



Research papers

Gas-phase applications of metal hydrides

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ABSTRACT

Applications of metal hydrides (MHs) utilise a reversible interaction of hydride-forming metals, alloys and intermetallic compounds with hydrogen. The reversible process of the formation-decomposition of the MH when interacting with hydrogen allows to utilise several unique features of the hydrogenation-dehydrogenation process. These features enable efficient storage of hydrogen gas resulting in a high volumetric efficiency of hydrogen storage while also storing thermal energy and converting it to the energy of compressed hydrogen gas or utilising the hydrides for the electrochemical energy conversion and storage. Thus, MH applications are very important as the components of the hydrogen energy systems integrating hydrogen supply from the metal hydride store and PEM fuel cells. Compact and safe hydrogen storage together with utilisation of the waste heat opens up for the commercial market of the hydrogen energy systems of green energy storage and supply.

1. Introduction: historical outlook

The revolutionary discovery in 1866 by Thomas Graham of the ability of palladium metal to reversibly absorb significant amounts of hydrogen [1,2] resulted in several practical applications of this phenomenon. Later a similar behaviour was observed for several other metals [3], and unique properties of the “metal – hydrogen” systems became a subject of numerous detailed studies. As mentioned by Sandrock in his published 30 years ago review [4], during the early period of the studies of metal hydrides, already in 1866–1946, there were published around 1500 works on the topic “Hydrogen in Metals”. Later, the intensity of research in this field steadily increased until discovery of the hydrides of intermetallic compounds (ZrNiH₃, Libowitz et al., 1958 [5]; LaNi₅H_{6.7}, Philips Research Laboratories, 1970s [6]) which initiated a dramatic growth of the R&D activities in the field. The well-known IEA/DOE/SNL hydride database [7,8] includes 2706 records on (pseudo)binary, intermetallic and complex hydrides published in 1616 references, while 373 records are related to the hydride applications, even though systematic introduction of new entries was discontinued in the first decade of 2000s. Thus, the authors who compiled this database [7] were well aware that the collected information is incomplete.

The volume and variety of the metal hydride-related activities evaluated when using Scopus database (Fig. 1) are very significant.

Since 1918 until January 2023, 11,591 relevant publications have been published of which >20 % (2465 entries for 1924–2023) are based on the applications of these materials. Since 1950s, the metal hydride publication activities exhibit exponential growth. Similar growth of the applications of the metal hydrides is now taking place, even though being less intense while starting after a gap of two decades.

The first comprehensive monograph [3] describing the applications of the metal hydrides was published in 1968 and focused on binary hydrides for nuclear technologies. Besides, the monograph also considered various applied aspects including use of metal hydrides as laboratory sources of pure hydrogen, preparation of the fine metal powders and metal foams, deposition of coatings, creating ceramic – metal junctions, as well as considering hydrogen embrittlement issues.

An important milestone in the development of the metal hydride applications was achieved in 1970s. As already mentioned, that time was characterised by a rapid growth of the research of newly discovered intermetallic hydrides characterised by reversible and very fast formation/decomposition at near-ambient conditions. Apart from the fundamental studies, this resulted in the development of prototypes of hydrogen storage and compression systems on the basis of intermetallic hydrides [9]. During the same time, a new concept of hydrogen energy systems suggesting transition of energy supply, industry and transport to use of hydrogen as an energy carrier appeared being catalysed by the

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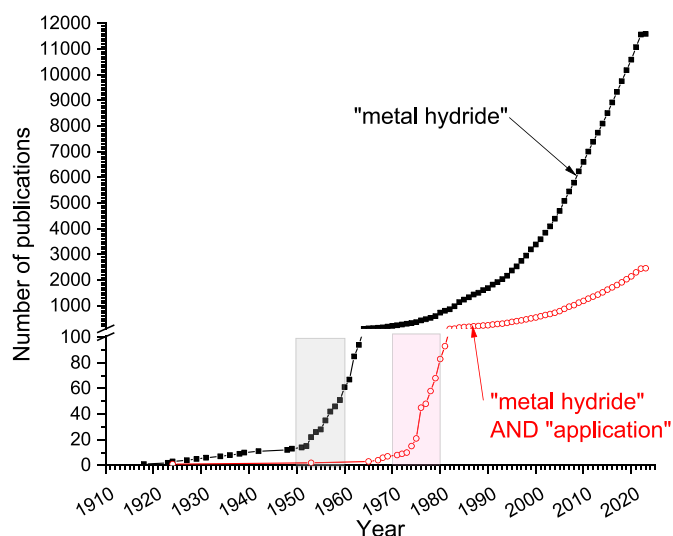


Fig. 1. Cumulative number of Scopus-indexed publications on metal hydrides and their applications. The search topics included the fields “Article Title”, “Abstract” and “Keywords”. The shaded areas correspond to the beginning of the exponential growth. Retrieved on 11 January 2023.

global oil supply crisis. Metal hydride technologies related to the development of compact and safe hydrogen storage systems were one of the key focus areas in this concept [10]. The time interval 1975–1990 was characterised by in-depth fundamental research, and a large number of the works on the topic were published worldwide. These studies were reviewed by Buschow, Bouten and Miedema [11], Lynch and Snape [12], Reilly and Wiswall [13,14], Buchner [15], Podgorny [16,17], and many others. The applications covered hydrogen storage, purification and extraction of hydrogen from the gas mixtures, thermal-sorption compression of hydrogen together with its supply at controlled required pressures. Some works (e.g., [17]) demonstrated an advantage of combining several working functions in a unified multipurpose metal hydride apparatus that allows to benefit from the advantages of the metal hydride technologies against the alternative available technology solutions. Various potential consumers spanned among power engineering, metallurgy, chemical industry, petrol refineries and other industries.

In the second half of 1980s, the changes in the world market of energy supply resulted in a decline of the growth rates in the R&D related to hydrogen energy technologies, first of all of the topic related to the broad use of metal hydrides. This was caused by economic factors related to a high market price of hydrogen as compared to the conventional energy carriers. This motivated the work towards improvements of techno-economic parameters of hydrogen production and increase of the efficiency of the processes of its utilisation. The issues of hydrogen storage were not prioritised, when compared to the focus area of joint hydrogen production and utilisation at a particular chemical plant/enterprise [18].

After the environment impact started to be seriously accounted and later prioritised from the societal considerations, the environment friendly nature of hydrogen utilisation improved profitability of the industrial processes [19]. At the same time, a broader implementation of the concept of hydrogen energy faces challenges in realising its efficient storage and transportation. Thus, various related applications of the metal hydrides including hydrogen storage, hydrogen separation and purification, and thermally driven compression of hydrogen gas attracted a significant interest of the international community of academia and industry [20–23].

Beginning of 1990s was marked by an explosive development of the metal hydrides batteries using MH as anode electrodes. Based on in-depth international fundamental and applied research, commercial

production of nickel – metal hydride (NiMH) batteries started in Japan [24]. Presently, NiMH batteries represent the most important global application of the metal hydrides. Furthermore, other applications of metal hydride technologies demonstrate a transition from the prototypes to the commercialisation. Though the speed of this process is slower than expected, the worldwide continuous growth remains stable.

In 1980s – early 2000s, there were published numerous reviews which presented R&D results on the fundamentals and applications of the metal hydrides (MH). The most significant contributions to the topic were made by Sandrock [9,25–28], Dantzer [29,30], Suda [25,31], Züttel [32–34], Bowman, Jr. [27,28,35], Latroche [36,37] and the authors of the present review [38–41]. Reviews and book chapters published during 2007–2017 covered various aspects of MH applications including; application-related properties of hydrogen storage materials [42–48], hydrogen storage using metal hydrides [49–53] and other gas-phase applications including hydrogen compression [54–57], heat management [56,58–60], hydrogen separation and purification [54,61,62], as well as electrochemical applications of MH [43,46–48,52,60] in the NiMH batteries.

Recently, several comprehensive reviews on fundamentals and applications of metal hydrides have been delivered by the International Energy Agency (IEA) expert groups (Tasks 32 “Hydrogen Based Energy Storage” and 40 “Energy Storage and Conversion based on Hydrogen”) [63–66]. Various applications of metal hydrides have been also reviewed by other research teams [67–73].

MH applications are very important for hydrogen-based energy storage and conversion technologies including hydrogen driven PEM fuel cells. They allow to combine the processes of compact and safe hydrogen storage and supply, along with the utilisation of the waste heat released during operation of other system components [52].

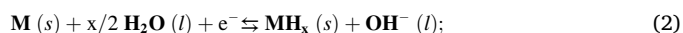
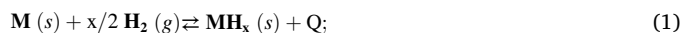
This article aims at overview of the gas-phase applications of the metal hydrides that utilise several unique features of the hydrogenation/dehydrogenation reaction and focuses on the following topics:

- Safe, compact and technologically flexible hydrogen storage.
- Thermally driven hydrogen compression.
- Efficient heat management (refrigeration, heat storage, heat upgrade and conversion) with a focus on the utilisation of the low-potential heat ($T < 160$ °C).
- Hydrogen separation and purification at near ambient conditions.
- Hydrogen getters and sources of low-pressure hydrogen and its heavy isotopes.

2. Fundamentals of the hydrogen – metal interaction

2.1. General considerations

The process of formation/decomposition of the MH involves two mechanisms. The first one (Eq. (1)) is the interaction of the parent metal/intermetallic compound with hydrogen gas while the second (Eq. (2)) is electrochemical hydrogenation of the metal (or hydride decomposition) in an electrolyte, e.g., aqueous alkaline solution:



where M is hydride-forming metal (intermetallic); Q is heat released during hydride formation or absorbed during its decomposition; the indexes s, g and l correspond to solid, gas and liquid phases, respectively. Both reactions are reversible, so it is possible to change their direction by small changes of the external conditions (temperature and hydrogen pressure for Eq. (1); electrode potential and temperature for Eq. (2)).

The principal difference between the mechanisms (1) and (2) is in the source of atomic hydrogen which is required in both Eqs. (1) and (2) and in a way this atomic hydrogen is generated either by splitting

molecular H₂ (process 1) or from water molecules (process 2).

Accordingly, the applications of MHs can be generally classified as the gas-phase (Eq. (1)) and electrochemical (Eq. (2)) ones. The latter include NiMH batteries; air – MH batteries and fuel cells and are a subject of a separate consideration [46,67,69].

The hydride formation processes taking place during the hydrogenation are schematically shown in Fig. 2. Hydrogen penetration into hydride forming metal is preceded by dissociative chemisorption of H₂ molecules on its surface followed by further diffusion of H atoms into the bulk through the interstitials in the metal matrix. It results in the formation of interstitial solid solution (α -phase) of hydrogen in the host metal. As the concentration of hydrogen in the α -solid solution increases, a phase transition is taking place in the M–H system causing the formation of hydride (β -phase) characterised by a high H/M ratio (from ~ 1 for M = Pd [74] to 3.75 for M = Th [75]) and partially (intermetallic hydrides) or completely (binary hydrides) ordered hydrogen sublattice.¹ Metal sublattice expands when accommodating H atoms, most frequently without changes in its original symmetry (see example in the mid-bottom inset).

The H – M interactions can be described by the following features:

- Fast and reversible hydrogen uptake and release take place.
- Host metal/ally matrix accommodates H atoms in the interstitial sites forming MH.
- Volume density of the accommodated H atoms by 1.5–2.0 times exceeds the value for the liquid H₂.
- The MH can be formed and decomposed within very broad ranges of the operating temperatures (from <0 to >300 °C) and hydrogen pressures (from <1 mbar to >1 kbar), as defined by the alloy's composition and structure type.
- Significant heat effects, Q, accompany the exothermic hydrogenation and endothermic decomposition of the hydride. They vary between <25 and >70 kJ/mol H₂. The Q's depend on the alloy's composition.
- Significant volume change of the host metal occurs upon the hydrogenation/dehydrogenation (dilatation effects).
- The effects associated with non-equilibrium state of the gas phase when hydrogenation/dehydrogenation reaction takes place, including high catalytic activity of the MH in the hydrogen transfer reactions [76].
- 100 % selectivity of hydrogen absorption from the H₂-rich gas mixtures.

2.2. Thermodynamic features and application requirements

Operating temperatures and hydrogen pressures are the most important parameters of the gas phase applications of the metal hydrides defined by their thermodynamic properties.

Thermodynamics of Reaction (1) follows the relationship between the hydrogen equilibrium pressure (P_{eq}), hydrogen concentration in the solid ($C=H/M$) and temperature (T) described by a PCT diagram built as a family of pressure – composition isotherms. An example of such a family is presented in Fig. 3(a) and describes an equilibrium condition during hydrogen desorption in the H₂–LaNi_{4.8}Sn_{0.2} system [78]. At moderate temperatures each isotherm has three segments two of which show a pronounced increase of P_{eq} with the increase of H/M and correspond to the formation of solid solution of hydrogen in the host metal (α) and in the hydride (β). The third segment is characterised by a constant equilibrium pressure ($P_{eq} = P_0$; plateau) and shows the area where the saturated α -solution and β -hydride coexist, that resembles a transformation of gas (α) into a liquid (β phase). The temperature

¹ The values of H/M for the α -solid solution (<0.1) and β -hydride (>1) presented in Fig. 2 show their typical values exhibiting a significant difference between the H concentrations in these phases at temperatures well below the critical temperature of α – β transition (see Fig. 3(a)).

increase causes the “shrinking” of the miscibility gap ($\alpha + \beta$ region) as shown by the dashed line in Fig. 3(a), and degeneration of the plateau into the slopy dependence with an inflection point at a critical temperature (T_C).

The temperature dependence of plateau pressure, $P_0(T)$, exhibits linearity in coordinates $1/T - \ln(P_0)$. Here the intercept of the straight line with the Y-axis and its slope are proportional to the negated standard entropy and the standard enthalpy of the α – β transition, respectively. The linear dependence between $1/T$ and $\ln(P_0)$ (van't Hoff plot; see Fig. 3(b)) is described by a well-known equation:

$$\ln(P_0) = -\frac{\Delta S^0}{R} + \frac{\Delta H^0}{RT}, \quad (3)$$

where P_0 [atm] is the plateau pressure, T [K] is temperature, ΔS^0 [J/(mol H₂ K)] and ΔH^0 [J/mol H₂] are standard enthalpy and entropy of the α – β transition, respectively, and $R = 8.314$ J/(mol K) is the universal gas constant.

Additional features of the real hydrogen – metal systems include hysteresis of the plateau pressures for H₂ absorption and desorption, sloping plateaux, as well as frequent appearance of the multiplateau segments. For further details please consult [79] and references therein.

The gas phase applications of metal hydrides include:

- Hydrogen stores. These provide benefits of compact hydrogen storage and supply systems operating at ambient pressure-temperature conditions.
- Metal hydride compressors. These compressors convert thermal energy into the energy of compressed H₂ gas. Hydrogen can be compressed from 1 bar to 800 bar by performing a multistage compression and by using appropriate composition of the MH alloys.
- Heat storage and conversion.
- Hydrogen getters and vacuum-plasma technologies.

The corresponding ranges for some of them are shown as rectangular regions in Fig. 4. As it can be seen, for every application a suitable MH material for which equilibrium conditions of Reaction (1) match well into the corresponding range can be found.

Table 1 presents main types of MH materials used in gas-phase applications. Suitability of a particular material for a particular target application mostly depends on the matching between the range of operating temperatures/hydrogen pressures determined by the thermodynamics of H–M interaction (Fig. 4) and the pressure/temperature operation conditions for the specific application. Obviously, a number of the additional application-related properties of the MHs should be taken into account to achieve the required efficiency and reliability of the end-user system.

The interrelation between the properties of hydrogen – metal systems and their performances in specific applications have been considered in detail in numerous reviews [25–30,42,55,65,67].

2.3. Application-related properties of metal hydrides

The most comprehensive consideration of application-related properties of MHs has been given by Dantzer [29]. According to the proposed classification, these include:

- Thermochemical reactivity, viz:
 - Thermodynamics of H–M interaction.
 - Surface effects affecting hydrogen sorption performance by impurities present in H₂ gas.
 - Cycling stability.
- Transport properties – hydrogenation/dehydrogenation kinetics.
- Thermal properties – heat transfer efficiency.
- Dynamics of heat-and-mass exchange between the MH bed and its surrounding.

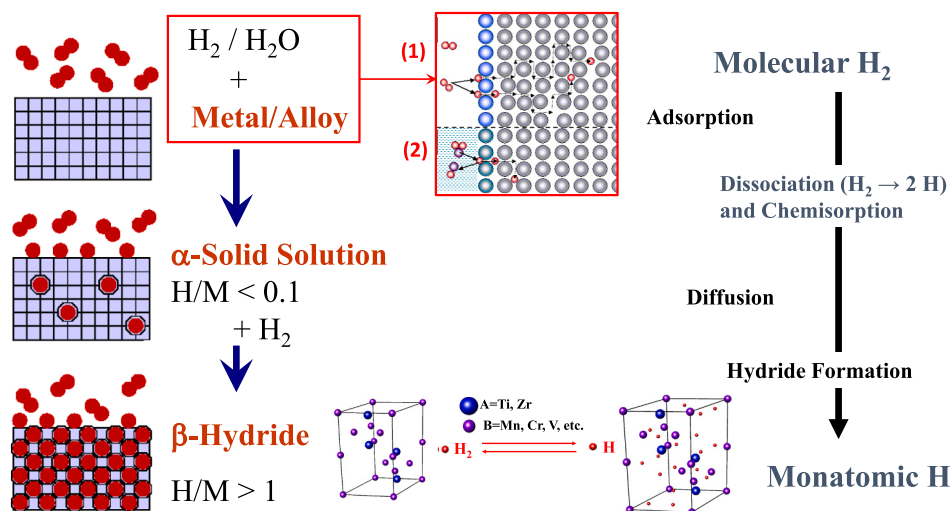


Fig. 2. Schematic representation of hydride formation process (left) and its main stages (right). The mid-top inset illustrates H – M interactions that correspond to the Reactions (1) and (2). The mid-bottom inset shows the changes of the unit cell of the metallic matrix (example for C14-AB₂ intermetallic [77] during Reaction (1)).

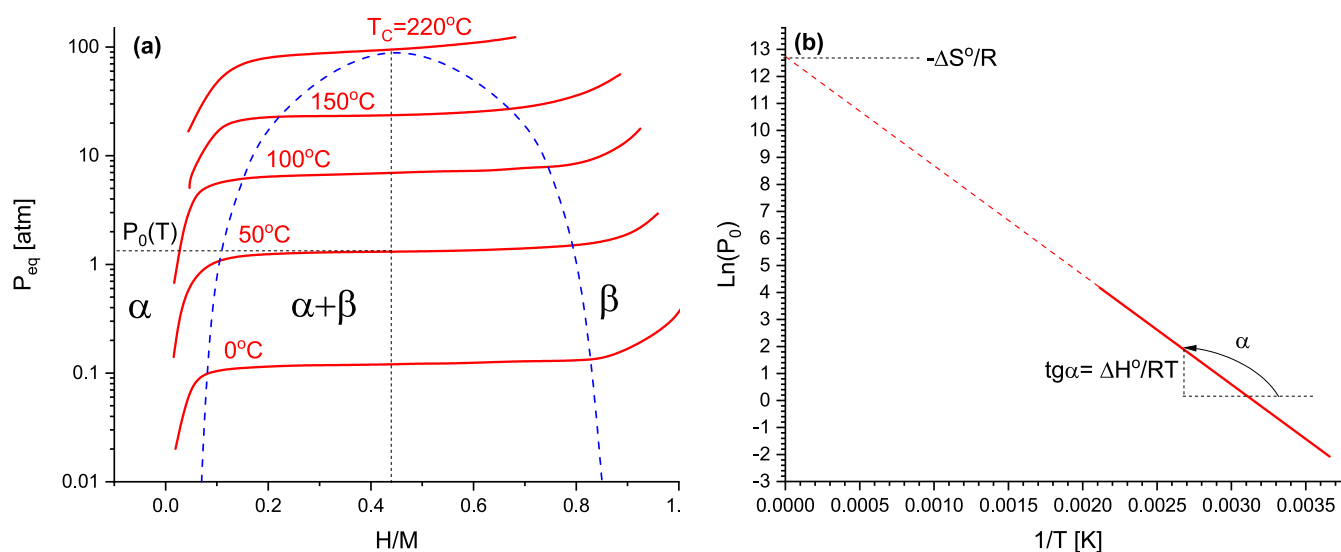


Fig. 3. Pressure–composition isotherms (a) and van't Hoff plot (b) for H₂–LaNi_{4.6}Sn_{0.2} system [78].

Of the listed groups of properties, the thermochemical reactivity (a) and hydrogen absorption/desorption kinetics (b) are related to the properties of the hydride-forming material while the other ones (c, d) – to the design and operational performance of the MH reactors whose hydrogen charge/discharge dynamics is mainly limited by macrokinetics determined by heat transfer performance of the MH beds.

Furthermore, the material-related features include the preparation routes of the alloys and hydrides [77,83,84], activation of the metal-hydrogen interaction [9,61,85–89], as well as the dilatation effects related to the expansion of the unit cells upon the hydrogenation [90–99]. The latter feature was recently reviewed by Gillia [99] and is very important for achieving the safe operation of the MH containers since the dilatation effects may cause unacceptably high stresses of their walls if the filling density of the MH material is too high. At the same time, increasing the filling density results in the improvement of hydrogen sorption capacity and dynamic performance of H₂ charge and discharge [55]. To achieve a compromise between the successful performances and safety, a careful design of the MH container including specification of the acceptable MH filling density and some technological procedures providing a uniform distribution of the material in the

container should be drawn. The most reliable starting data for this stage of development include the quantitative information about the structure of the parent and hydrogenated material and lattice periods of the constituent phases to allow the calculations of the ideal (crystallographic) density of the material in the non-hydrogenated and hydrogenated states.

Another material-related feature important for the gas phase applications of MHs is the stability of their hydrogen sorption properties during the cyclic hydrogenation-dehydrogenation. Most of hydride-forming metals and alloys exhibit degradation of their reversible hydrogen sorption capacities, gradual transformation of their pressure – composition isotherms and deterioration of hydrogen absorption/desorption kinetics during the repeated cycling in H₂. The cycle stability issues may be related to the influence of several factors including surface poisoning by the impurities present in H₂ (will be considered in Section 3.4) and sintering of the solid particles at high temperatures which results in the elongation of H diffusion pathways (typical for the MgH₂-based materials [100]). However, the most frequently observed degradation phenomenon is related to the disproportionation of the multi-component intermetallic hydrides during performing multiple H

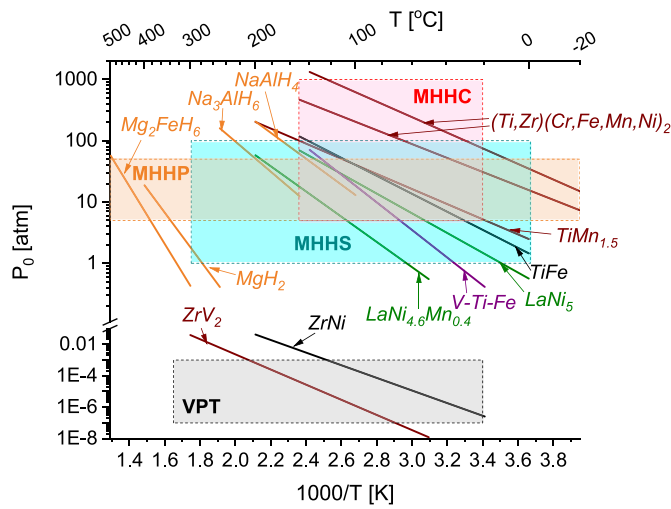


Fig. 4. Van't Hoff plots for several pseudo-binary, complex and intermetallic hydrides and the related gas-phase applications: VPT – vacuum-plasma technologies (getters and low-pressure sources of H isotopes), MHHS – MH hydrogen storage systems MHHP – MH heat management systems (heat storage, conversion & upgrade), MHHC – thermally driven MH H₂ compressors. (Adopted from [77].)

absorption/desorption cycles that negatively impacts hydrogen compression (Section 3.2) and heat management (Section 3.3) applications.

The disproportionation of the intermetallic AB_n alloy in hydrogen results in the formation of a stable binary hydride of the A-component along with a release of the component B in elemental or B-enriched alloy forms; the latter two do not form hydrides at the applied experimental conditions. This process is thermodynamically favourable (see Fig. 5) but it requires a diffusion of the metallic atoms enabling phase

separation. As the diffusion is slow or hindered at low temperatures, then the formation of the insertion type homogeneous intermetallic hydride AB_nH_Y prevails. However, the disproportionation quickly accelerates when the temperature increases, and even a minor extent of the disproportionation process when accumulated from cycle to cycle becomes very pronounced after a completion of several thousand hydrogenation/dehydrogenation cycles or when the intermetallic alloy is subjected to high temperatures and high hydrogen pressures.

The disproportionation process of the hydride-forming intermetallics was intensively studied since the 1970s, see Refs. [101–105] (1970s–1980s), [106–110] (1990s), and [111–115] (2000 and later) representing the studies that made a noticeable contribution to the subject.

As it can be seen from the Fig. 5, the disproportionation is favoured by the increased values of the heat (negated enthalpy) of formation of the binary hydride, AH_Y, and the decreased values of heat of formation of AB_n intermetallic. Thus, the disproportionation is more pronounced for the A-components which form stable hydrides (REH₂ where RE is a

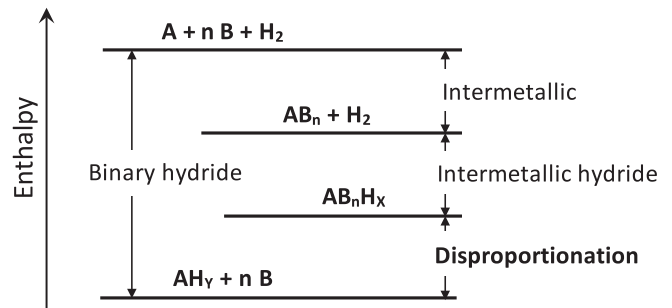


Fig. 5. Schematic energy (enthalpy) diagram illustrating thermodynamic favourability of the disproportionation reaction. (Adopted from refs. [101, 102].)

Table 1

Types of MH materials for the gas-phase applications [9,29,52,56,61,63,67,71,77,80–82].

Type	Operating temperatures [°C]	Operating H ₂ pressures [bar]	H storage capacity [wt %]	Hydrogenation heat effect (Q in Eq. (1)) [kJ/mol H ₂]	Suitable for applications	Notes
Binary (e.g., MgH ₂) and complex (e.g., NaAlH ₄ , Mg ₂ FeH ₆) hydrides	150...500	<1...200	4...7.6	45...80	High-temperature (T > 200 °C) heat management Weight-efficient H storage	Nanostructuring and/or use of catalysts is required to provide reversibility and improve H absorption/desorption kinetics
AB ₅ (A = RE; B=Ni,Al, Sn,Mn, ...)	0...200	<1...200	1.2...1.5	25...40	Efficient H storage at ambient conditions Metal hydride hydrogen compression Heat management at low temperatures (T < 200 °C) H ₂ separation and purification	Operating pressures can be tuned by variation of alloy composition
AB ₂ (A = Zr; B=V, V + Fe)	20...300	10 ⁻⁷ ...10 ⁻³	1.9...2.2	~80	Hydrogen getters and sources of H isotopes Efficient H storage at ambient conditions Metal hydride hydrogen compression Heat management at low temperatures (T < 100 °C)	Operating pressures can be tuned in very broad ranges by varying the alloy's composition
AB ₂ (A = Ti,Zr; B=Mn, Cr,Fe,V, ...)	-50...150	1...1000	1.5...1.9	15...30	Hydrogen getters and sources of H isotopes Efficient H storage at ambient conditions Metal hydride hydrogen compression Heat management at low temperatures (T < 100 °C)	
AB (A = Zr; B=Ni,Co)	20...250	10 ⁻⁶ ...10 ⁻³	0.7...1.9	45...75	Hydrogen getters and sources of H isotopes	Performance is very sensitive to impurities in both H ₂ gas and host alloy
AB (A = Ti; B=Fe,Mn, V)	0-150	1...100	1.7...2.0	28...32	Efficient H storage at ambient conditions	
BCC solid solution alloys on the basis of V and Ti-Cr	0 ... 100	<1 ... 300	2.5...3.0	30...40		Difficulties in the preparation and further processing

rare-earth element or CaH_2 ; $\Delta H = -(180\text{--}200)$ kJ/mol H_2 [3]), and for the relatively less stable intermetallics (e.g., LaNi_2 , $\Delta H = -90$ kJ/mol [116] against LaNi_5 , $\Delta H = -159$ kJ/mol [117]). Thus, the possibilities to suppress the disproportionation process include increase of the stability of the parent intermetallic alloy (e.g., by a substitution of La by Ce [112], or Ni with Sn [108,118], Co [113] or Al [119,120] in LaNi_5) and/or decrease of the stability of the binary hydrides formed by A-components of the intermetallic (e.g., by substituting a rare-earth element with Mg in RENi_3 [121]).

We note that the stability of AB_n intermetallic compounds and, accordingly, the resistance against the disproportionation increases with an increase of the B/A ratio, i.e., the value of n in AB_n [11]. The disproportionation may include several intermediate processes comprising of lattice disordering/appearance of defects, amorphization, and formation of intermetallics enriched with B-component [118,122,123].

AB- [124–126] and, particularly, AB_2 -type [109,110] intermetallics where $A = \text{Ti}$ and/or Zr^2 were shown to be less prone to the disproportionation as compared to the intermetallic compounds of the rare-earth elements and calcium. The origin of this difference is in a lower stability of TiH_2 and ZrH_2 ($\Delta H = -131$ and -160 kJ/mol H_2 , respectively [3]) as compared to the RE and calcium dihydrides (see above). However, taking into account the lower stability of the Ti- and/or Zr-based AB- and AB_2 -type intermetallics as compared to the RE-based AB_5 -type ones [11], the thermodynamic considerations alone are insufficient. As an example, the Gibbs free energy of hydrogen-induced disproportionation of TiFe calculated at $T = 300$ °C (-83.7 kJ/mol H_2 assuming formation of TiH_2 and TiFe_2) was found to be not much less negative than that for LaNi_5 (-96.2 kJ/mol H_2 assuming formation of LaH_2 and Ni) while for TiFe the disproportionation at $T = 300$ °C and 40 bar H_2 was not observed, in contrast to LaNi_5 which exhibits a noticeable disproportionation at the same conditions [124]. Studies clarifying the effect of additional factors (e.g., diffusivity of the metal atoms) which contribute to the disproportionation mechanism of AB- and AB_2 -type alloys where $A = \text{Ti}$ and/or Zr are, therefore, required to further enlighten the controlling features of the interaction process.

The degradation effects upon cycling also occur for the individual hydride-forming BCC metal vanadium and solid solution type BCC alloys. As it was noted in the review paper describing fundamental and applied features of the use of the metal hydrides in the MH compressors published by the authors of this article (ML, VY) [55], the origin of the degradation is in the structural-morphological changes of the metallic matrix resulting in the reduction of H sorption capacity, particularly at the stage of the lower pressure/temperature H absorption. Recent studies of the V–Ti–Cr BCC alloys [115,127] showed that their cycling in hydrogen results in a significant drop of the H absorption capacity at room temperature, along with the significant increase of the plateau slope at the pressure-composition isotherms. The cycling was accompanied by a leaching of Ti and V from the metal matrix appearing in the form of their hydrides, similar to the hydrogen-induced disproportionation of intermetallics. The increase of Cr content in the alloy makes the degradation even more pronounced. Furthermore, the decrease of the low-temperature hydrogen saturation of the alloys inhibits the degradation effect.

Hydrogen sorption properties of the AB_5 -type intermetallics can be recovered by several hours-long heating in vacuum or under near-atmospheric H_2 pressure [104,110,118]. This is caused by the recombination reaction when the stable binary hydride decomposes and the initial intermetallic alloy forms upon a completion of the hydrogen desorption process. However, upon further cycling, the recovered alloys

frequently degrade faster than the “fresh” ones [104].

Advanced *in situ* diffraction studies contribute as a highly valuable tool to probe the structure and reacting mechanisms of hydrogen and energy storage materials including hydrogenation–disproportionation–desorption–recombination (HDDR) [128]. A completeness of the HDDR process when using *in situ* studies has been demonstrated for a broad range of chemical compositions of hydrogen storage alloys. These include Zr-rich Zr_2Fe , Zr_3Fe and $\text{Zr}_4\text{Fe}_2\text{O}_{1-x}$ [129], Mg-rich LaMg_{12} [130,131], and MgCo_2 [132]. Furthermore, hydrogen desorption properties of a series of binary hydrides of the rare earth metals have been characterised [133,134] and related to the HDDR behaviours in the rare-earth rich $\text{Nd}_5\text{Fe}_2\text{B}_6$ [135] and $\text{Nd}_5\text{Fe}_2\text{Co}_6$ [136]. All these studies showed that because of the nanostructured morphologies of the hydrogenated materials typical for the alloys subjected to the HDDR process and increased diffusion mobility of the metal atoms caused by hydrogen dissolved in the metal lattice, the recombination process in the multi-component disproportionated mixtures often proceeds at much lower temperatures as compared to the binary hydrides. One example is Mg-assisted low temperature hydrogen desorption from the disproportionated in hydrogen LaMg_{12} when initial intermetallic LaMg_{12} recombines already below 450 °C which is 400 °C lower as compared to the binary hydride LaH_2 releasing hydrogen at 850 °C only [131].

The material-related information about thermodynamics of H–M interaction including reaction heat effect, equilibrium pressure–concentration–temperature (PCT) relationships, as well as kinetics of hydrogen uptake and release is a starting point in the design optimisation of the MH reactors where these parameters along with other properties of the hydride-forming material (particle size distribution, density, heat capacity, etc.) are used during optimisation of the MH reactors via modelling of heat-and-mass transfer (refs [137–150] represent typical articles from several dozen of the works published since 2015).

2.4. From material to system

We can conclude that MH material properties are the key factors defining the development of any gas-phase application of metal hydrides, and the general strategy of the system development should realise the down-top approach “From material to system” (see Fig. 6) when the first stage includes a comprehensive studies of various properties of the selected MH materials followed by the development of the MH reactors and their integration in the end-use hydrogen energy systems. At the same time, selection criteria of the MH materials should account conditions of their use in the specific applications (dashed arrow in Fig. 6) including ranges of operating temperatures and hydrogen pressures, system size and weight, presence of impurities gas species in the hydrogen feed, required cycle and calendar lifetime. These requirements are application-specific and will be considered later in this review.

3. Main applications of MHs using hydrogen gas

3.1. Hydrogen storage

Hydrogen produced by water electrolysis with the use of green energy is a clean and zero-emission fuel. As is well recognised, one main challenge limiting the widespread use of hydrogen fuel cell technology in various applications is in the development of efficient hydrogen storage and supply systems [150–156]. The main problem is in finding an efficient way to deliver hydrogen to the consumer as at normal conditions H_2 is a low-density gas (0.09 kg/ m^3), thus requiring a densification by using physical (compression or liquefaction) or chemical methods. Even at high pressures, the density of compressed H_2 remains too low, about 20 kg/ m^3 at $P = 350$ bar and $T = 25$ °C. Accordingly, the size of the high-pressure cylinders for the storage of necessary amount of hydrogen becomes too large that prevents their use

² The discrepancies between the data related to the disproportionation of ZrNi observed in [125] after 50 cycles and not observed in [126] after 24,000 cycles can be explained by significantly higher temperatures (400–600 °C) applied in [125] as compared to the temperature range (7–177 °C) used in [126].

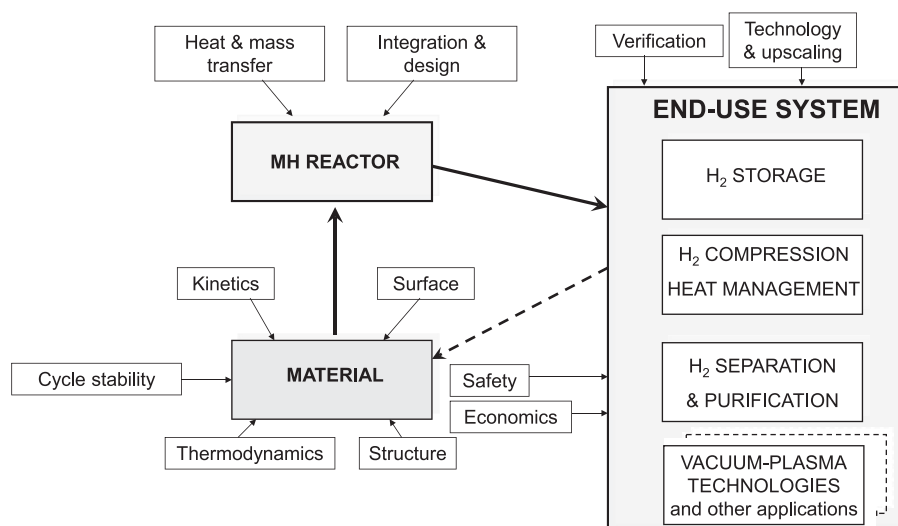


Fig. 6. Research – development – implementation strategy: From material to system.

in the applications which experience strict space constraints. Storage of hydrogen as a cryogenic liquid (density 70 kg/m^3 ; $T = -253 \text{ }^\circ\text{C}$) is associated with high energy consumption, up to 30 % of hydrogen higher heating value (HHV) for the liquefaction of H_2 gas. Similar energy consumption (up to 25 % HHV) is characteristic of the chemical hydrogen storage methods, e.g., Liquid Organic Hydrogen Carriers (LOHC).

Metal hydrides (hydrogen storage density up to 150 kg/m^3) present a promising alternative to the above-mentioned H_2 storage technologies, with a possibility to select materials compositions as required by the specification requirements from the end-use applications. Advantages of MHs as a hydrogen storage medium include simplicity, high safety, and flexibility of hydrogen storage systems on their basis (based on a proper selection of the H storage materials) which provides a high hydrogen storage density per unit volume and high purity of the supplied H_2 . Improvement of the operational safety is achieved due to the lower pressure of the stored hydrogen and the limited rate of hydrogen release in case of accidental leaks or even rupture of the hydrogen storage tank. Decomposition of “low-temperature” metal hydrides with release of H_2 consumes 20–30 kJ/mol H_2 [157] that is about two times lower than the energy necessary for the H_2 release from LOHC (55–70 kJ/mol H_2 [156]). Finally, thermal integration of the “low temperature” MHs based on AB_5 - and AB_2 -type intermetallics allows utilisation of heat produced during operation of the electrolyser and a fuel cell stack, thus improving the overall system efficiency [52,67,81,155,158]. Other advantages of MH-based hydrogen storage technologies include their flexibility and ability to be well-aligned with certain niche applications including combination of several functions in a unified MH system, in addition to hydrogen storage [17,35,52,67,73,155,158]. Competitive advantages of metal hydride hydrogen storage technologies over the alternative ones also include simpler and less expensive H_2 refuelling infrastructure due to a low standby H_2 pressure (1–50 bar at the ambient temperature). According to the estimations presented in ref. [159], the replacement of compressed gas H_2 storage tank ($P = 700 \text{ bar}$) with the MH one on-board of a fuel cell vehicle allows to achieve 36–39 % reduction of the refuelling costs due to significant reduction of the costs for H_2 compression.

The low weight capacity of the “low-temperature” (inter)metallic hydrides usually considered as the major disadvantage to their use in passenger vehicles [157], is not critical for the stationary applications and becomes an advantage for hydrogen storage on-board heavy duty utility vehicles, in maritime, railroad and other applications which require use of the ballast lowering centre of gravity of the donor vehicle [63].

The main problems hindering a broader commercialisation of the MH H_2 storage systems include [63,157,160–162]:

- (i) Excessive costs of the MH materials and MH reactors/containers.
- (ii) Necessity to shorten initially long charge/discharge time of the MH tanks.
- (iii) Insufficiently fast kinetics, particularly for H_2 absorption.
- (iv) Difficulties in aligning the compositions of the MH materials with thermodynamic properties of their interaction with H_2 gas, to provide matching with the pressure – temperature conditions required for the application, lowering hydrogenation enthalpy, and increasing the volumetric hydrogen storage density.

Due to the vast amount of the available experimental data on hydrogen sorption performance of various metallic hydride forming materials accumulated since the beginning of 1970s, empiric statistical analysis of the regularities in interrelations between the alloy’s composition and its hydrogenation/dehydrogenation properties can become a powerful tool for optimising compositions of hydrogen storage alloys in the specific hydrogen storage applications (iv). Such analyses including the use of machine-learning approach were carried out for a number of hydrogen storage alloys including AB_2 - [77,161,163–165] and AB_5 -type [166] intermetallics, “high-entropy” BCC solid solution alloys [167], as well as some “high-temperature” hydrides including Mg-based and complex compositions [168–170]. Furthermore, modelling attempts were undertaken to describe the performance of the hydrogen storage and compression MH materials belonging to the different types [157,171,172]. Successful correlations identified by the analysis of several hundred entries were obtained for the multi-component AB_2 -type alloys, well describing the relationships between their composition and the Gibbs energy of hydride formation, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = RT \ln P_0$, or characteristic temperature which corresponds to the atmospheric plateau pressure, $T_s = \frac{\Delta H^\circ}{\Delta S^\circ}$ [77].

Resolving kinetic issues (iii) is another important problem in the development of the MH hydrogen storage materials and systems. Studies of hydrogenation – dehydrogenation kinetics are in a focus of the metal hydrides research; a brief review of the application-related kinetic studies can be found in ref. [173]. Mostly, kinetics improvements are required for the “high-temperature” Mg-based and complex hydrides as they are generally characterised by the slow H absorption – desorption rates. The improvements are caused by adding of catalysts, nanostructuring or combination of these methods [64,65,174–184]. A very promising approach is in the preparation of hydrogen storage composites which include nanoscale carbon (e.g., graphene-like materials) with catalytic metal nanoparticles deposited onto it [185,186]. In addition to the accelerating hydrogenation/dehydrogenation kinetics due to the

facilitation of dissociative H₂ chemisorption/H recombination on the catalytic nanoparticles and shortening the H diffusion pathways in the nanostructured material, such composites are characterised by improved effective thermal conductivity of the MH beds on their basis and high stability of their hydrogen sorption performance during the cycling at high temperatures.

Hydrogenation/dehydrogenation kinetics and mechanisms are strongly dependent on the pressure acting as a driving force of the process [187]. This factor is particularly critical for the applications which require low-pressure H₂ absorption, for example, when storing H₂ supplied from a solid oxide electrolyser or another source of low-pressure (~1 bar absolute) hydrogen.

The decrease of pressure driving force also happens during the operation of the MH containers for hydrogen storage and other gas-phase applications (e.g., H₂ compression) due to the heating (exothermic H absorption) or cooling (endothermic H desorption) of the MH bed usually characterised by a low (<1 W/(m K)) effective thermal conductivity. As a result, the pressure/temperature conditions approach the equilibrium ones [188], and H absorption/desorption rates slow down, so the process becomes rate-limited by the heat transfer issues (issue ii). Detailed analysis of this effect requires numerical modelling of heat-and-mass transfer in the MH beds where PCT (iv) [79,189,190] and kinetic (iii) [191–193] relationships/models are included in the model as the governing equations [140–142,150,194–196].

Most of the methods for the acceleration of H₂ charge/discharge of metal hydride reactors are aimed at the increase of the effective thermal conductivity of the MH bed, by placing MH powder in a heat-conductive matrix (metal foam, internal finning or their combination [148,197–199]), compacting MH powder with a heat-conductive binder (metal, expanded natural graphite, carbon nanomaterials [200–205]), as well as introducing internal heat exchangers of various layouts [206–210], heat pipes [211–213], phase change materials [213–216]. These methods and corresponding designs of metal hydride hydrogen storage reactors have been recently reviewed in refs [217–219].

We note that the methods of heat transfer augmentation specified above are applicable to the most of the gas-phase applications of MH (hydrogen compression, heat storage and conversion systems), in addition to hydrogen storage.

Apart from the improvement of the charge/discharge dynamic performances by intensifying heat exchange between the MH bed and its heating/cooling means, special attention in the development of the MH containers for hydrogen storage and compression must be paid to avoid or mitigate the stresses which appear on the containment wall due to the dilatation of the MH material when it is hydrogenated. The main technological approach is in the keeping safe density of filling the MH material into container which roughly should not exceed 50 % of the crystallographic density of the material in the hydrogenated state [90]. Some increase of the safe filling density can be achieved by mixing the MH powder with a plastic additive like Expanded Natural Graphite (ENG). The mixture can be either left in the powdered form or further compacted [205,220–222]. Alternatively, the stress alleviation can be achieved by introducing minor additives which provide lubricating effect – a recent study [223] showed that addition of 3 wt% of silicone oil to AB₅-type MH powder almost eliminates stresses in the reactor at the filling density increased to 60 %.

Compact, safe, and flexible hydrogen storage remains the main gas-phase application of the metal hydrides. One example of a commercial product for the stationary applications is the integrated hybrid hydrogen battery recently developed by the company Lavo (Australia; <https://lavo.com.au>). The LAVO™ Energy Storage System intended for the use in residential applications consumes renewable energy from the PV panels and a tap water which is further purified inside the system. Hydrogen generated by an electrolyser is stored in four metal hydride containers at a pressure about 30 bar and further supplied to a PEM fuel cell stack which, together with Li-ion battery, provides on-demand supply of up to 5 kW power of electricity. The system can store 40

kWh of electricity. The details about the system performance and cost can be found in [224,225].

In summary, the use of metal hydrides allows to build various hydrogen energy systems. The companies involved in the manufacturing and sales of the metal hydride hydrogen storage systems for the laboratory and stationary applications include GRZ Technologies/Switzerland (<https://grz-technologies.com/>), GKN Hydrogen/Germany (<https://www.gknhydrogen.com/>), Pragma Industries/France (<https://www.pragma-industries.com/hydrogen-storage/>), HBank/Taiwan (<http://www.hbank.com.tw>), Whole Bin (Beijing)/China (<http://www.bjhaoyun.com/indexen.php>).

Metal hydrides allow to create compact, safe and technologically flexible hydrogen storage systems for portable, stationary and mobile applications ranged in the amount of the stored H₂ from several grams to several dozens of kilograms. Some examples representing developments at HySA Systems Centre of Competence in South Africa [222,226,227] are described below.

Fig. 7 shows a cartridge-type MH tank for hydrogen storage on-board of a light fuel cell vehicle (scooter) [226]. The tank has hydrogen storage capacity of up to 1 Nm³ (90 g) H₂ and comprises of two MH containers made of aluminium, filled with AB₂-type hydrogen storage alloy powder and equipped with internal copper and external aluminium heat-conductive fins which provide the rated performance of the H₂ charge (~1 h time at supply pressure up to 40 bar) and discharge (2 tanks connected in parallel provide stable operation of 1.1 kW fuel cell stack) when cooled and heated with ambient air at $T = 15–25$ °C. H₂ input/output pipeline of the tank is equipped with quick connector which allows for a quick replacement of the used tank with the one refuelled off-board.

The MH tank for the storage of up to 1.8 kg (20 Nm³) H₂ on-board of a 3-t fuel cell forklift (see Fig. 8) is made as an assembly of eight metal hydride cassettes each comprising of 5 tubular (ø48x800 mm) MH containers filled with the AB₂-type hydrogen storage alloy powder and equipped with internal heat conductive copper fins. To provide a safe operation of the forklift when lifting the maximum load, each liquid heated/cooled cassette is encased in a lead thus combining the functions of hydrogen storage unit and vehicle ballast. The tank is characterised by a reasonable refuelling time (up to 20 min at the refuelling pressure up to 150 bar and ambient temperature) and provides stable operation of 11 kW fuel cell stack at the maximum load [227].

Recently HySA Systems has developed a prototype hydrogen storage tank for the stationary fuel cell applications (Fig. 9). The liquid heated/cooled tank filled with AB₅-type hydrogen storage alloy stores up to 4 kg (45 Nm³) H₂ and is made of a stainless-steel pipe (ø219x2500 mm) with flanged ends. One of the flanges is intended for H₂ input/output while the other carries an internal heat exchanger. For the temperature measurements in different points of the MH bed, the tank is equipped with several thermocouple probes installed at the ports of the cylindrical containment.

Fig. 10(a–c) presents the estimated breakdowns of the costs incurred by HySA Systems for the making the MH tanks described above.

As it can be seen, a frequently expressed opinion that the cost of the metal hydride hydrogen storage systems is mainly determined by the cost of MH material is valid only for the large MH tanks made as individual containers (Fig. 10(c)). For the tanks made as assemblies of several small-size MH containers in order to improve the H₂ charge/discharge dynamic performance (Fig. 10(a, b)), quite labour-intensive MH containers, due to their individual manufacturing in a larger number by a custom order, become the main cost component. Taking into account that high costs for the MH containers are mainly related to not yet well-established market associated with absence of the mass production, it is expected that when mass produced, the cost of the containers will become lower than the one for the MH material. The latter might be further reduced due to the increase of its market demand associated with the increase of the production volume, and/or by the use of cheaper MH materials, e.g., based on TiFe which can potentially be

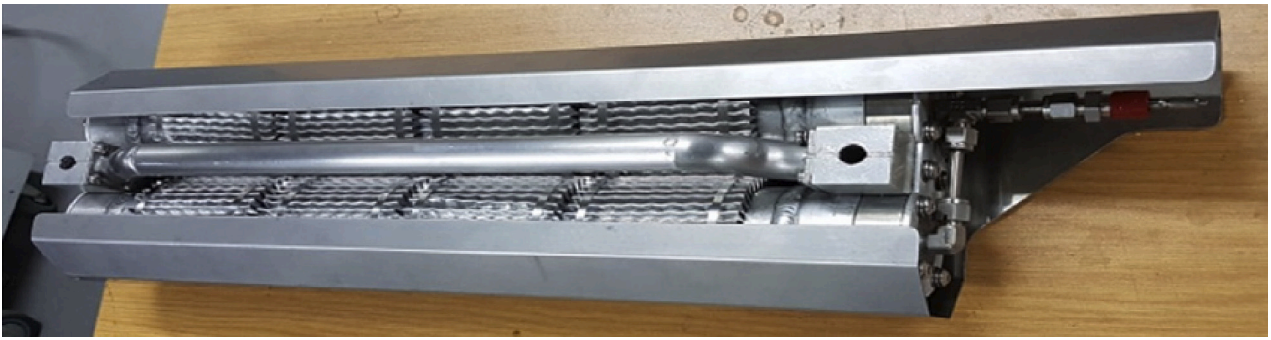


Fig. 7. Air heated/cooled cartridge-type MH tank developed by HySA Systems for hydrogen storage on-board fuel cell scooter [226].



Fig. 8. HySA Systems tank made as an assembly of lead-encased MH cassettes for hydrogen storage on-board of fuel cell forklift [227].

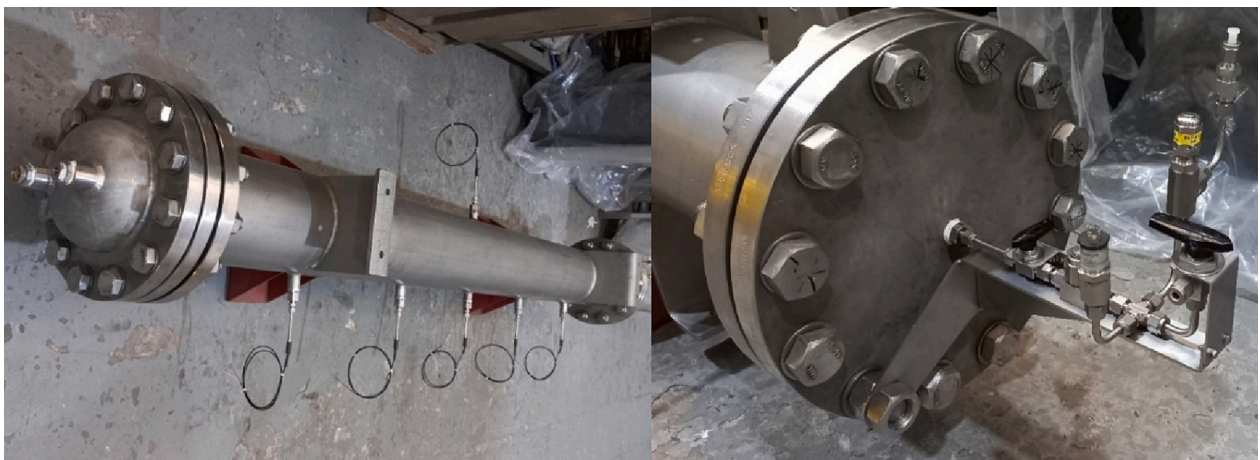


Fig. 9. General view of the assembled hydrogen storage tank with the heating/cooling flange on the forefront (left) and gas input/output flange (right).

3–5 times cheaper (per unit weight of the stored H_2) than the AB_5 - and AB_2 -type hydrogen storage alloys conventionally used for hydrogen storage applications due to their favourable hydrogen sorption performances [9]. However, inexpensive methods of the improvement of the

activation performance, hydrogenation/dehydrogenation kinetics and poisoning tolerance of TiFe [9,85,87–89,228] are necessary to be developed first.

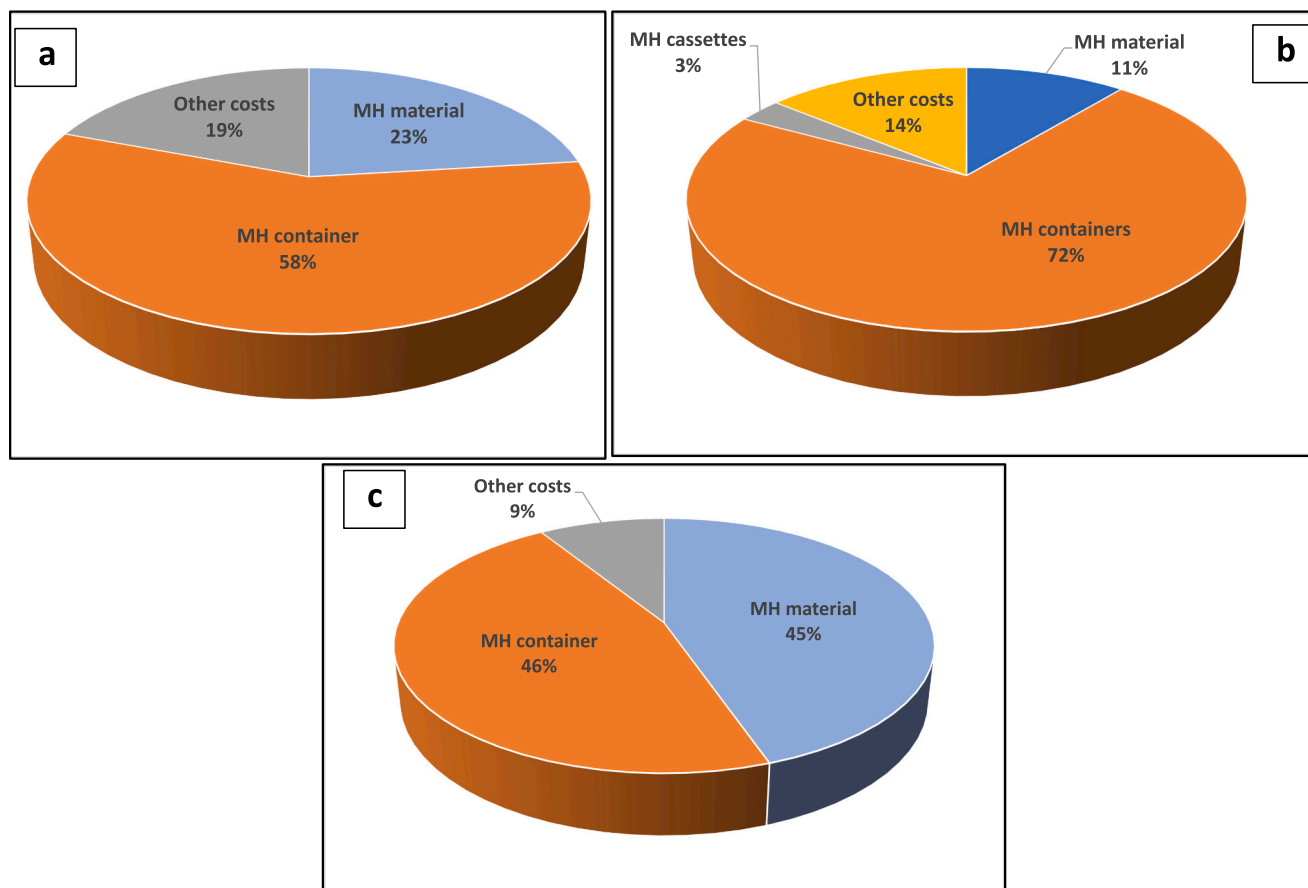


Fig. 10. Breakdown of the costs incurred by HySA Systems for the manufacturing of the MH hydrogen storage tanks: a – 90 g H₂ MH tank for scooter (Fig. 7), b – 1.8 kg H₂ MH tank for forklift (Fig. 8), c – stationary 4 kg H₂ MH tank (Fig. 9).

3.2. Thermally driven hydrogen compression

Almost any application of hydrogen gas requires its compression. The major problems in hydrogen compression technologies are in achieving high safety, reliability, and energy efficiency of the compressor systems [229]. The use of conventional mechanical hydrogen compressors is associated with unacceptably high capital and operational costs and frequent safety-related incidents. For hydrogen refuelling stations with dispensing pressures 350 to 700 bar, hydrogen compressors take from 48 to 58 % of the capital costs, up to 65 % of the operational costs (including service and maintenance which take about 1/4 of the total maintenance hours) and cause 18 % of the incidents [160,188,230].

Thermally driven hydrogen compression utilising metal hydrides has several advantages over conventional methods, including simple compressor design, the absence of moving parts, high purity of the delivered hydrogen, the possibility of utilisation of low-potential heat, reliability and safety in operation [55,57,63,66,160,188,231]. The main disadvantages of the MH hydrogen compressors include low efficiency limited by Carnot efficiency in the operating temperature range [232], as well as limited cycle and calendar life of the MH materials for hydrogen compression [112,233].

Metal hydride technology of hydrogen compression is in demand for several applications including:

- H₂ filling stations.
- Space exploration.
- Utilisation of low-potential heat.
- Powder metallurgy and other special H₂-consuming technological processes.
- Laboratory supply of compressed H₂.

- Temperature sensors & actuators.

Despite a possibility to generate very high, up to 7.5 kbar, H₂ discharge pressures utilising vanadium hydride as a hydrogen compression material [234], the hydrogen compression productivity acceptable for medium-to-large scale applications (e.g., hydrogen refuelling stations) is presently limited by the pressures 200–250 bar H₂ [160,188,230]. On-going R&D activities are aimed at further increase of the discharge pressure while reaching the productivity suitable for the refuelling of fuel cell buses and utility vehicles (>350 bar) and passenger vehicles (>700 bar) [63,160,161,188]. The relevant recent publications are mainly focused on the development of MH materials suitable for high-pressure hydrogen compression mostly based on C14-AB₂-type intermetallics where A = Ti or Ti + Zr [235–245]; in some works [246,247] the application of V–Ti–Cr BCC alloys for hydrogen compression has also been studied.

Fig. 11(a) presents the isotherms of hydrogen absorption at $T = 20\text{ }^{\circ}\text{C}$ and hydrogen desorption at $T = 150\text{ }^{\circ}\text{C}$ for C14-AB₂ intermetallic (A = Ti + Zr, B = Cr + Fe + Mn + Ni) recently developed by HySA Systems in South Africa. The isotherms were calculated on the basis of fitting the experimental PCT data for this alloy taken in the range $T = -20\text{ }^{\circ}\text{C} \dots +20\text{ }^{\circ}\text{C}$, $P = 0.1 \dots 200$ bar, using the model of phase equilibria in hydrogen–metal systems which allows for the realistic extrapolation of the results outside pressure–temperature ranges where the experimental data were collected [79]. As it can be seen, this alloy allows for hydrogen compression from $P_L = 100$ bar ($T_L = 20\text{ }^{\circ}\text{C}$) to $P_H = 500$ bar ($T_H = 150\text{ }^{\circ}\text{C}$) with cycle productivity $\Delta C = 115$ NL/kg.

Fig. 11(b) illustrates hydrogen discharge performance (backpressure regulator setpoint of 500 bar) of a prototype composite metal hydride container for high-pressure hydrogen compression developed by HySA

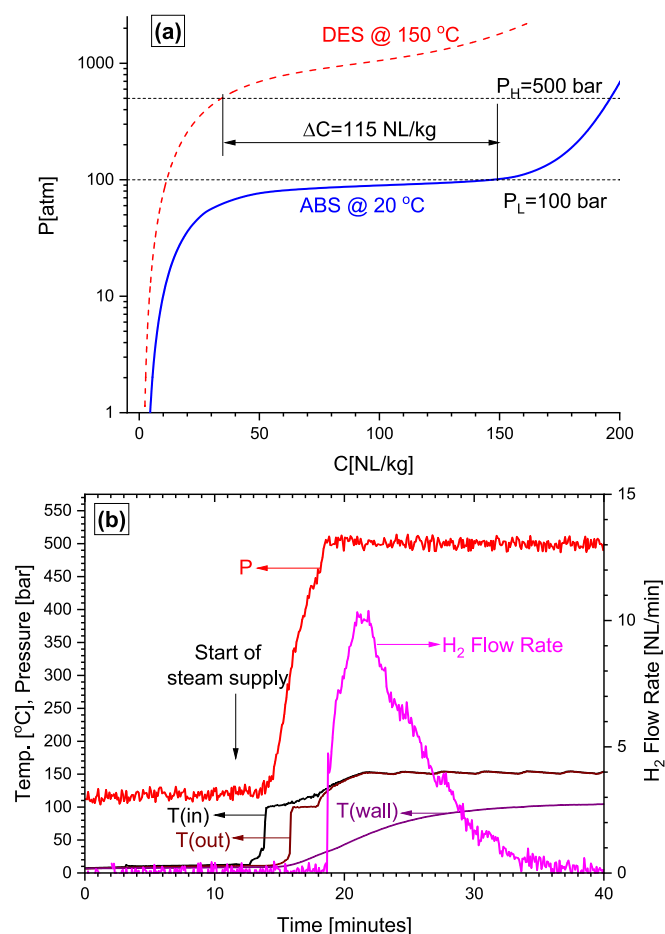


Fig. 11. Calculated PCT diagrams in the system $H_2 - C14-(Ti,Zr)(Cr,Fe,Mn,Ni)_2$ (a) and discharge performance of the composite MH container filled with 0.86 kg of this alloy and charged with H_2 at $P = 100$ bar and $T = 15$ °C (b).

Systems and its industrial partner [188]. The container filled with 0.86 kg of the C14- AB_2 intermetallic mentioned above and charged with hydrogen at $P(H_2) = 100$ bar and $T = 10-15$ °C was heated to $T = 150$ °C with steam supplied to the inner heat exchanger of the container. It is seen that the increase of pressure (P) in the container begins after 2 min from starting steam supply, and after 6.5 min it reaches backpressure setpoint accompanied by the start of hydrogen release at $P = 500$ bar. The hydrogen flow rate measured at the exit of the backpressure regulator quickly increases to ~ 20 NL/min followed by the gradual decrease to zero during ~ 25 min from start of the heating. During the operation in high-pressure H_2 discharge mode, the temperature of container wall (carbon fibre wrapping), $T(wall)$, does not exceed 100 °C while the steam temperature at the input ($T(in)$) and output ($T(out)$) of the container's heat exchanger is close to 150 °C. The amount of hydrogen desorbed at $P = 500$ bar was of 86 NL, or 75 % of the theoretical/equilibrium cycle productivity (see Fig. 11(a)).

Apart from a possibility to achieve very high hydrogen discharge pressures at moderate heating temperatures, development of metal hydride hydrogen compressors with low suction pressure is also in a great demand. This is caused by the fact that many chemical industries including chlorine production are characterised by huge, up to several tons a day, emissions of hydrogen as a byproduct released at a pressure close to the atmospheric pressure, and utilisation of this hydrogen may bring significant benefits. The same motivation is related to a possibility of utilisation of hydrogen produced using high temperature solid oxide electrolyzers normally providing low output H_2 pressures.

To achieve a reasonably high hydrogen compression productivity, the pressure driving force, i.e., the difference between the operating

pressure (1 bar absolute) and the hydrogen equilibrium pressure at the cooling temperature for the metal hydride used at the low-pressure H_2 compression stage, should be as high as possible. At the same time, the used metal hydride should provide sufficiently high H_2 discharge pressure (at least, 3–5 bar necessary for the suction in the next compression stage) when heated up to a reasonable temperature, from 90 °C (provided by solar collectors) to 150 °C (low-grade industrial steam).

The most suitable hydride-forming materials which satisfy these requirements are AB_5 -type intermetallics on the basis of $LaNi_5$ where Ni is substituted with elements (Al, Mn, Co, etc.) increasing the thermal stability of the intermetallic hydride as compared to $LaNi_5H_x$. Recent studies related to the use of this kind of materials for hydrogen compression can be found in refs [248, 249].

A significant number of the recent publications was focused on the modelling of single- and multi-stage MH compressors where PCT relationships for the used MH materials were included in the governing equations [250–257].

3.3. Heat management

Heat management applications utilising metal hydrides include thermal energy storage (TES) [64,65,70,150,208], as well as heat conversion comprising of cooling, heat transforming and heat upgrade [56,58,70,158]. These applications use the concept of metal hydride heat pump (MHHP) which is a heat engine similar to a metal hydride hydrogen compressor, however, operating in the reverse mode. Then, depending on the hydrogen pressure applied to MH bed, Reaction (1) proceeds either directly (heat release) or in reverse direction (heat absorption). Thermodynamics of MHHPs was analysed by Dantzer and Orgaz [258,259]; more recent works include refs [58, 70, 260].

The cyclic operation of a metal hydride bed in MHHP is illustrated by Fig. 12 and includes two stages: H_2 absorption at a higher pressure, P_H , accompanied by the release of heat, Q_H , at a higher temperature, T_H (a), followed by H_2 desorption at a lower pressure, P_L , accompanied by absorption of heat, Q_L , at a lower temperature, T_L (b). An idealized (not accounting H_2 absorption/desorption hysteresis) van't Hoff plot for the used MH material is presented in Fig. 12(c).

The principle of operation described above is used for the thermal energy storage ($T_L \approx T_H$) and heat conversion ($T_L < T_H$).

The MH-based TES is a highly competitive solution as compared to the systems utilising molten salts. The use of “high-temperature” binary and complex hydrides allows to store medium-to-high grade heat including the one supplied by concentrated solar energy plants at $T = 300... > 1000$ °C with energy storage densities per unit volume and weight close to and even exceeding the values for the alternative thermochemical heat storage materials ([261–264]; see Fig. 13). Storage and conversion of heat at lower temperatures is also possible using “low-temperature” intermetallic hydrides [263].

The use of heat pumps on the basis of “low temperature” MH allows to utilise low-grade heat with temperature potential below 100 °C. This is a promising energy saving technology for industrial and domestic applications, particularly in the case of combined cooling, heating and power (CCHP) systems.

Most frequently used configurations of MHHPs include one-bed compressor-driven and multi-bed thermally driven systems which use two or more MH materials differing by their thermal stabilities [58,70,260].

The one-bed MHHPs (Fig. 12) are mainly used for the cooling purposes (refrigeration and air conditioning) [265–268]. The technical solution is simple in the implementation and has the highest efficiency (above 80 %) and coefficient of performance (3.85) among alternative configurations of the MHHPs [260]. At the same time, it seems to be quite challenging to use this configuration in large-scale applications due to consumption of expensive electricity to drive hydrogen compressor, as well as other problems associated with its operation (see Section 3.2).

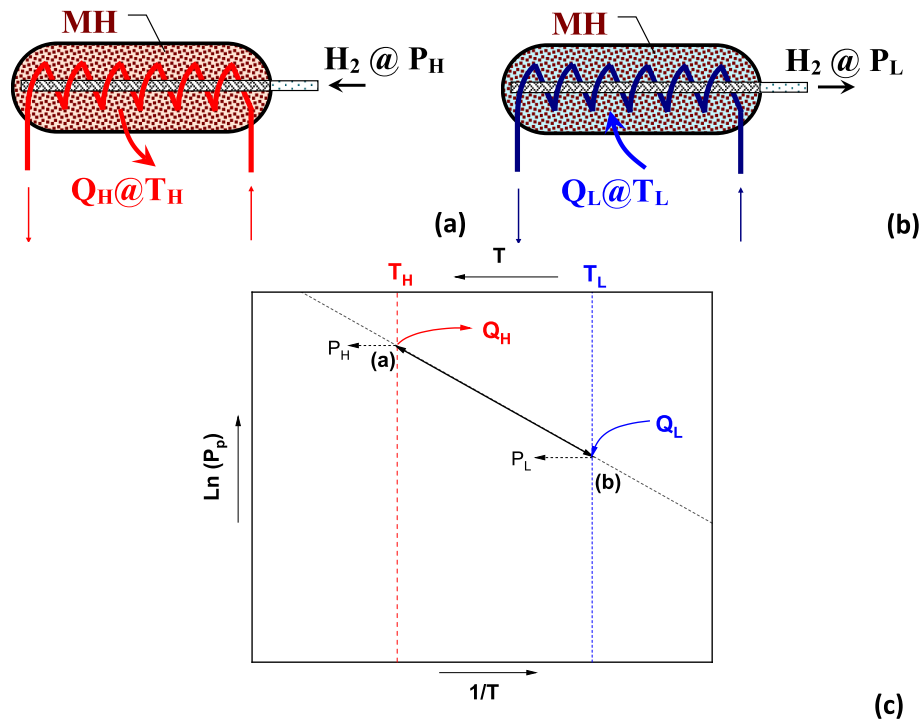


Fig. 12. Operation of MH bed in H₂ charge/heat generation (a) and H₂ discharge/heat absorption (b) modes; (c) – simplified representation of the operation in the van't Hoff plot.

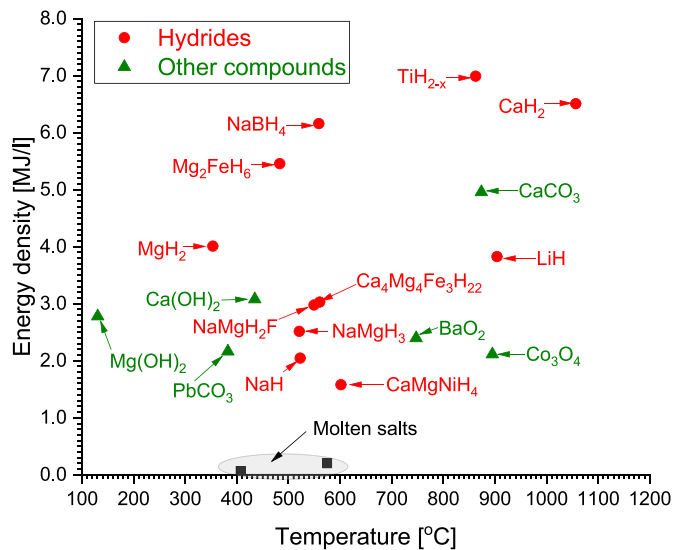


Fig. 13. Theoretical heat storage capacity of various thermochemical systems per unit volume. (Adopted from [261].)

In the multi-bed configuration, hydrogen compression from P_L to P_H (see Fig. 12(a, b)) is provided by another MH bed which uses low-grade heat to compress H₂. The simplest case is a two-bed configuration (Figs. 14, 15) which includes the less stable (LT-MH) and more stable (HT-MH) hydride beds forming the “cold” and “hot” sides of the MHHP, respectively. The gas spaces above the beds are connected allowing the hydrogen gas to flow between them, and the operation is driven by the heating and/or cooling the MH beds maintaining them at three temperature levels: high (T_H), medium (T_M) and low (T_L); T_L < T_M < T_H. As it can be seen from the bottom parts of Figs. 14 and 15, the operation follows the cycle ABCD coupling van't Hoff plots (simplified similar to

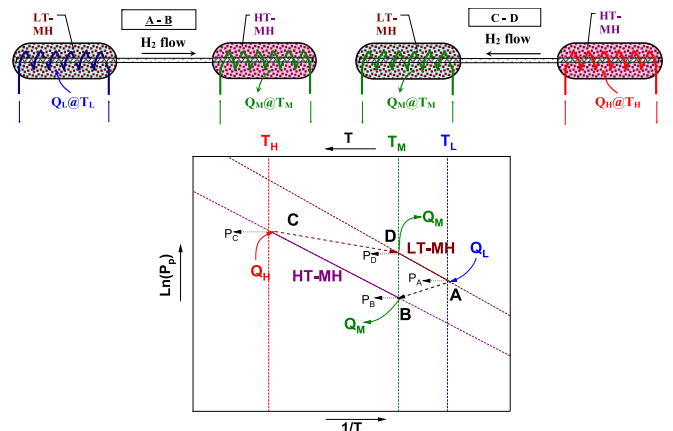


Fig. 14. Operation of two-bed MHHP in the cooling and heat upgrade mode.

the Fig. 12) for HT-MH between T_M and T_H and LT-MH between T_L and T_M. Generally, the mode of operation of the two-bed MHHP depends on the values of T_L, T_M and T_H, and thermodynamic properties of LT-MH and HT-MH. These parameters determine the differences between hydrogen equilibrium pressures in points A (LT-MH at T_L) and B (HT-MH at T_M), and in points C (HT-MH at T_H) and D (LT-MH at T_M). Consequently, the pressure differences determine direction of H₂ flow between the two beds.

When P_A > P_B and P_C > P_D, the hydrogen flow follows the paths A → B and C → D as shown in Fig. 14, and the cyclic process ABCD provides cooling of the “cold” side to the lower temperature T_L driven by the heating of the “hot” side to the higher temperature T_H while a periodic cooling of the “cold” and “hot” sides set the equilibrium at the medium temperature T_M. Accordingly, the MHHP provides cooling of the LT-MH to T_L driven by the heating of HT-MH to T_H and the cooling of both beds to T_M. Alternatively, this mode can provide heat upgrade at T_M by the heat transfer from both “hot” (T_H) and “cold” (T_L) sides.

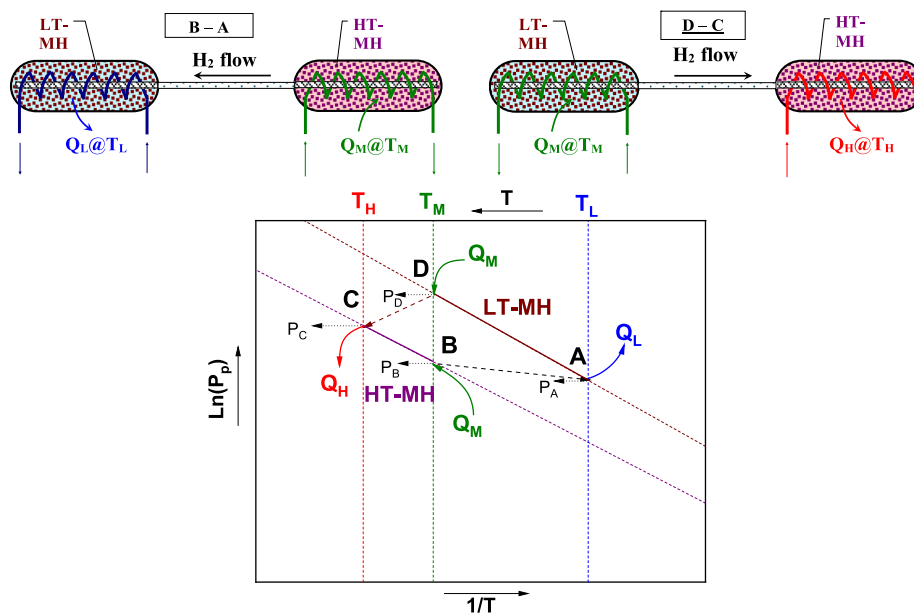


Fig. 15. Operation of two-bed MHHP in the heat transformer mode.

When $P_A < P_B$ and $P_C < P_D$ (Fig. 15), the cycle ABCD changes its direction. Indeed, hydrogen transfer between HT-MH at T_M and LT-MH at T_L follows the path $B \rightarrow A$ thus absorbing heat at T_M and releasing heat at T_L . The reverse H_2 transfer from LT-MH to HT-MH follows the path $D \rightarrow C$ accompanied by heat absorption in LT-MH at T_M and heat release from HT-MH at T_H . In doing so, the heat transforming mode is realised: the release of heat from HT-MH at T_H is driven by its heating to T_M and cooling of LT-MH to T_L followed by its heating to T_M .

The first and the main task in the development of the multi-bed MHHP is a proper selection of the pairs of MH materials for the connected LT-MH and HT-MH beds. The thermodynamic performances of the materials in the pair should be carefully aligned towards achievement of maximum efficiency and coefficient of performance (COP) for the selected mode of operation at the specified operating temperatures (T_L , T_M and T_H). They should also provide maximum absolute values of pressure driving forces ($P_A - P_B$) and ($P_C - P_D$) and, in turn, to improve dynamics of hydrogen transfer. Additionally, the operating pressures should not be too high to minimise the material consumption of the MH containment thus reducing losses for its alternating heating and cooling.

The approach for the selection of hydride pairs for MHHPs [259] was significantly extended by accounting the vast growth of the amount of the available data on the properties of the MH materials and development of the advanced data processing algorithms. The work [269] reported screening of the suitable pairs based on the analysis of 336 (pseudo)binary, complex and intermetallic hydrides for the heat management applications. The study also included dynamic simulations allowing to select around 1900 (from >10,000 available) hydride pairs characterised by the dynamic COP above 1 and specific heating power between 25 and 60 W/kg in the temperature range 25 to 140 °C.

Industrial-scale implementation of the metal hydride heat pumps started in the first decade of 2000s in Japan. One example is a freezer/refrigerator system developed by the Japan Steel Works, Ltd. and comprising of two rooms, 67 m³ each, cooled to -30 and 0–5 °C, respectively. The system uses four MH beds, two (120 kg each) for the “cold” and two (137 kg each) for the “hot” side, based on AB₂-type materials. The system is driven by industrial heat at $T_H = 160$ °C and intermediate cooling to $T_M = 10$ –17 °C using ground water [270].

The reference data describing the recent developments in the application of metal hydrides for heat storage and conversion can be found in the Refs [70,73,271–275].

3.4. Hydrogen separation and purification

Selectivity of the reversible interaction of gaseous hydrogen with hydride forming metals and intermetallics (Reaction (1)) when subjecting the metals to the mixtures of hydrogen-containing gases allows for the development of simple and low energy-consuming absorption/desorption systems for hydrogen separation and purification based on pressure – temperature swing [25,27,29,54,61,62,276–281].

The main problem of the application of metal hydrides for hydrogen separation and purification is in a high sensitivity of the MH materials towards poisoning by the selected gas impurities of active gases including carbon dioxide and, particularly, carbon monoxide which may be present as an admixture in hydrogen synthesized from hydrocarbons [61,62,73,282–286]. The Ti-based hydride forming alloys (TiFe and AB₂-type) are also sensitive to oxygen and water vapour/moisture which may be present in H_2 produced by electrolysis [9,287–290].

The origin of “poisoning” of hydride materials with gas impurities is in the passivation of active centres responsible for the dissociative H_2 chemisorption on the material surface (see Fig. 2) by forming strong bonds with active gases thus making these centres inaccessible for the splitting of hydrogen molecules.

Accordingly, the poisoning tolerance of the MH substrate can be improved by either preventing the migration of the impurities to its surface, or by a creation of the additional catalytically active centres thereon. These approaches are schematically illustrated by Fig. 16. The first approach (1) is in covering the particles of the MH substrate with a very fine polycrystalline fluoride layer which is permeable for hydrogen but not for the species of the active gases, O₂, H₂O, CO, CO₂, which may cause the degradation of the hydrogen sorption performance. The protecting layer is formed during the treatment of the substrate powder with an aqueous solution of a soluble fluoride in presence of HF. The best results have been obtained for the rare-earth containing AB₅- and A₂B₇-type substrate materials and for hydrogen storage alloys (e.g., AB₂-type intermetallics) doped by rare-earth elements [291–294].

The second approach (2) is in the surface deposition of the metals capable to catalyse a dissociative chemisorption of H_2 . Efficient catalysts include Platinum Group Metals (PGM), with Pd being most abundantly utilised [295–301]. The most frequently applied technique is electroless plating which results in a discontinuous coating of the substrate by the PGM particles with the size of x10 nm [302]. Improvement of the PGM deposition process allowed increasing of the PGM loading and the

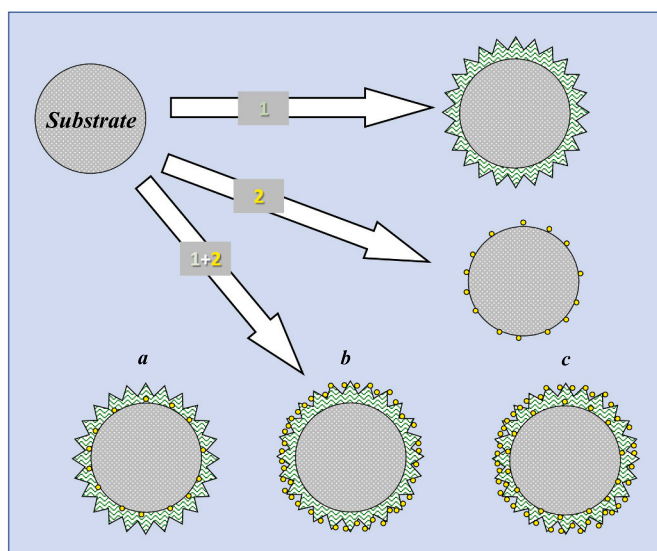


Fig. 16. Approaches to increase the tolerance of the MH substrate towards “poisoning” with gas species by blocking the H_2 chemisorption active centres. 1 – covering with the protective fluoride layer not permeable to the species of active gases but permeable to H_2 molecules. 2 – deposition of the catalytically active metals. 1 + 2 – combination of the above techniques.

coating density (and, in turn, poisoning tolerance of the surface-modified MH), even at a low concentration of the PGM plating solution, can be achieved by functionalisation of the oxidised substrate surface by aqueous solutions of aminosilanes [299,303].

A combination of the approaches described above (1 + 2 in Fig. 16) provides a very pronounced synergetic effect [61,302]. Of the possible options of realisation of this approach (a–c), the deposition of PGM onto fluoride layer (b) seems to be the most promising. It was shown [302] that electroless deposition of Pd onto fluorinated AB_5 -type material results in plugging the micro-cavities of the fluoride layer by Pd nanoparticles to form advanced composite material characterised by exceptionally good hydrogenation performance. These materials even after long (several months) exposure of the AB_5 powder to air actively form the hydrides without a need for the preliminary activation.

Table 2 presents the data allowing to compare hydrogen absorption characteristics of the same AB_5 -type alloy surface modified by different methods. It can be seen that the hydrogenation performance is improved following the series “unmodified \ll Pd coating without aminosilane functionalisation \approx fluorination $<$ Pd coating with aminosilane functionalisation $<$ fluorination followed by aminosilane functionalisation and Pd coating”.

Surface modification by fluorination and deposition of metallic catalysts significantly improves both gas-phase and electrochemical hydrogenation properties of MH materials including easy activation and suppression of the degradation rate during the cycling [293,304,305].

A prototype hydrogen separation unit based on the AB_5 -type

Table 2

Characteristics of hydrogenation at $P(H_2) = 5$ bar and $T = 20$ °C of the non-activated air exposed AB_5 -type intermetallic [61,302].

Surface modification route	Hydrogenation rate constant [h^{-1}]	Incubation period [h]
No modification	$\sim 10^{-5}$	–
Pd coating	0.19	0
Fluorination	0.28	1
Pd coating after aminosilane functionalisation	1.3	0
Pd coating after fluorination and aminosilane functionalisation	3.7	0

material surface-modified using “fluorination – aminosilane functionalisation – Pd coating” route showed a stable hydrogen separation and purification performances over ~ 200 cycles when exposed to the feedstocks containing CO_2 and CO at the concentrations of up to 30 % and 100 ppm, respectively [62,282].

The recent studies (2020–2023) on hydrogen separation and purification utilising MH materials were mainly focused on the experimental investigations of the influence of gas admixtures (up to 50 % of CH_4 or CO_2) on hydrogen sorption properties of the AB_5 -type alloys [286,306–308]. Interesting data concerning the influence of the temperature on the poisoning tolerance of AB_5 -type alloys when exposed to $H_2 + CO$ mixtures were reported in ref. [285]. It was shown that the increase of the operating temperatures improved poisoning tolerance towards CO . Similar results were reported in ref. [309]. The work [310] which studied the poisoning resistance of fluorinated Mg/MgH_2 during the hydrogenation using the mixture $H_2 + CO$ (up to 50 %) + CO (up to 100 ppm) at $T \sim 300$ °C is also of interest.

Many recent works reported modelling approaches describing MH hydrogen separation and purification systems [309,311–314]. The problems related to the selection of the suitable MH materials and design of hydrogen purification reactors were considered in the Ref. [315].

3.5. MH getters and low-pressure sources of hydrogen isotopes used in vacuum-plasma technologies

One of the promising gas-phase applications of the metal hydrides is their use in the supply systems of vacuum-plasma facilities, which include ion sources for the accelerators, injectors for the fusion installations, and other components which use hydrogen isotopes as a working fluid. These materials can provide compact storage of a moderate amount (around $\times 100$ normal litres) of hydrogen (deuterium, tritium), evacuation of the excessive gas from an ion source to the pressure $P = 0.1$ – 10 Pa or from the vacuum systems to $P = 10^{-7}$ – 10^{-3} Pa, involving its purification and further supply to the ion source at $P = 0.1$ – 100 Pa. Additionally, the use of the MH in the vacuum-plasma technologies allows to significantly increase the efficiency and operation stability of the corresponding components of vacuum-plasma installations [316].

Reversibility of the Reaction (1) even for the very stable hydrides, e. g., formed by the multi-phase alloys α -Zr + $C14$ -Zr(V,Fe) $_2$ + η -Zr $_3$ V $_3$ (B, O) $_{1-x}$ [317] or α -Zr + $C15$ -ZrV $_2$ + η -Zr $_3$ V $_3$ O $_{1-x}$ [318], allows building of the very efficient sources of both positive (H^+ , H_2^+ , H_3^+) and negative (H^-) hydrogen ions comprising electrodes made of the hydrogenated getter type alloy. Schematic representation of a prototype ion source utilising such material as a part of anode of the gas discharge chamber is shown in Fig. 17. Introducing MH into the anode results in the significant improvements of the H ions generation including easier ignition (lower value of the discharge voltage, U_d) and higher stability of the discharge burning, as well as significant increase of the yield of hydrogen ions (by 30–50 % for H^+ and by 15 % for H^-) [316,319]. The later feature was associated with the effect of hydrogen “activation” during the H_2 desorption from a MH [76], via vibrational excitation of the H_2 molecules formed by recombination of H atoms on the MH surface [320,321].

Introducing reversible MH getters into cathode of the gas discharge chamber is particularly efficient. The bombardment of the MH cathode by positive ions of the discharge plasma results in hydrogen desorption, and the desorption rate increases with the increase of intensity of the ion bombardment. As a result, the processes in hydrogen plasma contacting with the MH cathode acquire internal dynamic feedback between the discharge current and hydrogen pressure established in a closed gas discharge chamber. The so-called “pressure auto-stabilisation” effect [322] is promising in the development of very efficient applications of MH (reversible hydrogen getters) in vacuum-plasma technologies by the creation of compact, autonomous, and simple in operation facilities characterised by a high gas efficiency [323–326].

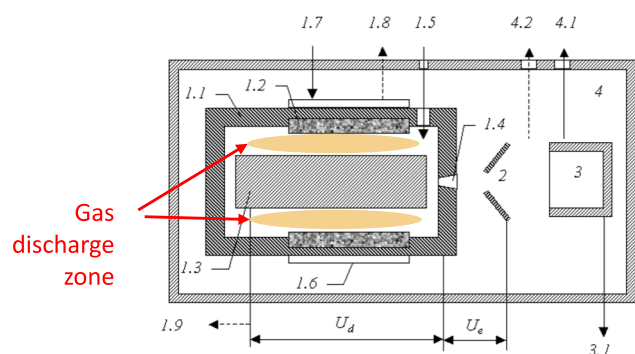


Fig. 17. Schematic representation of a prototype ion source utilising MH as a part of anode of gas discharge chamber (1): 1.1 – anode, 1.2 – MH insertion, 1.3 – cathode, 1.4 – emission aperture, 1.5 – external H_2 supply, 1.6 – heating element, 1.7 – powering of the heating element, 1.8 – temperature feedback signal, 1.9 – logging of the discharge current; 2 – extraction electrode; 3 – ion collector; 3.1 – logging of the ion beam current; 4 – vacuum chamber; 4.1 – evacuation, 4.2 – vacuum logging. (Adopted from [316,319].)

Feasibility of a thin film source of H_2^+ ions formed due to electron stimulated hydrogen desorption from TiH_2 thin films followed by H_2 ionisation has been demonstrated in ref. [327].

Applications of MH hydrogen getters in vacuum-plasma technologies also include targets for the laser sources of protons (MgH_2 , ZrH_2) [328] and neutron generators (titanium tritide); the latter application also uses deuterium-saturated getter alloy for the supply of low-pressure deuterium gas [329].

Recently published review [330] considers Zr and V-based intermetallics and multiphase alloys as promising non-evaporable hydrogen getters. Other recent publications on the topic can be found in the references of the corresponding section of review [77], as well as in the refs [331–336].

4. Discussion

Use of metal hydrides because of versatility of their thermodynamic properties thus covering an extremely broad range of hydrogen pressures spanning 10 orders of magnitude (see Fig. 4), allows to efficiently utilise them for hydrogen storage, hydrogen compression, heat storage and conversion, and in vacuum-plasma technologies.

The rich chemistry of metal hydrides extends this application landscape to the processes of hydrogen generation by the hydrolysis of the MH [337–340], catalysis of the chemical reactions involving transfer of hydrogen [73,341–343], powder metallurgy processing of the metals including HDDR route [132,136,344,345]. Each of these mentioned applications owns a vast amount of individual specific features and deserves to be considered in separate reviews.

Use of the approach “From material to system” (Fig. 6), allows to properly select relevant for the specific application MH and to optimise their properties making them suitable to fulfil the requirements of the targeted engineering solutions. When developing various gas-phase applications of metal hydrides, a joint use of the metal hydride technologies together with other suitable hydrogen energy technologies appears to be particularly fruitful because of their synergy thus bringing benefits by mitigating the effect of disadvantageous features while amplifying the advantages of the combined methods. One example is the development of hybrid hydrogen compression technology by integrating electrochemical hydrogen supply system providing hydrogen gas with an output pressure of 10–200 bar and metal hydride hydrogen compression technology boosting this pressure to 200–875 bar. Such integrated system offers a higher reliability and energy efficiency as compared to 10–875 bar electrochemical and metal hydride hydrogen compressors when operating separately [346]. Another example is the

application of AB_5 -type hydride-forming material surface-modified by Pd acting as a very efficient catalyst in the hydrogenation/dehydrogenation of liquid organic hydrogen carriers [347].

We believe that further R&D in the development of gas phase applications of metal hydrides will be focused on addressing system integration issues by introducing multi-functional MH units into balance of plant (BoP) of small-to-medium (up to 100–200 kW) hydrogen-based renewable energy systems [348]. Along with compact hydrogen storage, such units can provide utilisation of heat losses from the system components (e.g., electrolyser and fuel cell), heat storage and conversion, hydrogen compression for dispensing to the fuel cell vehicles, together with other useful features which will eventually result in the extension of system functionality and increase of the round-trip efficiency.

Successful implementation of this approach requires in-depth application-targeted studies of MH materials including:

- Selection of the compositions of multi-component hydride-forming alloys and catalysed hydride composites whose hydrogen sorption properties will be well aligned with the requirements of end-use applications as concerns of operating temperatures and hydrogen pressures. The search could be done using computer modelling (including machine learning tools) followed by the experimental validation of the PCT behaviours of the selected materials.
- In-depth experimental studies of hydrogen absorption – desorption kinetics for the promising MH materials including the influence of impurities in H_2 gas and H_2 absorption/desorption cycling on the kinetic parameters.
- Studies of the upscaling on the preparation of the MH materials as related to their phase-structural characteristics, morphology, and hydrogen sorption properties.

Along with the material studies, in-depth investigations of the engineering aspects of the use of MH materials will be continued. The focus will be on the augmentation of heat-and-mass transfer in the MH reactors, by the optimisation based on their simulation results together with the experimental validation. Special attention in these works should be paid to simplified modelling approaches which would allow to adequately predict H_2 charge/discharge dynamic performances of the MH reactors without excessive workload to assess the data concerning, e.g., spatial temperature distributions requiring use of significant computation resources and not always helpful in optimising the reactors design. This approach should provide a set of criterial equations where dimensionless criteria would describe the principal reactor parameters responsible for the charge/discharge dynamics. Examples of use of such approach can be found in refs [196, 349].

An extra component contributing to the improvement of H_2 charge/discharge dynamics via acceleration of reaction kinetics and optimisation of the heat transfer is in the development of advanced MH-based composites with additives which combine functions of hydrogenation/dehydrogenation catalyst and increase of the effective thermal conductivity of the MH bed. One good example is in use of graphene-like materials doped by nanoparticles of catalytically active metals [186].

Development of the MH reactors should also focus on addressing the safety concerns associated with the dilatation effects in MH materials, and, at the same time, maximising the MH loading density. Furthermore, elaboration of efficient and labour-saving procedures of the MH loading into the reactors is in a great demand.

For the high-pressure hydrogen compression applications, development of the MH containers for hydrogen compression combining sufficient strength with minimal material consumption (to reduce energy losses during the thermal cycling) is required.

Finally, future breakthroughs in the gas-phase metal hydride technologies can be achieved by proposing new solutions of their combination with the alternative technologies as has been already mentioned in this section.

5. Conclusions

The unique features of the reversible processes of formation/decomposition of metal hydrides make possible to efficiently use these materials for various applications. The applications based on heat-driven reversible interaction of hydride-forming materials with hydrogen gas are the most versatile. The MH systems for the gas-phase applications allow to tailor operating H₂ pressures in extremely broad range, while being compact, safe in operation, offering excellent absorption/desorption kinetics, and being easy to scale up based on the concept of modular design. Further to hydrogen storage, several other important technologies, including hydrogen compression, heat management, H₂ separation and purification, should be in focus in the development of the MH technologies. A success in realising this approach will be in a fine tuning of the properties of the MH materials, and in the optimisation of the system design addressing consumer's specification. MH applications are very important for energy storage and conversion technologies including hydrogen and fuel cell-based hydrogen energy systems. They allow to combine the processes of compact and safe hydrogen storage and its supply, along with the utilisation of waste heat released during operation of other system components.

Future progress in the gas-phase applications of metal hydrides will include in-depth application-targeted studies of metal hydride materials and development of advanced engineering solutions of the efficient metal hydride reactors aimed at integration of multi-functional metal hydride units into balance of plant of hydrogen-based renewable energy systems.

CRediT authorship contribution statement

I hereby state that the manuscript EST-D-23-01209R1 "Gas-phase applications of metal hydrides" has been jointly reviewed by all the co-authors, Mykhaylo Lototskyy, Boris Tarasov and Volodymyr Yartys, who agreed with the introduced updates.

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.

Data availability

No data was used for the research described in the article.

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References

- [1] T. Graham, On the absorption and dialytic separation of gases by colloid septa, *Philos. Trans. R. Soc. Lond.* 156 (1866) 399–439.
- [2] T. Graham, On the occlusion of hydrogen gas by metals, *Proc. R. Soc. Lond.* 16 (1868) 422–427.
- [3] W.M. Mueller, J.P. Blackledge, G.G. Libowitz, *Metal Hydrides*, Academic Press, New York – London, 1968.
- [4] G. Sandrock, Hydrogen – metal systems, in: Y. Yürüm (Ed.), *Hydrogen Energy System. Production and Utilization of Hydrogen and Future Aspects (NATO ASI, Series E)*, Kluwer Acad. Publ., Dordrecht – Boston – London, 1994, pp. 135–166.
- [5] G.G. Libowitz, H.F. Hayes, T.R.P. Gibb, The system zirconium–nickel and hydrogen, *J. Phys. Chem.* 62 (1958) 76–79, <https://doi.org/10.1021/j150559a019>.
- [6] H.H. Van Mal, K.H.J. Buschow, A.R. Miedema, Hydrogen absorption in LaNi₅ and related compounds: experimental observations and their explanation, *J. Less Common Metals* 35 (1974) 65–76, [https://doi.org/10.1016/0022-5088\(74\)90146-5](https://doi.org/10.1016/0022-5088(74)90146-5).
- [7] G. Sandrock, G. Thomas, *The IEA/DOE/SNL On-line Hydride Databases*, 2001.
- [8] Hydrogen Storage Materials Database. <http://Hydrogenmaterialssearch.Govtools.Us/>, 2010.
- [9] G. Sandrock, A panoramic overview of hydrogen storage alloys from a gas reaction point of view, *J. Alloys Compd.* 293 (1999) 877–888, [https://doi.org/10.1016/S0925-8388\(99\)00384-9](https://doi.org/10.1016/S0925-8388(99)00384-9).
- [10] T.N. Veziroglu, Twenty years of the hydrogen movement: 1974–1994, in: Y. Yürüm (Ed.), *Hydrogen Energy System. Production and Utilization of Hydrogen and Future Aspects (NATO ASI, Series E)*, Kluwer Acad. Publ., Dordrecht – Boston – London, 1994, pp. 1–14.
- [11] K.H.J. Buschow, P.C.P. Bouten, A.R. Miedema, Hydrides formed from intermetallic compounds of two transition metals: a special class of ternary alloys, *Rep. Prog. Phys.* 45 (1982) 937–1039, <https://doi.org/10.1088/0034-4885/45/9/001>.
- [12] F.E. Lynch, E. Snape, The role of metal hydrides in hydrogen storage and utilization, in: T.N. Veziroglu, W. Seifritz (Eds.), *Hydrogen Energy System: Proc. 2-Nd World Hydrogen Energy Conf*, Pergamon Press, Zurich, 1978, pp. 1475–1524.
- [13] R. Wiswall, Hydrogen storage in metals, in: G. Alefeld, J. Völkl (Eds.), *Hydrogen in Metals II. Application-Oriented Properties, Topics in Applied Physics*, Springer Verlag, Berlin–Heidelberg, 1978, pp. 201–242.
- [14] J.J. Reilly, Metal hydride technology, *Z. Phys. Chem.* 117 (1979) 155–184, <https://doi.org/10.1524/zpch.1979.117.117.155>.
- [15] H. Buchner, Perspectives for metal hydride technology, *Prog. Energy Combust. Sci.* 6 (1980) 331–346, [https://doi.org/10.1016/0360-1285\(80\)90009-X](https://doi.org/10.1016/0360-1285(80)90009-X).
- [16] A. Podgorny, Hydride systems in power engineering and motor transport, *Int. J. Hydrog. Energy* 14 (1989) 599–602, [https://doi.org/10.1016/0360-3199\(89\)90119-5](https://doi.org/10.1016/0360-3199(89)90119-5).
- [17] A.N. Podgorny, Y.F. Shmal'ko, V.V. Solovey, M.V. Lototsky, Metal hydride technology of hydrogen processing, in: T.N. Veziroglu, A.N. Protsenko (Eds.), *Hydrogen Energy Progress VII. Proc. 7-Th World Hydrogen Energy Conf*, Pergamon Press, Moscow, 1988, pp. 1401–1417.
- [18] B.P. Tarasov, M.V. Lototskii, Hydrogen energetics: past, present, prospects, *Russ. J. Gen. Chem.* 77 (2007), <https://doi.org/10.1134/S1070363207040299>.
- [19] J.O. Bockris, J.C. Wass, About the real economics of massive hydrogen production at 2010 A.D., in: T.N. Veziroglu, A.N. Protsenko (Eds.), *Hydrogen Energy Progress VII. Proc. 7-Th World Hydrogen Energy Conf*, Pergamon Press, Moscow, 1988, pp. 101–151.
- [20] K. Hoffman, J. Reilly, F. Salzano, C. Waide, R. Wiswall, W. Winsche, Metal hydride storage for mobile and stationary applications, *Int. J. Hydrog. Energy* 1 (1976) 133–151, [https://doi.org/10.1016/0360-3199\(76\)90067-7](https://doi.org/10.1016/0360-3199(76)90067-7).
- [21] E.L. Huston, G.D. Sandrock, Engineering properties of metal hydrides, *J. Less Common Metals* 74 (1980) 435–443, [https://doi.org/10.1016/0022-5088\(80\)90182-4](https://doi.org/10.1016/0022-5088(80)90182-4).
- [22] O. Bernauer, C. Halene, Properties of metal hydrides for use in industrial applications, *J. Less Common Metals* 131 (1987) 213–224, [https://doi.org/10.1016/0022-5088\(87\)90521-2](https://doi.org/10.1016/0022-5088(87)90521-2).
- [23] O. Bernauer, Metal hydride technology, *Int. J. Hydrog. Energy* 13 (1988) 181–190, [https://doi.org/10.1016/0360-3199\(88\)90017-1](https://doi.org/10.1016/0360-3199(88)90017-1).
- [24] I. Uehara, T. Sakai, H. Ishikawa, The state of research and development for applications of metal hydrides in Japan, *J. Alloys Compd.* 253–254 (1997) 635–641, [https://doi.org/10.1016/S0925-8388\(96\)03090-3](https://doi.org/10.1016/S0925-8388(96)03090-3).
- [25] G. Sandrock, S. Suda, L. Schlapbach, Applications, in: L. Schlapbach (Ed.), *Hydrogen in Intermetallic Compounds. II. Surface and Dynamic Properties, Applications*, Springer-Verlag, 1992, pp. 197–258.
- [26] G. Sandrock, Application of hydrides, in: Y. Yürüm (Ed.), *Hydrogen Energy System. Production and Utilization of Hydrogen and Future Aspects (NATO ASI, Series E)*, Kluwer Acad. Publ., Dordrecht – Boston – London, 1994, pp. 25–280.
- [27] G. Sandrock, R.C. Bowman, Gas-based hydride applications: recent progress and future needs, *J. Alloys Compd.* 356–357 (2003) 794–799, [https://doi.org/10.1016/S0925-8388\(03\)00090-2](https://doi.org/10.1016/S0925-8388(03)00090-2).
- [28] R.C. Bowman Jr., G. Sandrock, Metal hydrides for energy storage and conversion applications, in: *Global 2003: Atoms for Prosperity: Updating Eisenhower's Global Vision for Nuclear Energy*, New Orleans, 2003, pp. 1176–1177.
- [29] P. Dantzer, Metal-hydride technology: a critical review, in: H. Wipf (Ed.), *Hydrogen in Metals. III. Properties and Applications, Topics in Applied Physics*, Springer-Verlag, Berlin – Heidelberg, 1997, pp. 279–340.
- [30] P. Dantzer, Properties of intermetallic compounds suitable for hydrogen storage applications, *Mater. Sci. Eng. A* 329–331 (2002) 313–320, [https://doi.org/10.1016/S0921-5093\(01\)01590-8](https://doi.org/10.1016/S0921-5093(01)01590-8).
- [31] S. Suda, What is required for the commercialization of metal hydride refrigerators and heat pumps, *Heat Recovery Syst. CHP.* 13 (1993) 309–314, [https://doi.org/10.1016/0890-4332\(93\)90054-Y](https://doi.org/10.1016/0890-4332(93)90054-Y).

- [32] L. Schlapbach, A. Züttel, Hydrogen-storage materials for mobile applications, *Nature* 414 (2001) 353–358, <https://doi.org/10.1038/35104634>.
- [33] A. Züttel, Materials for hydrogen storage, *Mater. Today* 6 (2003) 24–33, [https://doi.org/10.1016/S1369-7021\(03\)00922-2](https://doi.org/10.1016/S1369-7021(03)00922-2).
- [34] A. Züttel, A. Remhof, A. Borgschulte, O. Friedrichs, Hydrogen: the future energy carrier, *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 368 (2010) 3329–3342, <https://doi.org/10.1098/rsta.2010.0113>.
- [35] R.C. Bowman, B. Fultz, Metallic hydrides I: hydrogen storage and other gas-phase applications, *MRS Bull.* 27 (2002) 688–693, <https://doi.org/10.1557/mrs2002.223>.
- [36] J.-M. Joubert, M. Lacroche, A. Percheron-Guégan, Metallic hydrides II: materials for electrochemical storage, *MRS Bull.* 27 (2002) 694–698, <https://doi.org/10.1557/mrs2002.224>.
- [37] M. Lacroche, Structural and thermodynamic properties of metallic hydrides used for energy storage, *J. Phys. Chem. Solids* 65 (2004) 517–522, <https://doi.org/10.1016/j.jpcs.2003.08.037>.
- [38] V. Yartys, V. Burnasheva, K. Semenenko, N. Fadeeva, S. Solovev, Crystal chemistry of $RT_5H(D)x$, $RT_2H(D)x$ and $RT_3H(D)x$ hydrides based on intermetallic compounds of $CaCu_5$, $MgCu_2$, $MgZn_2$ and $PuNi_3$ structure types, *Int. J. Hydrog. Energy* 7 (1982) 957–965, [https://doi.org/10.1016/0360-3199\(82\)90164-1](https://doi.org/10.1016/0360-3199(82)90164-1).
- [39] V.A. Yartys, V.V. Burnasheva, K.N. Semenenko, Structural chemistry of hydrides of intermetallic compounds, *Russ. Chem. Rev.* 52 (1983) 299–317, <https://doi.org/10.1070/RC1983v05n04ABEH002818>.
- [40] 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), <https://doi.org/10.1134/S1070363207040329>.
- [41] B.P. Tarasov, Metal-hydride accumulators and generators of hydrogen for feeding fuel cells, *Int. J. Hydrog. Energy* 36 (2011) 1196–1199, <https://doi.org/10.1016/j.ijhydene.2010.07.002>.
- [42] B. Sakintuna, F. Lamari-Darkrim, M. Hirscher, Metal hydride materials for solid hydrogen storage: a review, *Int. J. Hydrog. Energy* 32 (2007) 1121–1140, <https://doi.org/10.1016/j.ijhydene.2006.11.022>.
- [43] D. Chandra, W.-M. Chien, A. Talekar, Metal hydrides for NiMH battery applications, *Mater. Matters* 6 (2011) 48–53.
- [44] G. Walker, M. Bououdina, Z.X. Guo, D. Fruchart, Overview on hydrogen absorbing materials: structure, microstructure, and physical properties, in: M. Bououdina, J.P. Davim (Eds.), *Handbook of Research on Nanoscience, Nanotechnology, and Advanced Materials*, IGI Global, 2014, pp. 312–342.
- [45] N.A.A. Rusman, M. Dahari, A review on the current progress of metal hydrides material for solid-state hydrogen storage applications, *Int. J. Hydrog. Energy* 41 (2016) 12108–12126, <https://doi.org/10.1016/j.ijhydene.2016.05.244>.
- [46] V. Yartys, D. Noreus, M. Lacroche, Metal hydrides as negative electrode materials for Ni–MH batteries, *Appl. Phys. A Mater. Sci. Process.* 122 (2016) 1–11, <https://doi.org/10.1007/s00339-015-9538-9>.
- [47] S. Sartori, F. Cuevas, M. Lacroche, Metal hydrides used as negative electrode materials for Li-ion batteries, *Appl. Phys. A Mater. Sci. Process.* 122 (2016) 135, <https://doi.org/10.1007/s00339-016-9674-x>.
- [48] R. Mohtadi, S. Orimo, The renaissance of hydrides as energy materials, *Nat. Rev. Mater.* 2 (2016) 16091, <https://doi.org/10.1038/natrevmats.2016.91>.
- [49] R. Bhattacharyya, S. Mohan, Solid state storage of hydrogen and its isotopes: an engineering overview, *Renew. Sust. Energ. Rev.* 41 (2015) 872–883, <https://doi.org/10.1016/j.rser.2014.09.004>.
- [50] S.S. Makridis, Hydrogen storage and compression, in: R. Carrière, D.S.-K. Ting (Eds.), *Methane and Hydrogen for Energy Storage*, IET, 2016, pp. 1–28.
- [51] H. Barthelemy, M. Weber, F. Barbier, Hydrogen storage: recent improvements and industrial perspectives, *Int. J. Hydrog. Energy* 42 (2017) 7254–7262, <https://doi.org/10.1016/j.ijhydene.2016.03.178>.
- [52] M.V. Lototskyy, I. Tolj, L. Pickering, C. Sita, F. Barbir, V. Yartys, The use of metal hydrides in fuel cell applications, *Prog. Nat. Sci. Mater. Int.* 27 (2017), <https://doi.org/10.1016/j.pnsc.2017.01.008>.
- [53] K.T. Møller, T.R. Jensen, E. Akiba, H. Li, Hydrogen - a sustainable energy carrier, *Prog. Nat. Sci. Mater. Int.* 27 (2017) 34–40, <https://doi.org/10.1016/j.pnsc.2016.12.014>.
- [54] H. Itoh, T. Kautomori, H. Takeda, Other applications (actuator, hydrogen purification, and isotope separation), in: *Encyclopedia of Life Support Systems (EOLSS)*. Energy Carriers and Conversion Systems 2, 2013. <http://www.eolss.net/ebooklib> (accessed December 31, 2022).
- [55] M.V. Lototskyy, V.A. Yartys, B.G. Pollet, R.C. Bowman Jr., Metal hydride hydrogen compressors: a review, *Int. J. Hydrog. Energy* 39 (2014), <https://doi.org/10.1016/j.ijhydene.2014.01.158>.
- [56] M. Lototskyy, B. Satya Sekhar, P. Muthukumar, V. Linkov, B.G. Pollet, Niche applications of metal hydrides and related thermal management issues, *J. Alloys Compd.* 645 (2015) S117–S122, <https://doi.org/10.1016/j.jallcom.2014.12.271>.
- [57] V.A. Yartys, M. Lototskyy, V. Linkov, D. Grant, A. Stuart, J. Eriksen, R. Denys, R. C. Bowman, Metal hydride hydrogen compression: recent advances and future prospects, *Appl. Phys. A Mater. Sci. Process.* 122 (2016), <https://doi.org/10.1007/s00339-016-9863-7>.
- [58] P. Muthukumar, M. Groll, Erratum to “Metal hydride based heating and cooling systems: a review” [International Journal of Hydrogen Energy (2010) 35: 3817–3831], *Int. J. Hydrog. Energy* 35 (2010) 8816–8829, <https://doi.org/10.1016/j.ijhydene.2010.04.087>.
- [59] X. Qu, Y. Li, P. Li, Q. Wan, F. Zhai, The development of metal hydrides using as concentrating solar thermal storage materials, *Front. Mater. Sci.* 9 (2015) 317–331, <https://doi.org/10.1007/s11706-015-0311-y>.
- [60] E.C.E. Rönnebro, E.H. Majzoub, Recent advances in metal hydrides for clean energy applications, *MRS Bull.* 38 (2013) 452–458, <https://doi.org/10.1557/mrs.2013.132>.
- [61] M.V. Lototskyy, M. Williams, V.A. Yartys, Y.V. Klochko, V.M. Linkov, Surface-modified advanced hydrogen storage alloys for hydrogen separation and purification, *J. Alloys Compd.* 509 (2011), <https://doi.org/10.1016/j.jallcom.2010.09.206>.
- [62] K.D. Modibane, M. Williams, M. Lototskyy, M.W. Davids, Y. Klochko, B.G. Pollet, Poisoning-tolerant metal hydride materials and their application for hydrogen separation from CO_2/CO containing gas mixtures, *Int. J. Hydrog. Energy* 38 (2013) 9800–9810, <https://doi.org/10.1016/j.ijhydene.2013.05.102>.
- [63] J. Bellosta von Colbe, J.R. Ares, J. Barale, M. Baricco, C. Buckley, G. Capurso, N. Gallandat, D.M. Grant, M.N. Guzik, I. Jacob, E.H. Jensen, T. Jensen, J. Jepsen, T. Klassen, M.V. Lototskyy, K. Manickam, A. Montone, J. Puszkiel, S. Sartori, D. A. Sheppard, A. Stuart, G. Walker, C.J. Webb, H. Yang, V. Yartys, A. Züttel, M. Dornheim, Application of hydrides in hydrogen storage and compression: achievements, outlook and perspectives, *Int. J. Hydrog. Energy* 44 (2019) 7780–7808, <https://doi.org/10.1016/j.ijhydene.2019.01.104>.
- [64] V.A. Yartys, M.V. Lototskyy, E. Akiba, R. Albert, V.E. Antonov, J.R. Ares, M. Baricco, N. Bourgeois, C.E. Buckley, J.M. Bellosta von Colbe, J.C. Crivello, F. Cuevas, R.V. Denys, M. Dornheim, M. Felderhoff, D.M. Grant, B.C. Hauback, T. D. Humphries, I. Jacob, T.R. Jensen, P.E. de Jongh, J.M. Joubert, M. A. Kuzovnikov, M. Lacroche, M. Paskevicius, L. Pasquini, L. Popilevsky, V. M. Skripnyuk, E. Rabkin, M.V. Sofianos, A. Stuart, G. Walker, H. Wang, C. J. Webb, M. Zhu, Magnesium based materials for hydrogen based energy storage: past, present and future, *Int. J. Hydrog. Energy* 44 (2019) 7809–7859, <https://doi.org/10.1016/j.ijhydene.2018.12.212>.
- [65] L. Pasquini, K. Sakaki, E. Akiba, M.D. Allendorf, E. Alvares, J.R. Ares, D. Babai, M. Baricco, J. Bellosta von Colbe, M. Berezniytsky, C.E. Buckley, Y.W. Cho, F. Cuevas, P. de Rango, E.M. Dematteis, R.V. Denys, M. Dornheim, J. F. Fernández, A. Hariyadi, B.C. Hauback, T.V. Heo, M. Hirscher, T.D. Humphries, J. Huot, I. Jacob, T.R. Jensen, P. Jerabek, S.Y. Kang, N. Keilbart, H. Kim, M. Lacroche, F. Leardini, H. Li, S. Ling, M.V. Lototskyy, R. Mullen, S. Orimo, M. Paskevicius, C. Pistidda, M. Polanski, J. Puszkiel, E. Rabkin, M. Sahlberg, S. Sartori, A. Santhosh, T. Sato, R.Z. Shneck, M.H. Sorby, Y. Shang, V. Stavila, J.-Y. Suh, S. Suwarno, L. Thi Thu, L.F. Wan, C.J. Webb, M. Witman, C. Wan, B. C. Wood, V.A. Yartys, Magnesium- and intermetallic alloys-based hydrides for energy storage: modelling, synthesis and properties, *Progress Energy* 4 (2022), <https://doi.org/10.1088/2516-1083/ac7190>.
- [66] M. Dornheim, L. Baetcke, E. Akiba, J.R. Ares, T. Autrey, J. Barale, M. Baricco, K. Brooks, N. Chalkiadakis, V. Charbonnier, S. Christensen, J. Bellosta Von Colbe, M. Costamagna, E. Dematteis, J.F. Fernandez, T. Gennett, D. Grant, T.W. Heo, M. Hirscher, K. Hurst, M. Lototskyy, O. Metz, P. Rizzi, K. Sakaki, S. Sartori, E. Stamatakis, A. Stuart, A. Stubos, G. Walker, C.J. Webb, B. Wood, V. Yartys, E. Zoulias, Research and development of hydrogen carrier based solutions for hydrogen compression and storage, *Progress Energy* 4 (2022), <https://doi.org/10.1088/2516-1083/ac7cb7>.
- [67] P. Modi, K.F. Aguey-Zinsou, Room temperature metal hydrides for stationary and heat storage applications: a review, *Front. Energy Res.* 9 (2021), <https://doi.org/10.3389/fenrg.2021.616115>.
- [68] L. Wang, J. Wang, L. Wang, M. Zhang, R. Wang, C. Zhan, A critical review on nickel-based cathodes in rechargeable batteries, *Int. J. Miner. Metall. Mater.* 29 (2022) 925–941, <https://doi.org/10.1007/s12613-022-2446-z>.
- [69] J. Monnier, J. Zhang, F. Cuevas, M. Lacroche, Hydrides compounds for electrochemical applications, *Curr. Opin. Electrochem.* 32 (2022), <https://doi.org/10.1016/j.coelec.2021.100921>.
- [70] K. Malleswararao, P. Dutta, S. Murthy, Applications of metal hydride based thermal systems: a review, *Appl. Therm. Eng.* 215 (2022), <https://doi.org/10.1016/j.applthermaleng.2022.118816>.
- [71] S.K. Dewangan, M. Mohan, V. Kumar, A. Sharma, B. Ahn, A comprehensive review of the prospects for future hydrogen storage in materials-application and outstanding issues, *Int. J. Energy Res.* 46 (2022) 16150–16177, <https://doi.org/10.1002/er.8322>.
- [72] Y. Zhang, S. Wu, L. Wang, X. Zhang, Chemisorption solid materials for hydrogen storage near ambient temperature: a review, *Front. Energy* (2022), <https://doi.org/10.1007/s11708-022-0835-7>.
- [73] M.S. Salman, Q. Lai, X. Luo, C. Prathana, N. Rambhujun, M. Costalin, T. Wang, P. Sapkota, W. Liu, A. Grahame, J. Tupe, K.F. Aguey-Zinsou, The power of multifunctional metal hydrides: a key enabler beyond hydrogen storage, *J. Alloys Compd.* 920 (2022), <https://doi.org/10.1016/j.jallcom.2022.165936>.
- [74] D.S. dos Santos, S. Miraglia, D. Fruchart, A high pressure investigation of Pd and the Pd–H system, *J. Alloys Compd.* 291 (1999) L1–L5, [https://doi.org/10.1016/S0925-8388\(99\)00281-9](https://doi.org/10.1016/S0925-8388(99)00281-9).
- [75] R. Caton, C.B. Satterthwaite, Preparation and characterization of massive Th_4H_{15} and Th_4D_{15} , *J. Less Common Metals* 52 (1977) 307–321, [https://doi.org/10.1016/0022-5088\(77\)90011-X](https://doi.org/10.1016/0022-5088(77)90011-X).
- [76] Yu.F. Shmal'ko, M.V. Lototskyy, Ye.V. Klochko, V.V. Solovey, The formation of excited H species using metal hydrides, *J. Alloys Compd.* 231 (1995), [https://doi.org/10.1016/0925-8388\(95\)01772-0](https://doi.org/10.1016/0925-8388(95)01772-0).
- [77] V.A. Yartys, M.V. Lototskyy, Laves type intermetallic compounds as hydrogen storage materials: a review, *J. Alloys Compd.* (2022), 165219, <https://doi.org/10.1016/j.jallcom.2022.165219>.
- [78] S. Luo, W. Luo, J.D. Clewley, T.B. Flanagan, R.C. Bowman, Thermodynamic and degradation studies of $LaNi_{4.8}Sn_{0.2}H$ using isotherms and calorimetry, *J. Alloys Compd.* 231 (1995) 473–478, [https://doi.org/10.1016/0925-8388\(95\)01870-0](https://doi.org/10.1016/0925-8388(95)01870-0).

- [79] M.V. Lototskyy, New model of phase equilibria in metal - hydrogen systems: features and software, *Int. J. Hydrog. Energy* 41 (2016) 2739–2761, <https://doi.org/10.1016/j.ijhydene.2015.12.055>.
- [80] M. Lototskyy, V.A. Yartys, Comparative analysis of the efficiencies of hydrogen storage systems utilising solid state H storage materials, *J. Alloys Compd.* 645 (2015), <https://doi.org/10.1016/j.jallcom.2014.12.107>.
- [81] M. Kölbig, C. Weckerle, M. Linder, I. Bürger, Review on thermal applications for metal hydrides in fuel cell vehicles: operation modes, recent developments and crucial design aspects, *Renew. Sust. Energ. Rev.* 162 (2022), <https://doi.org/10.1016/j.rser.2022.112385>.
- [82] A. Kumar, P. Muthukumar, P. Sharma, E.A. Kumar, Absorption based solid state hydrogen storage system: a review, *Sust. Energy Technol. Assess.* 52 (2022), <https://doi.org/10.1016/j.seta.2022.102204>.
- [83] B. Friedrich, Large-scale production and quality assurance of hydrogen storage (battery) alloys, *J. Mater. Eng. Perform.* 3 (1994) 37–46, <https://doi.org/10.1007/BF02654497>.
- [84] S. Fashu, M. Lototskyy, M.W. Davids, L. Pickering, V. Linkov, S. Tai, T. Renheng, X. Fangming, P.V. Fursikov, B.P. Tarasov, A review on crucibles for induction melting of titanium alloys, *Mater. Des.* 186 (2020), 108295, <https://doi.org/10.1016/j.matdes.2019.108295>.
- [85] F. Guo, K. Namba, H. Miyaoka, A. Jain, T. Ichikawa, Hydrogen storage behavior of TiFe alloy activated by different methods, *Mater. Lett.* X 9 (2021), <https://doi.org/10.1016/j.mblux.2021.100061>.
- [86] K. Panwar, S. Srivastava, Enhancement in hydrogenation properties of ball-milled AB₅-type hydrogen storage alloy through catalyst, *J. Phys. Conf. Ser. Inst. Phys.* (2022), <https://doi.org/10.1088/1742-6596/2267/1/012052>.
- [87] D.M. Dreistadt, L. Thi-Thu, G. Capurso, J.M. Bellosta von Colbe, A. Santhosh, C. Pistidda, N. Scharnagl, H. Ovir, C. Milanese, P. Jerabek, T. Klassen, J. Jepsen, An effective activation method for industrially produced TiFeMn powder for hydrogen storage, *J. Alloys Compd.* 919 (2022), <https://doi.org/10.1016/j.jallcom.2022.165847>.
- [88] C. Li, Y. Lan, X. Wei, W. Zhang, B. Liu, X. Gao, Z. Yuan, Improvement of hydrogen absorption and desorption properties of TiFe-based alloys by adding yttrium, *J. Alloys Compd.* 927 (2022), <https://doi.org/10.1016/j.jallcom.2022.166992>.
- [89] H. Liu, J. Zhang, P. Sun, C. Zhou, Y. Liu, Z.Z. Fang, Effect of oxygen addition on phase composition and activation properties of TiFe alloy, *Int. J. Hydrog. Energy* (2022), <https://doi.org/10.1016/j.ijhydene.2022.11.353>.
- [90] K. Nasako, Y. Ito, N. Hiro, M. Osumi, Stress on a reaction vessel by the swelling of a hydrogen absorbing alloy, *J. Alloys Compd.* 264 (1998) 271–276, [https://doi.org/10.1016/S0925-8388\(97\)00246-6](https://doi.org/10.1016/S0925-8388(97)00246-6).
- [91] C.-K. Lin, S.-M. Huang, Y.-H. Jhang, Effects of cyclic hydriding–dehydriding reactions of Mg₂Ni alloy on the expansion deformation of a metal hydride storage vessel, *J. Alloys Compd.* 509 (2011) 7162–7167, <https://doi.org/10.1016/j.jallcom.2011.04.038>.
- [92] M. Okumura, K. Terui, A. Ikado, Y. Saito, M. Shoji, Y. Matsushita, H. Aoki, T. Miura, Y. Kawakami, Investigation of wall stress development and packing ratio distribution in the metal hydride reactor, *Int. J. Hydrog. Energy* 37 (2012) 6686–6693, <https://doi.org/10.1016/j.ijhydene.2012.01.097>.
- [93] 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. Hydrog. Energy* 37 (2012) 16031–16041, <https://doi.org/10.1016/j.ijhydene.2012.07.091>.
- [94] B. Charlas, F. Kneib, O. Gillia, D. Imbault, P. Doremus, A tool for modelling the breathing of hydride powder in its container while cyclically absorbing and desorbing hydrogen, *Int. J. Hydrog. Energy* 40 (2015) 2283–2294, <https://doi.org/10.1016/j.ijhydene.2014.11.077>.
- [95] A.R. Galvis Escobar, A. Chaise, V. Iosub, B. Salque, J.F. Fernandez, O. Gillia, Stress effect on the swelling/shrinking behavior of an AB₂ alloy during hydrogenation cycles, *Int. J. Hydrog. Energy* 42 (2017) 22422–22431, <https://doi.org/10.1016/j.ijhydene.2017.03.145>.
- [96] F. Heubner, A. Hilger, N. Kardjilov, I. Manke, B. Kieback, L. Gondek, J. Banhart, L. Röntsch, In-operando stress measurement and neutron imaging of metal hydride composites for solid-state hydrogen storage, *J. Power Sources* 397 (2018) 262–270, <https://doi.org/10.1016/j.jpowsour.2018.06.093>.
- [97] V.I. Borzenko, I.A. Romanov, D.O. Dunikov, A.N. Kazakov, Hydrogen sorption properties of metal hydride beds: effect of internal stresses caused by reactor geometry, *Int. J. Hydrog. Energy* 44 (2019) 6086–6092, <https://doi.org/10.1016/j.ijhydene.2019.01.052>.
- [98] C. Briki, P. de Rango, S. Belkhiria, M.H. Dhaou, A. Jemni, Measurements of expansion of LaNi₅ compacted powder during hydrogen absorption/desorption cycles and their influences on the reactor wall, *Int. J. Hydrog. Energy* 44 (2019) 13647–13654, <https://doi.org/10.1016/j.ijhydene.2019.04.010>.
- [99] O. Gillia, Hydride breathing and its consequence on stresses applied to containers: a review, *Int. J. Hydrog. Energy* 46 (2021) 35594–35640, <https://doi.org/10.1016/j.ijhydene.2021.07.082>.
- [100] M. Lototskyy, R. Denys, V.A. Yartys, J. Eriksen, J. Goh, S.N. Nyamsi, C. Sita, F. Cummings, An outstanding effect of graphite in nano-MgH₂-TiH₂ on hydrogen storage performance, *J. Mater. Chem. A Mater.* 6 (2018) 10740–10754, <https://doi.org/10.1039/c8ta02969e>.
- [101] K.N. Semenenko, V.V. Burnasheva, Synthesis and phase transformations of hydrogen compounds with metals, *Vestn. Mosk. Univ., Khim.* 18 (1977) 618–632.
- [102] K.N. Semenenko, V.V. Burnasheva, Physicochemistry and crystallochemistry of intermetallic hydrides containing rare earths and transition metals, *J. Less Common Metals* 105 (1985) 1–11, [https://doi.org/10.1016/0022-5088\(85\)90121-3](https://doi.org/10.1016/0022-5088(85)90121-3).
- [103] P.D. Goodell, Stability of rechargeable hydriding alloys during extended cycling, *J. Less Common Metals* 99 (1984) 1–14, [https://doi.org/10.1016/0022-5088\(84\)90330-8](https://doi.org/10.1016/0022-5088(84)90330-8).
- [104] J.-M. Park, J.-Y. Lee, The intrinsic degradation phenomena of LaNi₅ and LaNi_{4.7}Al_{0.3} by temperature induced hydrogen absorption-desorption cycling, *Mater. Res. Bull.* 22 (1987) 455–465, [https://doi.org/10.1016/0025-5408\(87\)90255-8](https://doi.org/10.1016/0025-5408(87)90255-8).
- [105] G.D. Sandrock, P.D. Goodell, E.L. Huston, P.M. Golben, On the disproportionation of intermetallic hydrides, *Z. Phys. Chem.* 164 (1989) 1285–1290, <https://doi.org/10.1524/zpch.1989.164.Part.2.1285>.
- [106] Y. Josephy, E. Bershadsky, M. Ron, Investigation of LaNi₅ after prolonged cycling, *J. Less Common Metals* 172–174 (1991) 997–1008, [https://doi.org/10.1016/S0022-5088\(06\)80005-6](https://doi.org/10.1016/S0022-5088(06)80005-6).
- [107] D. Chandra, S. Bagchi, S.W. Lambert, W.N. Cathey, F.E. Lynch, R.C. Bowman, Long-term thermal cycling studies on LaNi_{5.2}, *J. Alloys Compd.* 199 (1993) 93–100, [https://doi.org/10.1016/0925-8388\(93\)90432-M](https://doi.org/10.1016/0925-8388(93)90432-M).
- [108] R.C. Bowman, C.H. Luo, C.C. Ahn, C.K. Witham, B. Fultz, The effect of tin on the degradation of LaNi₅-Sn metal hydrides during thermal cycling, *J. Alloys Compd.* 217 (1995) 185–192, [https://doi.org/10.1016/0925-8388\(94\)01337-3](https://doi.org/10.1016/0925-8388(94)01337-3).
- [109] G. Friedlmeier, A. Manthey, M. Wanner, M. Groll, Cyclic stability of various application-relevant metal hydrides, *J. Alloys Compd.* 231 (1995) 880–887, [https://doi.org/10.1016/0925-8388\(95\)01776-3](https://doi.org/10.1016/0925-8388(95)01776-3).
- [110] M. Wanner, G. Friedlmeier, G. Hoffmann, M. Groll, Thermodynamic and structural changes of various intermetallic compounds during extended cycling in closed systems, *J. Alloys Compd.* 253–254 (1997) 692–697, [https://doi.org/10.1016/S0925-8388\(96\)03041-1](https://doi.org/10.1016/S0925-8388(96)03041-1).
- [111] J.-M. Joubert, M. Lacroche, R. Černý, A. Percheron-Guégan, K. Yvon, Hydrogen cycling induced degradation in LaNi₅-type materials, *J. Alloys Compd.* 330–332 (2002) 208–214, [https://doi.org/10.1016/S0925-8388\(01\)01640-1](https://doi.org/10.1016/S0925-8388(01)01640-1).
- [112] B.P. Tarasov, M.S. Bocharnikov, Y.B. Yanenko, P.V. Fursikov, M.V. Lototskyy, Cycling stability of RNi₅ (R = La, La+Ce) hydrides during the operation of metal hydride hydrogen compressor, *Int. J. Hydrog. Energy* 43 (2018) 4415–4427, <https://doi.org/10.1016/j.ijhydene.2018.01.086>.
- [113] Z. Zhu, S. Zhu, H. Lu, J. Wu, K. Yan, H. Cheng, J. Liu, Stability of LaNi₅-Co alloys cycled in hydrogen — part I evolution in gaseous hydrogen storage performance, *Int. J. Hydrog. Energy* 44 (2019) 15159–15172, <https://doi.org/10.1016/j.ijhydene.2019.04.111>.
- [114] S. Nayeboossadri, D. Book, Compositional effects on the hydrogen cycling stability of multicomponent Ti-Mn based alloys, *Int. J. Hydrog. Energy* 44 (2019) 10722–10731, <https://doi.org/10.1016/j.ijhydene.2019.02.138>.
- [115] F. Guo, A. Jain, H. Miyaoka, Y. Kojima, T. Ichikawa, Critical temperature and pressure conditions of degradation during thermochemical hydrogen compression: a case study of V-based hydrogen storage alloy, *Energies (Basel)* 13 (2020) 2324, <https://doi.org/10.3390/en13092324>.
- [116] J.H. Zhu, C.T. Liu, L.M. Pike, P.K. Liaw, Enthalpies of formation of binary Laves phases, *Intermetallics (Barking)* 10 (2002) 579–595, [https://doi.org/10.1016/S0966-9795\(02\)00030-4](https://doi.org/10.1016/S0966-9795(02)00030-4).
- [117] W.N. Hubbard, P.L. Rawlins, P.A. Connick, R.E. Stedwell, P.A.G. O'Hare, The standard enthalpy of formation of LaNi₅ the enthalpies of hydriding of LaNi_{5-x}Al_x, *J. Chem. Thermodyn.* 15 (1983) 785–798, [https://doi.org/10.1016/0021-9614\(83\)90145-3](https://doi.org/10.1016/0021-9614(83)90145-3).
- [118] R.C. Bowman, E.A. Payzant, P.R. Wilson, D.P. Pearson, A. Ledovskikh, D. Danilov, P.H.L. Notten, K. An, H.D. Skorpenske, D.L. Wood, Characterization and analyses of degradation and recovery of LaNi_{4.78}Sn_{0.22} hydrides following thermal aging, *J. Alloys Compd.* 580 (2013) S207–S210, <https://doi.org/10.1016/j.jallcom.2013.03.129>.
- [119] K. Suzuki, K. Ishikawa, K. Aoki, Degradation of LaNi₅ and LaNi_{4.7}Al_{0.3} hydrogen-absorbing alloys by cycling, *Mater. Trans. JIM* 41 (2000) 581–584, <https://doi.org/10.2320/matertrans1989.41.581>.
- [120] J. Liu, K. Li, H. Cheng, K. Yan, Y. Wang, Y. Liu, H. Jin, Z. Zheng, New insights into the hydrogen storage performance degradation and Al functioning mechanism of LaNi₅-Al alloys, *Int. J. Hydrog. Energy* 42 (2017) 24904–24914, <https://doi.org/10.1016/j.ijhydene.2017.07.213>.
- [121] R.V. Denys, V.A. Yartys, C.J. Webb, Hydrogen in La₂MgNi₉D₁₃: the role of magnesium, *Inorg. Chem.* 51 (2012) 4231–4238, <https://doi.org/10.1021/ic202705u>.
- [122] V. Paul-Boncour, C. Lartigue, A. Percheron-Guégan, J.C. Achard, J. Pannetier, In situ neutron powder diffraction measurements of the absorption and desorption of hydrogen (deuterium) in (La,Ce)Ni₂ compounds: amorphization and recrystallization, *J. Less Common Metals* 143 (1988) 301–313, [https://doi.org/10.1016/0022-5088\(88\)90052-5](https://doi.org/10.1016/0022-5088(88)90052-5).
- [123] X. Dong, Y. Chen, J. Su, T. Gao, Y. Ma, X. Li, Research progress on hydrogen-induced amorphization in hydrogen storage alloys, *Mater. Rep.* 34 (2020) 15110–15115.
- [124] H.Y. Zhu, J. Wu, Q.D. Wang, Disproportionation of LaNi₅ and TiFe in 4 MPa H₂ at 300 °C, *J. Alloys Compd.* 185 (1992) 1–6, [https://doi.org/10.1016/0925-8388\(92\)90546-L](https://doi.org/10.1016/0925-8388(92)90546-L).
- [125] K. Watanabe, M. Hara, M. Matsuyama, I. Kanesaka, T. Kabutomori, Stability of ZrCo and ZrNi to heat cycles in hydrogen atmosphere, *Fusion Technol.* 28 (1995) 1437–1442, <https://doi.org/10.13182/FST95-A30614>.
- [126] M. Prina, R.C. Bowman, J.G. Kulleck, Degradation study of ZrNiH_{1.5} for use as actuators in gas gap heat switches, *J. Alloys Compd.* 373 (2004) 104–114, <https://doi.org/10.1016/j.jallcom.2003.10.053>.
- [127] S. Selvaraj, A. Jain, S. Kumar, T. Zhang, S. Isobe, H. Miyaoka, Y. Kojima, T. Ichikawa, Study of cyclic performance of V-Ti-Cr alloys employed for hydrogen

- compressor, *Int. J. Hydrog. Energy* 43 (2018) 2881–2889, <https://doi.org/10.1016/j.ijhydene.2017.12.159>.
- [128] V.A. Yartys, C.J. Webb, F. Cuevas, In situ diffraction studies of phase-structural transformations in hydrogen and energy storage materials: an overview, *J. Alloys Compd.* 953 (2023), 170133, <https://doi.org/10.1016/j.jallcom.2023.170133>.
- [129] V.A. Yartys, H. Fjellvåg, I.R. Harris, B.C. Hauback, A.B. Riabov, M.H. Sorby, I. Yu. Zavalii, Hydrogen ordering and H-induced phase transformations in Zr-based intermetallic hydrides, *J. Alloys Compd.* 293–295 (1999) 74–87, [https://doi.org/10.1016/S0925-8388\(99\)00304-7](https://doi.org/10.1016/S0925-8388(99)00304-7).
- [130] R.V. Denys, A.A. Poletaev, J.P. Maehlen, J.K. Solberg, B.P. Tarasov, V.A. Yartys, Nanostructured rapidly solidified LaMg₁₁Ni alloy. II. In situ synchrotron X-ray diffraction studies of hydrogen absorption–desorption behaviours, *Int. J. Hydrog. Energy* 37 (2012) 5710–5722, <https://doi.org/10.1016/j.ijhydene.2011.12.133>.
- [131] A.A. Poletaev, R.V. Denys, J.K. Solberg, B.P. Tarasov, V.A. Yartys, Microstructural optimization of LaMg₁₂ alloy for hydrogen storage, *J. Alloys Compd.* 509 (2011) S633–S639, <https://doi.org/10.1016/j.jallcom.2010.09.172>.
- [132] C. Wan, V.E. Antonov, R.V. Denys, V.I. Kulakov, V.A. Yartys, MgCo₂-D₂ and MgCoNi-D₂ systems synthesized at high pressures and interaction mechanism during the HDDR processing, *Progress Nat. Sci. Mater. Int.* 27 (2017) 74–80, <https://doi.org/10.1016/j.pnsc.2017.01.007>.
- [133] V.A. Yartys, O. Gutfleisich, V.V. Panasyuk, I.R. Harris, Desorption characteristics of rare earth (R) hydrides (R=Y, Ce, Pr, Nd, Sm, Gd and Tb) in relation to the HDDR behaviour of R–Fe-based-compounds, *J. Alloys Compd.* 253–254 (1997) 128–133, [https://doi.org/10.1016/S0925-8388\(96\)03097-6](https://doi.org/10.1016/S0925-8388(96)03097-6).
- [134] S. Suwarno, M.V. Lototsky, V.A. Yartys, Thermal desorption spectroscopy studies of hydrogen desorption from rare earth metal trihydrides REH₃ (RE=Dy, Ho, Er), *J. Alloys Compd.* 842 (2020), 155530, <https://doi.org/10.1016/j.jallcom.2020.155530>.
- [135] V.A. Yartys, O. Gutfleisich, I.R. Harris, Further studies of hydrogenation, disproportionation, desorption and recombination processes in a Nd₅Fe₂B₆ boride, *J. Alloys Compd.* 253–254 (1997) 134–139, [https://doi.org/10.1016/S0925-8388\(96\)02996-9](https://doi.org/10.1016/S0925-8388(96)02996-9).
- [136] V.A. Yartys, R.V. Denys, O. Gutfleisich, I.I. Bulyk, Y.B. Kuz'ma, I.R. Harris, Studies of hydrogen absorption-desorption properties and HDDR behaviour of a Nd₅Co₂B₆ ρ-boride, *Int. J. Hydrog. Energy* 24 (1999) 189–194, [https://doi.org/10.1016/S0360-3199\(98\)00074-3](https://doi.org/10.1016/S0360-3199(98)00074-3).
- [137] S.S. Mohammadshahi, E. MacA, C.J. Webb Gray, A review of mathematical modelling of metal-hydride systems for hydrogen storage applications, *Int. J. Hydrog. Energy* 41 (2016) 3470–3484, <https://doi.org/10.1016/j.ijhydene.2015.12.079>.
- [138] S.S. Mohammadshahi, T. Gould, E.M.A. Gray, C.J. Webb, An improved model for metal-hydrogen storage tanks - part 1: model development, *Int. J. Hydrog. Energy* 41 (2016) 3537–3550, <https://doi.org/10.1016/j.ijhydene.2015.12.050>.
- [139] A. Singh, M. Prakash Maiya, S. Srinivasa Murthy, Performance of a solid state hydrogen storage device with finned tube heat exchanger, *Int. J. Hydrog. Energy* 42 (2017) 26855–26871, <https://doi.org/10.1016/j.ijhydene.2017.06.071>.
- [140] V. Keshari, M.P. Maiya, Design and investigation of hydridding alloy based hydrogen storage reactor integrated with a pin fin tube heat exchanger, *Int. J. Hydrog. Energy* 43 (2018) 7081–7095, <https://doi.org/10.1016/j.ijhydene.2018.02.100>.
- [141] K.B. Minko, M.S. Bocharnikov, Y.B. Yanenko, M.V. Lototsky, A. Kolesnikov, B. P. Tarasov, Numerical and experimental study of heat-and-mass transfer processes in two-stage metal hydride hydrogen compressor, *Int. J. Hydrog. Energy* (2018) 21874–21885, <https://doi.org/10.1016/j.ijhydene.2018.09.211>.
- [142] F. Bouzgarrou, F. Askri, S. Ben Nasrallah, Prediction of heat and mass transfer within a metal-hydrogen reactor using the Lattice Boltzmann method, in: *Green Energy and Technology*, Springer Verlag, 2018, pp. 371–381, https://doi.org/10.1007/978-3-319-62572-0_26.
- [143] X. Lin, Q. Zhu, H. Leng, H. Yang, T. Lyu, Q. Li, Numerical analysis of the effects of particle radius and porosity on hydrogen absorption performances in metal hydride tank, *Appl. Energy* 250 (2019) 1065–1072, <https://doi.org/10.1016/j.apenergy.2019.04.181>.
- [144] L. Tong, J. Xiao, T. Yang, P. Bénard, R. Chahine, Complete and reduced models for metal hydride reactor with coiled-tube heat exchanger, *Int. J. Hydrog. Energy* (2019) 15907–15916, <https://doi.org/10.1016/j.ijhydene.2018.07.102>.
- [145] R. Aruna, S.T. Jaya Christa, Modeling, system identification and design of fuzzy PID controller for discharge dynamics of metal hydride hydrogen storage bed, *Int. J. Hydrog. Energy* 45 (2020) 4703–4719, <https://doi.org/10.1016/j.ijhydene.2019.11.238>.
- [146] X. Lin, W. Xie, Q. Zhu, H. Yang, Q. Li, Rational optimization of metal hydride tank with LaNi_{4.25}Al_{0.75} as hydrogen storage medium, *Chem. Eng. J.* 421 (2021), <https://doi.org/10.1016/j.cej.2020.127844>.
- [147] D. Wang, Y. Wang, F. Wang, S. Zheng, S. Guan, L. Zheng, L. Wu, T. Fang, X. Yang, M. Lv, Hydrogen storage in branch mini-channel metal hydride reactor: optimization design, sensitivity analysis and quadratic regression, *Int. J. Hydrog. Energy* 46 (2021) 25189–25207, <https://doi.org/10.1016/j.ijhydene.2021.05.051>.
- [148] X.S. Bai, W.W. Yang, X.Y. Tang, Z.Q. Dai, F.S. Yang, Parametric optimization of coupled fin-metal foam metal hydride bed towards enhanced hydrogen absorption performance of metal hydride hydrogen storage device, *Energy* 243 (2022), <https://doi.org/10.1016/j.energy.2021.123044>.
- [149] M. Chai, J. Tan, L. Gao, Z. Liu, Y. Chen, K. He, M. Jiang, Effects of different heat transfer conditions on the hydrogen desorption performance of a metal hydride hydrogen storage tank, *Energies (Basel)*. 15 (2022), <https://doi.org/10.3390/en15228375>.
- [150] S. Tiwari, P. Sharma, Integration of metal hydride reactor with thermo-cline based heat storage system, *J. Energy Storage* 59 (2023), <https://doi.org/10.1016/j.est.2022.106506>.
- [151] S.P. Filippov, A.B. Yaroslavtsev, Hydrogen energy: development prospects and materials, *Russ. Chem. Rev.* 90 (2021) 627–643, <https://doi.org/10.1070/rcr5014>.
- [152] T. Amirthan, M.S.A. Perera, The role of storage systems in hydrogen economy: a review, *J. Nat. Gas Sci. Eng.* 108 (2022), <https://doi.org/10.1016/j.jngse.2022.104843>.
- [153] M.R. Usman, Hydrogen storage methods: review and current status, *Renew. Sust. Energ. Rev.* 167 (2022), <https://doi.org/10.1016/j.rser.2022.112743>.
- [154] F. Qureshi, M. Yusuf, M. Arham Khan, H. Ibrahim, B.C. Ekeoma, H. Kamyab, M. M. Rahman, A.K. Nadda, S. Chelliapan, A state-of-the-art review on the latest trends in hydrogen production, storage, and transportation techniques, *Fuel* 340 (2023), <https://doi.org/10.1016/j.fuel.2023.127574>.
- [155] S.A. Cetinkaya, T. Dishi, G. Soyuturk, O. Kizilkan, C.O. Colpan, A review on thermal coupling of metal hydride storage tanks with fuel cells and electrolyzers, *Energies (Basel)* 16 (2023), <https://doi.org/10.3390/en16010341>.
- [156] J.W. Makepeace, T. He, C. Weidenthaler, T.R. Jensen, F. Chang, T. Vegge, P. Ngene, Y. Kojima, P.E. de Jongh, P. Chen, W.I.F. David, Reversible ammonia-based and liquid organic hydrogen carriers for high-density hydrogen storage: recent progress, *Int. J. Hydrog. Energy* 44 (2019) 7746–7767, <https://doi.org/10.1016/j.ijhydene.2019.01.144>.
- [157] Q. Lai, Y. Sun, T. Wang, P. Modi, C. Cazorla, U.B. Demirci, J.R. Ares Fernandez, F. Leardini, K.F. Aguey-Zinsou, How to design hydrogen storage materials? Fundamentals, synthesis, and storage tanks, *Adv. Sustain. Syst.* 3 (2019), <https://doi.org/10.1002/advs.201900043>.
- [158] M. Bhourri, M. Linder, I. Bürger, Metal hydride reactor for dual use: hydrogen storage and cold production, *Int. J. Hydrog. Energy* 43 (2018) 23357–23371, <https://doi.org/10.1016/j.ijhydene.2018.10.194>.
- [159] E.D. Frank, A. Elgowainy, Y.S. Khalid, J.-K. Peng, K. Reddi, Refueling-station costs for metal hydride storage tanks on board hydrogen fuel cell vehicles, *Int. J. Hydrog. Energy* 44 (2019) 29849–29861, <https://doi.org/10.1016/j.ijhydene.2019.09.206>.
- [160] M. Hirscher, V.A. Yartys, M. Baricco, J. Bellosta von Colbe, D. Blanchard, R. C. Bowman, D.P. Broom, C.E. Buckley, F. Chang, P. Chen, Y.W. Cho, J.C. Crivello, F. Cuevas, W.I.F. David, P.E. de Jongh, R.V. Denys, M. Dornheim, M. Felderhoff, Y. Filinchuk, G.E. Froudakis, D.M. Grant, E.M.A. Gray, B.C. Hauback, T. He, T. D. Humphries, T.R. Jensen, S. Kim, Y. Kojima, M. Latroche, H.W. Li, M. V. Lototsky, J.W. Makepeace, K.T. Møller, L. Naheed, P. Ngene, D. Noréus, M. M. Nygård, S. Ichi Orimo, M. Paskevicius, L. Pasquini, D.B. Ravnsbæk, M. Veronica Sofianos, T.J. Udovic, T. Vegge, G.S. Walker, C.J. Webb, C. Weidenthaler, C. Zlotea, Materials for hydrogen-based energy storage – past, recent progress and future outlook, *J. Alloys Compd.* 827 (2020), <https://doi.org/10.1016/j.jallcom.2019.153548>.
- [161] V.A. Yartys, M.V. Lototsky, V. Linkov, S. Pasupathi, M.W. Davids, I. Tolj, G. Radica, R.V. Denys, J. Eriksen, K. Taube, J. Bellosta von Colbe, G. Capurso, M. Dornheim, F. Smith, D. Mathebuta, D. Swanepoel, S. Suwarno, HYDRIDE4MOBILITY: an EU HORIZON 2020 project on hydrogen powered fuel cell utility vehicles using metal hydrides in hydrogen storage and refuelling systems, *Int. J. Hydrog. Energy* 46 (2021) 35896–35909, <https://doi.org/10.1016/j.ijhydene.2021.01.190>.
- [162] M.D. Allendorf, V. Stavila, J.L. Snider, M. Witman, M.E. Bowden, K. Brooks, B. L. Tran, T. Autrey, Challenges to developing materials for the transport and storage of hydrogen, *Nat. Chem.* 14 (2022) 1214–1223, <https://doi.org/10.1038/s41557-022-01056-2>.
- [163] S.V. Mitrokhin, Regularities of hydrogen interaction with multicomponent Ti(Zr)-Mn-V Laves phase alloys, *J. Alloys Compd.* 404–406 (2005) 384–387, <https://doi.org/10.1016/j.jallcom.2005.02.078>.
- [164] M. Gheytaanzadeh, F. Rajabhasani, A. Baghban, S. Habibzadeh, O. Abida, A. Esmaeili, M.T. Munir, Estimating hydrogen absorption energy on different metal hydrides using Gaussian process regression approach, *Sci. Rep.* 12 (2022), <https://doi.org/10.1038/s41598-022-26522-2>.
- [165] S. Suwarno, G. Dicky, A. Suyuthi, M. Effendi, W. Witantyo, L. Noerochim, M. Ismail, Machine learning analysis of alloying element effects on hydrogen storage properties of AB₂ metal hydrides, *Int. J. Hydrog. Energy* 47 (2022) 11938–11947, <https://doi.org/10.1016/j.ijhydene.2022.01.210>.
- [166] S.V. Mitrokhin, A.A. Tepanov, V.N. Verbetsky, Hydrogen interaction with alloys of NdNi_{5-x}Al_x system, *Int. J. Hydrog. Energy* 42 (2017) 22353–22357, <https://doi.org/10.1016/j.ijhydene.2017.05.098>.
- [167] N. Pineda-Romero, M. Witman, V. Stavila, C. Zlotea, The effect of 10 at.% Al addition on the hydrogen storage properties of the Ti_{0.33}V_{0.33}Nb_{0.33} multi-principal element alloy, *Intermetallics (Barking)* 146 (2022), <https://doi.org/10.1016/j.intermet.2022.107590>.
- [168] K.A. Rana, J.A. Acantillado, J.E. Santos, R.R. Tan, K.B. Aviso, A binary hyperbox classifier model for hydrogen storage in metal hydrides, *Chem. Eng. Trans.* 88 (2021) 637–642, <https://doi.org/10.3303/CET2188106>.
- [169] A. Rahnawa, G. Zepson, S. Sridhar, Machine learning based prediction of metal hydrides for hydrogen storage, part I: prediction of hydrogen weight percent, *Int. J. Hydrog. Energy* 44 (2019) 7337–7344, <https://doi.org/10.1016/j.ijhydene.2019.01.261>.
- [170] K. Batalović, J. Radaković, B. Paskaš Mamula, B. Kuzmanović, M. Medić Ilić, Predicting the heat of hydride formation by graph neural network - exploring the structure–property relation for metal hydrides, *Adv. Theory Simul.* 5 (2022) 2200293, <https://doi.org/10.1002/adts.202200293>.

- [171] J.R. Hattrick-Simpers, K. Choudhary, C. Corngale, A simple constrained machine learning model for predicting high-pressure-hydrogen-compressor materials, *Mol. Syst. Des. Eng.* 3 (2018) 509–517, <https://doi.org/10.1039/c8me00005k>.
- [172] A. Rahnama, G. Zepón, S. Sridhar, Machine learning based prediction of metal hydrides for hydrogen storage, part II: prediction of material class, *Int. J. Hydrog. Energy* 44 (2019) 7345–7353, <https://doi.org/10.1016/j.ijhydene.2019.01.264>.
- [173] Q. Li, X. Lin, Q. Luo, Y. Chen, J. Wang, B. Jiang, F. Pan, Kinetics of the hydrogen absorption and desorption processes of hydrogen storage alloys: a review, *Int. J. Miner. Metall. Mater.* 29 (2022) 32–48, <https://doi.org/10.1007/s12613-021-2337-8>.
- [174] A.A. Poletaev, R.V. Denys, J.P. Maehlen, J.K. Solberg, B.P. Tarasov, V.A. Yartys, Nanostructured rapidly solidified LaMg₁₁Ni alloy: microstructure, crystal structure and hydrogenation properties, *Int. J. Hydrog. Energy* 37 (2012) 3548–3557, <https://doi.org/10.1016/j.ijhydene.2011.11.054>.
- [175] A. Jain, S. Agarwal, T. Ichikawa, Catalytic tuning of sorption kinetics of lightweight hydrides: a review of the materials and mechanism, *Catalysts* 8 (2018), <https://doi.org/10.3390/catal8120651>.
- [176] F. Guo, T. Zhang, L. Shi, L. Song, Composition dependent microstructure evolution, activation and de-/hydrogenation properties of Mg–Ni–La alloys, *Int. J. Hydrog. Energy* 44 (2019) 16745–16756, <https://doi.org/10.1016/j.ijhydene.2019.05.019>.
- [177] H. Yong, S. Guo, Z. Yuan, Y. Qi, D. Zhao, Y. Zhang, Catalytic effect of in situ formed Mg₂Ni and REH_x (RE: Ce and Y) on thermodynamics and kinetics of Mg-RE-Ni hydrogen storage alloy, *Renew. Energy* 157 (2020) 828–839, <https://doi.org/10.1016/j.renene.2020.05.043>.
- [178] Y. Zhang, Y. Li, W. Zhang, Z. Yuan, Z. Hou, Y. Qi, S. Guo, Gaseous hydrogen storage properties of Mg-Y-Ni-Cu alloys prepared by melt spinning, *J. Rare Earths* 37 (2019) 750–759, <https://doi.org/10.1016/j.jre.2018.10.003>.
- [179] C. Zhou, K. Li, T. Huang, P. Sun, L. Wang, Y. Lu, Z.Z. Fang, In situ formation of nanocrystalline MgH₂ through room temperature hydrogenation, *Mater. Des.* 218 (2022), <https://doi.org/10.1016/j.matdes.2022.110729>.
- [180] Y. Luo, Q. Wang, J. Li, F. Xu, L. Sun, Y. Zou, H. Chu, B. Li, K. Zhang, Enhanced hydrogen storage/sensing of metal hydrides by nanomodification, *Mater Today Nano* 9 (2020), <https://doi.org/10.1016/j.mtnano.2019.100071>.
- [181] Y. Shang, C. Pistidda, G. Gizer, T. Klassen, M. Dornheim, Mg-based materials for hydrogen storage, *J. Magnes. Alloys* 9 (2021) 1837–1860, <https://doi.org/10.1016/j.jma.2021.06.007>.
- [182] Y.J. Cho, H. Cho, E.S. Cho, Nanointerface engineering of metal hydrides for advanced hydrogen storage, *Chem. Mater.* (2022), <https://doi.org/10.1021/acs.chemmater.2c02628>.
- [183] T.R. Somo, T.C. Ma ponya, M.W. Davids, M.J. Hato, M.V. Lototskyy, K. D. Modibane, A comprehensive review on hydrogen absorption behaviour of metal alloys prepared through mechanical alloying, *Metals (Basel)*. 10 (2020) 562, <https://doi.org/10.3390/met10050562>.
- [184] K. Edalati, E. Akiba, W.J. Botta, Y. Estrin, R. Floriano, D. Fruchart, T. Grosdidier, Z. Horita, J. Huot, H.W. Li, H.J. Lin, A. Révész, M.J. Zehetbauer, Impact of severe plastic deformation on kinetics and thermodynamics of hydrogen storage in magnesium and its alloys, *J. Mater. Sci. Technol.* 146 (2023) 221–239, <https://doi.org/10.1016/j.jmst.2022.10.068>.
- [185] B.P. Tarasov, A.A. Arbutov, S.A. Mozhhuhin, A.A. Volodin, P.V. Fursikov, M. V. Lototskyy, V.A. Yartys, Hydrogen storage behavior of magnesium catalyzed by nickel-graphene nanocomposites, *Int. J. Hydrog. Energy* 44 (2019) 29212–29223, <https://doi.org/10.1016/j.ijhydene.2019.02.033>.
- [186] B.P. Tarasov, A.A. Arbutov, A.A. Volodin, P.V. Fursikov, S.A. Mozhhuhin, M. V. Lototskyy, V.A. Yartys, Metal hydride – graphene composites for hydrogen based energy storage, *J. Alloys Compd.* 896 (2022), <https://doi.org/10.1016/j.jallcom.2021.162881>.
- [187] F. Guo, T. Zhang, L. Shi, Y. Chen, L. Song, Mechanisms of hydrides' nucleation and the effect of hydrogen pressure induced driving force on de-/hydrogenation kinetics of Mg-based nanocrystalline alloys, *Int. J. Hydrog. Energy* 47 (2022) 1063–1075, <https://doi.org/10.1016/j.ijhydene.2021.10.104>.
- [188] M. Lototskyy, V. Linkov, Thermally driven hydrogen compression using metal hydrides, *Int. J. Energy Res.* 46 (2022) 22049–22069, <https://doi.org/10.1002/er.8189>.
- [189] G. Zepón, B.H. Silva, C. Zlotea, W.J. Botta, Y. Champion, Thermodynamic modelling of hydrogen-multicomponent alloy systems: calculating pressure-composition-temperature diagrams, *Acta Mater.* 215 (2021), 117070, <https://doi.org/10.1016/j.actamat.2021.117070>.
- [190] Z.K. Simelane, A. Kolesnikov, M. Lototskyy, Application of artificial neural network (ANN) for calculations of pressure–concentration–temperature (PCT) diagrams in hydrogen – metal hydride systems, in: *Advances in Mechanical and Power Engineering. CAMPE 2021. Lecture Notes in Mechanical Engineering*, Springer, 2023, pp. 137–146, https://doi.org/10.1007/978-3-031-18487-1_14.
- [191] I.A. Chernov, High-throughput identification of hydride phase-change kinetics models, *Comput. Res. Model.* 12 (2020) 171–183, <https://doi.org/10.20537/2076-7633-2020-12-1-171-183>.
- [192] F. Wang, Z. Huang, Y. Wang, D. Wang, L. Zheng, L. Wu, X. Ding, D. Li, Z. Zhang, Simulation and prediction study of hydrogenation/dehydrogenation kinetics based on the universal changing-volume model, *Chem. Eng. Sci.* 251 (2022), 117428, <https://doi.org/10.1016/j.ces.2022.117428>.
- [193] A. Hariyadi, S. Suwarno, R.V. Denys, J.B. von Colbe, T.O. Sætre, V. Yartys, Modeling of the hydrogen sorption kinetics in an AB₂ laves type metal hydride alloy, *J. Alloys Compd.* 893 (2022), 162135, <https://doi.org/10.1016/j.jallcom.2021.162135>.
- [194] D.G. Oliva, M. Fuentes, E.M. Borzone, G.O. Meyer, P.A. Aguirre, Hydrogen storage on LaNi_{5-x}Sn_x. Experimental and phenomenological Model-based analysis, *Energy Convers. Manag.* 173 (2018) 113–122, <https://doi.org/10.1016/j.enconman.2018.07.041>.
- [195] S. Nyallang Nyamsi, Z. Wu, Z. Zhang, A. Kolesnikov, M.V. Lototskyy, S. Pasupathi, Dehydrogenation performance of metal hydride container utilising MgH₂-based composite, *Appl. Therm. Eng.* 209 (2022), 118314, <https://doi.org/10.1016/j.applthermaleng.2022.118314>.
- [196] C.-S. Wang, J. Brinkerhoff, Low-cost lumped parameter modelling of hydrogen storage in solid-state materials, *Energy Convers. Manag.* 251 (2022), 115005, <https://doi.org/10.1016/j.enconman.2021.115005>.
- [197] X.-S. Bai, W.-W. Yang, Y.-J. Yang, K.-R. Zhang, F.-S. Yang, Multi-variable optimization of metal hydride hydrogen storage reactor with gradient porosity metal foam and evaluation of comprehensive performance, *Int. J. Hydrog. Energy* 47 (2022) 35340–35351, <https://doi.org/10.1016/j.ijhydene.2022.08.123>.
- [198] H. Wang, G. Yi, J. Ye, X. Feng, Z. Li, S. Wang, Z. Gao, Intensification of hydrogen absorption process in metal hydride devices with novel corrugated fins: a validated numerical study, *J. Alloys Compd.* 926 (2022), 166759, <https://doi.org/10.1016/j.jallcom.2022.166759>.
- [199] J. Sunku Prasad, P. Muthukumar, Performance and energy efficiency of a solid-state hydrogen storage system: an experimental study on La_{0.7}Ce_{0.1}Ca_{0.3}Ni₅, *Appl. Therm. Eng.* 216 (2022), 119030, <https://doi.org/10.1016/j.applthermaleng.2022.119030>.
- [200] E. Anil Kumar, Y. Madaria, K. Sarath Babu, S. Srinivasa Murthy, Influence of effective thermal conductivity on hydrogen sorption in Mg-LaNi_{4.6}Al_{0.4} composite hydride beds for thermal energy storage, *Therm. Sci. Eng. Prog.* 19 (2020), 100653, <https://doi.org/10.1016/j.tsep.2020.100653>.
- [201] I.A. Romanov, V.I. Borzenko, A.N. Kazakov, Use of carbon nano fibers in the production of metal hydride compacts, *Nanotechnol. Russ.* 15 (2020) 314–318, <https://doi.org/10.1134/S1995078020030118>.
- [202] I.A. Romanov, V.I. Borzenko, A.N. Kazakov, Comparing hydrogen absorption kinetics of the samples of intermetallic compound and metal hydride compact on its basis, *J. Phys. Conf. Ser.* 2057 (2021), 012043, <https://doi.org/10.1088/1742-6596/2057/1/012043>.
- [203] C.S. Park, K. Jung, S.U. Jeong, K.S. Kang, Y.H. Lee, Y.-S. Park, B.H. Park, Development of hydrogen storage reactor using composite of metal hydride materials with ENG, *Int. J. Hydrog. Energy* 45 (2020) 27434–27442, <https://doi.org/10.1016/j.ijhydene.2020.07.062>.
- [204] Z. Zhu, Z. Bao, D. Wu, Optimization of the content distribution of expanded natural graphite in a multilayer metal hydride bed for thermochemical heat storage, *Appl. Therm. Eng.* 216 (2022), 119115, <https://doi.org/10.1016/j.applthermaleng.2022.119115>.
- [205] U.R. Singh, S. Bhogilla, Performance analysis of LaNi₅ added with expanded natural graphite for hydrogen storage system, *Int. J. Hydrog. Energy* (2022), <https://doi.org/10.1016/j.ijhydene.2022.05.244>.
- [206] X.-S. Bai, W.-W. Yang, W.-Y. Zhang, F.-S. Yang, X.-Y. Tang, Hydrogen absorption performance of a novel cylindrical MH reactor with combined loop-type finned tube and cooling jacket heat exchanger, *Int. J. Hydrog. Energy* 45 (2020) 28100–28115, <https://doi.org/10.1016/j.ijhydene.2020.04.209>.
- [207] R. Sreeraj, A.K. Aadithiyani, S. Anbarasu, Comparison, advancement, and performance evaluation of heat exchanger assembly in solid-state hydrogen storage device, *Renew. Energy* 198 (2022) 667–678, <https://doi.org/10.1016/j.renene.2022.08.051>.
- [208] A. Mathew, N. Nadim, T.T. Chandratilleke, T.D. Humphries, M. Paskevicius, C. E. Buckley, Performance analysis of a high-temperature magnesium hydride reactor tank with a helical coil heat exchanger for thermal storage, *Int. J. Hydrog. Energy* 46 (2021) 1038–1055, <https://doi.org/10.1016/j.ijhydene.2020.09.191>.
- [209] S. Nyallang Nyamsi, M.V. Lototskyy, V.A. Yartys, G. Capurso, M.W. Davids, S. Pasupathi, 200 NL H₂ hydrogen storage tank using MgH₂-TiH₂-C nanocomposite as H storage material, *Int. J. Hydrog. Energy* 46 (2021) 19046–19059, <https://doi.org/10.1016/j.ijhydene.2021.03.055>.
- [210] X. Mou, Z. Bao, W. Huang, Performance investigation of metal hydride reactor equipped with helically coiled heat exchanger during hydrogen absorption and desorption, *Therm. Sci. Eng. Prog.* 38 (2023), 101656, <https://doi.org/10.1016/j.tsep.2023.101656>.
- [211] A.P. Tetuko, B. Shabani, R. Omrani, B. Paul, J. Andrews, Study of a thermal bridging approach using heat pipes for simultaneous fuel cell cooling and metal hydride hydrogen discharge rate enhancement, *J. Power Sources* 397 (2018) 177–188, <https://doi.org/10.1016/j.jpowsour.2018.07.030>.
- [212] F.A.M. Elhamshri, M. Kayfeci, Enhancement of hydrogen charging in metal hydride-based storage systems using heat pipe, *Int. J. Hydrog. Energy* 44 (2019) 18927–18938, <https://doi.org/10.1016/j.ijhydene.2018.10.040>.
- [213] F. Bouzgarrou, S. Mellouli, T. Alqahtani, S. Algarni, Parametric study of a metal hydride reactor with phase change materials and heat pipes, *Int. J. Energy Res.* 46 (2022) 4588–4598, <https://doi.org/10.1002/er.7451>.
- [214] H. El Mghari, J. Huot, L. Tong, J. Xiao, Selection of phase change materials, metal foams and geometries for improving metal hydride performance, *Int. J. Hydrog. Energy* 45 (2020) 14922–14939, <https://doi.org/10.1016/j.ijhydene.2020.03.226>.
- [215] Y. Ye, Y. Yue, J. Lu, J. Ding, W. Wang, J. Yan, Enhanced hydrogen storage of a LaNi₅ based reactor by using phase change materials, *Renew. Energy* 180 (2021) 734–743, <https://doi.org/10.1016/j.renene.2021.08.118>.
- [216] A. Chibani, S. Merouani, C. Bougriou, The performance of hydrogen desorption from a metal hydride with heat supply by a phase change material incorporated in porous media (metal foam): heat and mass transfer assessment, *J. Energy Storage* 51 (2022), 104449, <https://doi.org/10.1016/j.est.2022.104449>.

- [217] S. Jana, P. Muthukumar, Design and performance prediction of a compact $\text{MmNi}_{4.6}\text{Al}_{0.4}$ based hydrogen storage system, *J. Energy Storage* 39 (2021), 102612, <https://doi.org/10.1016/j.est.2021.102612>.
- [218] R. Sreeraj, A.K. Aadithiyani, S. Anbarasu, Integration of thermal augmentation methods in hydride beds for metal hydride based hydrogen storage systems: review and recommendation, *J. Energy Storage* 52 (2022), 105039, <https://doi.org/10.1016/j.est.2022.105039>.
- [219] Y. Cui, X. Zeng, J. Xiao, H. Kou, The comprehensive review for development of heat exchanger configuration design in metal hydride bed, *Int. J. Hydrog. Energy* 47 (2022) 2461–2490, <https://doi.org/10.1016/j.ijhydene.2021.10.172>.
- [220] C. Pohlmann, L. Röntzsch, F. Heubner, T. Weißgärber, B. Kieback, Solid-state hydrogen storage in hydralloy–graphite composites, *J. Power Sources* 231 (2013) 97–105, <https://doi.org/10.1016/j.jpowsour.2012.12.044>.
- [221] K. Herbrig, L. Röntzsch, C. Pohlmann, T. Weißgärber, B. Kieback, Hydrogen storage systems based on hydride–graphite composites: computer simulation and experimental validation, *Int. J. Hydrog. Energy* 38 (2013) 7026–7036, <https://doi.org/10.1016/j.ijhydene.2013.03.104>.
- [222] M.V. Lototskyy, M.W. Davids, I. Tolj, Y.V. Klochko, B.S. Sekhar, S. Chidziva, F. Smith, D. Swanepoel, B.G. Pollet, Metal hydride systems for hydrogen storage and supply for stationary and automotive low temperature PEM fuel cell power modules, *Int. J. Hydrog. Energy* 40 (2015), <https://doi.org/10.1016/j.ijhydene.2015.01.095>.
- [223] Q. Li, G. Tang, B. Cai, K. Wu, L. Qin, D. Chen, Y. Huang, Effect of silicone oil additive on swelling stress alleviation in the metal hydride reactor, *Int. J. Hydrog. Energy* 47 (2022) 10308–10314, <https://doi.org/10.1016/j.ijhydene.2022.01.114>.
- [224] S. Carrol, LAVO launches first commercially ready hydrogen energy storage solution. <https://electricalconnection.com.au/lavo-launches-first-commercially-ready-hydrogen-energy-storage-solution/>, 2021. (Accessed 21 January 2023).
- [225] A. Malewar, World's first home hydrogen battery powers an average home for two days. <https://www.inceptivemind.com/lavo-worlds-first-home-hydrogen-battery-powers-average-home-two-days/17778/>, 2021 (accessed January 22, 2023).
- [226] M.W. Davids, M. Lototskyy, M. Malinowski, D. van Schalkwyk, A. Parsons, S. Pasupathi, D. Swanepoel, T. van Niekerk, Metal hydride hydrogen storage tank for light fuel cell vehicle, *Int. J. Hydrog. Energy* (2019), <https://doi.org/10.1016/j.ijhydene.2019.01.227>.
- [227] M. Lototskyy, I. Tolj, Y. Klochko, M.W. Davids, D. Swanepoel, V. Linkov, Metal hydride hydrogen storage tank for fuel cell utility vehicles, *Int. J. Hydrog. Energy* 45 (2020) 7958–7967, <https://doi.org/10.1016/j.ijhydene.2019.04.124>.
- [228] H. Liu, J. Zhang, C. Zhou, P. Sun, Y. Liu, Z.Z. Fang, Hydrogen storage properties of Ti-Fe-Zr-Mn-Nb alloys, *J. Alloys Compd.* 938 (2023), 168466, <https://doi.org/10.1016/j.jallcom.2022.168466>.
- [229] G. Sdanghi, G. Maranzana, A. Celzard, V. Fierro, Review of the current technologies and performances of hydrogen compression for stationary and automotive applications, *Renew. Sust. Energy. Rev.* 102 (2019) 150–170, <https://doi.org/10.1016/j.rser.2018.11.028>.
- [230] M. Lototskyy, M.W. Davids, D. Swanepoel, G. Louw, Y. Klochko, F. Smith, F. Haji, I. Tolj, S. Chidziva, S. Pasupathi, V. Linkov, Hydrogen refuelling station with integrated metal hydride compressor: layout features and experience of three-year operation, *Int. J. Hydrog. Energy* 45 (2019) 5415–5429, <https://doi.org/10.1016/j.ijhydene.2019.05.133>.
- [231] C. Corgnale, R.C. Bowman, T. Motyka, Thermal hydrogen compression based on metal hydride materials, in: *Advances in Sustainable Energy*, Springer International Publishing, Cham, 2021, pp. 171–192, https://doi.org/10.1007/978-3-030-74406-9_6.
- [232] A.V. Rusanov, V.V. Solovey, M.V. Lototskyy, Thermodynamic features of metal hydride thermal sorption compressors and perspectives of their application in hydrogen liquefaction systems, *J. Phys. Energy* 2 (2020), 021007, <https://doi.org/10.1088/2515-7655/ab7bf4>.
- [233] B.P. Tarasov, M.S. Bocharnikov, Y.B. Yanenko, P.V. Fursikov, K.B. Minko, M. V. Lototskyy, Metal hydride hydrogen compressors for energy storage systems: layout features and results of long-term tests, *J. Phys. Energy* 2 (2020), 024005, <https://doi.org/10.1088/2515-7655/ab6465>.
- [234] A.N. Golubkov, A.A. Kononenko, A.A. Yukhimchuk, Thermodesorption of vanadium-hydride-based hydrogen isotope sources, *Fusion Sci. Technol.* 48 (2005) 527–533, <https://doi.org/10.13182/FST05-A981>.
- [235] Z. Peng, Q. Li, L. Ouyang, W. Jiang, K. Chen, H. Wang, J. Liu, Z. Li, S. Wang, M. Zhu, Overview of hydrogen compression materials based on a three-stage metal hydride hydrogen compressor, *J. Alloys Compd.* 895 (2022), 162465, <https://doi.org/10.1016/j.jallcom.2021.162465>.
- [236] L. Ouyang, Z. Peng, H. Wang, J. Liu, M. Zhu, Design of a three-stage metal hydride hydrogen compressor and progress of hydrogen compression materials, *Mater. Rep.* 36 (2022) 21030081, <https://doi.org/10.11896/cldb.21030081>.
- [237] M. Piao, X. Xiao, Z. Cao, P. Zhou, L. Zhan, J. Qi, Z. Li, L. Jiang, L. Chen, Low-cost vanadium-free Ti–Zr–Cr–Mn–Fe based alloys for metal hydride hydrogen compressor under mild conditions, *Mater. Chem. Phys.* 297 (2023), 127407, <https://doi.org/10.1016/j.matchemphys.2023.127407>.
- [238] Z. Cao, M. Piao, X. Xiao, L. Zhan, P. Zhou, Z. Li, S. Wang, L. Jiang, F. Xu, L. Sun, L. Chen, Development of (Ti–Zr)1.02(Cr–Mn–Fe)2-based alloys toward excellent hydrogen compression performance in water-bath environments, *ACS Appl. Energy Mater.* 6 (2023) 1913–1925, <https://doi.org/10.1021/acsaem.2c03857>.
- [239] V. Charbonnier, H. Enoki, K. Asano, H. Kim, K. Sakaki, Improvement of hydrogenation sorption properties of $\text{Ti}_{0.90}\text{V}_{0.30}\text{Mn}_{1.00}\text{Ni}_{0.80}$ for ultra-high pressure metal-hydride compressor, *Int. J. Hydrog. Energy* 47 (2022) 32252–32261, <https://doi.org/10.1016/j.ijhydene.2022.07.111>.
- [240] W. Jiang, C. He, X. Yang, X. Xiao, L. Ouyang, M. Zhu, Influence of element substitution on structural stability and hydrogen storage performance: a theoretical and experimental study on $\text{TiCr}_2\text{-xMn}_x$ alloy, *Renew. Energy* 197 (2022) 564–573, <https://doi.org/10.1016/j.renene.2022.07.113>.
- [241] Z. Peng, Q. Li, J. Sun, K. Chen, W. Jiang, H. Wang, J. Liu, L. Ouyang, M. Zhu, Ti–Cr–Mn–Fe-based alloys optimized by orthogonal experiment for 85 MPa hydrogen compression materials, *J. Alloys Compd.* 891 (2022), 161791, <https://doi.org/10.1016/j.jallcom.2021.161791>.
- [242] Q. Li, Z. Peng, W. Jiang, L. Ouyang, H. Wang, J. Liu, M. Zhu, Optimization of Ti–Zr–Cr–Fe alloys for 45 MPa metal hydride hydrogen compressors using orthogonal analysis, *J. Alloys Compd.* 889 (2021), 161629, <https://doi.org/10.1016/j.jallcom.2021.161629>.
- [243] V. Charbonnier, H. Enoki, K. Asano, H. Kim, K. Sakaki, Tuning the hydrogenation properties of $\text{Ti}_{1-y}\text{Cr}_2\text{-xMn}_x$ laves phase compounds for high pressure metal-hydride compressors, *Int. J. Hydrog. Energy* 46 (2021) 36369–36380, <https://doi.org/10.1016/j.ijhydene.2021.08.143>.
- [244] Z. Cao, P. Zhou, X. Xiao, L. Zhan, Z. Li, S. Wang, L. Chen, Investigation on Ti–Zr–Cr–Fe–V based alloys for metal hydride hydrogen compressor at moderate working temperatures, *Int. J. Hydrog. Energy* 46 (2021) 21580–21589, <https://doi.org/10.1016/j.ijhydene.2021.03.247>.
- [245] D.B. Smith, R.C. Bowman, L.M. Anovitz, C. Corgnale, M. Sulic, Isotherm measurements of high-pressure metal hydrides for hydrogen compressors, *J. Phys. Energy* 3 (2021), 034004, <https://doi.org/10.1088/2515-7655/abeab5>.
- [246] K. Goshome, N. Endo, T. Maeda, Demonstration of a single-stage metal hydride hydrogen compressor composed of BCC V_{40}TiCr alloy, *Int. J. Hydrog. Energy* 46 (2021) 28180–28190, <https://doi.org/10.1016/j.ijhydene.2021.06.069>.
- [247] K. Goshome, N. Endo, T. Maeda, Evaluation of the pressure dependence of the cycle durability and thermodynamics of a metal hydride compressor composed of ternary V_{40} and V_{70}TiCr , *Int. J. Hydrog. Energy* 46 (2021) 9479–9487, <https://doi.org/10.1016/j.ijhydene.2020.12.101>.
- [248] D. Dashbabu, E.A. Kumar, I.P. Jain, Thermodynamic analysis of a metal hydride hydrogen compressor with aluminium substituted LaNi_5 hydrides, *Int. J. Hydrog. Energy* (2022), <https://doi.org/10.1016/j.ijhydene.2022.09.094>.
- [249] L. Lv, J. Lin, G. Yang, Z. Ma, L. Xu, X. He, X. Han, W. Liu, Hydrogen storage performance of $\text{LaNi}_{3.95}\text{Al}_{0.75}\text{Co}_{0.3}$ alloy with different preparation methods, *Progress Nat. Sci. Mater. Int.* 32 (2022) 206–214, <https://doi.org/10.1016/j.pnsc.2022.02.001>.
- [250] S. Gupta, V.K. Sharma, Performance investigation of a multi-stage sorption hydrogen compressor, *Int. J. Hydrog. Energy* 46 (2021) 1056–1075, <https://doi.org/10.1016/j.ijhydene.2020.09.249>.
- [251] M.V. Lototskyy, V.A. Yartys, B.P. Tarasov, M.W. Davids, R.V. Denys, S. Tai, Modelling of metal hydride hydrogen compressors from thermodynamics of hydrogen – metal interactions viewpoint: part I. Assessment of the performance of metal hydride materials, *Int. J. Hydrog. Energy* 46 (2021) 2330–2338, <https://doi.org/10.1016/j.ijhydene.2020.10.090>.
- [252] M.V. Lototskyy, V.A. Yartys, B.P. Tarasov, R.V. Denys, J. Eriksen, M. S. Bocharnikov, S. Tai, V. Linkov, Modelling of metal hydride hydrogen compressors from thermodynamics of hydrogen – metal interactions viewpoint: part II. Assessment of the performance of metal hydride compressors, *Int. J. Hydrog. Energy* 46 (2021) 2339–2350, <https://doi.org/10.1016/j.ijhydene.2020.10.080>.
- [253] E. MacA. Gray, Alloy selection for multistage metal-hydride hydrogen compressors: a thermodynamic model, *Int. J. Hydrog. Energy* 46 (2021) 15702–15715, <https://doi.org/10.1016/j.ijhydene.2021.02.025>.
- [254] V.K. Sharma, A. Sathesh, E.A. Kumar, Performance investigation of a two-stage sorption hydrogen compressor, *Int. J. Hydrog. Energy* 46 (2021) 17282–17294, <https://doi.org/10.1016/j.ijhydene.2021.02.155>.
- [255] E.I. Gkanas, E. Stamatakis, C.N. Christodoulou, G. Tzamalidis, G. Karagiorgis, A. Chronos, N. Kuganathan, M. Khzouz, A.K. Stubos, Study on the operation and energy demand of dual-stage metal hydride hydrogen compressors under effective thermal management, *Int. J. Hydrog. Energy* 46 (2021) 29272–29287, <https://doi.org/10.1016/j.ijhydene.2021.02.062>.
- [256] M.V. Lototskyy, E.E. Fokina, I.E. Bessarabskaya, B.P. Tarasov, Calculation of two-stage metal hydride hydrogen compressors using a model of intermetallic compound–hydrogen phase equilibria, *Inorg. Mater.* 58 (2022) 1227–1234, <https://doi.org/10.1134/S0020168522110097>.
- [257] A. Parida, P. Muthukumar, Reactor design and numerical study on metal hydride based finned reactor configurations for hydrogen compression application, *Int. J. Hydrog. Energy* (2023), <https://doi.org/10.1016/j.ijhydene.2022.10.183>.
- [258] P. Dantzer, E. Orgaz, Thermodynamics of the hydride chemical heat pump: model (I), *J. Chem. Phys.* 85 (1986) 2961–2973, <https://doi.org/10.1063/1.451006>.
- [259] P. Dantzer, E. Orgaz, Thermodynamics of hydride chemical heat pump—II. How to select a pair of alloys, *Int. J. Hydrog. Energy* 11 (1986) 797–806, [https://doi.org/10.1016/0360-3199\(86\)90176-X](https://doi.org/10.1016/0360-3199(86)90176-X).
- [260] S.P. Jenne, S. Jana, M. Palanisamy, Thermal and compressor-driven metal hydride based coupled system for thermal storage, cooling and thermal upgradation, *Therm. Sci. Eng. Prog.* 21 (2021), 100800, <https://doi.org/10.1016/j.tsep.2020.100800>.
- [261] D.A. Sheppard, M. Paskevicius, T.D. Humphries, M. Felderhoff, G. Capurso, J. Bellosta von Colbe, M. Dornheim, T. Klassen, P.A. Ward, J.A. Teprovich, C. Corgnale, R. Zidan, D.M. Grant, C.E. Buckley, Metal hydrides for concentrating solar thermal power energy storage, *Appl. Phys. A Mater. Sci. Process.* 122 (2016) 395, <https://doi.org/10.1007/s00339-016-9825-0>.

- [262] R. Urbanczyk, M. Meggouh, R. Moury, K. Peinecke, S. Peil, M. Felderhoff, Demonstration of Mg_2FeH_6 as heat storage material at temperatures up to 550 °C, *Appl. Phys. A Mater. Sci. Process.* 122 (2016) 315, <https://doi.org/10.1007/s00339-016-9811-6>.
- [263] M.S. Choudhari, V.K. Sharma, M. Paswan, Metal hydrides for thermochemical energy storage applications, *Int. J. Energy Res.* 45 (2021) 14465–14492, <https://doi.org/10.1002/er.6818>.
- [264] M. Adams, C.E. Buckley, M. Busch, R. Bunzel, M. Felderhoff, T.W. Heo, T. D. Humphries, T.R. Jensen, J. Klug, K.H. Klug, K.T. Möller, M. Paskevicius, S. Peil, K. Peinecke, D.A. Sheppard, A.D. Stuart, R. Urbanczyk, F. Wang, G.S. Walker, B. C. Wood, D. Weiss, D.M. Grant, Hydride-based thermal energy storage, *Progress Energy* 4 (2022), 032008, <https://doi.org/10.1088/2516-1083/ac72ea>.
- [265] J. Park, The development of compressor-driven metal hydride heat pump (CDMHP) system as an air conditioner, *Int. J. Hydrog. Energy* 27 (2002) 941–944, [https://doi.org/10.1016/S0360-3199\(01\)00187-2](https://doi.org/10.1016/S0360-3199(01)00187-2).
- [266] S. Bedbak, M. Ram Gopal, Performance analysis of a compressor driven metal hydride cooling system, *Int. J. Hydrog. Energy* 30 (2005) 1127–1137, <https://doi.org/10.1016/j.ijhydene.2004.10.014>.
- [267] P. Bansal, E. Vineyard, O. Abdelaziz, Status of not-in-kind refrigeration technologies for household space conditioning, water heating and food refrigeration, *Int. J. Sustain. Built Environ.* 1 (2012) 85–101, <https://doi.org/10.1016/j.ijsbe.2012.07.003>.
- [268] P. Muthukumar, M.S. Patil, N.N. Raju, M. Imran, Parametric investigations on compressor-driven metal hydride based cooling system, *Appl. Therm. Eng.* 97 (2016) 87–99, <https://doi.org/10.1016/j.applthermaleng.2015.10.155>.
- [269] T.G. Voskuilen, E.L. Waters, T.L. Pourpoint, A comprehensive approach for alloy selection in metal hydride thermal systems, *Int. J. Hydrog. Energy* 39 (2014) 13240–13254, <https://doi.org/10.1016/j.ijhydene.2014.06.119>.
- [270] H. Uchida, A metal hydride (MH) freezer system as human environment conscious eco-technology, in: *Proceedings International Hydrogen Energy Congress and Exhibition IHEC 2007, Istanbul, Turkey, 13–15 July 2007, Istanbul, 2007*.
- [271] T. Brestović, N. Jasminská, M. Lázár, Measurements of operating parameters of a metal hydride compressor with a heat pump, *Appl. Sci.* 12 (2022) 3302, <https://doi.org/10.3390/app12073302>.
- [272] P. Krane, D. Ziviani, J.E. Braun, N. Jain, A. Marconnet, Techno-economic analysis of metal-hydride energy storage to enable year-round load-shifting for residential heat pumps, *Energy Build.* 256 (2022), 111700, <https://doi.org/10.1016/j.enbuild.2021.111700>.
- [273] Y.T. Ge, P.Y. Lang, Alloy selections in high-temperature metal hydride heat pump systems for industrial waste heat recovery, *Energy Rep.* 8 (2022) 3649–3660, <https://doi.org/10.1016/j.egyr.2022.02.279>.
- [274] P. Krane, A.L. Nash, D. Ziviani, J.E. Braun, A.M. Marconnet, N. Jain, Dynamic modeling and control of a two-reactor metal hydride energy storage system, *Appl. Energy* 325 (2022), 119836, <https://doi.org/10.1016/j.apenergy.2022.119836>.
- [275] J. Sunku Prasad, P. Muthukumar, Design of metal hydride reactor for medium temperature thermochemical energy storage applications, *Therm. Sci. Eng. Prog.* 37 (2023), 101570, <https://doi.org/10.1016/j.tsep.2022.101570>.
- [276] X.Y. Chen, L.X. Wei, L. Deng, F.S. Yang, Z.X. Zhang, A review on the metal hydride based hydrogen purification and separation technology, *Appl. Mech. Mater.* 448–453 (2013) 3027–3036, <https://doi.org/10.4028/www.scientific.net/AMM.448-453.3027>.
- [277] X.Y. Chen, L.X. Wei, L. Deng, F.S. Yang, Z.X. Zhang, A review on the metal hydride based hydrogen purification and separation technology, *Appl. Mech. Mater.* 448–453 (2013) 3027–3036, <https://doi.org/10.4028/www.scientific.net/AMM.448-453.3027>.
- [278] P. Hao, S. Li, S. Li, Y. Shi, N. Cai, Hydrogen direct adsorptive separation: development status and trends, *Energy Fuel* 34 (2020) 15126–15140, <https://doi.org/10.1021/acs.energyfuels.0c02317>.
- [279] Z. Du, C. Liu, J. Zhai, X. Guo, Y. Xiong, W. Su, G. He, A review of hydrogen purification technologies for fuel cell vehicles, *Catalysts* 11 (2021) 393, <https://doi.org/10.3390/catal11030393>.
- [280] T. Kim, Y. Song, J. Kang, S.K. Kim, S. Kim, A review of recent advances in hydrogen purification for selective removal of oxygen: Deoxo catalysts and reactor systems, *Int. J. Hydrog. Energy* 47 (2022) 24817–24834, <https://doi.org/10.1016/j.ijhydene.2022.05.221>.
- [281] M. Amin, A.S. Butt, J. Ahmad, C. Lee, S.U. Azam, H.A. Mannan, A.B. Naveed, Z.U. R. Farooqi, E. Chung, A. Iqbal, Issues and challenges in hydrogen separation technologies, *Energy Rep.* 9 (2023) 894–911, <https://doi.org/10.1016/j.egyr.2022.12.014>.
- [282] M. Lototsky, K.D. Modibane, M. Williams, Y. Klochko, V. Linkov, B.G. Pollet, Application of surface-modified metal hydrides for hydrogen separation from gas mixtures containing carbon dioxide and monoxide, *J. Alloys Compd.* 580 (2013), <https://doi.org/10.1016/j.jallcom.2013.02.096>.
- [283] E.M. Borzone, M.V. Blanco, G.O. Meyer, A. Baruj, Cycling performance and hydriding kinetics of $LaNi_5$ and $LaNi_{4.73}Sn_{0.27}$ alloys in the presence of CO, *Int. J. Hydrog. Energy* 39 (2014) 10517–10524, <https://doi.org/10.1016/j.ijhydene.2014.05.004>.
- [284] N. Hanada, H. Asada, T. Nakagawa, H. Higa, M. Ishida, D. Heshiki, T. Toki, I. Saita, K. Asano, Y. Nakamura, A. Fujisawa, S. Miura, Effect of CO₂ on hydrogen absorption in Ti-Zr-Mn-Cr based AB₂ type alloys, *J. Alloys Compd.* 705 (2017) 507–516, <https://doi.org/10.1016/j.jallcom.2017.02.067>.
- [285] Z. Wu, L. Guo, J. Yao, P. Zhu, H. Wang, S. Gao, Y. Yang, F. Yang, H. Yan, Z. Zhang, Absorption of poisoned hydrogen from metal hydride under CO+H₂ mixture gas for the production of clean, high purity hydrogen, *J. Clean. Prod.* 365 (2022), 132751, <https://doi.org/10.1016/j.jclepro.2022.132751>.
- [286] A. Kumar, P. Muthukumar, Experimental studies on poisoning of $La_{0.9}Ce_{0.1}Ni_5$ based hydrogen purification system with CO₂ as impurity, *Int. J. Hydrog. Energy* (2022), <https://doi.org/10.1016/j.ijhydene.2022.10.137>.
- [287] G.D. Sandrock, P.D. Goodell, Cyclic life of metal hydrides with impure hydrogen: overview and engineering considerations, *J. Less Common Metals* 104 (1984) 159–173, [https://doi.org/10.1016/0022-5088\(84\)90452-1](https://doi.org/10.1016/0022-5088(84)90452-1).
- [288] X.-N. Yu, Z. Lin, Surface properties on hydrogen storage material TiFeMm, *J. Less Common Metals* 130 (1987) 535–540, [https://doi.org/10.1016/0022-5088\(87\)90153-6](https://doi.org/10.1016/0022-5088(87)90153-6).
- [289] P. Lv, Z. Liu, Effect of high zirconium content on hydrogenation properties and anti-poisoning ability of air-exposed TiFe alloy, *J. Mater. Res. Technol.* 8 (2019) 5972–5983, <https://doi.org/10.1016/j.jmrt.2019.09.072>.
- [290] D. Feng, J. Kuang, X. Sun, Q. Yuan, Z. Yuan, Y. Zhang, Research and Progress in FeTi based hydrogen storage materials, *Chin. J. Rare Metals* 45 (2021) 363–371, <https://doi.org/10.13373/j.cnki.cjrm.XY20010013>.
- [291] X.-L. Wang, S. Suda, Surface characteristics of fluorinated hydriding alloys, *J. Alloys Compd.* 231 (1995) 380–386, [https://doi.org/10.1016/0925-8388\(95\)01851-4](https://doi.org/10.1016/0925-8388(95)01851-4).
- [292] D.S. Rodriguez, G. Meyer, Improvement of the activation stage of $MmNi_{4.7}Al_{0.3}$ hydride-forming alloys by surface fluorination, *J. Alloys Compd.* 293–295 (1999) 374–378, [https://doi.org/10.1016/S0925-8388\(99\)00405-3](https://doi.org/10.1016/S0925-8388(99)00405-3).
- [293] H.Y. Park, W.I. Cho, B.W. Cho, S.R. Lee, K.S. Yun, Effect of fluorination on the lanthanum-doped AB₂-type metal hydride electrodes, *J. Power Sources* 92 (2001) 149–156, [https://doi.org/10.1016/S0378-7753\(00\)00527-9](https://doi.org/10.1016/S0378-7753(00)00527-9).
- [294] Y. Li, C. Wang, Y. Tao, Z. Dong, S. Yang, S. Han, Effect of complex surface treatment on morphology and electrochemical properties of La–Mg–Ni-based alloys, *J. Electrochem. Soc.* 164 (2017) A2611–A2616, <https://doi.org/10.1149/2.1281712jes>.
- [295] D.B. Willey, I.R. Harris, A.S. Pratt, The improvement of the hydrogenation properties of nickel-metal hydride battery alloy by surface modification with platinum group metals (PGMs), *J. Alloys Compd.* 293–295 (1999) 613–620, [https://doi.org/10.1016/S0925-8388\(99\)00353-9](https://doi.org/10.1016/S0925-8388(99)00353-9).
- [296] D.B. Willey, D. Pederzoli, A.S. Pratt, J. Swift, A. Walton, I.R. Harris, Low temperature hydrogenation properties of platinum group metal treated, nickel metal hydride electrode alloy, *J. Alloys Compd.* 330–332 (2002) 806–809, [https://doi.org/10.1016/S0925-8388\(01\)01475-X](https://doi.org/10.1016/S0925-8388(01)01475-X).
- [297] O. Gutfleisch, N. Schlorke-de Boer, N. Ismail, M. Herrich, A. Walton, J. Speight, I. R. Harris, A.S. Pratt, A. Züttel, Hydrogenation properties of nanocrystalline Mg- and Mg₂Ni-based compounds modified with platinum group metals (PGMs), *J. Alloys Compd.* 356–357 (2003) 598–602, [https://doi.org/10.1016/S0925-8388\(02\)01283-5](https://doi.org/10.1016/S0925-8388(02)01283-5).
- [298] E.M.B. Heller, A.M. Vredenberg, D.O. Boerma, Hydrogen uptake kinetics of Pd coated FeTi films, *Appl. Surf. Sci.* 253 (2006) 771–777, <https://doi.org/10.1016/j.apsusc.2006.01.004>.
- [299] M. Williams, A.N. Nechaev, M.V. Lototsky, V.A. Yartys, J.K. Solberg, R.V. Denys, C. Pineda, Q. Li, V.M. Linkov, Influence of aminosilane surface functionalization of rare earth hydride-forming alloys on palladium treatment by electroless deposition and hydrogen sorption kinetics of composite materials, *Mater. Chem. Phys.* 115 (2009), <https://doi.org/10.1016/j.matchemphys.2008.11.049>.
- [300] M. Williams, M.V. Lototsky, M.W. Davids, V. Linkov, V.A. Yartys, J.K. Solberg, Chemical surface modification for the improvement of the hydrogenation kinetics and poisoning resistance of TiFe, *J. Alloys Compd.* 509 (2011) S770–S774, <https://doi.org/10.1016/j.jallcom.2010.11.063>.
- [301] K. Hubkowska, M. Soszko, M. Krajewski, A. Czerwiński, Enhanced kinetics of hydrogen electroadsorption in AB₅ hydrogen storage alloy decorated with Pd nanoparticles, *Electrochem. Commun.* 100 (2019) 100–103, <https://doi.org/10.1016/j.elecom.2019.02.007>.
- [302] M. Williams, M.V. Lototsky, V.M. Linkov, A.N. Nechaev, J.K. Solberg, V.A. Yartys, Nanostructured surface coatings for the improvement of AB₅-type hydrogen storage intermetallics, *Int. J. Energy Res.* 33 (2009), <https://doi.org/10.1002/er.1609>.
- [303] M. Williams, M.V. Lototsky, A.N. Nechaev, V.M. Linkov, Method of Surface Modification of Metallic Hydride Forming Materials, Patent (2013). US8354552B2.
- [304] Y. Zhang, Y. Ding, X. Zhao, Improvement of electrochemical properties of modified unitized regenerative fuel cells through a fluorination technique, *J. Renew. Sust. Energy* 10 (2018), 044302, <https://doi.org/10.1063/1.5024702>.
- [305] K. Hubkowska, M. Soszko, M. Krajewski, A. Czerwiński, Enhanced kinetics of hydrogen electroadsorption in AB₅ hydrogen storage alloy decorated with Pd nanoparticles, *Electrochem. Commun.* 100 (2019) 100–103, <https://doi.org/10.1016/j.elecom.2019.02.007>.
- [306] D.V. Blinov, A.A. Bezdudny, D.O. Dunikov, A.N. Kazakov, V.N. Kuleshov, Experimental studies of hydrogen-absorbing properties of intermetallic compound $LaNi_{4.4}Fe_{0.3}Al_{0.3}$ for hydrogen purification, *J. Phys. Conf. Ser.* 1683 (2020), 032036, <https://doi.org/10.1088/1742-6596/1683/3/032036>.
- [307] D. Dunikov, D. Blinov, Extraction of hydrogen from a lean mixture with methane by metal hydride, *Int. J. Hydrog. Energy* 45 (2020) 9914–9926, <https://doi.org/10.1016/j.ijhydene.2020.01.201>.
- [308] A. Kumar, P. Muthukumar, Experimental investigation on the poisoning characteristics of methane as impurity in $La_{0.9}Ce_{0.1}Ni_5$ based hydrogen storage and purification system, *Energy* 259 (2022), 124888, <https://doi.org/10.1016/j.energy.2022.124888>.
- [309] P. Hao, Y. Shi, N. Cai, Elevated temperature pressure swing adsorption using $LaNi_{4.3}Al_{0.7}$ for efficient hydrogen separation, *Int. J. Hydrog. Energy* 46 (2021) 697–708, <https://doi.org/10.1016/j.ijhydene.2020.09.233>.

- [310] H. Wang, Y. Liu, J. Zhang, Hydrogen purification by Mg alloy hydrogen adsorbent, *Adsorption* 28 (2022) 85–95, <https://doi.org/10.1007/s10450-021-00348-2>.
- [311] M.D. Nashchekin, M.V. Minko, S.B. Morgunova, K.B. Minko, Enhancement of heat- and mass-transfer processes in a metal-hydride flow-through hydrogen-purification reactor, *Int. J. Hydrog. Energy* 45 (2020) 25013–25029, <https://doi.org/10.1016/j.ijhydene.2020.06.233>.
- [312] K.A.J. Koua, L. Tong, T. Yang, J. Xiao, High purity hydrogen production by metal hydride system: a parametric study based on the lumped parameter model, *J. Wuhan Univ. Technol. Mater. Sci. Ed.* 36 (2021) 127–135, <https://doi.org/10.1007/s11595-021-2385-y>.
- [313] M.D. Nashchekin, K.B. Minko, Numerical investigation into the effectiveness of internal finning of a flow-type metal-hydride reactor for purifying hydrogen of impurities, *Therm. Eng.* 69 (2022) 490–502, <https://doi.org/10.1134/S0040601522070059>.
- [314] L. Guo, Z. Wu, H. Wang, H. Yan, F. Yang, G. Cheng, Z. Zhang, Efficient hydrogen recovery and purification from industrial waste hydrogen to high-purity hydrogen based on metal hydride powder, *Chem. Eng. J.* 455 (2023), 140689, <https://doi.org/10.1016/j.cej.2022.140689>.
- [315] D.V. Blinov, V.I. Borzenko, A.V. Bezdudny, A.N. Kazakov, Metal hydride hydrogen storage and purification technologies, *J. Phys. Conf. Ser.* 2039 (2021), 012005, <https://doi.org/10.1088/1742-6596/2039/1/012005>.
- [316] Yu.F. Shmal'ko, V.V. Solovei, M.V. Lotots'kiy, E.V. Klochko, I.Yu. Zavaliy, O. B. Ryabov, V.A. Yartys', Metal-hydride systems for processing hydrogen isotopes for power plants, *Mater. Sci.* 37 (2001) 689–706, <https://doi.org/10.1023/A:1015041406755>.
- [317] V.A. Yartys', I.Yu. Zavaliy, M.V. Lototsky, A.B. Riabov, Yu.F. Shmal'ko, Oxygen-, boron- and nitrogen-containing zirconium-vanadium alloys as hydrogen getters with enhanced properties, *Z. Phys. Chem.* 183 (1994) 485–489, https://doi.org/10.1524/zpch.1994.183.Part_1_2.485.
- [318] M.V. Lototsky, V.A. Yartys, Ye.V. Klochko, V.N. Borisko, R.I. Starovoitov, V. M. Azhazha, P.N. V'yugov, Applications of Zr–V hydrogen getters in vacuum-plasma devices: phase-structural and hydrogen sorption characteristics, *J. Alloys Compd.* 404–406 (2005) 724–727, <https://doi.org/10.1016/j.jallcom.2005.02.086>.
- [319] Yu.F. Shmal'ko, M.V. Lototsky, V.V. Solovey, V.A. Yartys', A.P. Strokach, Application of metal hydrides in hydrogen ion sources, *Z. Phys. Chem.* 183 (1994) 479–483, https://doi.org/10.1524/zpch.1994.183.Part_1_2.479.
- [320] Y. Shmal'ko, V.V. Solovey, M.V. Lototsky, Y.V. Klochko, Mass spectrometry determination of vibrationally excited states of molecules of hydrogen desorbed from the surface of metal hydrides, *Int. J. Hydrog. Energy* 20 (1995) 357–360, [https://doi.org/10.1016/0360-3199\(94\)00058-8](https://doi.org/10.1016/0360-3199(94)00058-8).
- [321] Y.F. Shmal'ko, Y.V. Klochko, M.V. Lototsky, Influence of isotopic effect on the shift of the ionization potentials of hydrogen desorbed from the metal hydride surface, *Int. J. Hydrog. Energy* 21 (1996) 1057–1059, [https://doi.org/10.1016/S0360-3199\(96\)00040-7](https://doi.org/10.1016/S0360-3199(96)00040-7).
- [322] Y. Klochko, M.V. Lototsky, V.V. Popov, Y.F. Shmal'ko, V.N. Borisko, Investigation of hydrogen plasma interaction with metal hydride, *Int. J. Hydrog. Energy* 24 (1999) 169–174, [https://doi.org/10.1016/S0360-3199\(98\)00073-1](https://doi.org/10.1016/S0360-3199(98)00073-1).
- [323] V.N. Borisko, Y.V. Klochko, V.I. Lapshin, I.N. Sereda, Peculiarities of sectioned metal-hydride hollow cathode applying in penning discharge, in: *AIP Conf Proc*, AIP, 2006, pp. 337–340, <https://doi.org/10.1063/1.2168856>.
- [324] I.V. Borgun, D.L. Ryabchikov, I.N. Sereda, A.F. Tseluyko, PIG charged particle source with hydrogen supply from a metal-hydride cathode, *J. Phys. Conf. Ser.* 514 (2014), 012051, <https://doi.org/10.1088/1742-6596/514/1/012051>.
- [325] I. Sereda, A. Tseluyko, D. Ryabchikov, Ya. Hrechko, N. Azarenkov, The increasing of H– current from penning ion source with electrically biased metal hydride cathode, *Vacuum* 162 (2019) 163–167, <https://doi.org/10.1016/j.vacuum.2019.01.046>.
- [326] I. Sereda, Y. Hrechko, I. Babenko, M. Azarenkov, The emission of H– ions from penning-type ion source with metal hydride cathode in pulsating regime, *Vacuum* 200 (2022), 111006, <https://doi.org/10.1016/j.vacuum.2022.111006>.
- [327] R.H. Reuss, B.R. Chalamala, Feasibility of thin film microfabricated hydrogen ion sources, *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.–Process., Meas., Phenom.* 20 (2002) 1132, <https://doi.org/10.1116/1.1473181>.
- [328] M. Sekine, K. Kondo, M. Okamura, N. Hayashizaki, A study of H⁺ production using metal hydride and other compounds by means of laser ion source, *Rev. Sci. Instrum.* 83 (2012) 02B318, <https://doi.org/10.1063/1.3675385>.
- [329] J.L. Ellsworth, S. Falabella, J. Sanchez, V. Tang, H. Wang, Compact deuterium-tritium neutron generator using a novel field ionization source, *J. Appl. Phys.* 116 (2014), 193301, <https://doi.org/10.1063/1.4901830>.
- [330] F. Cuevas, M. Lacroche, Intermetallic alloys as hydrogen getters, *J. Alloys Compd.* 905 (2022), 164173, <https://doi.org/10.1016/j.jallcom.2022.164173>.
- [331] I.I. Okseniuk, V.O. Litvinov, D.I. Shevchenko, R.L. Vasilenko, S.I. Bogatyrenko, V. V. Bobkov, Hydrogen interaction with Zr-based getter alloys in high vacuum conditions: in situ SIMS-TPD studies, *Vacuum* 197 (2022), 110861, <https://doi.org/10.1016/j.vacuum.2021.110861>.
- [332] V.A. Litvinov, I.I. Okseniuk, D.I. Shevchenko, V.V. Bobkov, Study of secondary-ion emission during the interaction of Zr₂Fe getter alloy with oxygen, *J. Surf. Investig. X-Ray Synchrotron Neutron Tech.* 16 (2022) 789–796, <https://doi.org/10.1134/S102745102205010X>.
- [333] J. Zhang, H. Song, J. Fang, X. Hou, S. Huang, J. Xiang, T. Lu, C. Zhou, Study on coated Zr-V-Cr getter with pore gradient structure for hydrogen masers, *Materials* 15 (2022) 6147, <https://doi.org/10.3390/ma15176147>.
- [334] Z. Luo, H. Leng, X. Han, W. Liu, G. Yang, Z. Ma, Influence of preparation methods on the hydrogen absorption properties of Zr₇V₅Fe getter alloy, *J. Alloys Compd.* 926 (2022), 166739, <https://doi.org/10.1016/j.jallcom.2022.166739>.
- [335] Y. Xiong, H. Wu, X. Liu, Hydrogen absorption performance and mechanism of low-temperature activated Ti-Co-Ce bulk getter, *J. Alloys Compd.* 888 (2021), 161541, <https://doi.org/10.1016/j.jallcom.2021.161541>.
- [336] Q. Cao, X. Wang, S. Wang, B. Xiao, J. Wu, S. Gan, X. Yuan, P. Li, Development and characterization of an improved Ti-Zr-V thin-film getter with 3D porous nano-scaffolds, *Vacuum* 209 (2023), 111747, <https://doi.org/10.1016/j.vacuum.2022.111747>.
- [337] Yu.V. Verbovitsky, V.V. Berezovets, A.R. Kytysa, I.Yu. Zavaliy, V.A. Yartys, Hydrogen generation by the hydrolysis of MgH₂, *Mater. Sci.* 56 (2020) 1–14, <https://doi.org/10.1007/s11003-020-00390-5>.
- [338] L. Ouyang, M. Liu, K. Chen, J. Liu, H. Wang, M. Zhu, V. Yartys, Recent progress on hydrogen generation from the hydrolysis of light metals and hydrides, *J. Alloys Compd.* 910 (2022), 164831, <https://doi.org/10.1016/j.jallcom.2022.164831>.
- [339] N. Ruslan, M.S. Yahya, Md.N.I. Siddique, A.P. Yengantiwar, M. Ismail, Md. R. Awal, M.Z. Mohd Yusoff, M.F.A. Abdul Halim Yap, N.S. Mustafa, Review on magnesium hydride and sodium borohydride hydrolysis for hydrogen production, *Crystals (Basel)* 12 (2022) 1376, <https://doi.org/10.3390/cryst12101376>.
- [340] M. Liu, Z. Yao, J. Gu, C. Li, X. Huang, L. Zhang, Z. Huang, M. Fan, Issues and opportunities facing hydrolytic hydrogen production materials, *Chem. Eng. J.* 461 (2023), 141918, <https://doi.org/10.1016/j.cej.2023.141918>.
- [341] V.S. Marakatti, E.M. Gaigneaux, Recent advances in heterogeneous catalysis for ammonia synthesis, *ChemCatChem* 12 (2020) 5838–5857, <https://doi.org/10.1002/cctc.202001141>.
- [342] C. Zhou, J. Zhang, R.C. Bowman, Z.Z. Fang, Roles of Ti-based catalysts on magnesium hydride and its hydrogen storage properties, *Inorganics (Basel)* 9 (2021) 36, <https://doi.org/10.3390/inorganics9050036>.
- [343] X. Zhang, Y. Cao, Q. Chen, C. Shen, L. He, Recent Progress in homogeneous reductive carbonylation of carbon dioxide with hydrogen, *Acta Phys.-Chim. Sin.* 0 (2020), <https://doi.org/10.3866/PKU.WHXB202007052>, 2007052–0.
- [344] T. Takeshita, Some applications of hydrogenation-decomposition-desorption-recombination (HDDR) and hydrogen-decrepitation (HD) in metals processing, *J. Alloys Compd.* 231 (1995) 51–59, [https://doi.org/10.1016/0925-8388\(95\)01873-5](https://doi.org/10.1016/0925-8388(95)01873-5).
- [345] T. Iwaki, T. Kuriwa, A. Kamegawa, H. Takamura, M. Okada, Grain-size refinements of Cu-3 mass%Ti alloys by HDDR treatments in correlating with their electrical and mechanical properties, *Mater. Trans.* 50 (2009) 499–505, <https://doi.org/10.2320/matertrans.MBW200807>.
- [346] C. Corgnale, S. Greenway, T. Motyka, M. Sulic, B. Hardy, T. Molten, D. Ludlow, Technical performance of a hybrid thermo-electrochemical system for high pressure hydrogen compression, *ECS Trans.* 80 (2017) 41–54, <https://doi.org/10.1149/08010.0041ecst>.
- [347] H. Yu, Y. Wu, S. Chen, Z. Xie, Y. Wu, N. Cheng, X. Yang, W. Lin, L. Xie, X. Li, J. Zheng, Pd-modified LaNi₅ nanoparticles for efficient hydrogen storage in a carbazole type liquid organic hydrogen carrier, *Appl Catal B.* 317 (2022), 121720, <https://doi.org/10.1016/j.apcatb.2022.121720>.
- [348] B.P. Tarasov, P.V. Fursikov, A.A. Volodin, M.S. Bocharnikov, Y.Y. Shimkus, A. M. Kashin, V.A. Yartys, S. Chidziva, S. Pasupathi, M.V. Lototsky, Metal hydride hydrogen storage and compression systems for energy storage technologies, *Int. J. Hydrog. Energy* 46 (2021) 13647–13657, <https://doi.org/10.1016/j.ijhydene.2020.07.085>.
- [349] C.-S. Wang, J. Brinkerhoff, Is there a general time scale for hydrogen storage with metal hydrides or activated carbon? *Int. J. Hydrog. Energy* 46 (2021) 12031–12034, <https://doi.org/10.1016/j.ijhydene.2021.01.067>.