



Improving solid-state hydriding and dehydriding properties of the LiBH₄ plus MgH₂ system with the addition of Mn and V dopants

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ABSTRACT

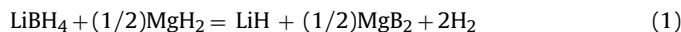
The hydriding process of the 2LiH + MgB₂ mixture is controlled by outward diffusion of Mg and inward diffusion of Li and H within MgB₂ crystals to form LiBH₄. This study explores the feasibility of using transition metal dopants, such as Mn and V, to enhance the diffusion rate and thus the hydriding kinetics. It is found that Mn can indeed enhance the hydriding kinetics of the 2LiH + MgB₂ mixture, while V does not. The major factor in enhancing the diffusion rate and thus the hydriding kinetics is related to the dopant's ability to induce the lattice distortion of MgB₂ crystals. This study demonstrates that the kinetics of the diffusion controlled solid-state hydriding process can be improved by doping if the dopant is properly selected.

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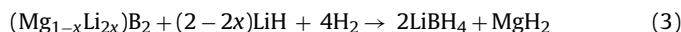
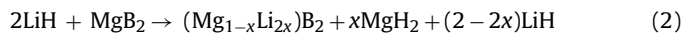
1. Introduction

Renewable hydrogen fuel sources are of considerable importance in the wake of present global energy shortages. While advances have been made in the application of compressed gas and liquid state hydrogen storage for mobile applications, solid-state reversible hydrogen storage possesses the potential to surpass the gaseous and liquid state storage in both volumetric and gravimetric storage capacities. Lithium borohydride (LiBH₄) is one of the solid-state storage materials that have generated great interest because of its high gravimetric hydrogen density (18.5 wt.% H₂) at room temperature [1–3]. However, LiBH₄ has a high chemical stability [3–14]. As a result, temperatures as high as 400 °C are often required to release most of the hydrogen stored in LiBH₄. Material advances aimed at decreasing the chemical stability and/or increasing reaction kinetics of LiBH₄ are currently pursued by (i) addition of novel catalysts [3,4,9], (ii) nanoengineering to confine LiBH₄ in mesoporous scaffolds or mix LiBH₄ with nano-tubes and mesoporous gels [10–13], (iii) thermodynamic destabilization of LiBH₄ via the partial substitution of Li⁺ cations by other cations with larger electronegativities [15–20], and (iv) using additives to stabilize the dehydrogenated state [5–8,21–28]. Addition of MgH₂, as an example of approach (iv), represents a material approach being technologically important as well as scientifically interesting because this approach has reduced the hydrogenation and

dehydrogenation temperatures to near 350 °C with the following reversible reaction [7]



Recently, it has been shown that solid-state hydriding and dehydriding via Eq. (1) is possible [29]. Through long-time ball milling of 2LiH + MgB₂ mixtures, 8.3 wt.% hydrogen uptake at 265 °C has been demonstrated, whereas the maximum theoretical uptake for the mixture is 11.4 wt.%. Hydrogen release, although slower than uptake, can also be attained in the solid state (e.g., 2.0 wt.% H₂ at 265 °C). Furthermore, it is found that both solid-state hydriding and dehydriding are diffusion controlled [29]. With the aid of nuclear magnetic resonance (NMR), it is found that long-time ball milling has led to the partial exchange of the Mg²⁺ ions in the MgB₂ crystal by the Li⁺ ions from the LiH crystal [30,31]. This partial ion exchange results in the formation of a compound with a composition of (Mg_{1-x}Li_{2x})B₂ where x is a variable changing from 0 to less than 1. It is the formation of this intermediate compound (Mg_{1-x}Li_{2x})B₂ that greatly enhance the subsequent hydriding reaction because the reaction pathway to form LiBH₄ and MgH₂ in the solid state is through the following two elementary reactions [32].



As shown in Eq. (2), the first step in the solid-state hydriding is the ion exchange between Mg and Li ions within MgB₂ to form an intermediate compound (Mg_{1-x}Li_{2x})B₂, and MgH₂. This reaction can take place during ball milling [30,31]. As a result, the hydriding reaction can be enhanced by long-time ball milling. The

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second step in the solid-state hydriding is the continuous Mg–Li ion exchange and simultaneous hydrogenation of the intermediate compound $(\text{Mg}_{1-x}\text{Li}_x)_2\text{B}_2$, to form the final product LiBH_4 – a compound that does not contain any Mg ions [32]. The Mg ions rejected from $(\text{Mg}_{1-x}\text{Li}_x)_2\text{B}_2$ react with H to form crystalline MgH_2 . These prior studies [29–32] reveal unambiguously that hydriding of the $\text{LiH} + \text{MgB}_2$ mixture is controlled by diffusion and the major diffusing species are Mg, Li and H ions. Therefore, the potential approaches to enhance the solid-state hydriding of this promising hydrogen storage material system are (i) nanoengineering to minimize the diffusion distance, (ii) mechanical activation to introduce lattice defects and thus increase the diffusion coefficient, and (iii) doping to increase the vacancy concentration and lattice distortion and thus the diffusion rate.

In this study, the approach of adding dopants to increase the diffusion rate is investigated. Mn and V dopants have been chosen for several reasons. First, MnH and VH are thermodynamically less stable than MgH_2 [33]. Thus, dissolution of Mn and V in MgH_2 , if taking place, will lead to thermodynamic destabilization of MgH_2 and possible reduction in the decomposition temperature of MgH_2 . Second, Mn has a reasonable solubility in Mg (~0.5 wt.% at room temperature) whereas the solubility of V in Mg is negligible [34]. Since no data of the solubilities of Mn and V in MgB_2 are available, the solubilities of Mn and V in Mg are taken as indicators of the possible difference in the solubility properties. Finally, a recent *ab initio* density functional theory calculation [35] reveals that Mn has the potential to enhance the diffusion rate of Mg vacancies in MgB_2 , whereas V does not. The favorable effect of Mn is due to its large atomic radius that induces the lattice distortion of MgB_2 , thereby decreasing the migration barrier and increasing the diffusion rate of Mg vacancies. In contrast, the atomic radius of V is closer to that of Mg. As a result, V exerts little or no influence on the diffusion rate of Mg vacancies in MgB_2 [35]. The present study is motivated by this theoretical prediction, and the findings from this study are reported below.

2. Experimental

LiH (95% purity), MgB_2 (~98% purity), Mn (99.95% purity), and V (100% purity) were purchased from Alfa Aesar and used as received. The LiH and MgB_2 particles were sub-micrometers, whereas the Mn and V particles were micrometers in the as-received condition. All materials handling and sample preparation was done in an argon-filled glovebox to prevent H_2O and O_2 contamination. Ball milling was performed under argon atmosphere using a modified Szegvari attritor that is effective in producing a highly uniform product while preventing the formation of a dead zone in the milling product [36]. The canister of the attritor with an inner volume of 700 ml and the balls (6.4 mm in diameter) were made of a stainless steel. The $\text{LiH} + \text{MgB}_2$ mixtures of ~10 g per batch were prepared using a 2:1 molar ratio according to Eq. (1). For the cases with the manganese and vanadium addition, the same 2:1 molar ratio of $\text{LiH} + \text{MgB}_2$ was utilized, but in each case 5 mol% of the additive was applied. The ball-to-powder weight ratio was 60:1, the milling speed was 600 rpm, the milling atmosphere was argon of 99.999% purity, and the milling temperature was maintained at 20 °C, achieved by water cooling at a flowing rate of 770 ml min⁻¹. Ball milling time was 3, 24, or 120 h, depending on the specific experiment.

Hydriding and subsequent dehydriding of the $\text{LiH} + \text{MgB}_2$ mixture were carried out using a commercial Sieverts'-type pressure-composition-temperature (PCT) unit (Advanced Materials Corporation, PA). For hydrogenation, the ball-milled $\text{LiH} + \text{MgB}_2$ mixture of ~600 mg was loaded into the pressure cell of the PCT unit in a glovebox filled with Ar of 99.999% purity. The loaded pressure cell was evacuated to 10⁻³ bar at room temperature before back

filled with H_2 of 99.99% purity at 90 bar. The temperature of the cell was then increased from ambient to 265 °C at a rate of 2 °C min⁻¹ and maintained at that temperature for 5 h. For dehydrogenation, the hydrogenated powder described above was first cooled down to room temperature, and then the pressure cell was evacuated to 10⁻³ bar before heating to and holding at 265 °C with the same heating rate and holding time as those in the hydrogenation treatment. The hydrogen pressure in the sample cell was maintained at approximately 0.01 bar during the dehydrogenation holding at 265 °C by evacuating the cell in every 30 min of holding.

The $2\text{LiH} + \text{MgB}_2$ mixtures before and after ball milling, dehydrogenation and re-hydrogenation were analyzed using a D8 ADVANCE X-ray diffractometer. The operation conditions for the X-ray diffraction (XRD) data collection were $\text{Cu K}\alpha$ radiation, 40 kV, 40 mA, 0.005° min⁻¹, and 0.01° per step. To prevent oxidation during XRD data collection, the sample was sealed in a capillary quartz tube of 1.5 mm in diameter and the loading of the sample to the tube was performed in a glovebox filled with argon. The wall of the capillary quartz tube is 0.01 mm in thickness and thus transparent to the X-ray. To detect any peak shifting of LiH and MgB_2 induced by ball milling and the subsequent hydriding treatment, ~15 wt.% coarse-grained Si of 99.9% purity was added as the internal standard to each sample. The use of the Si within the capillary tube as the internal standard not only provided the reference position, but also avoided the possible effect of the curved front of the powder compact caused by the capillary tube on the peak positions of all the compounds in the powder mixture. In analyzing XRD patterns, the “Peakfit” software was used to fit a XRD peak with the assumption of the line profile being a Lorentzian function. The fitting process was stopped when the R^2 value was larger than 0.95 for the ball milled powders and larger than 0.98 for the un-milled powders. The peak position was then determined from the fitted curve. The typical standard deviation for our peak fit was ±0.0036°.

In addition to monitoring the peak shifting and new phase formation, XRD was also used to estimate the crystallite sizes of LiH and MgB_2 and the lattice microstrain of MgB_2 crystals. The LiH (2 0 0) and MgB_2 (1 0 1) reflections with the diffraction angles at 44.35° and 42.41° are used to estimate their crystallite sizes using the Scherrer formula [37], respectively. The lattice microstrain within MgB_2 was estimated using the (1 1 0) reflection of MgB_2 at the diffraction angle of 59.89° with the aid of the Stokes and Wilson formula [38]. The correction for instrumental broadening was conducted using the procedure described in [39] with the aid of ~15 wt.% coarse-grained silicon (Si) of 99.9% purity as the internal standard in each sample. Note that low-angle reflections (e.g., MgB_2 (1 0 1) peak) were used to estimate the crystallite size, whereas high angle reflections (such as MgB_2 (1 1 0) peak) were utilized to determine the lattice microstrain. This was done in order to minimize the error introduced by neglecting the interplay between broadenings due to the lattice microstrain and nanograins. This procedure is justified by the fact that the XRD broadening approaches pure grain size broadening at low 2θ angles, and approximates to pure lattice microstrain broadening at large 2θ angles [38,39]. Recently, a detailed XRD analysis [40] using the Rietveld method in conjunction with Levenberg–Marquardt non-linear least-square fit (LM-fit) and line-broadening analysis, demonstrates that this approach is indeed the case for nanocrystalline Al alloys that have been subjected to severe plastic deformation. The estimation of the lattice microstrain of LiH was not feasible in this study because its high angle reflections disappeared after ball milling.

Fourier transform infrared (FTIR) analysis (Nicolet, Magna-IR 560) was conducted on the hydrogenated samples in order to check if LiBH_4 was generated during hydrogenation. Around 1 wt.% hydrogenated powder was mixed and ground with KBr powder in a glovebox filled with Ar of 99.999% purity. The ground mixture was subsequently pressed into a pellet 1 cm in diameter in air very

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