Chemical activation of MgH_2; a new route to superior hydrogen storage materials†

Simon R. Johnson,[ab] Paul A. Anderson,*[a] Peter P. Edwards,*[b] Ian Gameson,[a] James W. Prendergast,[a] Malek Al-Mamouri,[c] David Book,*[c] I. Rex Harris,[c] John D. Speight[c] and Allan Walton[c]

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We report the discovery of a new, chemical route for 'activating' the hydrogen store MgH_2, that results in highly effective hydrogen uptake/release characteristics, comparable to those obtained from mechanically-milled material.

Hydrogen is widely regarded as a promising alternative to carbon-based fuels; it can be produced from a variety of renewable resources and, when coupled with fuel cells, offers the prospect of near-zero emission of pollutants and greenhouse gases.[1] However, the development of hydrogen as a major energy carrier will require solutions to many scientific and technological challenges.[2] Foremost among these is the issue of hydrogen storage; the lightest of all the chemical elements has an excellent energy content per unit weight, but a low energy content per unit volume.[3]

The current generation of solid state hydrogen stores employ metal hydrides (*e.g.* $LaNi_5H_6$) that have excellent volumetric storage densities—higher than for both compressed gas and liquid hydrogen—but which have poor gravimetric storage densities (1.37 wt% for $LaNi_5H_6$), thereby precluding their use for mobile storage applications in hydrogen fuel-cell vehicles, for which a capacity of 6–7 wt% is regarded as a minimum requirement.[2] Magnesium hydride offers the highest energy density of all reversible hydrides applicable for hydrogen storage.[4] However, hydrogen adsorption/desorption kinetics are too slow to form the basis of a practical hydrogen store. It has been demonstrated previously by a number of groups that the hydrogen sorption kinetics of Mg and Mg-based alloys can be greatly improved if the materials are prepared with a nanocrystalline microstructure through high velocity ball milling.[5] However, this technique is energy intensive, especially for batch-milling large quantities of material.

Recently, a number of new hydrogen storage systems have been proposed[6] based on the interaction between light metal hydrides and amides. Luo reported[7] that a 1 : 2 mixture of MgH_2 and $LiNH_2$ desorbed hydrogen reversibly at around 200 °C. Here we report a dramatic enhancement in the absorption/desorption kinetics of MgH_2 through reaction with small amounts of $LiBH_4$.[8]

MgH_2 and $LiBH_4$ (Sigma-Aldrich) were mixed together in a mole ratio of 1 : 0.1 in an argon atmosphere glove box (O_2 content < 10 ppm) and placed in a quartz tube. The tube was capped with a Young's tap, *via* an Ultra Torr fitting, removed from the glove box and placed on a vacuum line, where it was evacuated to 10^{-6} mbar before being sealed with a gas torch. The sealed evacuated tube was then placed in a muffle furnace and heated at 300 °C for 12 hours.

For comparison, MgH_2 (typical size $\sim$ 100 μm) was milled at 300 rpm (PM400 Retsch planetary ball mill) for 15 hours in an argon atmosphere in a stainless steel milling pot (250 ml) using 8 mm balls with a 10 : 1 ball to powder ratio. All samples were prepared for characterization in the glove box.

The hydrogen desorption kinetics of $MgH_2/LiBH_4$ after five hydrogen desorption and reabsorption cycles are shown in Fig. 1, compared to MgH_2 and MgH_2 milled for 15 h (i, ii and iii respectively).[9] It is apparent that $MgH_2/LiBH_4$ desorbed hydrogen significantly faster than both the MgH_2 and milled MgH_2. The average desorption rates, therefore, were 0.28×10^{-2} wt% s^{-1}, 0.01×10^{-2} wt% s^{-1} and 0.12×10^{-2} wt% s^{-1} for $MgH_2/LiBH_4$, MgH_2 and milled MgH_2 respectively.[10]

The subsequent sixth hydrogen absorption at 300 °C and 10 bar H_2 for the same three materials is shown in Fig. 2. Again the $MgH_2/LiBH_4$ material reabsorbed hydrogen faster than MgH_2, and at a rate comparable to MgH_2 milled for 15 hours. The wt% values of hydrogen absorbed at 60 min for $MgH_2/LiBH_4$, MgH_2 and ball milled MgH_2 were 5.86, 4.86 and 6.01 respectively, and the absorption rates within this time scale were 1.03×10^{-2} wt% s^{-1}, 0.16×10^{-2} wt% s^{-1} and 1.24×10^{-2} wt% s^{-1} respectively.[11]

Clearly, the reaction of MgH_2 with quite modest amounts of $LiBH_4$ resulted in a spectacular increase in the kinetics of hydrogen

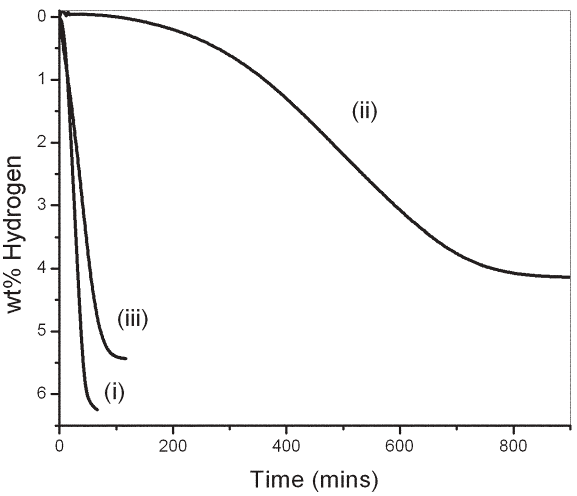

Fig. 1 Hydrogen desorption kinetics at 300 °C under 10 mbar H_2 of i) $MgH_2/LiBH_4$, ii) as-received MgH_2 and iii) MgH_2 milled for 15 h; all samples measured on the sixth hydrogen desorption.

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† Electronic supplementary information (ESI) available: XPS and ^{11}B NMR spectra. See http://www.rsc.org/suppdata/cc/b5/b503085d/

*peter.edwards@chemistry.oxford.ac.uk (Peter P. Edwards)
p.a.anderson@bham.ac.uk (Paul A. Anderson)
d.book@bham.ac.uk (David Book)

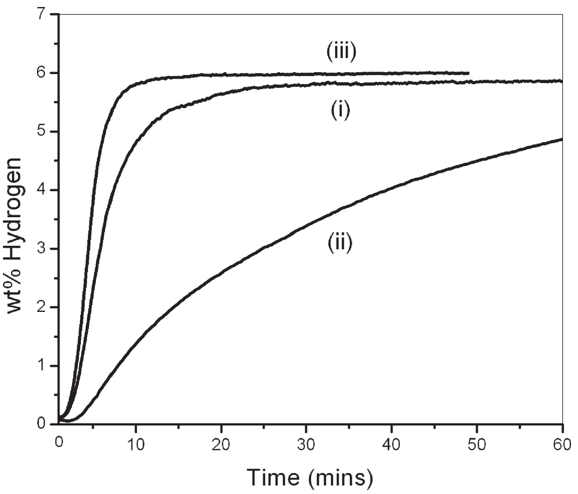

Fig. 2 Hydrogen absorption kinetics at 300 °C under 10 bar H_2 of i) $MgH_2/LiBH_4$, ii) MgH_2 and iii) MgH_2 milled for 15 h; all samples measured on the sixth hydrogen absorption.

desorption/absorption. This improvement, however, was not apparent in the 'as-prepared' material: importantly, the rate of hydrogen desorption/absorption increased with each successive cycle for the first 4–5 cycles before stabilizing. Both the heat treatment and the initial cycling were necessary to activate the material: cycling a simple mixture of MgH_2 and $LiBH_4$ did not result in such an 'active' material with fast kinetics.

There are a number of possible factors that could contribute to the observed enhancement in hydrogen absorption/desorption properties. Powder XRD studies revealed that $MgH_2/LiBH_4$ contained only phases with the tetragonal α-MgH_2 structure (rutile).[12] Evidently a change in the crystal structure of MgH_2 is not responsible. The XRD pattern of the as-prepared material exhibited narrow, split diffraction lines, indicating that the material contained two different phases with the same structure, present in roughly equal amounts. After cycling, the active material was apparently single phase but with noticeably broader lines, and a unit cell slightly expanded ($\sim$0.8%) from that of as-received MgH_2.[13] This expansion could contribute to enhanced diffusion of H atoms in Mg/MgH_2.

Previously observed enhancements in the hydrogen absorption/desorption kinetics of Mg and Mg-based alloys after ball milling have been attributed to a nanocrystalline microstructure with an increased volume of grain boundary material, which acts as a preferred pathway for hydrogen diffusion.[14] Changes in sample morphology and particle size may also be important. SEM images of $MgH_2/LiBH_4$, before and after six hydrogen desorption/absorption cycles, are shown in Fig. 3, along with those of as-received and milled MgH_2.[15] Before cycling, $MgH_2/LiBH_4$ (Fig. 3i(c)) had a very similar appearance to MgH_2 (Fig. 3i(a)) consisting of large particles of up to 100 μm with a smooth surface. After six cycles of repeated crystallization of Mg and MgH_2, some finer particles were visible in MgH_2, but a significant proportion of larger lumps remained (Fig. 3ii(a)). $MgH_2/LiBH_4$ (Fig. 3ii(c)) in contrast consisted of a fine, apparently porous material of coral-like appearance with characteristic length scale *ca.* 2 μm. This is roughly the same as the particle size of MgH_2 milled for 15 hours (Fig. 3i(b) & ii(b)), although the morphologies were noticeably different.

The fine powder structure observed may be a factor in the fast kinetics of both $MgH_2/LiBH_4$ and milled MgH_2 materials, but this may not be the most important factor in the former, as it differs chemically, owing to the presence of $LiBH_4$. Analysis of $MgH_2/LiBH_4$ after the sixth hydrogen absorption by XPS[16] indicated that lithium and boron were still present in the sample. The FTIR spectrum[17] of $MgH_2/LiBH_4$ before cycling exhibited peaks at 1126 cm^{-1}, which corresponds to a BH_2 deformation, and four peaks at 2225 cm^{-1}, 2238 cm^{-1}, 2291 cm^{-1} and 2386 cm^{-1}, corresponding to B–H_t (terminal) stretching.[18] This may be compared to $LiBH_4$, which showed peaks at 1120 cm^{-1} (BH_2

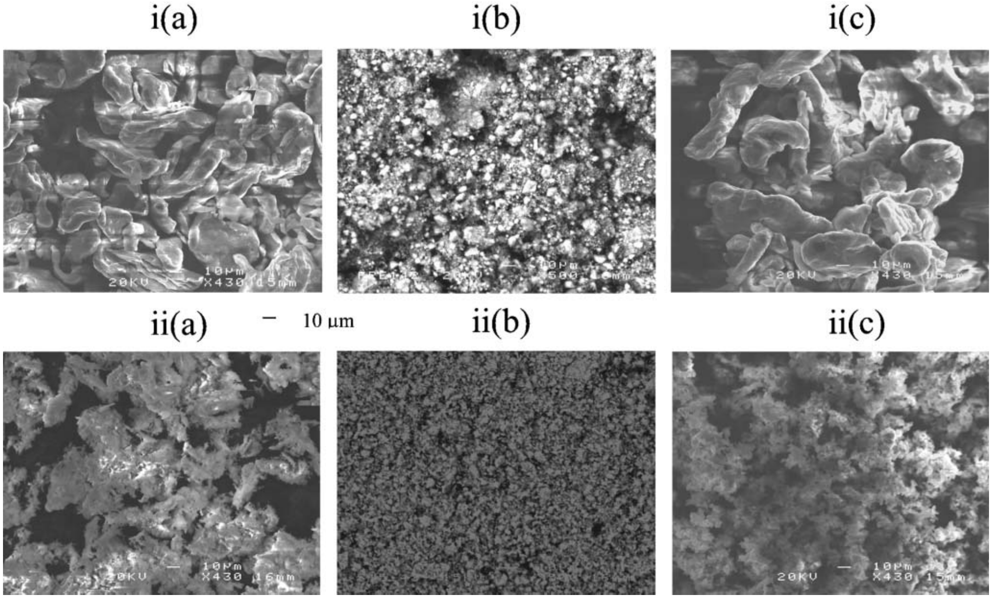

Fig. 3 Scanning electron microscope images, i) before hydrogen desorption of a) MgH_2, b) MgH_2 milled for 15 h and c) $MgH_2/LiBH_4$ and ii) taken after the sixth hydrogen reabsorption of a) MgH_2, b) MgH_2 milled for 15 h and c) $MgH_2/LiBH_4$.

deformation) and 2220 cm^{-1}, 2231 cm^{-1}, 2282 cm^{-1} and 2381 cm^{-1} (B–H$_t$ stretches). The spectrum of the same material after six hydrogen desorption/absorption cycles contained no B–H vibrations, suggesting that BH_4^- anions did not persist at this stage. This conclusion was supported by proton-decoupled solid state ^{11}B NMR spectra[19] of the MgH_2/$LiBH_4$ before and after cycling. Before hydrogen desorption the spectrum was very similar to that of $LiBH_4$ with a single central transition at *ca.* −41 ppm. After the first hydrogen desorption the spectrum was transformed with peaks at 12.7 ppm, 0.9 ppm, −16.0 ppm and −43.3 ppm, and retained multiple peaks on subsequent absorption/desorption cycles.

The decomposition of BH_4^- after the first hydrogen desorption at 300 °C is to be expected as compounds such as $LiBH_4$ and $NaBH_4$ are well known to lose hydrogen at temperatures lower than this.[20] The fact that the anion did not reform on subsequent hydrogen adsorption, however, is significant, indicating that $LiBH_4$ served as a convenient method for introducing both lithium and boron into the system, but that BH_4^- compounds were not present in the active material. In fact, it was possible to make a material with identical properties starting from a mixture of magnesium powder and $LiBH_4$. Although the presence of both Li and B in MgH_2/$LiBH_4$ after cycling is not in doubt, their exact chemical role in the fast hydrogen absorption/desorption has not yet been identified. One suggestion is that these elements might have a catalytic effect at the surface of the magnesium or magnesium hydride particles, but preliminary XPS data suggest that boron enters the subsurface layers of the material and is not just confined to the surface.

Doping of boron and/or lithium into MgH_2 could also be consistent with the small increase observed in lattice parameters and could change the thermodynamic properties of the compound. So far, however, there is little evidence for significant thermodynamic differences from MgH_2, as there was no observed shift in the hydrogen plateau pressure at 300–350 °C. The observation that use of $NaBH_4$ in the reaction instead of $LiBH_4$ resulted in no improvement in the hydrogen absorption/desorption kinetics, however, suggests that lithium doping of MgH_2 could be significant. The presence of Li^+ in the MgH_2 lattice might lead to hydride anion vacancies which could facilitate diffusion of hydrogen in the hydride phase. More detailed characterization including measurements of thermodynamic parameters and microstructural studies of MgH_2/$LiBH_4$ is in progress.

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Simon R. Johnson,[ab] Paul A. Anderson,*[a] Peter P. Edwards,*[b]
Ian Gameson,[a] James W. Prendergast,[a] Malek Al-Mamouri,[c]
David Book,*[c] I. Rex Harris,[c] John D. Speight[c] and Allan Walton[c]
[a]*School of Chemistry, The University of Birmingham, Edgbaston, Birmingham, UK B15 2TT. E-mail: p.a.anderson@bham.ac.uk*
[b]*Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX3 3QR.*
E-mail: peter.edwards@chemistry.oxford.ac.uk
[c]*Department of Metallurgy and Materials, School of Engineering, The University of Birmingham, Edgbaston, Birmingham, UK B15 2TT.*
E-mail: d.book@bham.ac.uk

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9 Hydrogen absorption/desorption properties were measured on a constant pressure thermogravimetric balance (Hiden IGA). The desorption kinetics were monitored at 10 mbar of hydrogen and 300 °C, absorption at 10 bar and 300 °C. Samples were transferred quickly from the glove box to the IGA to minimize contact with the atmosphere.

10 The desorption rates were calculated as the ratio between the amount desorbed and time taken to go from 80 to 20% of full capacity. The error in the wt% was ±0.05, while the error in the desorption rate was $\pm 0.01 \times 10^{-2}$ wt% s^{-1}.

11 The absorption rates were calculated as the ratio between the amount absorbed and time taken to go from 20 to 80% of capacity measured at 60 min. The error in the wt% was ±0.05, while the error in the absorption rate was $\pm 0.01 \times 10^{-2}$ wt% s^{-1}.

12 In addition to α-MgH_2, a number of other crystal structures, observed and predicted, have been reported for MgH_2; see M. Bortz, B. Bertheville, G. Bøttger and K. Yvon, *J. Alloys Compd.*, 1999, 287L4. α-MgH_2 is sometimes referred to in the literature as the 'β-MgH_2 phase', which is not to be confused with the proposed high temperature, high pressure β-MgH_2 structure.

13 Structural characterisation of the samples was carried out on a Siemens D5000 X-ray diffractometer, using a CuK$_\alpha$ source. The structure of α-MgH_2 is tetragonal (space group $P4_2mnm$) with $a = 4.508 \pm 0.001$ Å, $c = 3.017 \pm 0.001$ Å; MgH_2/$LiBH_4$ as-prepared contained two phases with $a = 4.510 \pm 0.001$ Å, $c = 3.017 \pm 0.001$ Å and $a = 4.502 \pm 0.001$ Å, $c = 3.011 \pm 0.001$ Å; MgH_2/$LiBH_4$ after cycling, $a = 4.522 \pm 0.003$ Å, $c = 3.025 \pm 0.003$ Å.

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15 SEM images were recorded on a JEOL 6300 electron microscope.

16 XPS measurements were carried out at the Johnson Matthey Technology Centre, UK on a VG ESACLAB 250 instrument. A monochromatic Al K$_\alpha$ X-ray source at 1464.6 eV was used.

17 FTIR spectra were acquired at a resolution of 2 cm^{-1}, from KBr disks containing the samples, on a Nicolet Magna FTIR spectrometer, equipped with a liquid nitrogen cooled MCTB detector.

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19 Solid state ^{11}B NMR spectra were acquired on a 400 MHz Varian Inova spectrometer. Samples were packed into 3.2 mm o.d. rotors and spun at the magic angle at rates of 10 to 15 KHz. A pulse width of 0.4 to 1.4 μs was employed for data acquisition.

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