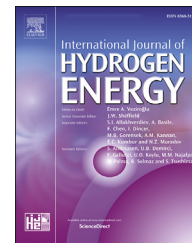




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# Metal hydride hydrogen storage and compression systems for energy storage technologies



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## HIGHLIGHTS

- Use of metal hydride storage and compression in hydrogen energy storage systems.
- AB<sub>5</sub>- and AB<sub>2</sub>-type hydrides for hydrogen storage and compression applications.
- Development of the energy storage systems and their metal hydride based components.

## ARTICLE INFO

### Article history:

Received 29 February 2020

Received in revised form

6 July 2020

Accepted 9 July 2020

Available online 6 August 2020

### Keywords:

Energy storage

Hydrogen

Metal hydrides

Hydrogen storage

Hydrogen compression

Integrated systems

## ABSTRACT

Along with a brief overview of literature data on energy storage technologies utilising hydrogen and metal hydrides, this article presents results of the related R&D activities carried out by the authors. The focus is put on proper selection of metal hydride materials on the basis of AB<sub>5</sub>- and AB<sub>2</sub>-type intermetallic compounds for hydrogen storage and compression applications, based on the analysis of PCT properties of the materials in systems with H<sub>2</sub> gas. The article also presents features of integrated energy storage systems utilising metal hydride hydrogen storage and compression, as well as their metal hydride based components developed at IPCP and HySA Systems.

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<https://doi.org/10.1016/j.ijhydene.2020.07.085>

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## Introduction

Imbalance between energy production and consumption calls for a great demand for efficient energy storage technologies [1], particularly when using renewables as primary energy sources [2]. The renewable energy sources are characterised by non-uniformity of power generation which fluctuates in time. In order to manage the fluctuations and utilize surplus electric power, the most promising way is in the use of hydrogen as an efficient energy carrier. When the surplus power is available, hydrogen is produced by water electrolysis. When the power generation is insufficient (e.g. during periods of low solar radiation), hydrogen is oxidized in a fuel cell (FC) to produce on-demand electricity.

The hydrogen based energy storage is beneficial in energy intensive systems ( $\geq 10$  kWh) operating in a wide range of unit power (1–200 kW), especially when the footprint of the system has to be limited. The cost of ownership for backup power systems (10 kW/120 kWh) with hydrogen energy storage becomes lower than for alternative energy storage methods when the operating time exceeds 5 years [3].

The main challenge hindering implementation of the hydrogen energy storage systems is safe and efficient hydrogen storage and supply [4,5].

Hydrogen storage in metal hydrides (MH) based on reversible reaction of hydrogen with metals, alloys and intermetallic compounds is a promising option for small-to-medium-scale applications ( $0.01$ – $30$  Nm<sup>3</sup> H<sub>2</sub>) [6–19].<sup>1</sup> Apart from compact hydrogen storage at modest pressures, MH systems can utilize heat released during fuel cell operation for H<sub>2</sub> desorption thus improving overall system efficiency [15,18–20]. The integration of MH in “electrolyser – fuel cell” energy system also allows for the efficient heat management providing end-user with heating and cooling in addition to electric power supply [21–25]. The available heat can also be used to drive metal hydride hydrogen compressor which provides storage of H<sub>2</sub> as compressed gas. Thermally driven hydrogen compression utilising MH is particularly promising due to several other advantages including absence of moving parts, simplicity in design and operation, high purity of the delivered hydrogen [26,27].

There is a number of existing or recently completed projects worldwide related to the implementation of MH compressors for different applications. Typical examples include the EU-funded ATLAS-H2 [28], ATLAS-MHC [29], COSMHYC and COSMHYC XL [30] projects. Another example is a US DoE funded project aimed at the development of MH compressor for high-pressure ( $>875$  bar) hydrogen delivery to refuel fuel cell powered vehicles [31]. The companies and institutions involved in the development of industrial-scale MH hydrogen compressors include HYSTORSYS AS (Norway, <http://hystorsys.no/>), HYSTORE Technologies Ltd. (Cyprus, <https://www.hystoretechnologies.com/>), South African Institute for

<sup>1</sup> These values represent typical hydrogen storage capacities of individual MH containers. Due to modular design of MH hydrogen storage tanks, they can be built as several containers connected in parallel thus providing the required amount of the stored H<sub>2</sub>. For example, a 7 Nm<sup>3</sup> H<sub>2</sub> MH hydrogen storage tank used in Refs. [13] comprises of seven MH containers, 1 Nm<sup>3</sup> H<sub>2</sub> each.

Advanced Materials Chemistry (<https://www.uwc.ac.za/Faculties/NS/SAIAMC/>) and HySA Systems Centre of Competence (<http://hysasystems.com/>), both hosted by the University of the Western Cape (South Africa), as well as SKTBE OAO (Russia, <https://intelhim.ru/>).

In this work, we summarise our results of development of integrated energy storage systems utilising metal hydride hydrogen storage and compression, as well as their metal hydride based components.

## Metal hydride materials

Selection criteria of metal hydride materials for hydrogen storage and compression applications depend on a number of factors. First of all, the processes of hydride formation and decomposition must be reversible in the range of operating temperatures and hydrogen pressures specific for the application.<sup>2</sup> Secondly, the material has to have high reversible hydrogen storage capacity at the operating conditions. These properties are determined by pressure – composition – temperature (PCT) characteristics in the systems of H<sub>2</sub> gas with hydride-forming materials when the reversible capacity is associated with plateau width on the pressure – composition isotherm and the process direction (hydrogenation/H<sub>2</sub> uptake or dehydrogenation/H<sub>2</sub> release) depends on the relation between the actual H<sub>2</sub> pressure and the plateau pressure at the actual temperature [26,32]. Plateau slope and hysteresis specific to the PCT behaviour of most of the real systems are very important for hydrogen compression applications since they result in the significant decrease of the compression ratio [26] and process efficiency [33] achieved in the given temperature range.

Other important properties of the MH materials for hydrogen storage and compression include fast hydrogen absorption and desorption kinetics, tolerance to poisoning with impurities in the feed H<sub>2</sub>, easy activation, cyclic stability, low cost and ease of the manufacturing [26,32].

Table 1 presents summary of hydrogen storage performances of various metal hydride materials used in hydrogen storage and compression systems. The typical values were taken from previously published data analysed by the authors [7,15,26,34–41].

As it can be seen, most commonly used “low-temperature” intermetallic hydrides are characterised by weight hydrogen storage density between 1.5 and 1.9 wt%, while the use of BCC solid solution alloys on the basis of Ti–Cr–V system allows to reach H storage capacity up to ~2.5 wt%; the latter materials, as well as some AB<sub>2</sub>-type intermetallics, can be used in “hybrid” hydrogen storage systems charged with H<sub>2</sub> gas at high pressures and subzero temperatures [36,38]. Hydrogen storage materials on the basis of MgH<sub>2</sub> are characterised by significantly higher weight hydrogen storage densities but require high operating temperatures that limits their application by only several cases when the high-temperature heat source, e.g. SOFC [22,23], is available.

<sup>2</sup> We do not consider hydrogen storage systems with off-board regeneration of the hydrogen storage material.

**Table 1 – Summary on performances of metal hydride materials for hydrogen storage and compression systems.**

Parameter [units]	Typical range/value				
	AB <sub>5</sub>	AB <sub>2</sub>	AB <sup>a</sup>	BCC-Ti–Cr–V	MgH <sub>2</sub> <sup>b</sup>
Operating temperatures [°C]	0 to 200	–50 to 150	0 to 100	–20 to 30	250 to 400
Operating H <sub>2</sub> pressures [atm]	0.1 to 500	1 to >1000	1 to 30	10 to 300	1 to 20
Gravimetric hydrogen storage density [wt.%]	1.50	1.90	1.75	2.5	5.5 to 7.5
Volumetric hydrogen storage density [kg/L]	Material	0.10	0.09	0.11	0.11
	System <sup>c</sup>	0.063	0.055	0.069	0.066

<sup>a</sup> TiFe and related intermetallics.

<sup>b</sup> Including alloys and nanocomposites on the basis of Mg.

<sup>c</sup> According to the analysis of reference data presented in Ref. [35].

In spite of very high volumetric hydrogen storage density in the considered hydride materials significantly (typically by half) exceeding the density of liquid hydrogen (~0.07 kg/L), the volumetric hydrogen storage density on the system level will be lower due to the limited safe densities of filling the materials in the containment, as well as differences in the densities of the parent materials [35]. As a result, the system volumetric hydrogen storage densities will take similar (though still high) values for the different materials (last row in Table 1), and for stationary energy storage systems the material selection criteria will be mainly related to conditions and performances of their operation (e.g. pressure/temperature ranges, ease of activation, hydrogen absorption/desorption kinetics, cycle stability) rather than the hydrogen storage densities.

AB<sub>5</sub>- and AB<sub>2</sub>-type intermetallics are the most frequently used hydride materials in hydrogen storage and its supply to fuel cell systems [15], as well as in hydrogen compression applications [26]. The main reason for that is the tunability of hydrogen sorption properties of these types of materials by small variations of their composition. This gives an opportunity to align the pressure/temperature operating performances of these materials with the application conditions.

AB<sub>5</sub>-type intermetallics where A = rare earth metal (RE), B = Ni, Co, Al, Mn, Sn, etc., are characterised by easy activation, fast kinetics of hydrogen absorption and desorption, and relatively high stability of hydrogen sorption properties during cyclic hydrogenation/dehydrogenation (including the operation in H<sub>2</sub> gas containing impurities of oxygen and water vapours in moderate concentrations).

For the parent intermetallic, LaNi<sub>5</sub>, the plateau pressure is equal to 1.8 atm at T = 25 °C [32]. The plateau pressure can be decreased by the substitution of Ni with Al, Sn, Mn, Co, while the substitution of La with Ce (or Mm/mischmetal), Y, Ca results in the pressure increase [26,32,42–45]. The substitution with Sn [42], Al [43], or Ce [45] also improves stability of LaNi<sub>5</sub> towards disproportionation during prolonged pressure/temperature cycling while Ca substitution worsens the cycle stability [45].

As a rule, pressure – composition isotherms in H–AB<sub>5</sub> systems exhibit one flat plateau with not very high H<sub>2</sub> absorption-desorption hysteresis which, however, increases in the substituted alloys. As an example, for LaNi<sub>5</sub> at T = 20–25 °C, the ratio of H<sub>2</sub> absorption (P<sub>A</sub>) and desorption (P<sub>D</sub>) pressures at the H concentration corresponding to plateau midpoint is about 1.45; for La<sub>0.5</sub>Ce<sub>0.5</sub>Ni<sub>5</sub> the ratio P<sub>A</sub>/P<sub>D</sub> increases to 3.55 at the same conditions [45].

AB<sub>2</sub> type materials used for H<sub>2</sub> storage and compression are C14 (less frequently, C15 and C36) Laves phase intermetallic

compounds mostly formed by Ti and Zr as A component, and B component is usually represented by several transition metals including Mn, Cr, Fe, V, etc. AB<sub>2+x</sub> intermetallics are even more flexible than AB<sub>5</sub>'s in the tuning of their PCT properties by the variation of the composition [26,46,47]. The equilibrium H<sub>2</sub> desorption pressures for hydrides of the AB<sub>2</sub>-type alloys cover practically unlimited range: from ~3·10<sup>–3</sup> atm at T = 227 °C for ZrV<sub>2</sub> (calculated from the values ΔS° = –88.4 J/(mol H<sub>2</sub>K), ΔH° = –78 kJ/mol H<sub>2</sub> [48]) to >5000 atm at the room temperature for TiFe<sub>2</sub> (calculated in Ref. [49]). The thermal stability of the hydrides (the absolute value of their formation enthalpy, |ΔH°|) can be increased by the increase of Zr:Ti atomic ratio from the A-side and/or by introducing V as one of the B-components. Conversely, the AB<sub>2</sub> hydride stability can be decreased by the decrease of the Zr:Ti ratio, decrease of V content or its elimination, increase of Fe content, as well as increase of stoichiometric B:A ratio. The balancing between the content of other components (e.g. Cr and Mn) allows to further modify the PCT properties [46,47,50,51]. Usually H–AB<sub>2</sub> interaction is characterised by a sloping plateau on the pressure – composition isotherms and small hysteresis, with values of P<sub>A</sub>/P<sub>D</sub> at T = 20–25 °C in the plateau midpoint ranging from 1.14 to 1.46, even in the multi-component alloys when A = Ti<sub>x</sub>Zr<sub>1–x</sub> (x = 0.15–0.85) and B is a mixture of 4–5 transition metals including Cr, Mn, Ni, Fe and V [47,52].

The AB<sub>2</sub>-type alloys are generally less easy activated than AB<sub>5</sub> ones, and for facilitation of their activation they can be doped by small amounts (~1 at%) of rare earth elements [53]. Once activated, they exhibit excellent hydrogenation/dehydrogenation kinetics and a good cycle stability [32,54]. Their components are less expensive than the ones used for the making of RE-based AB<sub>5</sub>'s, but manufacturing of the AB<sub>2</sub>-type alloys experiences some metallurgical difficulties due to higher melting temperatures, high reactivity of the components and other factors [32,55]. When activated, the AB<sub>2</sub>-type alloys, particularly those ones which contain Zr and Mn, are highly pyrophoric; these materials are also more sensitive to impurities in H<sub>2</sub> than AB<sub>5</sub>'s [32].

The La<sub>1–x</sub>RE<sub>x</sub>Ni<sub>5</sub> (RE = Ce, Mm) and Ti<sub>1–x</sub>Zr<sub>x</sub>(Mn,Cr,Fe,V,Ni)<sub>2</sub> intermetallics were used by the authors in a number of MH hydrogen storage systems operating at near-ambient temperatures and hydrogen pressures above 1 atm, as well as for thermally-driven H<sub>2</sub> compression from 3 to 35 to 100–150 atm (AB<sub>5</sub>) and from 50 to 100 to 200–500 atm (AB<sub>2</sub>) at T = 15–150 °C (will be discussed in Sections [Hydrogen storage](#) and [Hydrogen compression](#) below).

For the determination of hydrogen concentrations in the studied materials at variable temperatures and H<sub>2</sub> pressures, we applied earlier developed model of phase equilibria in metal – hydrogen systems [56]. Within this model, the pressure – composition isotherms were constructed as pseudo-convolutions of an “ideal” isotherm built according to the model of van der Waals lattice gas (hydrogen – metal phase diagram), with two modified asymmetric pseudo Voight distribution functions (one for H desorption and another for H absorption) modelling plateau slope and hysteresis. In doing so, the median of the absorption distribution was shifted from the one of the desorption distribution towards higher pressures, by the value related to a minimum of a hysteresis free energy loss and an excessive chemical potential of hydrogen in over-saturated  $\alpha$ -solid solution. According to the model, the PCT diagram as a whole is described by a set of parameters (16 per a plateau segment) some of which (e.g. critical temperature, hysteresis energy loss, enthalpy and entropy of hydride formation) have a clear physical sense and others, describing temperature- and concentration-dependent plateau slope, are semi-empirical.

Table 2 presents characteristics of the studied MH materials including hydrogen absorption capacities at the room temperature (20 °C) and the specified H<sub>2</sub> pressures, as well as temperatures which correspond to the specified plateau pressures of H<sub>2</sub> desorption at H concentrations which correspond to the plateau midpoint. The presented values were calculated from hydrogen absorption and desorption isotherms for the specified materials built at different temperatures using the authors’ experimental PCT data further processed by the model [56]; so as the fitted model parameters allowed to build the isotherm at any selected temperature.

As it can be seen from Table 2, the AB<sub>5</sub>-type materials with different Ce/La ratios and AB<sub>2</sub>-type ones with different Zr/Ti ratios (both from the A side) allow to develop on their basis various hydrogen storage and compression systems operating in various ranges of temperatures and H<sub>2</sub> pressures. However, the presented data do not allow to estimate the useable hydrogen storage capacities for the hydrogen storage, as well as cycle productivities of the hydrogen compressors. These estimations can also be derived from the PCT diagrams of the used MH materials and will be presented in the next sections. The calculations of reversible hydrogen storage capacities or the materials assumed to be close to the useable hydrogen storage capacities of hydrogen storage systems (Section Hydrogen storage) or cycle productivities of H<sub>2</sub> compressors (Section Hydrogen compression), were carried out similarly, from the modelled hydrogen absorption (ABS) and desorption (DES) isotherms (see example in Fig. 1 (D)).

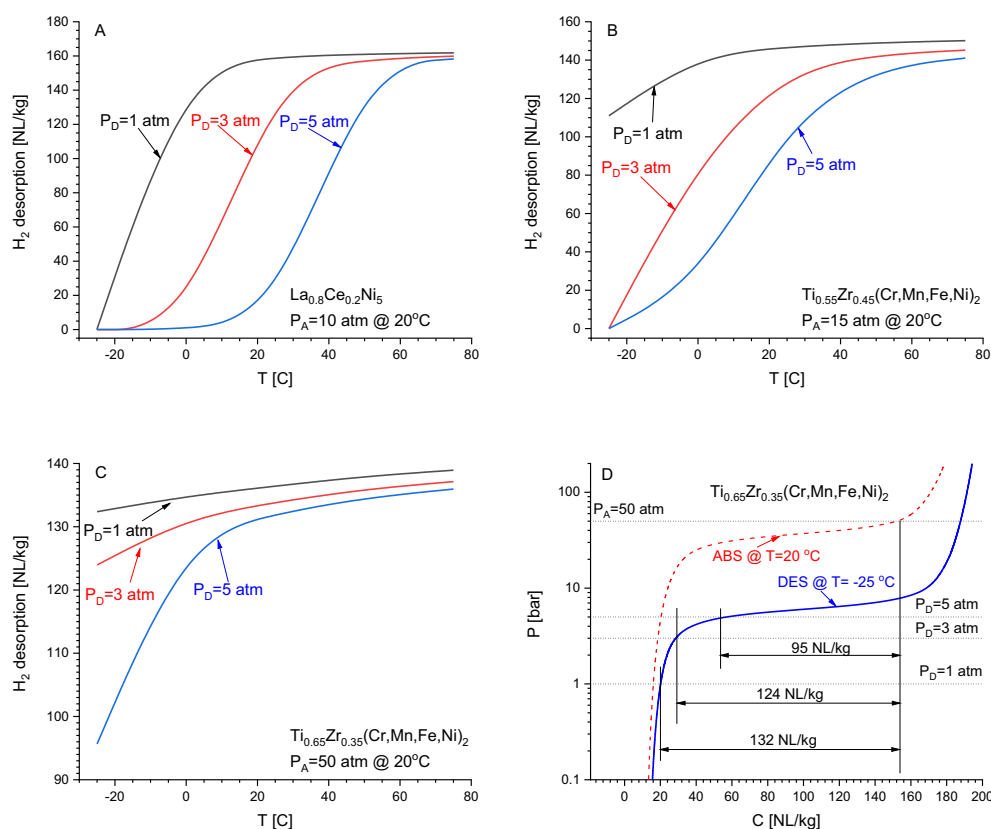
## Hydrogen storage

Fig. 1(A–C) shows the useable (reversible) hydrogen storage capacities for AB<sub>5</sub>- and AB<sub>2</sub>-type materials in the hydrogen storage systems which were developed at the author’s institutions.

When charged with H<sub>2</sub> at T = 20 °C and the pressure corresponding to the end of H absorption plateau on the pressure – composition isotherm, all the materials allow to use ~90% of

**Table 2 – Characteristics of metal hydride materials used by ICP and HysA Systems in the developed hydrogen storage and compression systems.**

Characteristic [unit]	MH material					
	LaNi <sub>5</sub>	La <sub>0.8</sub> Ce <sub>0.2</sub> Ni <sub>5</sub>	La <sub>0.5</sub> Ce <sub>0.5</sub> Ni <sub>5</sub>	Ti <sub>0.55</sub> Zr <sub>0.45</sub> (Cr,Mn,Fe,Ni) <sub>2</sub>	Ti <sub>0.65</sub> Zr <sub>0.35</sub> (Cr,Mn,Fe,Ni) <sub>2</sub>	
H <sub>2</sub> absorption at T=20 °C	Pressure [atm]	10	10	40	15	50
	Full H absorption capacity [NL/kg]	158	165	129	158	153
H <sub>2</sub> desorption temperature [°C] at the plateau pressure [atm] of:	1	18	-8	-30	-34	-60
	10	77	52	24	42	-10
	100	168	145	111	196	70
200	206	186	150	281	105	



**Fig. 1 – A–C: amounts of desorbed H<sub>2</sub> (useable H storage capacity) for some AB<sub>5</sub>- and AB<sub>2</sub>-type materials as functions of operating temperature at different H<sub>2</sub> desorption pressures (P<sub>D</sub>); H<sub>2</sub> absorption pressures (P<sub>A</sub>) are specified in the graphs. D: Example of determination of the amounts of the desorbed H<sub>2</sub> for Ti<sub>0.65</sub>Zr<sub>0.35</sub>(Cr,Mn,Fe,Ni)<sub>2</sub> (C) at T = –25 °C.**

their full capacity at T = 50 °C and P(H<sub>2</sub>) = 5 atm that is enough to supply hydrogen to low-temperature PEM FC stack using the heat released during its operation for the heating of the MH bed [15]. Moreover, most of the MH materials are able to desorb H<sub>2</sub> at pressures above atmospheric and subzero temperatures (Fig. 1(D)) thus making it possible to start-up the FC power system even during winter time.

It has to be noted that the useable hydrogen storage capacities of MH materials shown in Fig. 1 are the maximum theoretical values. Real amounts of H<sub>2</sub> supplied from the MH to the FC stack also depend on the hydrogen supply flow rate and, in turn, the stack power. At the high rate, the endothermic H<sub>2</sub> desorption results in the cooling the MH bed thus slowing the H<sub>2</sub> release down. As a result, the useable H<sub>2</sub> capacity of the MH at a specified rate of H<sub>2</sub> desorption/stack power will decrease; this effect can be minimised by the improvement of the heat exchange between the MH and the heating fluid, as well as by other engineering solutions [12].

Table 3 summarises performances of several metal hydride hydrogen storage units for hydrogen energy storage systems developed at the Institute of Problems of Chemical Physics of Russian Academy of Sciences (IPCP) and "Hydrogen South Africa" System Integration and Technology Validation Centre of Competence (HySA Systems). The units use MH materials on the basis of La<sub>1-x</sub>RE<sub>x</sub>Ni<sub>5</sub> (RE = Ce, Mm) and multicomponent AB<sub>2</sub>-type alloys (A = Ti + Zr) characterised by H<sub>2</sub> equilibrium desorption pressures from 2.2 to 40 atm at the room temperature and can supply H<sub>2</sub> to PEM FC stacks, 1–15 kW in

the nominal power. The tanks number 1, 2 and 5 utilising more stable MH materials can be charged directly from a PEM electrolyser with H<sub>2</sub> output pressure 15–20 atm while for the tanks number 3 and 4 the feed H<sub>2</sub> should be compressed to 50 atm or higher, if a fast H<sub>2</sub> charge is necessary.

The units developed by IPCP (number 1–3; Fig. 2) use standard composite cylinders (carbon- or glass-fibre wound stainless steel liner) as a containment heated and cooled from the outside by natural air convection or flow of heating/cooling liquid; in the latter case the containment is enveloped in a stainless steel heating/cooling jacket. This solution is lightweight, simple and inexpensive but it is characterised by a poor heat exchange between the MH and the heating/cooling fluid that results in rather slow H<sub>2</sub> charge and discharge.

The HySA Systems MH tanks (number 4, 5) use multiple MH containers, ~40 mm in internal diameter, equipped with inner copper fins (see Fig. 3 (A)) and heated/cooled from the outside. Additionally, a small amount of expanded natural graphite was added to the MH powder that allowed to increase the safe MH filling density<sup>3</sup> and to further improve the heat transfer in the MH

<sup>3</sup> The limitation of the filling density is necessary to avoid appearance of stresses in the container walls due to expansion of the MH material upon hydrogenation. As a rule, the filling density of MH powders into HySA Systems containers for hydrogen storage and compression was about 55% of the density of the material in the hydrogenated state. The maximum safe limit of the filling density was reported as 61% (50% typically applied) [57].

**Table 3 – Performances of some metal hydride hydrogen storage units developed at IPCP and HySA Systems.**

Characteristic	Developer/Number of the unit (with reference to figure)			HySA Systems	
	1 (Fig. 2 (A))	2 (Fig. 2 (B))	3 (Fig. 2 (C))		4 (Fig. 3 (B))
Useable H <sub>2</sub> storage capacity [Nm <sup>3</sup> ]	0.5	3.5	6.0	10.0	20.0
MH material	La <sub>0.8</sub> Ce <sub>0.2</sub> Ni <sub>5</sub>	La <sub>0.8</sub> Ce <sub>0.2</sub> Ni <sub>5</sub>	La <sub>0.5</sub> Mm <sub>0.5</sub> Ni <sub>5</sub>	Ti <sub>0.65</sub> Zr <sub>0.35</sub> (Cr,Mn,Fe,Ni) <sub>2</sub>	Ti <sub>0.55</sub> Zr <sub>0.45</sub> (Cr,Mn,Fe,Ni) <sub>2</sub>
Features	Composite containment, external heating/cooling.	Composite containment, external heating/cooling.	Composite containment, external heating/cooling.	Stainless steel containment with inner finning, external heating/cooling.	Stainless steel containment with inner finning, external heating/cooling.
H <sub>2</sub> charge pressure [atm]	15–20	30	50–100	>50 (150–180) <sup>a</sup>	>15 (100–150) <sup>a</sup>
H <sub>2</sub> discharge pressure [atm]	>1.2	≥3	≥5	≥13	≥1.3
H <sub>2</sub> discharge flow rate [NL/min]	1.1	≤25	≤40	≤170	≤170
Operating temperature range [°C]	0–30 (environment)	0–80	0–90	0–60	0–60
Volume [dm <sup>3</sup> ]	1 (1 x 1 L cylinder)	7 (1 x 7 L cylinder)	70 (5 x 2 L cylinders + case)	80 (20 containers + water tank)	160 (40 containers + heat exchanger + encasing)
Weight [kg]	4.6	28	45	184	350/1200 <sup>b</sup>

<sup>a</sup> To achieve short refuelling time (10–15 min) at the ambient temperature (25–30 °C).

<sup>b</sup> For the lead-encased MH containers.

bed. Though this solution is more labour-consuming and expensive, it allowed to significantly increase H<sub>2</sub> supply rate to the fuel cell stack whose cooling system is thermally coupled with the heating system of the MH tank. A significant increase of the tank weight associated with the heat transfer improvements is not an issue for the stationary and even some special mobile applications. For example, in the HySA Systems MH tank (number 5; Fig. 3(C)) initially designed for hydrogen storage on-board fuel cell forklift, the weight was even intentionally increased by encasing the MH containers in lead to provide counterbalance weight necessary for the safe forklift operation [58].

## Hydrogen compression

When hydrogen energy storage system stores hydrogen in compressed gas cylinders or in metal hydrides whose equilibrium H<sub>2</sub> absorption pressure at the operating temperature for H<sub>2</sub> charge exceeds H<sub>2</sub> pressure provided by electrolyser, hydrogen compression is necessary. As it was mentioned in the Introduction, the use of MH for the H<sub>2</sub> compression brings a number of benefits including the increase of the overall system efficiency by the use of waste heat released during operation of the electrolyser.

Fig. 4(A–E) presents dependencies of cycle productivities of MH compression on the suction (P<sub>L</sub>) and discharge (P<sub>H</sub>) pressures, at the cooling temperature T<sub>L</sub> = 20 °C and heating temperature T<sub>H</sub> = 150 °C. The graphs similar to the ones presented in the review on MH H<sub>2</sub> compressors (see Refs. [26], Fig. 4) were built from the calculated isotherms (see Section [Metal hydride materials](#) for the details) for H<sub>2</sub> absorption at T<sub>L</sub> and H<sub>2</sub> desorption at T<sub>H</sub> (see example in Fig. 4(F)).

As it was shown in Refs. [26], if P<sub>L</sub> exceeds the plateau pressure at T = T<sub>L</sub>, very high compression ratios, P<sub>H</sub>/P<sub>L</sub>, can be achieved even for quite stable MH, though at low cycle productivities; and at P<sub>H</sub>/P<sub>L</sub> below ~5 the cycle productivity exceeds ~70% of the full capacity of the MH material (see examples in Fig. 4). As it can be seen from Fig. 4(A–C), at T<sub>L</sub> = 20 °C and T<sub>H</sub> = 150 °C and the target cycle productivity of 100 NL/kg, LaNi<sub>5</sub> can provide H<sub>2</sub> compression from 3 to 25 atm, La<sub>0.8</sub>Ce<sub>0.2</sub>Ni<sub>5</sub> from 10 to 100 atm, and La<sub>0.5</sub>Ce<sub>0.5</sub>Ni<sub>5</sub> from 40 to 170 atm. For the AB<sub>2</sub>-type H<sub>2</sub> compression alloys (Fig. 4(D and E)), the corresponding ranges of the operating pressures (P<sub>L</sub>–P<sub>H</sub>) are 50–270 and 70–350 atm, for Ti<sub>0.65</sub>Zr<sub>0.35</sub>(Cr,Mn,Fe,Ni)<sub>2</sub> and Ti<sub>0.7</sub>Zr<sub>0.3</sub>(Cr,Mn,Fe,Ni)<sub>2</sub>, respectively. Note that the values specified above are only estimations based on the analysis of PCT data for the MH materials and can vary depending on the design features of the MH compressors and their operating conditions. However, for the properly designed compressor the deviations are not very high. For example, for the two-stage compressor TSC2-3.5/150 (T<sub>L</sub> = 15 °C, T<sub>H</sub> = 150 °C, 15 Nm<sup>3</sup>/h) developed by Russian company SKTBE under IPCP supervision, the cycle productivity of the first stage (LaNi<sub>5</sub>, P<sub>L</sub> = 3.5 atm, P<sub>H</sub> ~ 35 atm) was about 75 NL/kg, and for the second stage (La<sub>0.5</sub>Ce<sub>0.5</sub>Ni<sub>5</sub>, P<sub>L</sub> ~ 35 atm, P<sub>H</sub> = 150 atm) about 100 NL/kg, taking into account cycle time 38 min and three H<sub>2</sub> compression sections in the compressor [27].

A summary of features and performances of MH hydrogen compressors for hydrogen energy storage systems developed

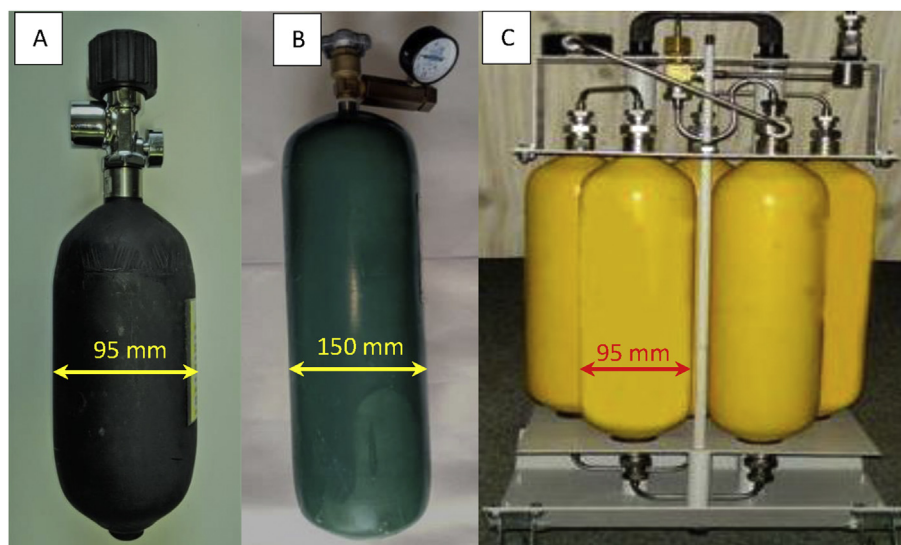


Fig. 2 – Examples of MH H<sub>2</sub> storage tanks with storage capacity of 0.5 (A), 3.5 (B) and 6 (C) Nm<sup>3</sup> H<sub>2</sub> developed at IPCP.

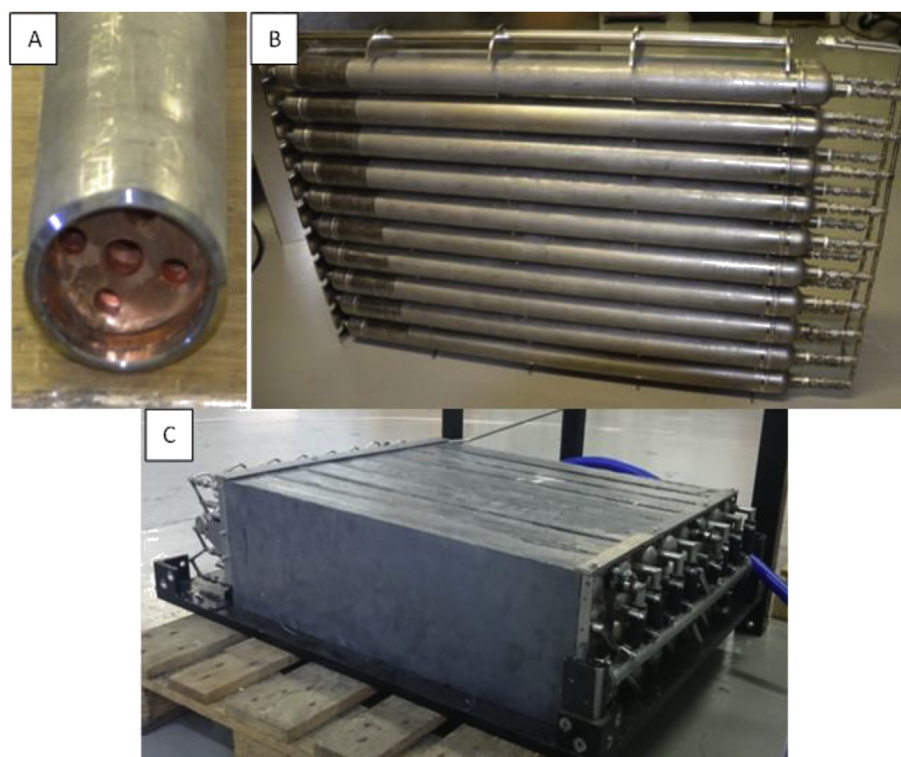


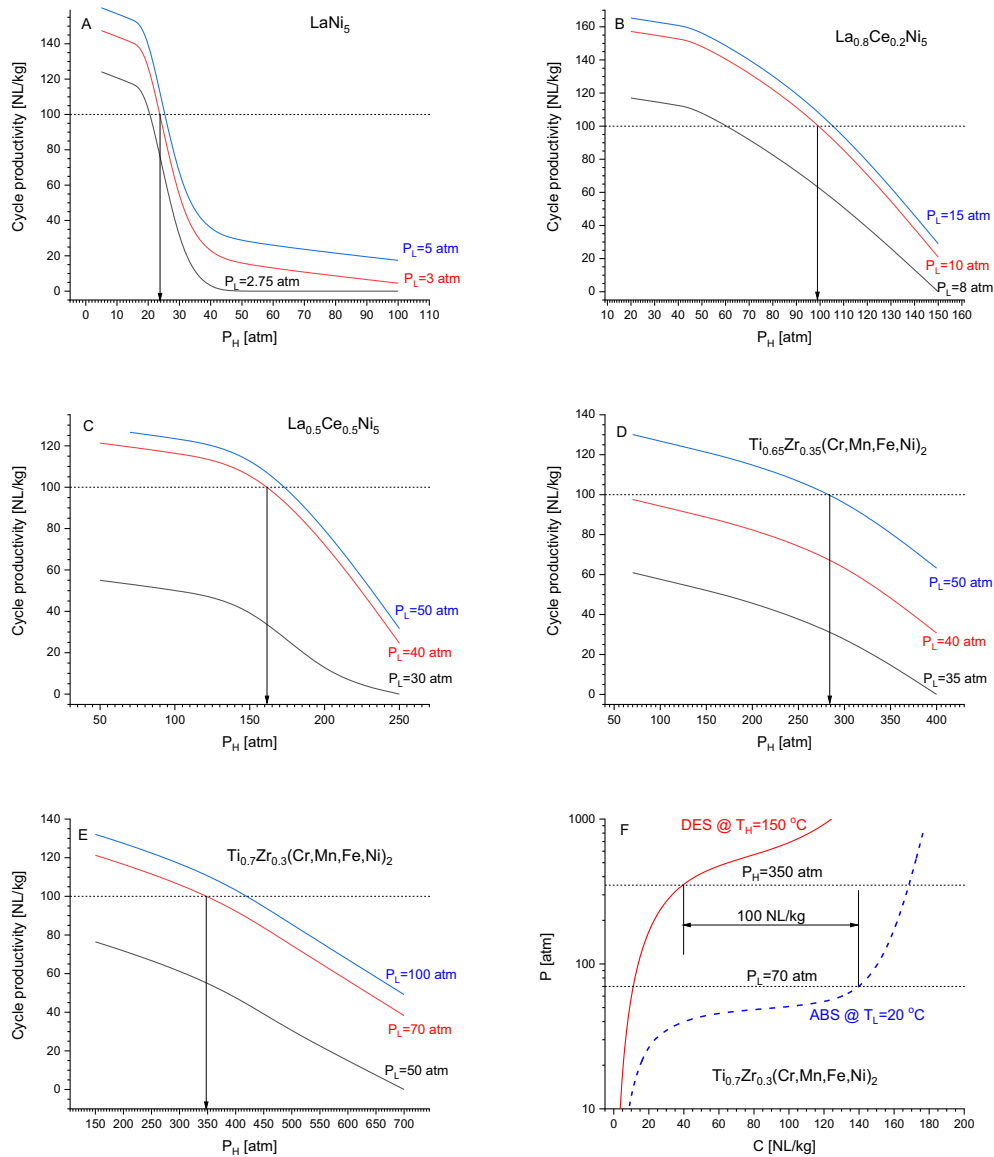
Fig. 3 – Inner layout of HySA Systems MH container for H<sub>2</sub> storage (A), assembly of the containers in 10 Nm<sup>3</sup> (B) and 20 Nm<sup>3</sup> H<sub>2</sub> (C) storage tanks.

under the authors' supervision has been presented in Ref. [27], as well as in a review [59] and references therein.

### System integration

Table 4 presents main features and performances of two integrated hydrogen energy storage systems developed under supervision of IPCP (number 1) and HySA Systems (number 2).

Both systems use gas cylinder packs as main and MH hydrogen storage units as auxiliary hydrogen storage facilities. The gas cylinder pack is filled with MH compressor during system operation. The MH units can be charged either from the output of the electrolyser (see example for system number 2 in Fig. 5) or, if the output pressure is not high enough (system number 1), from the discharge line of the compressor via reducer. When charged, the smaller-scale MH units can be moved to other premises where H<sub>2</sub> consuming fuel cell stacks



**Fig. 4 – A–E:** cycle productivities of MH hydrogen compressors for AB<sub>5</sub>- and AB<sub>2</sub>-type materials used in MH H<sub>2</sub> compressors developed at IPCP and HySA Systems as functions of suction ( $P_L$ ) and discharge ( $P_H$ ) pressures at  $T_L = 20$  °C and  $T_H = 150$  °C. **F:** Example of determination of the cycle productivity for  $Ti_{0.7}Zr_{0.3}(Cr,Mn,Fe,Ni)_2$  (E). The values of  $P_H$  are shown in X-axes while the values of  $P_L$  – as curve labels.

are installed. Alternatively, the bigger MH tanks (e.g. number 4, 5 in Table 3) can be permanently connected to a line supplying hydrogen to the fuel cell stacks. These tanks can also be used as buffers between the output of the electrolyser and the input of the MH compressor (Fig. 5).

System number 2 (HySA Systems; see Fig. 5) provides SAIAMC research facilities with hydrogen from H<sub>2</sub> cylinder pack equipped with a gas distributing system connected to three pipelines for H<sub>2</sub> supply to (i) fuel cell testing stations (10 atm), (ii) other experimental facilities consuming medium-pressure hydrogen (80 atm) and (iii) hydrogen dispensing (30–200 atm) for the refuelling of fuel cell vehicle prototypes (e.g. forklifts).

Though a big number of the integrated energy systems “electrolyser – metal hydride – fuel cell” has been developed

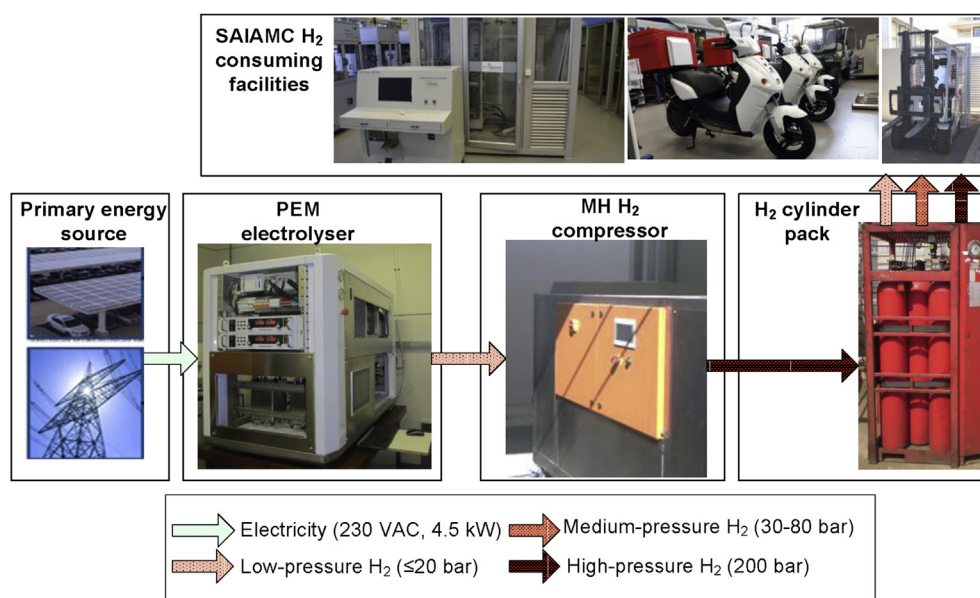
up to date, they mainly used metal hydrides for hydrogen storage (see e.g. Refs. [10,13,14,16,19]). As to the authors’ knowledge, there exists one development related to the integration of the MH compressor in a hydrogen-based power system undertaken under support of EU-funded ATLAS-MHC project [60]. The corresponding development of a prototype MH compressor for this application including techno-economic forecast was reported in Ref. [61]; a brief performance summary for the prototype was presented in the review [59]. The compressor developed by HYSTORE Technologies Ltd. (Cyprus) provides H<sub>2</sub> compression from 7 to 220 atm with a productivity up to 2.5 Nm<sup>3</sup>/h that is close to the characteristics of the MH compressor integrated in HySA Systems hydrogen production, storage and distribution system (number 2 in Table 4, Fig. 5). The advantage of the



**Table 4 – Integrated energy storage systems developed under supervision of IPCP and HySA Systems.**

Features, main components		Number/developer	
		1/IPCP [27]	2/HySA Systems (Fig. 5)
Primary energy source		Grid, solar panels, wind turbine (25 kW)	Grid, solar panels (4.5 kW)
Electrolyser	Type	Alkaline	PEM
	Power [kW]	23	4.3
	H <sub>2</sub> output pressure [atm]	4	≤20
	H <sub>2</sub> output flow rate [Nm <sup>3</sup> /h]	15	2
H <sub>2</sub> storage	Type	Gas cylinders <sup>a</sup> + MH	Gas cylinders <sup>a</sup>
	H <sub>2</sub> charge pressure [atm]	Gas cylinders: 150 MH units: 30–100	Gas cylinders: 200 MH unit: 15–20
	H <sub>2</sub> supply pressure [atm]	Gas cylinders: up to 150 MH units: 2–5	10 (FC stacks test stations) 80 (other H <sub>2</sub> consuming facilities) 30–200 (FCV refuelling)
	Capacity [Nm <sup>3</sup> ]	Gas cylinders: 72 MH tanks: 3.5–6	Gas cylinders: 180 MH tank: 20
	H <sub>2</sub> supply flow rate [NL/min]	Gas cylinders: unlimited MH units: 20–40	Gas cylinders: unlimited MH unit: up to 170
	MH H <sub>2</sub> compressor	Pressure range [atm]	3.5–150
	Temperature range [°C]	15–160	20–130
	Productivity [Nm <sup>3</sup> /h]	15	5
Hydrogen consumer		Various PEM FC stacks (1–10 kW)	PEM FC stacks test stations (up to 30 kW) FCV refuelling

<sup>a</sup> The gas cylinders of standard size (50 dm<sup>3</sup> in the volume) connected in parallel (up to 18 per a pack).



**Fig. 5 – Schematic representation of hydrogen production, storage and distribution system at HySA Systems/South African Institute for Advanced Materials Chemistry (SAIAMC) research facility. Additional details about the system components are presented in Table 4 (number 2).**

HYSTORE compressor is in the narrow range of the operating temperatures (10–80 °C) that allows to use simple and inexpensive source of heat (e.g. solar collectors) to drive H<sub>2</sub> compression. This advantage, however, has been achieved at the expense of the increase of number of stages (up to six) that is known to be detrimental from thermodynamic efficiency and reliability points of view [26]. Conversely, the MH compressors integrated in the operating energy storage systems presented in this study use two- (IPCP) and three-stage (HySA Systems) layouts. The problem of availability of heat with

rather high temperature potential (130–160 °C) necessary for these developments can be solved by appropriate heat management solutions, that is a subject for future studies.

## Conclusions

Metal hydride hydrogen storage and compression technologies have been shown to be efficient in small-to-medium scale energy storage systems. The approach for selection of AB<sub>5</sub>-

and AB<sub>2</sub>-type metal hydride materials for MH based hydrogen storage and compression systems developed in this work has been outlined. The approach is based on the analysis of PCT properties of the materials and takes into account useable H<sub>2</sub> capacity for hydrogen storage or cycle productivity for H<sub>2</sub> compression depending on temperatures and pressures of H<sub>2</sub> absorption and desorption.

Two medium-scale energy storage systems developed under supervision of IPCP and HySA Systems have been demonstrated. The systems can use various primary sources of electricity (grid, solar panels, wind turbine) for hydrogen production by water electrolysis. The produced low-pressure hydrogen is compressed by metal hydride hydrogen compressor and supplied to gas cylinder packs (150–200 atm) as main hydrogen storage facilities. Additionally, hydrogen is collected and stored at the pressure below 100 atm in metal hydride hydrogen storage units. Both hydrogen storage facilities supply hydrogen to PEM fuel cell stacks, up to 30 kW in the electric power; the high pressure cylinder packs can also supply hydrogen for the refuelling of fuel cell vehicles and for other needs.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgements

Russian co-authors are grateful to the Ministry of Science and Higher Education for the financial support (Agreement No. 05.574.21.0209, Unique identifier RFMEFI57418X0209).

SC, SP and ML acknowledge financial support of Department of Science and Innovation (DSI) of South Africa within Hydrogen South Africa (HySA) Program, HySA Systems projects KP6–S01 and KP6–S02. ML also acknowledges support of South African National Research Foundation (NRF), grant number 109092.

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