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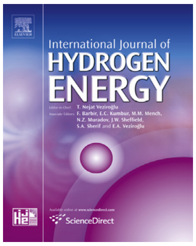

Review

Compaction pressure influence on material properties and sorption behaviour of $LiBH_4–MgH_2$ composite

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ABSTRACT

Among different Reactive Hydride Composites (RHCs), the combination of $LiBH_4$ and MgH_2 is a promising one for hydrogen storage, providing a high reversible storage capacity. During desorption of both $LiBH_4$ and MgH_2, the formation of MgB_2 lowers the overall reaction enthalpy. In this work, the material was compacted to pellets for further improvement of the volumetric hydrogen capacity. The influence of compaction pressure on the apparent density, thermal conductivity and sorption behaviour for the Li-based RHC during cycling was investigated for the first time. Although $LiBH_4$ melts during cycling, decrepitation or disaggregation of the pellets is not observed for any of the investigated compaction pressures. However, a strong influence of the compaction pressure on the apparent hydrogen storage capacity is detected. The influence on the reaction kinetics is rather low. To provide explanations for the observed correlations, SEM analysis before and after each sorption step was performed for different compaction pressures. Thus, the low hydrogen sorption in the first cycles and the continuously improving sorption for low pressure compacted pellets with cycling may be explained by some surface observations, along with the form stability of the pellets.

1. Introduction

Metal hydride systems can be used as heat storage units [1], for gas purification [2] or pumping systems [3] or directly for hydrogen storage (e.g. [4–6].). There are several hydride systems applicable for energy storage by hydrogen. Beside sodium aluminium hydride ($NaAlH_4$) [4] and magnesium hydride (MgH_2) [7], the group of reactive hydride composite (RHC) is currently most interesting and could play a major role in the future [8]. In RHCs, two materials react exothermically with each other, and form a new compound while releasing hydrogen. Among different RHCs, the combination of lithium boron hydride ($LiBH_4$) and MgH_2 is one promising combination for hydrogen storage, providing a high storage capacity [9].

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During desorption of both $LiBH_4$ and MgH_2, the exothermic formation of the new compound magnesium boride (MgB_2) lowers the overall reaction enthalpy [6,10]:

$$2\,LiBH_4 + MgH_2 \leftrightharpoons 2\,LiH + MgB_2 + 4\,H_2 \qquad (1.1)$$

The theoretical maximum hydrogen capacity is 13.04 wt.% based on the desorbed state and 11.54 wt.% based on the absorbed state.

For larger bed sizes of hydride systems, the heat transport and not the intrinsic kinetics can limit the overall reaction rate. Considering the reaction described in equation (1.1), an energy of 46 kJ mol^{-1} H_2 is theoretically released or needs to be provided, for the absorption or desorption, respectively [9]. To provide solutions for this heat transport problem, the materials in previous studies were mixed with additives that improve the thermal conductivity (e.g. expanded natural graphite) [11–14]. Hence, the transformation rate was successfully enhanced, but with the drawback of a reduced volumetric and gravimetric capacity due to the addition of inert material.

In this work the material was compacted to pellets as a start for further improvement of the volumetric hydrogen capacity. Beside the improvement of the volumetric capacity it is also expected that the compaction itself will lead to an improved thermal conductivity of the material.

The effect of the compaction is of particular interest for this system because, due to the melting of $LiBH_4$ [9] during the sorption process, decrepitation or disaggregation of the pellets is expected.

2. Experimental details

The desorbed state of the composite (right side of equation (1.1)) was chosen as initial material, and 5 mol-% of titanium chloride ($TiCl_3$) were added as a reaction speed enhancer. The theoretical maximum hydrogen capacity, based on the desorbed state, is thus reduced to 10.9 wt.%. Lithium hydride (LiH; ≥99.4% purity) and MgB_2 (99% purity) were purchased from Alfa Aesar, the additive material $TiCl_3$ (≥99.995% purity) was purchased from Sigma Aldrich. All the above quoted raw materials were purchased in powder form.

The materials were processed in a planetary ball mill (Fritsch, Pulverisette 5, Germany) for 20 h with a ball to powder ratio of 10:1. After milling, the material was compacted at different pressures and diameters. For the compaction, a uniaxial manual hydraulic press (Specac, Manual Hydraulic Press, United Kingdom) with a maximum force of 15 ton was used. The compaction was always performed in the same way: (i) The desired pressure was applied for 2 min; (ii) the pressure was released for 1 min; (iii) the desired pressure was again applied for another 2 min. To determine the apparent density as a function of the compaction pressure, different diameters, i.e. 5 mm, 8 mm, 10 mm, 13 mm and 20 mm, were used, while for the sorption measurements only pellets of 5 mm and 8 mm in diameter were tested. The height of all pellets was at least 50% and at most 150% of the diameter, thus the weight of the pellets was not always the same. Different diameters for the sorption measurement were chosen to investigate the correlation between the diameter and the sorption rate. For the fitting of the apparent density against the compaction pressure, different diameters and the 3-steps procedure of compaction was chosen to minimise the error due to inhomogeneity in the density of the pellets, which is expected in particular for pellets with larger diameters. However, according to the literature, cross section observations by optical micrograph for different hydrogen absorption materials show no clear inhomogeneity for pellets up to 14 mm in diameter [14–16].

For the calculation of the thermal properties of the material, the Transient Plane Source (TPS) method [17,18] was applied. For the measurement a TPS 1500 system (C3 Prozeβ- und Analysetechnik, Germany) was used with a sensor of 13 mm in diameter. The applied power was between 100 and 350 mW. The measurements were performed at room temperature with a measurement time of 80 s. All handlings and measurements were carried out under Argon atmosphere in a glove box to avoid any atmospheric impurities.

The sorption rate was measured using a Sievert's apparatus (HERA, Canada) based on the differential pressure method. The purity of the used hydrogen gas was 5.0 (99.999%). The measurements conditions were 350 °C and 50 bar hydrogen for the absorption and 400 °C and 5 to 2 bar of hydrogen for the desorption.

The observations by scanning electron microscope (SEM) were performed with an EvoMA10 (Zeiss, Germany) microscope equipped with a LaB_6 filament for X-ray analysis. The composition of the samples is determined by Energy Dispersion Microanalysis (EDS), using an INCA Energy 350 X Max detector from Oxford Instruments, equipped with a Be window. Cobalt standard is used for the calibration of the quantitative elementary analysis. To avoid oxidation during the handling of the sample, a special sample holder was used. Thereby the sample was placed inside the glove box in the sample holder and afterwards a vacuum was created inside the holder to transport the sample to the SEM.

3. Results

3.1. *Initial density and thermal conductivity*

Initially, and as a reference, the loose powder density of the desorbed material was determined at 0.6243 ± 0.018 g cm^{-3} by using a defined volume and measuring the mass of the powder that fits inside without compacting it. The maximum density was calculated theoretically by using the crystalline solid density and the molar mass of the two components LiH and MgB_2 for the desorbed state and $LiBH_4$ and MgH_2 for the absorbed state (Table 1).

The stoichiometric composition of the desorbed and absorbed material follows the simplified reaction equation (1.1) [9]. For this equation and for the calculation of the maximum density, the addition of $TiCl_3$ was neglected.

The maximum density was calculated to be 0.83 g cm^{-3} for the absorbed state and 1.66 g cm^{-3} for the desorbed state, which was defined, for practical purposes, as zero point of the porosity. Following this definition, the porosity of the loose

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