COMPARATIVE ANALYSIS OF THE EFFICIENCIES OF HYDROGEN STORAGE SYSTEMS UTILISING SOLID STATE H STORAGE MATERIALS

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ABSTRACT

Evaluation of the performances of hydrogen storage systems accommodating solid H storage materials should include characteristics on their reversible hydrogen storage capacity, operating pressures and temperatures, packing densities, and heat effects of hydrogen uptake and release. We have conducted a performance evaluation of the systems accumulating 5 kg of hydrogen in a containment of cylindrical geometry filled with a solid H storage material including such hydrides and reactive hydride composites as AlH_3 , MgH_2 , “low-temperature” (inter)metallic hydrides, NaAlH_4 , Na_3AlH_6 , $\text{LiBH}_4 + \text{MgH}_2$, and MOFs. The analysis yielded gravimetric and volumetric H storage capacities, and energy efficiencies of hydrogen stores. We conclude that the weight efficiency of hydrogen stores, apart from the gravimetric H storage capacity of the material, is greatly affected by its packing density, and by the pressure-temperature conditions which determine type and dimensions of the containment. The materials with low heat effects of H exchange, operating close to the ambient conditions, should be targeted in the course of the development of new hydrogen stores as offering the best energy efficiency of their operation.

Keywords: hydrogen storage; solid-gas reaction; system efficiency; metal hydrides

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1. INTRODUCTION

Hydrogen storage is a key enabling technology for the advancement of hydrogen and fuel cell power systems in transportation, stationary, and portable applications. The main challenge is in finding an efficient way to deliver hydrogen to the consumer, as at normal conditions it is a low density gas (0.09 kg/m^3), thus requiring a densification [1–4]. The improvements of the performances of H_2 stores can be achieved by minimising the volume and weight of the storage systems, as well as by reducing the energy consumption required to enable hydrogen uptake or release.

Obviously, the requirements to the performances of hydrogen storage systems are determined by the corresponding applications. The most strict constraints are imposed for hydrogen storage on board of hydrogen-powered vehicles, when the H_2 fuel tank should ensure the needed driving range, refuelling conditions, cost, safety, etc., without compromising the load carrying capacity and passenger / cargo space [5]. Typical target values for hydrogen storage for mobile applications are presented in the U.S. Department of Energy (DoE) National Hydrogen R&D Program. The Program envisages high energy storage densities to be achieved by 2017: $1.8 \text{ kW}\cdot\text{h/kg}$ (5.5 wt.% H) in the weight and $1.3 \text{ kW}\cdot\text{h/L}$ ($40 \text{ g}_\text{H}/\text{L}$) in the volume efficiencies. The ultimate hydrogen storage goals set by DoE are defined as $2.5 \text{ kW}\cdot\text{h/kg}$ (7.5 wt.% H) and $2.3 \text{ kW}\cdot\text{h/L}$ ($70 \text{ g}_\text{H}/\text{L}$) [6].

The specified target performances are related to the total mass and volume of the hydrogen storage system including hydrogen storage material, containment, auxiliary parts, etc. At the same time, in the publications on solid state hydrogen storage, the gravimetric and volumetric densities, as a rule, are presented for the material itself, without taking into account weight of the containment, shell volume, as well as differences between the actual and bulk / packing

densities of the hydrogen storage material. As we have shown earlier in [3], such an approach results in the overestimated efficiencies.

Thus, the studies evaluating real performances of the solid-state hydrogen storage systems are in a great demand. Only a limited number of the works considering these problems has been published so far. The most detailed studies [7,8] were focused on the evaluation of hydrogen storage performances of the “hybrid” hydrogen storage tanks comprising composite high pressure H₂ cylinder and a solid-state H storage material.

At ANL, Ahluwalia et al. [9] published a valuable analysis of hydrogen storage performances of various hydrogen storage systems, including solid-and-liquid-state materials: AlH₃ based slurry, AX-21 activated carbon, MOF-177 metal-organic framework, NaAlH₄, ammonia borane, liquid organic hydrides, and hydrolysis-type H₂ delivery system NaBH₄ + H₂O. The systems under consideration differ significantly in their layouts that complicates evaluation of the influence of the hydrogen storage material on the system performances.

The present study gives estimations of the influence of the main properties (operating pressure / temperature conditions, reversible weight hydrogen capacity, density and packing fraction) for a number of solid-state H storage materials on the performances of simple hydrogen storage units, when a storage container has a cylindrical geometry with hemispherical caps.

2. REFERENCE DATA AND CALCULATION PROCEDURE

2.1. Hydrogen storage materials

The following hydrogen storage materials were analysed.

2.1.1. Metal Organic Frameworks (MOF) belong to the high surface area crystalline porous materials suitable for gas storage and separation. MOF bind hydrogen via physical adsorption at low temperatures. Theoretically, hydrogen storage density in MOF can

approach 12.4 wt.% H [10], but the experimentally observed values do not exceed 7.5 wt.% H at $T = -196\text{ }^{\circ}\text{C}$ and $P = 70\text{ bar}$ [11]. Because of the “loose” MOF structure, there are various approaches in determining density of this type of materials, ρ , the parameter that defines the gravimetric and volumetric hydrogen storage densities in the material (see below). As example, for MOF-5 the theoretical crystallographic density is equal to 0.605 g/cm^3 while the skeletal density¹ determined by helium pycnometry is 2.03 g/cm^3 [12].

MOF-5 was chosen as a well-studied representative of hydrogen storage materials binding hydrogen via low-temperature physisorption [12–14]. In addition to the material taken as a loose powder, we included the available experimental data for the compacts of MOF-5 with Expanded Natural Graphite (ENG) [14].

2.1.2. “Low-temperature” metallic / interstitial hydrides on the basis of intermetallic compounds and alloys reversibly absorbing H_2 gas at ambient conditions, typically, at $T \leq 50\text{ }^{\circ}\text{C}$ and $P \leq 50\text{ bar H}_2$. The considered parent alloys included AB_5 - [15–19] and AB_2 -type intermetallics [15–18], as well as BCC solid solution alloys on the basis of Ti–Cr system modified by V [20,21].

2.1.3. Aluminium hydride, AlH_3 , combines high gravimetric (10 wt.% H) and volumetric ($164\text{ g}_\text{H}/\text{L}$) hydrogen storage densities with the low temperature hydrogen release around $100\text{ }^{\circ}\text{C}$. Decomposition of AlH_3 at realistic operating conditions is irreversible (direct hydrogenation of aluminium requires application of hydrogenation pressures exceeding 15 kBar [22]), and hydrogen storage systems on its basis should foresee off-board regeneration of the hydrogen storage material by organo-chemical methods. The starting data on the properties of AlH_3 were taken from [23–26].

¹ The skeletal density excludes pores volume from the volume of MOF’s in the density calculation, i.e., only space taken up by the MOF linker and secondary building unit are accounted for [12]

2.1.4. Sodium allanate. Complex hydride NaAlH_4 , when catalysed by Ti-containing catalysts, reversibly, with fast kinetics of hydrogen absorption and desorption, releases hydrogen in a two-stage process transforming first into a hexahydride Na_3AlH_6 and then into $\text{NaH} + \text{Al}$ [27–32].

The net reversible H storage density equals to 5.6 wt.% H / 111 $\text{g}_\text{H}/\text{cm}^3$. According to the PCT relations in $\text{NaH} + \text{Al} - \text{H}_2$ system, the process 1 takes place at hydrogen pressures above 100 bar ($T=170^\circ\text{C}$), and hydrogen release completes (reaction 2) at $T \geq 240^\circ\text{C}$ [27]. Lowering of the operating temperatures to $T=140\text{--}150^\circ\text{C}$ is possible with use of a proper catalyst. However, in this case the first step (reverse reaction) proceeds only partially, thus lowering the reversible H storage capacity of the material to just 3.5 wt.% H at $T=140^\circ\text{C}$ (150°C for the tanks) and $P=100$ bar [31] that only slightly exceeds hydrogen storage capacity corresponding to the reaction 2 (2.9 wt.% H).

For comparison with other materials, we took the operating conditions of NaAlH_4 corresponding to its maximum reversible H storage capacity, $T \leq 200^\circ\text{C}$, $P \leq 150$ bar. The data for the mixture $\text{Na}_3\text{AlH}_6 + 2 \text{ Al}$ (reaction 2; $T \leq 160^\circ\text{C}$, $P \leq 15$ bar) were also analysed; for convenience, this system will be called later in the paper as Na_3AlH_6 .

2.1.5. Magnesium hydride, MgH_2 , which is intensively studied as a hydrogen storage material, has practically attainable storage densities exceeding 7 wt.% H / 109 $\text{g}_\text{H}/\text{L}$ [32–34]. MgH_2 -based nanocomposites, prepared by high-energy reactive ball milling of Mg and catalysts in hydrogen gas, are able to quickly absorb H_2 even at ambient temperatures [35] that allows development of the efficient stationary H storage systems [36]. However, thermodynamic limitations do not allow operation of MgH_2 below $T=300^\circ\text{C}$ corresponding

to H₂ equilibrium pressure above 1 bar. We assume realistic operation conditions for MgH₂-based hydrogen storage systems as T ≤ 400 °C, P ≤ 20 bar H₂.

2.1.6. Reactive hydride composite of LiBH₄ and MgH₂ presents a different class of “high-temperature” reversible hydrogen storage materials. Hydrogen storage is achieved by the reversibility of the reaction:

Reaction 3 allows to store about 11.3 wt.% H, but the practically achieved reversible H storage capacity is about 9 wt.% H / 82 g_H/cm³; the operating conditions are T ≤ 400 °C, P ≤ 50 bar [37].

2.2. Evaluation of H storage performance

The gravimetric/weight, w , and volumetric, v , hydrogen storage densities in a solid state hydrogen storage material are defined by the following Equations:

$$w = \frac{m_S}{m_S + M'}, \text{ or} \quad (4)$$

$$M' = m_S \frac{(1-w)}{w}; \quad (5)$$

$$v = \frac{m_S}{V} = \frac{m_S \rho}{M'} = \frac{w \rho}{1-w}; \quad (6)$$

where m_S is the weight of hydrogen bound by the solid; and M' , V and $\rho = M'/V$ are weight², volume and maximum / theoretical density of the solid state material, respectively. Note that according to the equation (6) the weight and volumetric hydrogen storage densities are related via the material's density, ρ .

The reduction of the volumetric hydrogen storage density on the system level is mainly affected by a packing fraction, a , of the hydrogen storage material in the container:

² M' relates to the required weight of the hydrogen storage material calculated taking into account only hydrogen bound by the solid. Further accounting of the gaseous H₂ in the void space (see Equation (9) below) yields the weight of the material denoted as M .

$$a = \frac{\rho'}{\rho}; \quad (7)$$

where ρ' is a filling (bulk) density of the material in the container.

Usually hydrogenation – dehydrogenation reactions are accompanied by significant changes of the volume in the solid. During the formation of the metal hydrides, an average volume increase on hydrogenation is in a range 20-30 %, while for the complex hydrides (e.g. for NaAlH_4) or for alane these changes are much higher (100% for AlH_3). Obviously, to achieve safe operation of the hydrogen storage system, the packing fraction *must be related to the lowest density of the hydrogen storage material*. For the metal hydrides (MH), a safe packing fraction was determined as ~60% of the material density in the hydrogenated state [38,39], so in most cases we assume $a=0.6^3$, with exception of MOFs for which the bulk densities were explicitly presented in the reference data [12]. The value $a=0.6$ adopts a less dense packing as compared to the fraction of space (0.74) occupied by the closely-packed spheres of the same diameter. Obviously, the used assumption is a rough estimation only as such factors as particle size and shape distributions will also affect the threshold of the packing fraction where will appear unacceptable stresses in the containment. Thus, the precise determination of the packing fraction, a , and, in turn, the filling density, ρ' , must be based on the results of the experimental studies of the swelling effects in the beds containing hydrogenated / dehydrogenated hydrogen storage materials (see [40] as an example).

Obviously, in addition to hydrogen bound by the solid, the hydrogen storage system will also contain hydrogen gas in the void volume of the container. The amount of gaseous hydrogen, m_g , depends on the void volume, as well as on the pressure-temperature conditions of

³ For hydrogen storage materials of practical importance, in the hydrogenated state the materials have lower densities as compared to the hydrogen-free alloys ([39]; the corresponding values are presented in Table 1). For the materials undergoing volume changes upon hydrogenation / dehydrogenation, the minimum value of the density, ρ , has to be used in the calculations. The packing fraction, a , determined in equation (7) does not depend on the value of the volume change.

hydrogen storage. Accounting two contributions, the total amount, m , of the stored hydrogen will be:

$$m = m_s + m_g . \quad (8)$$

Taking into account the contribution of gaseous hydrogen and using equation (5) for the determination of the weight, M' [kg], of the solid state material for the storage of required amount, m [kg], of hydrogen, will determine a total amount of the stored hydrogen, M , as:

$$M = m \left(\frac{w}{1-w} + \frac{P \mu}{Z R T \rho} (1/a - 1) \right)^{-1} ; \quad (9)$$

where P [Pa] is hydrogen pressure, μ [kg/mol] is molecular weight of H_2 , $R = 8.3143$ J/(mol K) is a universal gas constant, T [K] is temperature, ρ [kg/m³] is the real density of the material, Z is H_2 compression factor at the pressure P and temperature T . More details are presented in Supplementary Information, Section S1.1.

Characteristics of the materials for hydrogen storage are presented in the Table 1. The data include operating temperature (T) and pressure (P)⁴, weight (w) and volumetric (v) hydrogen storage densities, maximum / theoretical (ρ) and bulk / filling (ρ') densities, packing fraction (a), hydrogenation enthalpy (ΔH), and specific heat capacity ($c_p^{(M)}$). The data also include the weight of the material (M) necessary for the storage of $m=5$ kg H (the contributions from m_s and m_g are specified separately), and volume (V_M) occupied by the material in the hydrogen storage container. Additional reference data were taken from [41,42]. The maximum / theoretical densities (ρ) were presented for the materials in the hydrogenated state, except of MOF-5. For NaH+Al – NaAlH₄ system ΔH and c_p are presented as weighted average values for the reactions 1 and 2.

⁴ The specified operating pressure – temperature conditions necessary for the selection of the suitable container material correspond to the maximum hydrogen pressure and minimum (MOF) or maximum (all others) temperature required for hydrogen sorption or desorption.

Table 1. Characteristics of hydrogen storage materials

From Table 1 it is clearly seen that the contribution of hydrogen stored in the gas phase (m_g) cannot be neglected and should be considered together with the data for m_s , particularly at low operating temperatures and high H_2 pressures. Indeed, for MOF-5 as a powder and as a composite with ENG, this latter contribution amounts 73.6 and 44 %, correspondingly, of the total amount of the accumulated H_2 . For the materials operating at $P \geq 50$ bar and temperatures above ambient, the contribution of m_g is much smaller and varies between 1.4 % ($LiH + MgB_2 / LiBH_4 + MgH_2$), 2.5 % (“low-temperature” MH) and 5.8 % ($(NaH+Al) / NaAlH_4$). Lower pressure hydrogen storage materials accommodate in the gaseous phase less than 1% of the stored H_2 .

2.3. Hydrogen storage containers

The hydrogen storage container (Figure 1) has been modelled as a cylinder of internal radius r and length L related as $L=l \cdot r$ where $l=L/r$ is an aspect ratio. Both ends of the cylinder have hemispherical caps of the same internal radius, r . The external radius, R , of the cylinder and caps is related with the internal radius, r , and wall thickness, s , as:

$$\alpha = \frac{R}{r} ; \quad (10)$$

$$s = (R - r) = r (\alpha - 1). \quad (11)$$

Figure 1. A schematic representation of the H storage container

The ratio between the external and internal radii, $\alpha = R / r$, is an important dimensionless parameter determining structural strength of the pressure container. Its determination requires

analysis of stresses which appear in the container's wall. According to [43], for the cylindrical container a simple estimation of the structural strength of the pressure container can be done, as related to the internal pressure, P_{max} ⁵, and a tensile strength of the material, σ_s , as follows:

$$\alpha = \sqrt{\frac{\sigma_s}{\sigma_s - P_{max}\sqrt{3}}}; \quad (12)$$

Equation (12) is used for the calculation of the pressure containers operating in the range of elastic deformations [43]. However, if to replace the tensile strength, σ_s , with equivalent allowable stress, σ^* , this will result in getting the values close to the ones adopted in the existing regulations for pressure safety for the seamless tubes in operation. As example, at room temperature the allowed working pressure for SS316 stainless steel tubing (ASTM A269; 2' OD x 0.109'WT, $\alpha=1.1223$) equals to 2000 psi (138 bar) [44]. At $\sigma_s=\sigma^*=137,800$ kPa (ASME B31.3, Process Piping) the solution of equation (12) yields $P_{max}=164$ bar. Similar calculations using equation (12) when substituting $\sigma_s=\sigma^*$ for different materials and pipe sizes show that the calculated values of P_{max} exceed the corresponding pressure ratings by not more than 15–20%. We consider such a difference as acceptable for the objective of comparison of the pressure containers.

Independently of the size and aspect ratio of the H storage container, its shell volume, V_s , will be equal to:

$$V_s = (V_e - V_i) = (\alpha^3 - 1) V_i; \quad (13)$$

where V_e and V_i are the external and internal volumes, respectively. The weight of the empty container, M_s , is proportional to the density of the container's material, ρ_s :

$$M_s = \rho_s(\alpha^3 - 1) V_i. \quad (14)$$

⁵ Assuming $P_{max} \gg P_0$ where P_0 is the pressure outside the container

More details are presented in Supplementary Information, Section S1.2.

Effect of auxiliary elements of the H storage units (mainly, internal heat exchangers) can be accounted by introducing a coefficient, f , describing the filling of the internal space of hydrogen storage containers (volume V_i) by these elements. Consequently,

$$V_{HE} = f V_i = \frac{f}{1-f} V_M ; \quad (15)$$

$$M_{HE} = \rho_{HE} V_{HE} ; \quad (16)$$

where V_M is the volume of the container occupied by the hydrogen storage material, V_{HE} and M_{HE} are volume and weight of the heat exchanger, respectively, ρ_{HE} is the density of the material of heat exchanger.

The weight, w' , and volumetric, v' , hydrogen densities of the material in a hydrogen storage container can be defined as:

$$w' = \frac{m}{m+M+M_S+M_{HE}} ; \quad (17)$$

$$v' = \frac{m}{V_i+V_S} = \frac{m}{V_M+V_{HE}+V_S} ; \quad (18)$$

where M_S and V_S are calculated by equations (13) and (14), respectively, and the structural strength, α , can be determined using equation (12) from the strength of the material (σ_S or σ^*) at the operating temperature taking into account maximum operating pressure, P_{max} .

As hydrogenation and dehydrogenation of a hydrogen storage material are, respectively, exothermic ($\Delta H < 0$) and endothermic ($\Delta H > 0$) processes and H storage materials require heating to the operation temperature to achieve hydrogen desorption, the associated energy consumption for these materials will include:

- Heating of the H storage material, containment and auxiliary elements (heat exchanger) from the ambient (T_0) to the operating (T) temperature;
- Supply of the heat of H desorption.

For the physisorption type materials operating at low temperatures, the associated energy consumption by the H₂ storage system includes:

- Cooling of the H storage material containment and the heat exchanger from the ambient (T_0) to the operating (T) temperature;
- Removal of the H₂ adsorption heat.

Accordingly, the energy consumption for hydrogen storage in the form of heat, Q , can be estimated as:

$$Q = c_p^{(M)} M \Delta T + c_p^{(S)} M_S \Delta T + c_p^{(HE)} M_{HE} \Delta T + |\Delta H| m_S ; \quad (19)$$

where c_p are specific heat capacities of the materials for hydrogen storage (M), containment (S) and heat exchanger (HE); M , M_S and M_{HE} are their weights; ΔT is the absolute value of ($T-T_0$); ΔH is the enthalpy of hydrogen absorption; and m_S is the weight of H₂ stored in the hydrogen storage material.

Even though equation (19) does not take into account the temperature dependence of the heat capacities and (for the hydrogen storage material) changes of hydrogen concentration with temperature, nevertheless, it can provide a useful estimate of energy/heat consumption with the main contributions coming from:

- The weights of materials used for the containment (M_S), heat exchanger (M_{HE}) and for hydrogen storage (M), see above;
- The enthalpy of hydrogen absorption, ΔH .

As we have mentioned earlier, the amount, m_g , of hydrogen stored in the void volume of hydrogen storage container as a pressurised gas cannot be neglected, and the additional energy input for hydrogen storage is associated with mechanical work, W , required for the compression of hydrogen gas from the initial pressure, P_0 , to the operating pressure, P , at the

temperature T_0 , with the efficiency η . The H_2 compression work can be expressed via the isothermal compression work as:

$$W = \frac{m_g}{\eta\mu} RT_0 \ln\left(\frac{P}{P_0}\right). \quad (20)$$

Table 2 presents properties of typical materials which can be used for the hydrogen storage containers, including SS316 stainless steel (SS), 6061-T6 aluminium alloy (Al) [44,45], as well as composite materials on the basis of epoxy reinforced with carbon (CFRP) or glass (GFRP) fibres [8,42,46]. In addition to the type of the container material, the data include allowed tensile stress (σ^*) taking into account its reduction at the elevated temperatures [44–46], density (ρ_s), and specific heat capacity ($c_P^{(S)}$).

Table 2. Properties of container materials.

Elevated operating temperatures and increased hydrogen pressures required for the operation of some hydrogen storage materials imply limitations for the use of the materials of hydrogen storage containers. As example, aluminium alloy and GFRP (maximum operating temperature $T_{max}=204^\circ\text{C}$) as well as CFRP ($T_{max}=120^\circ\text{C}$) are not suitable for building the containers accommodating MgH_2 and high-temperature reactive hydride composites⁶. In addition, CFRP cannot be utilised to build hydrogen stores accommodating AlH_3 and Na_3AlH_6 . In contrast, stainless steel containers ($T_{max}=537^\circ\text{C}$) are suitable for all considered materials.

Note that the reference data for the strength of the composites are strongly dependent on the technology used in the manufacturing of the composite structures and thus show significant

⁶ For (NaH+Al – NaAlH₄) system the operating temperature is very close to the T_{max} of the aluminium alloy and GFRP; this introduces limitations of use of the latter materials as the shells of the containers for the H storage systems based on sodium alanate.

variations. The σ^* values presented in Table 2 approximately correspond to ~80% of the tensile strength, σ_s , of unidirectional tape made of the corresponding composite and loaded along the fibres. Similar arguments concern the data on the maximum operating temperatures for the composites; here the thermal stability of the epoxy binder becomes a critical parameter and determines the overall performance [46]. Naturally, use of the binders (e.g., polyimides) with higher thermal stability will increase the maximum operating temperature of the composite materials and make them suitable for the solid state hydrogen storage systems operating at higher temperatures.

3. RESULTS AND DISCUSSION

The results on the estimation of hydrogen storage performances of the hydrogen storage materials for four types of hydrogen storage containers are summarised in Figures 2 and 3. The corresponding data are also presented in Tables S1–S4, see Supplementary Information. All calculations were performed for the storage of 5 kg H₂ using the following assumptions:

- (i) Internal heat exchangers are made of aluminium ($f=0.1$, $\rho_{HE}=2700 \text{ kg/m}^3$, $c_P^{(HE)}=0.90 \text{ kJ/(kg K)}$);
- (ii) H₂ compression work was calculated for $P_0=1 \text{ bar}$, $T_0=300 \text{ K}$, $\eta=0.5$.
- (iii) We also include estimations of the composite containers operating at temperatures higher than the presently allowed maxima (MgH₂ and LiBH₄ + MgH₂ for GFRP; AlH₃, Na₃AlH₆, NaAlH₄, MgH₂ and LiBH₄ + MgH₂ for CFRP) assuming that novel heat-resistant binders will be developed allowing operation at the required elevated temperatures.

For each series shown in the Figures 2A, 2B and 3A, the sequence of the stacked bars corresponds to the following container materials “SS – Al – GFRP – CFRP”; the sequence of

the points for a particular hydrogen storage material shows its weight and volumetric hydrogen storage densities (Figure 3B; from bottom-left to top-right) corresponds to the series “SS – Al – GFRP – CFRP – material alone”.

Figure 2. Volumes (A) and weights (B) of the hydrogen storage systems based on different solid state materials placed in the various containers (as shown for BCC-TiCr(V)): SS, Al (if suitable), GFRP, and CFRP.

Figure 3. Gravimetric and volumetric H storage densities (A) and energy consumptions (B) for hydrogen storage in different solid state materials taken alone (A) and placed into the various containers (as shown in B for BCC-TiCr(V)): SS, Al (if suitable), GFRP, and CFRP. The data for MOF in A (material alone) correspond to the crystallographic density $\rho=605 \text{ kg/m}^3$.

As it can be seen from the Figure 2A, total system volume mainly depends on the volumetric H storage density, v , of the material and typically varies from 58 (AlH_3 , $v=164 \text{ g}_\text{H}/\text{L}$) to ~200 L (MOF-5 , $v=36 \text{ g}_\text{H}/\text{L}$ ⁷). In most cases, the share of hydrogen storage material (V_M) in the total system volume ($V_M+V_{HE}+V_S$) is close to 80%. The share of the volume belonging to the hydrogen storage containers does not vary very much; it ranges from <1–3% for the systems operating at H_2 pressures up to 20 bar (AlH_3 , Na_3AlH_6 , MgH_2) and up to 8–13% for the other materials working at higher operating pressures. A contribution from a heat exchanger (V_{HE} , typically, from 8.2 to 9.7%) is close to the assumed in our evaluations space filling coefficient ($f=0.1$). The contribution of a container shell (V_S) into the total system volume varies in a much broader range, from 3% for the practically viable storage solutions to >20% for the solutions which, consequently, do not pass the requirements and were turned down as

⁷ As related to the crystal density of the material.

impractical hydrogen storage options. Naturally, this contribution is determined by the structural strength of the pressure container, α , (see equation (13)), which, in turn, is affected by the operating pressure and the strength of the container material at the operating temperature (see equation (12)). Accordingly, use of stronger container materials results in smaller shell volumes which increase in a series “CFRP < GRFP < SS < Al”; the differences become more pronounced at higher operating pressures and temperatures. When the strength of the container material becomes comparable with the operating pressure, as in the case of combination NaAlH₄ / Al ($T=200$ °C, $P=150$ bar, $\sigma_{Al}^*=408$ bar), the container must have thick walls ($\alpha=1.606$); that dramatically increases the shell volume (403 L, or 78% of the total system volume) and makes such systems interesting solely from the point of view of theoretical analysis.

The total system weight ($m_M+m_g+M+M_{HE}+M_S$) correlates with the gravimetric H storage density, w , in the material, and typically varies from 68–80 kg (AlH₃, $w=10\%$) to 350–420 kg (AB₅, $w=1.5\%$). The contribution of the system components (M , M_{HE} , M_S) into the total system weight significantly varies for the different hydrogen storage and container materials, depending on the number of contributing factors. The contribution of the containment, M_S , exhibits the highest variations, from 1.2–1.7% (“low-temperature” MH / CFRP) to ~50–75% (NaAlH₄, LiBH₄ + MgH₂ and MOF-5 in stainless steel containers) and even to >90% for NaAlH₄ / Al. Here the structural strength of the pressure container, α (see above), as well as the density of the container material, ρ_S , and the bulk density of hydrogen storage materials, ρ' , have the most significant contribution.

A comparison of the gravimetric and volumetric hydrogen storage densities for the considered materials taken alone and the corresponding parameters for the hydrogen storage systems “material + containment + heat exchanger” (Figure 3A) shows a significant

reduction of both weight and volumetric efficiencies of hydrogen storage on the system level. The reduction is more pronounced for the light-weight materials. Operation at high temperatures and hydrogen pressures poses most strict requirements on the material and wall thickness of the containment resulting in a further decrease of the volumetric and, especially, gravimetric hydrogen storage efficiencies. If for the materials themselves two light element-based options, AlH_3 and $\text{LiBH}_4+\text{MgH}_2$, meet the DoE requirements for the hydrogen storage densities (area marked by dash-dot line in Figure 3A), after taking into account containment and heat exchanger, only AlH_3 satisfies these requirements, with the gravimetric system storage density being close to the corresponding lower limit of the DoE requirements (7.5 wt.%).

As expected, the reduction of the volumetric hydrogen storage densities is determined by the packing fraction of the materials, a , in the containers. For the materials accommodated in the thin wall containers, the assumed safe packing fraction $a=0.6$, results in the ~40% decrease of the volumetric H storage density on the system level; additional decrease by ~10 % is caused by the heat exchanger ($f=0.1$), and in total the decrease in the volumetric efficiency of hydrogen storage is close to 50%. However, if the operating pressure and strength of the container material require thicker walls, the contribution of the shell volume reduces the volumetric H storage density dramatically. This effect is especially pronounced for $\text{NaAlH}_4 / \text{Al}$.

The influence of the container on the reduction of the weight hydrogen storage densities mainly depends on the strength of the container material at the operating conditions and its density. The least favourable situation here is a combination of high temperatures approaching maximum operation temperatures of the container material and high operation

pressures (we refer to the data for AlH_3/Al , $\text{Na}_3\text{AlH}_6/\text{Al}$ and NaAlH_4/Al). Unfortunately, application of CFRP and GFRP, which combine high strength and low density, being the best solution for the container material, does not suit the operation requirements for the “high-temperature” hydrogen storage materials.

The system performances for the containers made of CFRP and GFRP operating at modest hydrogen pressures, ≤ 150 bar, required for the solid state hydrogen storage systems, appear to be quite similar. However, taking into account (i) higher maximum operating temperature and (ii) lower cost, in our opinion, the glass fibre reinforced composite could be recommended as an optimal material for the H storage containment. Further improvements of the composite containers may be expected if a heat-resistant filler (e.g., polyimide) would be utilised.

Despite of the very small packing fractions, a , achievable for MOF-5 (0.06 for the loose powder and 0.25 for the material compacted with ENG), its volumetric hydrogen storage density in the containers, as compared to the material alone, decreases less significantly, by only 6.5–40%, while for the other materials with $a=0.6$ the decrease is about 50%. For MOF-5 powder accommodated in the light-weight composite containers, the gravimetric hydrogen storage density on the system level is almost same as for the individual material. This is caused by the significant contribution of gaseous hydrogen stored at high pressures and low temperatures in the void volume of the container (m_g), as can be seen from Figure 2B. Thus, the corresponding systems combine features of solid-state and cryo-compression hydrogen storage systems.

Figure 3B presents the energy consumption of the hydrogen storage systems, as a percentage of the higher heating value of the stored H_2 (HHV; 141.8 MJ/kg). AlH_3 -based systems are characterised by the lowest energy consumption ($<4.5\%$ of HHV) followed by the systems

based on MOF and “low-temperature” MH (10–15%), Na_3AlH_6 and NaAlH_4 (~23%), LiBH_4 + MgH_2 (31–35%), and MgH_2 (~40%). In most cases, the main part of the energy (up to 90–95% for “low-temperature” MH) is consumed to compensate the heat effects of hydrogen desorption. Additional energy has to be spent for the heating or cooling of the system components (hydrogen storage material, containment and heat exchanger); it increases with an extent of the deviation of the operation temperature from the ambient conditions, as well as with the increase of the total system weight. For MOF-5, hydrogen compression takes 30 to 60% of the total energy input.

CONCLUSIONS

Performance analysis of hydrogen storage efficiency (gravimetric and volumetric hydrogen storage densities, and energy consumption) for the systems on the basis of various solid state hydrogen storage materials has been carried out. The contributions of the containment and heat exchangers into the overall balance of hydrogen storage densities and energy consumption were evaluated.

The volumetric and, especially, gravimetric efficiencies of hydrogen storage at the system level, apart from the gravimetric hydrogen storage capacity of the material, are greatly affected by its bulk density, as well as the pressure-temperature conditions which determine type, size and wall thickness of the containment.

In the hydrogen storage systems based on high surface area materials operating at low temperatures and high H_2 pressures, which combine features of solid state and cryo-compression hydrogen storage, a significant contribution into the amount of stored hydrogen is introduced by compressed gaseous H_2 accommodated in the void space of hydrogen store.

The energy consumption during use of the hydrogen storage systems is mainly dependent on the type of hydrogen storage material and increases with the increase of the heat effect of

hydrogen sorption – desorption. Furthermore, but to a lesser extent, the energy consumption increases at high deviation of the operation temperature from the ambient conditions, for the increased total weight of the system and for the systems on the basis of high surface area materials, where a significant part of the consumed energy is associated with hydrogen compression.

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REFERENCES

- [1] L.Schlapbach, A.Züttel, Hydrogen-storage materials for mobile applications, *Nature* 414 (2001) 353-358
- [2] A.Züttel, Materials for hydrogen storage, *Materials Today* 6 (2003) 24-33
- [3] V.A.Yartys, M.V.Lototsky, An overview of hydrogen storage methods, in: T.N.Veziroglu, S.Yu.Zaginaichenko, D.V.Schur, B.Baranowski, A.P.Shpak, V.V.Skorokhod (Eds.), *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials*, Kluwer Academic Publ., Dordrecht, 2004, pp. 75-104
- [4] B.P.Tarasov, M.V.Lototskii, V.A.Yartys, Problem of hydrogen storage and prospective uses of hydrides for hydrogen accumulation, *Russ J Gen Chem* 77 (2007) 694-711
- [5] S.Satyapal, J.Petrovic, C.Read, G.Thomas, Grace Ordaz, The U.S. Department of Energy’s National Hydrogen Storage Project: Progress towards meeting hydrogen-powered vehicle requirements, *Catalysis Today* 120 (2007) 246-256
- [6] N.T.Stetson, K. O’Malley, C.Ahn, Hydrogen storage research and development efforts supported by the U.S. Department of Energy. International Symposium on the Metal-Hydrogen Systems MH2014, Manchester, July, 2014. .

- [7] N.Takeichi, H.Senoh, T.Yokota, H.Tsuruta, K.Hamada, H.T.Takeshita, et al, “Hybrid hydrogen storage vessel”, a novel high-pressure hydrogen storage vessel combined with hydrogen storage material, *Int J Hydrogen Energy* 28 (2003) 1121-1129
- [8] C.Corgnale, B.J.Hardy, D.L.Anton, Structural analysis of metal hydride-based hybrid hydrogen storage systems, *Int J Hydrogen Energy* 37 (2012) 14223-14233
- [9] R.K. Ahluwalia, T.Q. Hua, J.K. Peng, On-board and off-board performance of hydrogen storage options for light-duty vehicles, *Int J Hydrogen Energy* 37 (2013) 2891–2910
- [10] J. Goldsmith, A.G. Wong-Foy, M.J. Cafarella, D.J. Siegel, Theoretical limits of hydrogen storage in metal–organic frameworks: Opportunities and trade-offs, *Chem Mater* 25 (2013) 3373–3382
- [11] Y.H. Hu, L. Zhang. Hydrogen Storage in Metal–Organic Frameworks, *Adv Mater* 22 (2010) E117–E130
- [12] J.J. Purewal, D. Liu, J. Yang, A. Sudik, D.J. Siegel, S. Maurer, U. Muller, Increased volumetric hydrogen uptake of MOF-5 by powder densification, *Int J Hydrogen Energy* 37 (2012) 2723-2727
- [13] B.Panella, M.Hirscher, H.Pütter, U.Müller. Hydrogen adsorption in metal–organic frameworks: Cu-MOFs and Zn-MOFs compared, *Adv Funct Mater* 16 (2006) 520–524
- [14] D. Liu, J.J. Purewal, J. Yang, A. Sudik, S. Maurer, U. Mueller, J. Ni, D.J. Siegel, MOF-5 composites exhibiting improved thermal conductivity, *Int J Hydrogen Energy* 37 (2012) 6109-6117
- [15] G.Sandrock, A panoramic overview of hydrogen storage alloys from a gas reaction point of view, *J Alloys Compds* 293–295 (1999) 877–888
- [16] Y.Chen, C.A.C.Sequeira, C.Chen, X.Wang, Q.Wang, Metal hydride beds and hydrogen supply tanks as minitype PEMFC hydrogen sources, *Int J Hydrogen Energy* 28 (2003) 329– 333
- [17] V.A.Yartys, V.V.Burnasheva, K.N.Semenenko, Structural chemistry of intermetallic hydrides, *Uspekhi Khimii (Sov. Adv. Chemistry)* 52(4) (1983) 529-561
- [18] B.A.Kolachev, R.E.Shalin, A.A.Il'in, Hydrogen storage alloys: Reference book, “Metallurgia” Publ., Moscow, 1995

- [19] D.Ohlendorf, H.E.Floto, Experimental heat capacities of LaNi_5 , $\alpha\text{-LaNi}_5\text{H}_{0.36}$, and $\beta\text{-LaNi}_5\text{H}_{6.39}$ from 5 to 300 K. Thermodynamic properties of the $\text{LaNi}_5\text{-H}_2$ system, J Chem Phys 73(1980) 2937
- [20] E.Akiba, M.Okada. Metallic Hydrides III: Body-Centered-Cubic Solid- Solution Alloys, MRS Bull 27 (2002) 699–703
- [21] T.Tamura, T.Kazumi, A.Kamegawa, H.Takamura, M.Okada, Protium absorption properties and protide formation of Ti-Cr-V alloys, J Alloys Compds 356-357 (2003) 505-509
- [22] J. Graetz, J.J. Reilly, V.A. Yartys, J.P. Maehlen, B.M. Bulychiev, V.E. Antonov, B.P. Tarasov, I.E. Gabis, Aluminum hydride as a hydrogen and energy storage material: Past, present and future, J Alloys Compds 509S (2011) S517– S528
- [23] J.W.Turley, H.W.Rinn, Crystal structure of aluminum hydride, Inorg Chem 8 (1969) 18-22
- [24] G. Sandrock, J. Reilly, J. Graetz, W.-M. Zhou, J. Johnson, J.Wegrzyn, Accelerated thermal decomposition of AlH_3 for hydrogen-fueled vehicles, Appl Phys A 80 (2005) 687–690
- [25] J.Graetz, J.Reilly, G.Sandrock, J.Johnson, W.M.Zhou, J.Wegrzyn. Aluminum Hydride, AlH_3 , As a Hydrogen Storage Compound, Report BNL-77336-2006, Brookhaven National Laboratory, 2006
- [26] V.E Antonov, A.I.Kolesnikov, Yu.E.Markushkin, A.V.Palnichenko, Y.Ren, M.K.Sakharov, Heat capacity of $\alpha\text{-AlH}_3$ and $\alpha\text{-AlD}_3$ at temperatures up to 1000 K, J Phys Condens Matter 20 (2008) 275204
- [27] B. Bogdanović, R.A. Brand, A. Marjanovic, M. Schwickardi, J. Tölle, Metal-doped sodium aluminium hydrides as potential new hydrogen storage materials, J Alloys Compds 302 (2000) 36–58
- [28] B.Bogdanović, G.Sandrock, Catalyzed complex metal hydrides, MRS Bull 27 (2002) 712–716
- [29] P.Vajeeston, P.Ravindran, R.Vidya, H.Fjellvåg, A.Kjekshus, Pressure-induced phase of NaAlH_4 : A potential candidate for hydrogen storage? Appl Phys Lett 82 (2003) 2257-2259

- [30] G.Sandrock, K.Gross, G.Thomas, C.Jensen, D.Meeker, S.Takara. Engineering considerations in the use of catalyzed sodium alanates for hydrogen storage, *J Alloys Compds* 330–332 (2002) 696–701
- [31] D.A.Mosher, S.Arsenault, X.Tang, D.L.Anton, Design, fabrication and testing of NaAlH_4 based hydrogen storage systems, *J Alloys Compds* 446–447 (2007) 707–712
- [32] M.Felderhoff, B.Bogdanović, High temperature metal hydrides as heat storage materials for solar and related applications, *Int J Mol Sci* 10 (2009) 325–344
- [33] P.Selvam, B.Viswanathan, C.S.Swamy, V.Srinivasan. Magnesium and magnesium alloy hydrides, *Int J Hydrogen Energy* 11 (1986) 169–192
- [34] B.Bogdanović, B.Splithoff, Active MgH_2 -Mg-systems for hydrogen storage, *Int J Hydrogen Energy*, 12 (1987) 863–873
- [35] M.V. Lototsky, R.V. Denys, V.A. Yartys, Combustion-type hydrogenation of nanostructured Mg-based composites for hydrogen storage, *Int J Energy Research*, 33 (2009) 1114–1125
- [36] B.Delhomme, P.de Rango, P.Marty, M.Bacia, B.Zawilski, C.Raufast, S.Miraglia, D.Fruchart, Large scale magnesium hydride tank coupled with an external heat source, *Int J Hydrogen Energy* 37 (2012) 9103–9111
- [37] J.Jepsen, C.Milanese, A.Girella, G.A.Lozano, C.Pistidda, J.M.B. von Colbe, A.Marini, T.Klassen, M.Dornheim, Compaction pressure influence on material properties and sorption behaviour of LiBH_4 - MgH_2 composite, *Int J Hydrogen Energy* 38 (2013) 8357–8366
- [38] K. Nasako, Y. Ito, N. Hiro, M. Osumi, Stress on a reaction vessel by the swelling of a hydrogen absorbing alloy, *J Alloys Compds* 264 (1998) 271–276
- [39] M.V.Lototsky, V.A.Yartys, B.G.Pollet, R.C.Bowman, Jr., Metal hydride hydrogen compressors: a review, *Int J Hydrogen Energy* 39 (2014) 5818–5851
- [40] B.Charlas, O.Gillia, P.Doremus, D.Imbault, Experimental investigation of the swelling/shrinkage of a hydride bed in a cell during hydrogen absorption/desorption cycles, *Int J Hydrogen Energy* 37 (2012) 16031–16041
- [41] S.D.Beattie, A.Harris, A.Levchenko, J.Rudolph, C.D.Willson, G.S.McGrady, Thermal conductivity and specific heat measurements of metal hydrides, http://btinnovations.org/shanebeattie/Papers/Thermal_Conductivity_Measurement_of_Metal_Hydrides_Aug_21.pdf

- [42] The Engineering ToolBox, <http://www.engineeringtoolbox.com>
- [43] D.S.Tsiklis, Technique for physical-chemical investigations at high and super-high pressures. Fourth edition, “Khimia” Publ., Moscow, 1976
- [44] Swagelok Tubing Data, document MS-01-107, <http://www.swagelok.com>
- [45] ASM Material Data Sheets, ASM Aerospace Specification Metals, Inc.,
<http://asm.matweb.com>
- [46] Composite Materials Handbook; Volume 2. Polymer Matrix Composites Materials Properties, MIL-HDBK-17-2F, U.S. Department of Defence, 2002

Table 1. Characteristics of the hydrogen storage materials

Property / operating conditions	MATERIAL									
	MOF-5		AB ₅	AB ₂	BCC- TiCr(V)	AlH ₃	(NaH+Al) / 1/3Na ₃ AlH ₆ +2/3 Al	(NaH+Al) / NaAlH ₄	MgH ₂	LiH + MgB ₂ / LiBH ₄ + MgH ₂
	powder	compact								
<i>w</i> [%]	5.60	4.20	1.50	1.90	2.70	10.00	2.90	5.60	7.00	9.00
<i>v</i> [g _H /L] ⁽¹⁾	121 (36)	89 (27)	101	100	123	164	55	77	109	82
<i>ρ</i> [kg/m ³] ⁽¹⁾	2030 (605)		6660	5180	4420	1480	1830	1300	1450	830
<i>ρ'</i> [kg/m ³]	130	500	3996	3108	2652	888	1098	780	870	498
<i>a</i> ⁽¹⁾	0.06 (0.21)	0.25 (0.83)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
<i>m_s</i> [kg]	1.32	2.80	4.88	4.88	4.90	4.99	4.95	4.71	4.98	4.93
<i>m_g</i> [kg]	3.68	2.20	0.12	0.12	0.10	0.01	0.05	0.29	0.02	0.07
<i>M</i> [kg]	22	64	321	252	177	45	166	79	66	50
<i>V_M</i> [L]	172	128	80	81	67	51	151	102	76	100
<i>c_p</i> ^(M) [kJ/(kg K)]	0.7	0.75	0.49	0.5	0.5	1	1.23	1.38	1.36	2.78
−Δ <i>H</i> [kJ/mol H ₂]	4		26.8	25.4	35	6.6	47	43	74.5	46
−Δ <i>H</i> [MJ/kg H ₂]	2		13.4	12.7	17.5	3.3	23.5	21.5	37.25	23
<i>T</i> [°C]	-196		50			150	160	200	400	400
<i>P</i> [bar]	70		50			10	15	150	20	50

Note: ⁽¹⁾ For MOF the data are presented for skeletal densities of the material, as well as (in brackets) for the crystal ones.

Table 2. Properties of container materials

Property ⁽¹⁾		Material			
		Stainless steel SS316	Aluminium 6061-T6	CFRP ⁽²⁾	GFRP ⁽³⁾
σ_s [MPa]		290	276	1000–2000	500
σ^* [MPa]		137.8	96.5	828	400 ⁽⁴⁾
ρ_s [kg/m ³]		7900	2700	1550	1900
c_p [kJ/(kg K)]		0.50	0.90	0.84	0.86
T_{max} [°C]		537	204	120	204
$\sigma^*(T_{max}) / \sigma^*(T_0)$		0.76	0.40	~1	0.66
Suitability of use together with hydrogen storage materials	MOF-5	+	+	+	+
	AB ₅ , AB ₂ , BCC-TiCr(V)	+	+	+	+
	AlH ₃	+	+	–	+
	Na ₃ AlH ₆	+	+	–	+
	NaAlH ₄	+	(+)	–	(+)
	MgH ₂ , LiBH ₄ + MgH ₂	+	–	–	–

- Notes:
- (1) The values of tensile stresses, densities and specific heat capacities are given at the room temperature, T_0 .
 - (2) Carbon Fibre Reinforced Plastic (epoxy binder).
 - (3) Glass Fibre Reinforced Plastic (epoxy binder).
 - (4) Estimated

Figure

Figure 1.

Figure 2.

Figure 3.