

Assessing the impact of particle size modulation and graphite addition on H₂ storage properties of commercial MgH₂

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Abstract

Hydrogen (H₂) has been the subject of extensive discussion and research due to its potential to be a key energy vector on the way to a zero-carbon emissions scenario. Nevertheless, storage stage remains a major hindrance to the full development of the H₂ value-chain due to its low volumetric density under ambient conditions. Solid-state storage has been recommended as a safer and cheaper alternative to conventional methods, with special emphasis on metal hydrides, and particularly magnesium hydride, owing its high gravimetric storage capacity (7.6 wt%). Despite this, its application as H₂ storage media faces thermodynamic and kinetics limitations, for which ball-milling process and catalysts addition have been investigated as strategies to overcome them. Therefore, the aim of this work is to assess the impact of these strategies on hydrogen storage properties of commercial MgH₂. For this purpose, two samples were obtained by ball-milling, being one of them milled with 10 wt% of graphite, and their H₂ uptake examined at different temperatures. The uptakes and desorption data suggested that the reduction of particle size improved the H₂ uptake kinetics but affected slightly the temperature of H₂ imminent release. Lastly, the combination of milling with graphite addition seems to generate minor or irrelevant benefits compared to the milling process as isolated strategy in the conditions evaluated in this study.

Keywords: Hydrogen; Storage; Magnesium; Ball-milling.

1. Introduction

H₂ has been attracted a lot of attention in the energy transition scenario due to its high gravimetric energy density (120 MJ kg⁻¹) and the fact that it does not generate polluting compounds during its conversion into energy since water is the only exhaust product [1, 2]. However, H₂ has a low volumetric density (0.08 g L⁻¹) at ambient temperature and pressure, resulting in a very low energy density per unit volume, which makes its storage an important bottleneck to the development of hydrogen value-chain [3-5].

Conventionally, H₂ is storage as compressed gas or liquefied so that significant storage densities can be achieved, but both technologies present relevant limitations [6, 7]. Compression involves the application of high pressures (~350-700 bar), resulting in risk of gas leaks and explosion, whereas liquefaction requires cryogenic temperatures (-253 °C), leading to a

huge energy demand [8].

Thus, the solid-state storage has been suggested as a safer and cheaper alternative to the conventional methods. In this case, metal hydrides have demonstrated to be the most attractive materials considering the DOE (US Department of Energy) targets, such as system gravimetric capacity (6.5 wt%) and H₂ delivery temperatures (-40 - 85 °C) and pressures (5 - 12 bar) [9, 10]. Nevertheless, the application of these materials faced some difficult, mainly related to thermodynamics and kinetics [10].

Among the possible host metals, magnesium stands out due to its high gravimetric and volumetric capacities (7.6 wt% and 110 g L⁻¹), large abundance, low cost and non-toxicity [11, 12]. However, the high thermodynamic stability of Mg-H bonding ($\Delta H = 74 \text{ kJ mol}^{-1}$), which results in high desorption temperatures, and the poor H₂ release/uptake kinetics of magnesium hydride (MgH₂) hindering its application [2].

One strategy to minimize these obstacles is to reduce the particle size by ball milling, as smaller particles have been associated to kinetics improvements and lower enthalpies [10, 13, 14]. Another possibility, it is to combine elements with MgH₂ to act as catalysts, such as carbon compounds that are associated with inhibition of MgH₂ particles agglomeration during cycling, improvements of hydrogen diffusion and thermal conductivity [15, 16].

Hence, this work aims to evaluate the influence of particle size modulation and its association with carbon compounds addition on the H₂ storage properties of commercial MgH₂.

2. Methodology

Materials

MgH₂ powder (>99%, 1-5 μm) and graphite (< 20 μm) were purchased from Nanochemazone (Canada) and Sigma-Aldrich (USA), respectively. MgH₂ was used as received and with a reduced particle size obtained by ball milling without any additive and in the presence of graphite.

Ball-milling

This process was performed in a planetary ball-mill PM100 (Retsch, Germany) at 300 rpm and room temperature for 3 h. The ball-to-powder mass ratio (BPR) was 10:1 and the grinding jar rotation was paused and inverted every 15 min to limit the temperature increase inside the jar. MgH₂ was milled alone and with 10 wt% of graphite applying the stated conditions. It is worth to mention that the milling process was carried out in a glove box filled with argon (99.999%), as well as the samples handling, aiming to prevent oxidation. The samples were named as MgH₂-A (MgH₂-as received), MgH₂-BM (MgH₂ ball-milled) and MgH₂-BM-G (MgH₂ ball-milled with graphite).

Dehydrogenation/hydrogenation curves

These curves were performed in a suspension magnetic balance (Rubotherm, Germany). Prior to all hydrogenation curves, around 0.5 g of each sample was subjected to vacuum (10⁻³ bar) at 350 °C for 12 h applying a heating rate of 2 °C min⁻¹. This represents the dehydrogenation (or H₂

release) step. The hydrogenation curves were carried out at 200, 250 and 300 °C dosing 10 bar of H₂. Moreover, three consecutive cycles of release/uptake of hydrogen were performed at 300 °C to get preliminary information about the performance of this material during continuous use. Lastly, the H₂ uptake data was collected during approximately 24 h, aiming to properly observe the reaching of equilibrium; only for the curves at 200 °C a longer data recording was performed due to the slower uptake kinetics for this temperature.

3. Results and discussion

Figures 1 and 2 shows the hydrogenation curves obtained for MgH₂-A and MgH₂-BM at 200, 250 and 300 °C, respectively.

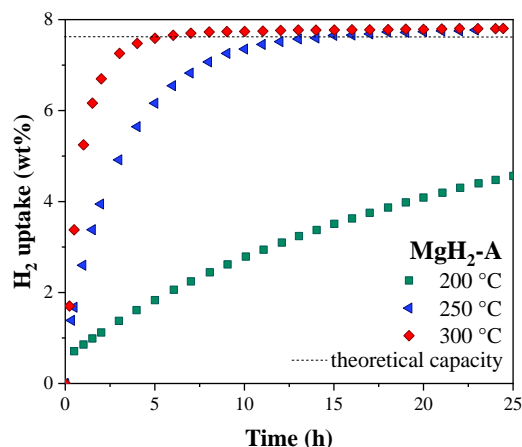


Fig. 1. H₂ uptake at 200, 250 and 300 °C for MgH₂-A.

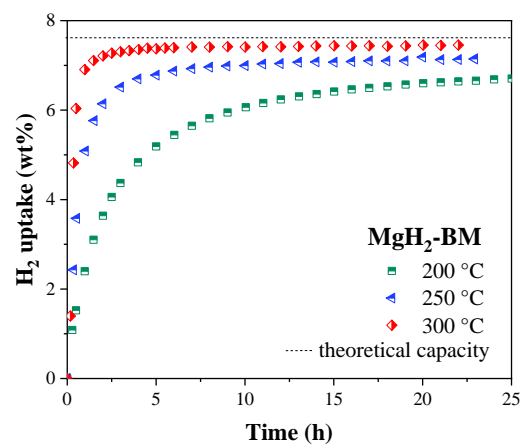


Fig. 2. H₂ uptake at 200, 250 and 300 °C for MgH₂-BM.

It is noticed that $\text{MgH}_2\text{-BM}$ achieved the theoretical storage capacity during the re-hydrogenation at 300 °C faster than $\text{MgH}_2\text{-A}$. However, even $\text{MgH}_2\text{-BM}$ demonstrating a faster uptake kinetics for all temperatures studied, it could not achieve the theoretical capacity for 200 and 250 °C. This could be related to sample contamination or presence of side products originated during the milling process. The cycles performed at 300 °C for $\text{MgH}_2\text{-A}$, as shown in Figure 3, might corroborate with this hypothesis, as well as pointing to the reversibility of H_2 storage process already expected for this material. Focusing on the initial 5 hours of these cycles, it could be observed a slightly difference in the kinetics of the first cycle compared to the subsequently. Therefore, the first cycle would be working as a cleaning/purification cycle, resulting in the minimization of the difference between the succeeding curves.

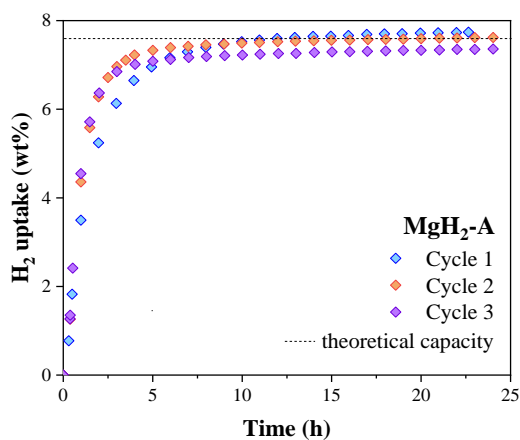


Fig. 3. Hydrogen uptake at 300 °C for $\text{MgH}_2\text{-A}$ for consecutive cycles of release/uptake.

Figure 4 shows a comparison between the H_2 uptake at 300 °C for $\text{MgH}_2\text{-A}$, $\text{MgH}_2\text{-BM}$ and $\text{MgH}_2\text{-BM-G}$ samples. It is noticed that the addition of graphite drives to a faster reaching of a capacity plateau related to unmodified sample, like what is observed because of the milling process with the $\text{MgH}_2\text{-BM}$ sample, and slightly more well-established than the others. However, it seems to present an undesirable effect of capacity reduction around 17%. However, since the data are presented in terms of mass and discounting the contribution of graphite to the total sample mass, this effect will be less relevant (~7%). This would shift the $\text{MgH}_2\text{-BM-G}$ curve upwards on the y-axis, bringing it

closer to the $\text{MgH}_2\text{-BM}$.

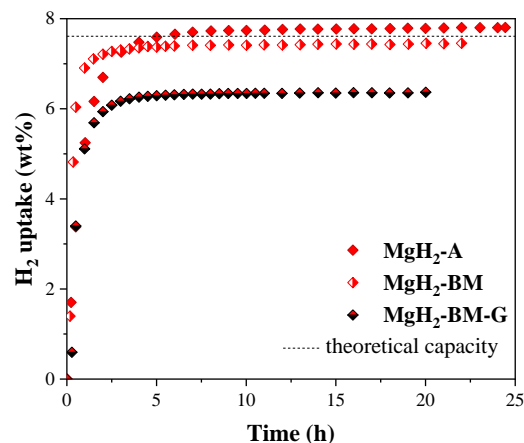


Fig. 4. Hydrogen uptake at 300 °C for $\text{MgH}_2\text{-A}$, $\text{MgH}_2\text{-BM}$ and $\text{MgH}_2\text{-BM-G}$.

In addition, according to the summary of these data, shown in Table 1, $\text{MgH}_2\text{-A}$ showed an uptake slightly higher than the theoretical capacity, which once again highlighting the possibility of contamination and/or the presence of side products in the samples.

Table 1. Summary of H_2 uptake at 300 °C for $\text{MgH}_2\text{-A}$, $\text{MgH}_2\text{-BM}$ and $\text{MgH}_2\text{-BM-G}$.

Sample	Uptake (wt%) / Time (h) (a)	Uptake (wt%) / Time (h) (b)
$\text{MgH}_2\text{-A}$	7.6 / 5.0	7.8 / 24
$\text{MgH}_2\text{-BM}$	7.4 / 7.0	7.4 / 22
$\text{MgH}_2\text{-BM-G}$	6.3 / 5.5	6.4 / 20

a-Uptake corresponding to the reaching of a plateau; b-Uptake obtained at the end of total experiment time.

Finally, Figure 5 shows a part of the desorption curves (only the heating step up to 350 °C) that were performed for $\text{MgH}_2\text{-A}$, $\text{MgH}_2\text{-BM}$ and $\text{MgH}_2\text{-BM-G}$ prior to H_2 uptake curves of Figure 4. There is a slightly difference between the curves for $\text{MgH}_2\text{-A}$ and $\text{MgH}_2\text{-BM}$ above 200 °C, which could suggest a reduction on the imminent release temperature of H_2 for $\text{MgH}_2\text{-BM}$. However, it is difficult to clearly state this, since the downward trend does not continue and is only observed again from around 285 °C, which is lower than that observed for $\text{MgH}_2\text{-A}$ (~300 °C).

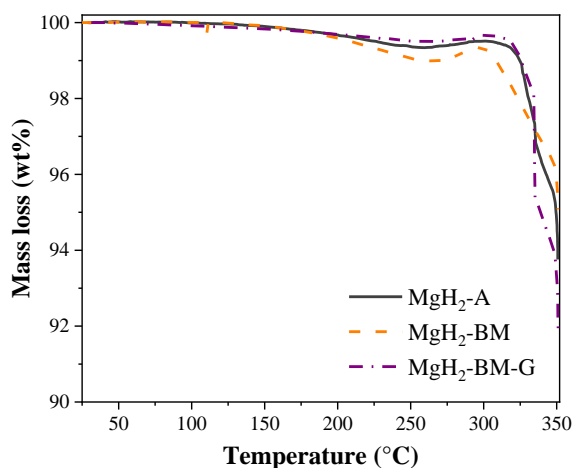


Fig. 5. H₂ desorption up to 350 °C for MgH₂-A, MgH₂-BM and MgH₂-BM-G.

5. Conclusion

In this work, it was evaluated the impact of particle size modulation and its combination with the incorporation of carbonaceous material on the hydrogen storage properties of a commercial MgH₂, focusing on storage capacity and hydrogen release/uptake kinetics. In summary, milling process resulted in improvement in uptake kinetics with a slight drop in capacity, confirming its potential as strategy to improve metal hydrides storage properties. However, its association with the addition of carbonaceous material seems did not bring relevant additional benefits for the proportion investigated regarding ball-milling as isolated strategy.

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