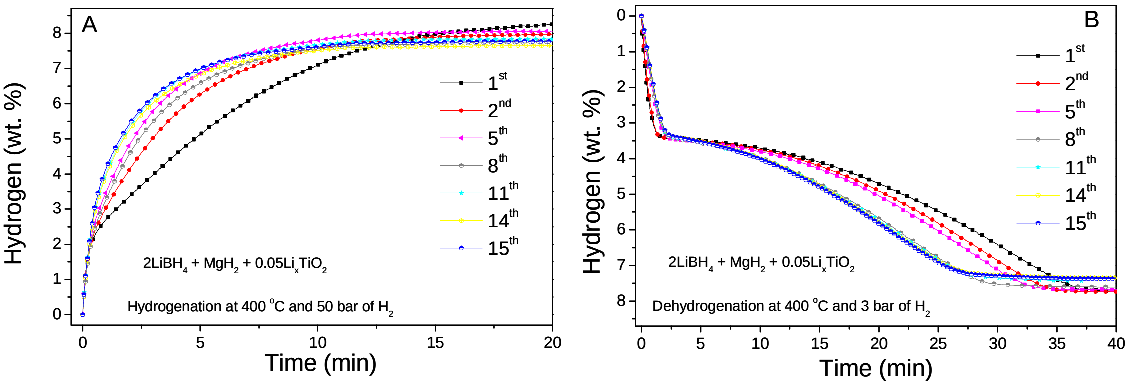

Fig. S7 Cycling at 400 °C for $2LiBH_4$ + MgH_2+$0.05Li_xTiO_2$: **A** Hydrogenation under 50 bar of H_2 and **B** Dehydrogenation under 3 bar of H_2

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