



Materials for hydrogen-based energy storage – past, recent progress and future outlook



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ABSTRACT

Globally, the accelerating use of renewable energy sources, enabled by increased efficiencies and reduced costs, and driven by the need to mitigate the effects of climate change, has significantly increased research in the areas of renewable energy production, storage, distribution and end-use. Central to this discussion is the use of hydrogen, as a clean, efficient energy vector for energy storage. This review, by experts of Task 32, "Hydrogen-based Energy Storage" of the International Energy Agency, Hydrogen TCP, reports on the development over the last 6 years of hydrogen storage materials, methods and techniques, including electrochemical and thermal storage systems. An overview is given on the background to the various methods, the current state of development and the future prospects. The following areas are covered; porous materials, liquid hydrogen carriers, complex hydrides, intermetallic hydrides, electrochemical storage of energy, thermal energy storage, hydrogen energy systems and an outlook is presented for future prospects and research on hydrogen-based energy storage.

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1. Introduction

The European Commission describes hydrogen as an energy carrier with a "great potential for clean, efficient power in stationary, portable and transport applications." Indeed, presently hydrogen is getting unprecedented focus not only in Europe but across the globe, and is on track to achieve its outstanding potential as a clean energy solution.

The growing applications of hydrogen fueled transportation started in the 20th century with high profile technology breakthroughs such as powering Apollo 11 to the moon. The area is maturing through a growing fleet of hydrogen fuel cell vehicles, hydrogen fuel cell trains commercially operating in Germany, France and the UK, and hydrogen driven ferries in Norway. This is in addition to the high capacity metal hydride fast recharging battery systems for trains and trams in France and in Japan. Hydrogen storage remains a key challenge in rolling out infrastructure to support hydrogen fueled transportation.

As the world's leading energy authority covering exploration of all fuels and related technologies, the International Energy Agency (IEA) is ideally placed to lead global policy on hydrogen. The IEA Technology Collaboration Program (TCP) supports advancing the research, development and commercialization of energy technologies. IEA Hydrogen TCP operates research on hydrogen within tasks. IEA Hydrogen Task 32 HYDROGEN-BASED ENERGY STORAGE has coordinated the efforts of the scientific community in various areas of energy storage based on hydrogen.

IEA Hydrogen Task 32 is the largest international collaboration in this field. It involves more than 50 experts coming from 17 countries. The task consists of seven working groups, working on porous materials, intermetallic alloys and magnesium-based hydrides as energy storage materials, complex and liquid hydrides, electrochemical storage of energy, heat storage and hydrogen storage systems for stationary and mobile applications.

This dynamic collaborative research effort has resulted not only in over 600 publications in international journals (including 20 in a topical collection in Applied Physics A in 2016 and seven in a special issue of International Journal of Hydrogen Energy in 2019) and presentations at international conferences and symposia in the field (lately in a special session at the 16th International Symposium on Metal-Hydrogen Systems (MH2018) on November 1, 2018 in Guangzhou, China), but has also led to the discoveries of new functional materials and their technologies, bridging the gap between fundamental science and real world applications.

Nanomaterials, materials for novel rechargeable batteries, for thermal storage, and the development of systems for hydrogen storage and compression of hydrogen gas using metal hydrides, together with beautiful chemistry, structure and properties of new materials attracted the interest of many leading researchers. These researchers are sharing the major outcomes of their work in this review paper, which summarizes the research efforts over the last 6 years, 2013–2018. The review is presented in the following sections. The multidisciplinary and collaborative work crosses many of these sections. The review is inevitably confined by size but it does summarize the most important results and contains an extensive list of references by the members of the IEA Hydrogen Task 32, which will allow the reader to find further details of the presented research effort.

2. Porous materials for H₂ storage

For technological applications, rapid kinetics and full reversibility enable short refuelling times and high cycle life, and so exploration into physisorption in materials is an important area. Hydrogen storage by physisorption in porous materials, using classical systems such as activated carbons and zeolites, has a long history. Maximum storage capacities are closely related to the surface area accessible to H₂ molecules. Gravimetric capacities therefore tend to follow Chahine's rule, which states that the hydrogen uptake is approximately 1 wt% H₂ per 500 m² g⁻¹ of surface area at 77 K and pressures above 20 bar. Super-activated, porous carbons with large surface areas have been developed in the past, but the field came to some stagnation around 20 years ago.

In the late 1990s, there was a certain amount of hype and hope surrounding hydrogen storage using carbon nanotubes and other carbon nanostructures; however, the initial results were later shown to be due to either contamination of the samples or erroneous measurements [1–3]. At the same time, an entirely new class of highly porous, crystalline materials called coordination polymers or Metal-Organic Frameworks (MOFs) was developed. Following promising results for methane in 2001, the first hydrogen storage results on MOF-5, published in 2003, showed a sharp increase in the H₂ uptake at very low pressures and a maximum of 4.5 wt% below 1 bar at 77 K [4]. However, this was corrected a year later by the same group to 1.3 wt% at 1 bar [5]. Soon after, more results on different MOFs were published showing high H₂ uptakes at 77 K and higher pressures, owing to the large pore volumes and high specific surface areas of these novel frameworks [6,7]. An additional

advantage of these materials is the open pore structure that makes the kinetics of hydrogen ad- and desorption very fast, and highly reversible since no structural change occurs in the framework [8].

The validity of Chahine's rule, which was originally proposed for carbons, was shown for MOFs independently by two groups at the same time [9,10]. Despite the different elements in the building blocks of MOFs, this result is reasonable since at pressures above 20 bar all adsorption sites will be occupied. This result then started a race to synthesize new MOFs with higher specific surface areas.

Over the next 15 years, many studies investigated the correlation between H₂ adsorption and the structure and composition of different MOFs. One example is the correlation of the heat of adsorption to pore size, due to overlapping of the van der Waals forces of neighbouring framework atoms [11,12]. Another is the influence of open metal sites, which adsorb strongly, due to polarization of the H₂ molecules [13,14]. High heats of adsorption have been observed for these sites; however, only a fraction of the total adsorption sites could be enhanced so far. A similar strategy is to post-synthetically exchange the linkers in the MOF structure, i.e. use functionalization, in order to change either the pore or aperture size, or enhance the interaction with H₂ [15–17].

The gravimetric H₂ uptakes at higher pressures above 20 bar and at 77 K, for all porous materials, are proportional to surface area, indicating that specific surface area is crucial for achieving high gravimetric storage capacities. The problem is that high-surface-area porous materials tend to have low material densities and therefore only modest volumetric hydrogen storage capacities. For crystalline materials, such as MOFs, the gravimetric H₂ uptake can easily be converted to volumetric uptake using the single crystal density obtained by X-Ray Diffraction (XRD) structure analysis. For experimental results, a phenomenological model for the volumetric absolute uptake as a function of the gravimetric absolute uptake has been developed [18]. For theoretical studies, via computational screening, a similar correlation was obtained using over 5000 MOF structures [19]. Fig. 1 shows the volumetric absolute uptake for a range of porous materials plotted against gravimetric uptake. The solid lines show the phenomenological model developed by Balderas-Xicohténcatl et al. [18].

So far most of the reported hydrogen storage capacities are still given as the maximum uptake at the upper measurement pressure, whereas for methane storage in porous materials the working or useable capacity is often reported. Useable capacity is defined as the difference between the capacity of the full tank at maximum pressure and the capacity remaining in the tank at the minimum pressure required to run the fuel cell. A detailed analysis based on experimental data of several MOFs has been reported by Schlichtenmayer and Hirscher [20]. Depending on the heat of adsorption, an optimum operating temperature was reported, which maximized the useable capacity for a particular material. Recently, Siegel and co-workers [21] screened half a million MOFs in a theoretical study and found an upper value of about 40 g H₂ L⁻¹ for the useable volumetric capacity. One strategy to increase the useable capacity has been recently demonstrated for methane storage through the use of flexible frameworks [22]. However, the lower isosteric heat of hydrogen compared to methane makes it more difficult to design and tailor a flexible MOF for which H₂ adsorption will induce a structural phase transition to an open structure with higher gas storage capacity.

As indicated earlier, measurement accuracy and reproducibility has been an issue in porous materials research [3]. H₂ adsorption is commonly measured using the manometric and gravimetric techniques [23], both of which are susceptible to errors associated with volume calibrations [24,25] and buoyancy corrections [26]. Problems, such as the use of insufficient sample sizes, gas purity, and equilibration times, have also affected measurements, and this has

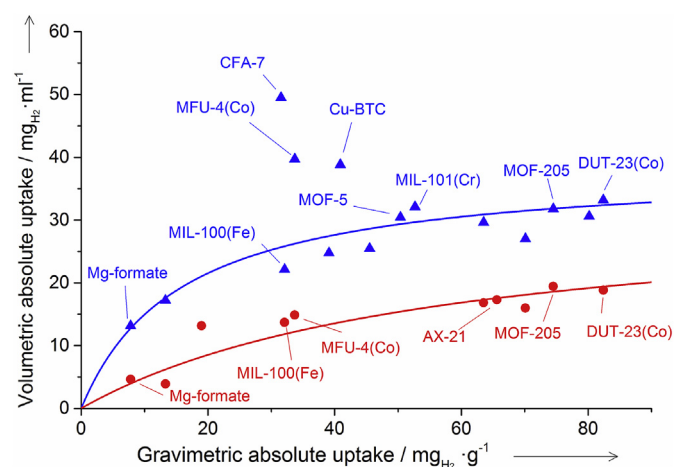


Fig. 1. Volumetric vs. gravimetric absolute hydrogen uptake of porous materials measured at 77 K and 2.0–2.5 MPa. The volumetric uptake was calculated using packing density (red) and single-crystal density (blue). Used with permission from Balderas-Xicohténcatl et al. [18]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

been demonstrated by interlaboratory exercises performed on both porous carbon [27] and doped MgH₂ [28]. Better agreement was found in a recent study, which reported high pressure H₂ adsorption measurements on two commercial porous carbons [29]. The use of small sample sizes in manometric instruments, inducing large errors, continues to be a problem in the literature. It has also not yet been demonstrated, via interlaboratory studies, that accurate measurements can be performed reproducibly at both 77 K and high pressures for a wide range of materials, such as MOFs, COFs and polymers [30]; since only porous carbons have been subject to such tests.

High pressure measurements, particularly above standard cylinder pressures of 200 bar, require specialist components, together with a hydrogen compressor [31–34]. As the pressure increases, uncertainties in the measurement increase [24] and problems associated with determining the volume of low density materials also increase [23]. This must be accounted for during instrument design [31]. Such high pressures are of interest due to the possibility of incorporating an adsorbent in the storage tanks of commercial 700 bar compressed gas systems, although this is made difficult by the tendency of adsorptive materials to have the majority of the useable capacity at low pressures. As an example, uptake isotherms for excess and net gravimetric capacity to 2000 bar at ambient temperature are shown in Fig. 2. This demonstrates that the maximum in the advantage of the adsorbing material over an empty tank occurs at only 100 bar, and that over 300 bar, the material constitutes a disadvantage compared to an empty tank.

An alternative approach for characterizing hydrogen adsorption in porous materials, by measuring one adsorption isotherm at 20 K, has been proposed by Streppel and Hirscher [35]. A single low-pressure, high-resolution isotherm of hydrogen at the boiling temperature can be used to analyze the specific surface area by applying the BET theory and to determine the upper physical limit for hydrogen uptake up to the filling of the pores by condensation [36]. Using compacted materials in the form of pellets allows direct measurement of the volumetric uptake based on the packing density.

Porous materials can also be used as substrates for metal nanoparticles. Several reports on noble metal particles finely dispersed inside porous materials claimed an enhanced hydrogen

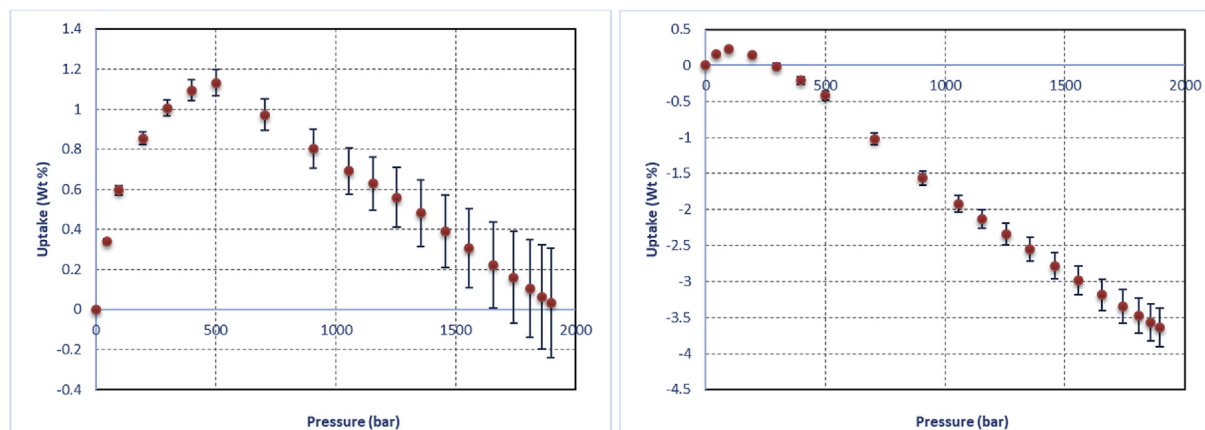


Fig. 2. Experimental excess (a) and net (b) isotherms of porous carbon Filtrasorb 400 at ambient temperature to 2000 bar. Net is defined as the amount of hydrogen due to adsorption over and above what would be in the same volume at the same pressure without the adsorptive material.

storage capacity at ambient temperature and ascribed it to a so-called “spillover effect”. None of these reports claiming high storage capacities could be independently reproduced [3]. If the spillover effect occurs at all, it is minor and technologically irrelevant [37–39]. On the other hand, noble metal particles in frameworks often exhibit special catalytic activities. Under hydrogen atmosphere organic gases or liquids can be hydrogenated under mild conditions in these metal-doped frameworks [40,41].

The inverse of this approach is the utilization of frameworks to nano-confine metal hydrides and use their structure as a scaffold [42,43]. While this does not add any adsorption contribution, this novel approach does offer the possibility that nanoconfinement may improve the thermodynamic and the kinetic properties of the hydride. In addition, by employing an oxygen-free porous metal scaffold that partially reacts with the nano-confined hydride, the remaining metal scaffold is expected to substantially improve the thermal conductivity of the hydride bed. Low thermal conductivity is a key constraint of hydrides as illustrated in the following sections. By carefully matching the amount of metal scaffold to the hydride encapsulated within it, enough of the metal scaffold remains upon reaction with the complex hydride to maintain structural integrity of the scaffold [44–49]. This also maintains the kinetic advantages of nanoconfinement by minimising segregation of the desorption products.

Together with the above experimental work, theory has also played a significant role in the development of the field, by helping explain experimental results and by leading experiments [50–58]. There are several methods for investigating gas storage in MOFs. For many years, multiscale modelling of various physical and chemical phenomena such as gas adsorption and diffusion has been developed. Multiscale modelling consists of applying different levels of theory depending on the length scale of the system under investigation and the time evolution of the physical phenomenon. In this way, the accuracy of the lower scale can be combined with the system size of the higher, without requiring prohibitively large computations. This approach has been undertaken in the modelling of H_2 physisorption in nanoporous materials. For example, Froudakis and co-workers developed a multiscale scheme presented in Fig. 3 – left [50–52]. At the lowest level, *ab-initio* techniques allow high accuracy calculation of the molecular H_2 interaction with the different building blocks of a MOF. At the next level, Potential Energy Surfaces (PES) are constructed, for fitting the classical interatomic potentials used in the highest level. These massive computations use either dispersion corrected Density Functional Theory (DFT) or Mixed Quantum Mechanics/Molecular Mechanics

(QM/MM) models. At the final level, classical Molecular Dynamics (MD) and Monte Carlo simulations in the Grand Canonical ensemble (GCMC) reveal the adsorption of H_2 in MOFs, taking into account several thousands of atoms. Such multiscale modelling of hydrogen storage in nanoporous materials has proved significant in developing our understanding, and has paved the way for further experimental studies [59,60]. One such study is the directed assembly of a high surface area 2D MOF displaying the augmented “kagomé dual” (kgd-a) layered topology. This showed a high H_2 uptake ($209.9 \text{ cm}^3(\text{STP}) \text{ g}^{-1}$ at 77 K and 1 bar).

Over the last couple of years, Machine Learning (ML) techniques have also been introduced, for predicting adsorption of different gases in MOFs. In the field of material science, the computational cost of ML methods is several orders of magnitude lower than that of the previously mentioned multiscale approaches. However, their ability to provide accurate predictions strongly depends on determining appropriate parameters (descriptors) to allow the algorithm to efficiently learn from existing data and the quality of the data fed in.

For ML techniques, shown in Fig. 3-right, a large dataset is needed for training and an algorithm is required to perform the training. Appropriate descriptors also have to be identified. While the training part may need computational time, the production runs for obtaining properties of unseen materials require only milliseconds. It has recently been shown that ML techniques are a powerful tool for the large-scale screening of materials [61,62]. An example is the chemically intuited large scale screening of MOFs by machine learning techniques done at the University of Crete in cooperation with the University of Huddersfield.

During IEA Hydrogen Task 32, the field of porous materials for hydrogen storage progressed from fundamental studies on synthesising, characterizing and understanding novel MOFs to improving and optimising technologically relevant parameters, such as volumetric, gravimetric and useable storage capacities. The first larger prototype storage tank systems have been built and operated introducing different heat-exchanger concepts. The achievements within the porous materials working group of IEA Hydrogen Task 32 are summarized in two recent articles [63,64].

3. Liquid hydrogen carriers

The liquid state is considered a practicable option for the large-scale transport and storage of hydrogen, towards an international hydrogen-based energy market [65]. Recent dramatic declines in auction prices for electricity from renewable energy installations

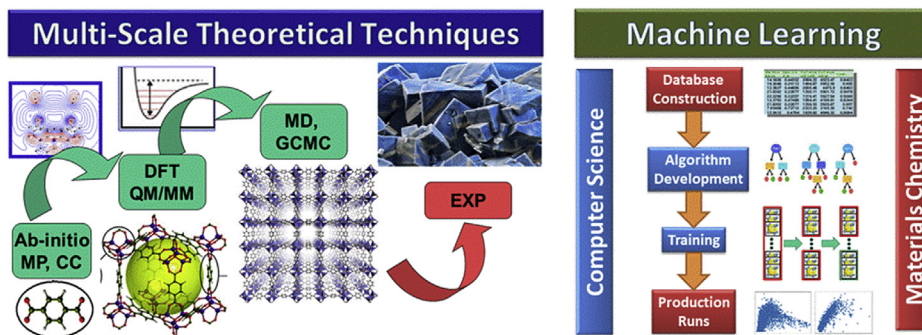


Fig. 3. Multiscale theoretical methodologies (left) vs Machine Learning techniques (right) for modelling hydrogen storage in MOFs.

have occurred in areas with favorable wind and solar conditions [66]. These low prices have highlighted the opportunity for energy supply chains which can transport renewable energy, via a carrier, from renewable rich areas such as Morocco, Saudi Arabia, UAE, Brazil, Chile and Australia (Fig. 4). The conversion of renewable electricity to hydrogen and long distance maritime transport of that hydrogen in a liquid form is seen as an economically attractive method of energy transport [67]. This may also be a viable option for remote areas with high renewable electricity generation potential, with no direct grid connections [68–70].

Liquid hydrogen storage is also an important component of domestic grid-balancing alongside electrochemical energy storage. A high energy density store which can be produced and stored at scale would help manage inter-seasonal imbalances in supply and demand, a task that is problematic for batteries due to self-discharge [71]. An example of this is the winter heating demand in the UK, which is around 200 TWh each year and is currently met by the natural gas grid [72]. Here again, production of hydrogen and storage either in geologic features or as a liquid is seen as the most viable means of achieving long-duration energy storage, giving advantages in volumetric energy density and cost of storage and distribution.

Liquid hydrogen is the most conceptually simple means of hydrogen storage; however, the complexity and cost associated with the extremely low temperature (20 K) required for hydrogen liquefaction [73,74] has prompted the consideration of other liquid carriers with moderate storage conditions. Most attention, including within IEA Task 32, has been given to two carriers in particular: ammonia and liquid organic hydrogen carriers (LOHCs) [75–80]. Both have more moderate storage requirements than liquid hydrogen which results in significantly lower projected transportation and storage costs [67,73,74]. This has led to the active development of hydrogen supply chains based on conversion to these carriers [65,67,81–84]. Most of the planned applications of liquid carriers do not involve dehydrogenation on-board a fuel cell vehicle, but rather models of either centralised dehydrogenation at ports or other facilities for local distribution as hydrogen gas, or

decentralised hydrogen release at refuelling stations.

While the synthesis costs of ammonia and LOHCs compare well with the cost of liquefying hydrogen [74,82,83], use of these liquid carriers introduces an extra step of converting the carrier back to hydrogen. The cost and efficiency losses associated with this reconversion step limit their use. As such, much of the research from Task 32 in this area has focused on improving the chemistry of hydrogen release through catalyst development.

3.1. LOHCs

The first LOHC compounds explored were cyclic alkane compounds, such as cyclohexane, methylcyclohexane and decalin, with dehydrogenation to the related aromatic compounds achieved largely with platinum-based catalysts at 300–350 °C [75,77,85]. These simple materials, which can release up to 6 wt% hydrogen with similar volumetric hydrogen density to 70 MPa hydrogen gas are attractive because they are already produced at commercial scale (e.g. benzene and toluene [86]) and have a high level of technological readiness. However, the high dehydrogenation temperature and the expensive catalysts required hinder their commercial application. As such, research on these carriers has focused on:

- Reducing the temperature of dehydrogenation by modification of the LOHC molecule to reduce the enthalpy of the reaction.
- Searching for more active, stable and earth-abundant catalysts for dehydrogenation.

Attempts to modify the enthalpy of dehydrogenation have largely centred on the introduction of heteroatoms, particularly nitrogen, into the cyclic structures [87–89]. A number of these materials (e.g. N-ethyl carbazole) have been shown to have superior hydrogen storage and release characteristics than unsubstituted systems [90,91].

Recently, a metallation strategy was employed to optimize the hydrogen storage properties of organic compounds through the replacement of their reactive H by alkali or alkaline earth metal to form the metallated counterparts. Crystalline lithiated amines were synthesised by ball milling primary amines with LiH, demonstrating a mild endothermic dehydrogenation and an enhanced selectivity to hydrogen release [92,93]. The sodium phenoxide-cyclohexanolate pair was also developed, which has an enthalpy change of dehydrogenation of 50.4 kJ/mol-H₂, substantially less than that of pristine phenol-cyclohexanol pair (64.5 kJ/mol-H₂). This enthalpy change was found to correlate with the electron delocalization from the oxygen to the benzene ring of phenoxide. Hydrogen uptake and release were achieved below 150 °C [94].

Ruthenium is the most active hydrogenation catalyst for these

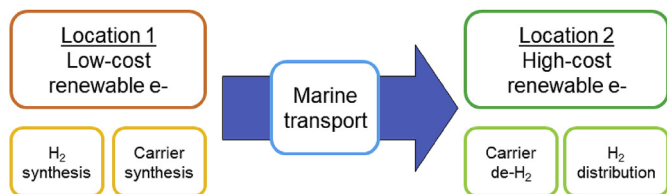


Fig. 4. Schematic of the use of liquid hydrogen carriers to store energy produced in areas with cheap renewable electricity for use in areas with more expensive local electricity.

N-substituted systems, while supported palladium has been found to be the most active catalyst for dehydrogenation. In some catalyzed dehydrogenations, complete reaction is not observed, producing partially-dehydrogenated products which limit the accessible hydrogen content [95]. Among the catalyst supports, materials have been found to increase the hydrogenation rate, as evidenced by the increased activity of palladium nanoparticles supported on a covalent triazine framework [96]. Homogeneous catalysts have also been investigated, with iridium pincer complexes used to catalyze the dehydrogenation of a number of heterocyclic species, showing appreciable activity at 150–200 °C [97,98].

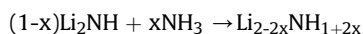
3.2. Ammonia

Ammonia is also an attractive liquid carrier for hydrogen storage. It is already one of the most consequential synthetic chemicals through its role as a fertiliser feedstock [99] – with production at around 180 Mt per year [100] – so this means existing synthesis and distribution infrastructure are technologically mature. However, there are several active research areas aiming to improve the cost and efficiency of ammonia-related hydrogen storage.

Hydrogen release from ammonia is not a well-established technology, as it does not form a significant part of the existing markets for ammonia. Ammonia decomposition catalysis has been studied in some depth for transition metal systems as a proxy for catalytic activity for ammonia synthesis. Ruthenium is the most active metal [101,102], but high performance is also achieved using more earth-abundant metals such as iron, cobalt and molybdenum [103–105]. In-situ diffraction techniques have proved valuable for understanding the formation of nitride phases in iron and manganese under ammonia decomposition conditions [106,107,107].

Temperature is also a consideration, with even the most active ruthenium-based catalysts requiring relatively high temperatures (>450 °C) to approach 100% conversion to hydrogen. Delivering significantly lower operating temperatures requires new catalysts to be developed. Recently, metal-nitrogen-hydrogen materials (principally light metal amides and imides) have been shown to effectively mediate ammonia decomposition achieving catalytic activities that are comparable to supported ruthenium catalysts [108–110].

For these new catalyst systems, two parallel paths of investigation have been explored: metal amide/imide as individual catalysts [108,110,111] and in composites with transition metals and their nitrides [109,112–116]. The catalytic activity has been rationalized by the cyclic formation and decomposition of ternary lithium nitrides (e.g. Li_7MnN_4 and Li_3FeN_2) in the transition metal composites (Fig. 5a) [109], or a metal/metal-rich species, such as sodium (Fig. 5b) or lithium nitride-hydride (Li_4NH) (Fig. 5c), in isolated metal imides [117]. Lithium imide (Li_2NH) containing species have been the most active catalysts reported to date. In-situ neutron and X-ray powder diffraction experiments have shown that the active state of the lithium imide is a solid solution of lithium amide and lithium imide, the precise stoichiometry of which depends on the reaction conditions [110,118].



Furthermore, isotope exchange reactions have revealed that both the hydrogen and nitrogen in the imide are exchangeable with ammonia under operating conditions [110,117], indicating a bulk exchange mechanism which is in contrast to transition metal nanoparticle catalysis and more closely related to the Mars van Krevelen mechanisms of metal nitride based ammonia synthesis [119].

Metal amides and imides have also recently been reported as part of novel ammonia synthesis pathways (Fig. 5d). They are hypothesized to be the mediating species in the lithium hydride – transition metal (nitride) composites, which are proposed to be two-site ammonia synthesis catalysts which break the scaling relations between nitrogen activation and the binding strength of intermediate species, achieving very high ammonia synthesis activity [120,121]. Additionally, they have been shown as part of a chemical looping approach to ammonia synthesis, where a combination of barium hydride (BaH_2) and nickel is able to produce ammonia from hydrogen and nitrogen through the formation and subsequent hydrogenation of barium imide (BaNH) at 1 bar and at a temperature as low as 100 °C [122].

These milder approaches to ammonia synthesis may well enable smaller-scale synthesis units which require much less capital investment and are better equipped to couple to variable renewable electricity supplies.

Electrochemical ammonia synthesis is another interesting approach [123], though a good electrocatalyst for nitrogen reduction has so far been elusive. Indeed, there is evidence that many published results are susceptible to ammonia derived from contaminants rather than from true nitrogen reduction, emphasizing the need for isotopically labelled experiments [124,125]. Theoretical approaches based on DFT have identified a range of nitrides as potential catalysts [126,127], if high activity catalysts which suppress the competing hydrogen evolution reaction can be identified [128,129].

Another challenge is preventing the release of ammonia from storage vessels or in hydrogen/exhaust streams to avoid: environmental effects of ammonia through toxicity in waterways and as an atmospheric pollutant [130]; shielding PEM fuel cells from degradation by ammonia [131]; and human exposure to corrosive ammonia gas. Approaches to purifying hydrogen to ensure ammonia levels are below the 0.1 ppm standard for mobile applications include absorption of ammonia by metal halides [132] or zeolites [133], or by filtering H_2 gas streams using membranes [134].

Sorption materials can also be used to store ammonia with a significantly reduced vapour pressure [135–138]. Metal halides ammine complexes can have ammonia densities similar to liquid ammonia. It has been shown that, by tailoring the combination of metal ions in a ternary metal halide system, the conditions for ammonia release can be matched to the desired application. Combinations of genetic algorithms and DFT calculations were used to identify mixed-metal systems which best matched a specific performance metric [139–142]. An example structure of a barium-strontium-calcium chloride ammine was then synthesised and demonstrated impressive agreement with the expected ammonia desorption behaviour [139,143,144]. Metal borohydride amines can also store significant quantities of ammonia [145,146], up to 6 ammonia groups per molecule in the case of $6\text{Mn}(\text{BH}_4)_2 \cdot 6(\text{NH}_3)$, forming often analogous structures to the metal halide ammine [147–149]. Thermal decomposition of these species can give either pure ammonia or mixtures of ammonia and hydrogen. While the factors governing this are not fully understood, it is hypothesized that the relative stability of the metal borohydride may play a significant role, with the amines of low-stability borohydrides more likely to release mixed gases [149]. These decomposition pathways could be of interest in tailoring gas release for particular applications like combustion of ammonia, where hydrogen is a useful co-fuel.

4. Complex metal hydrides

Complex metal hydrides are a class of materials containing an

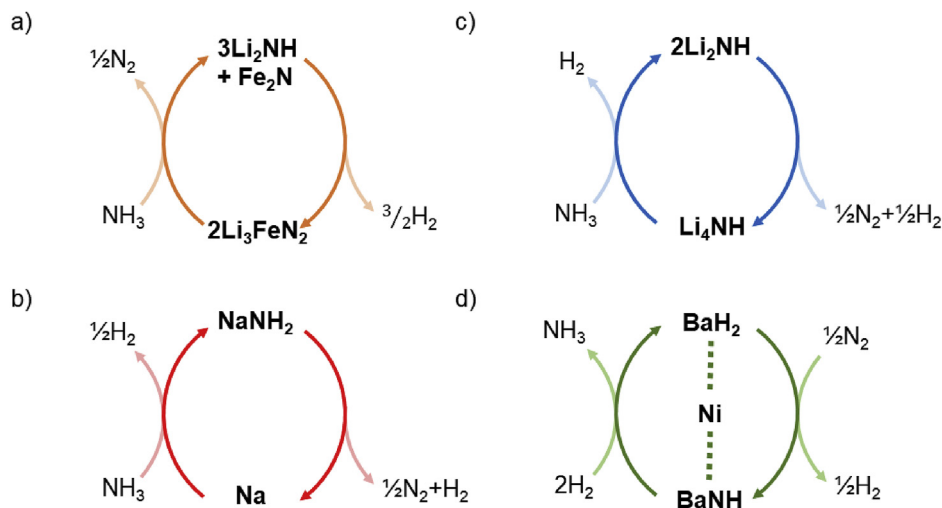


Fig. 5. Examples of proposed reaction cycles involving metal amides and imides in catalytic decomposition of ammonia using a) lithium imide – iron nitride composite b) sodium amide c) lithium imide and d) the catalytic or chemical looping synthesis of ammonia with barium hydride – nickel composite.

anion where hydrogen is covalently bonded to a metal or a non-metal. The late transition metals (TM) form homoleptic hydrido complexes with the general formula $[\text{TH}_n]^{m-}$ [150,151]. Theoretical studies have been undertaken to predict the probable existence of transition metal complex hydrides and a number have been synthesised and characterised including $\text{Na}_2\text{Mg}_2\text{NiH}_6$, $\text{Na}_2\text{Mg}_2\text{FeH}_8$, $\text{Na}_2\text{Mg}_2\text{RuH}_8$, YLiFeH_6 , and Li_4RuH_4 [152–167]. Research efforts in the past two decades have increasingly focused on solids with the light element complexes of boron, aluminium, and nitrogen, i.e. $[\text{BH}_4]^-$, $[\text{AlH}_4]^-$, $[\text{AlH}_6]^{3-}$, $[\text{NH}_2]^-$, or $[\text{NH}]^{2-}$ coordinated to one or more metals [168–174].

4.1. Synthesis and crystal structures

Originally, mechanochemistry (ball milling) was the dominant synthesis approach for complex metal hydrides, via a metathesis (double substitution) reaction [175,176]. This method has been used to synthesize a number of new rare-earth (RE) based borohydrides. These compounds have a very rich chemistry, structural diversity, and thermal properties. Recently, solvent-based approaches have produced more phase pure products [177,178]. Such methods often rely on the initial synthesis of an ionic or polar covalent hydride, which is then reacted with a borane (BH_3) donating solvent such as dimethylsulfideborane, $(\text{CH}_3)_2\text{SBH}_3$. The reaction occurs via a nucleophilic attack on the electron deficient boron on the metal hydride. This reaction is only possible for an ionic or polar covalent metal hydride, MH_x . The product is often a metal borohydride solvate ($\text{M}(\text{BH}_4)_x \cdot \text{solvent}$), which can be removed to obtain $\text{M}(\text{BH}_4)_x$ [177,179]. This approach allows purification by filtration, and to obtain a polymorphic pure product as well as the ability to recycle old samples of metal borohydrides. This was recently illustrated by synthesis of a series of rare earth metal borohydrides [180]. It was observed that only the ionic SmH_3 can react (and not the more metallic dihydride, SmH_2). The product, in this case, is $\text{Sm}(\text{BH}_4)_3 \cdot (\text{CH}_3)_2\text{S}$, which produces $\text{Sm}(\text{BH}_4)_2$ via reductive desolvation [177,180].

The crystal structures of monometallic borohydrides (Fig. 6) often resemble structures of metal oxides, illustrated by the structures of $\text{Ca}(\text{BH}_4)_2$ -polymorphs, which are isomorphous to TiO_2 polymorphs [172]. This structural analogy is because BH_4^- and O^{2-} are isoelectronic [181]. The most electropositive metals, e.g. Na, K, Rb, and Cs are the most ionic and have high melting points and

stabilities. Divalent rare earth (RE) metal borohydrides also form relatively ionic structures, and polymorphs of $\text{Yb}(\text{BH}_4)_2$ resemble polymorphs of $\text{Ca}(\text{BH}_4)_2$ [182]; whereas $\text{Sm}(\text{BH}_4)_2$ and $\text{Eu}(\text{BH}_4)_2$ are isostructural to different polymorphs of $\text{Sr}(\text{BH}_4)_2$ [183,184]. In contrast, more electronegative metals, such as Al and Zr, form molecular, covalent, and volatile compounds, e.g. $\text{Al}(\text{BH}_4)_3$ and $\text{Zr}(\text{BH}_4)_4$ [185]. Mono-metal borohydrides in between these two extremes have often pronounced directional bonding and some

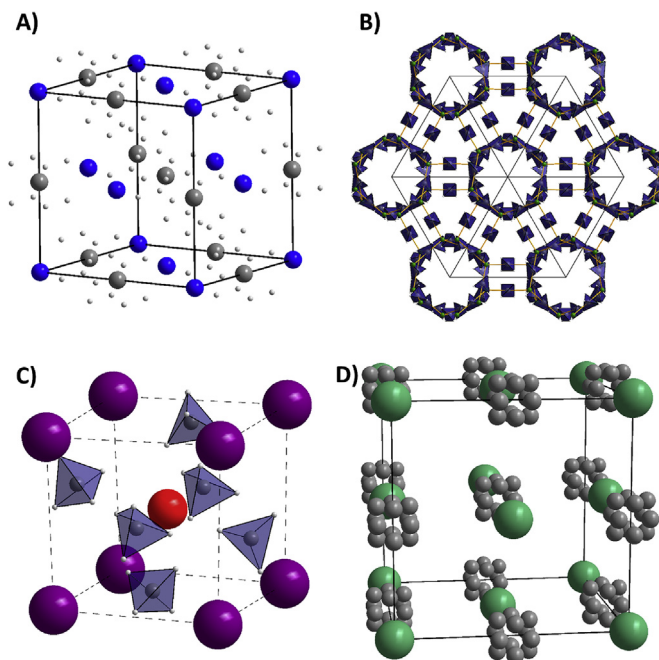


Fig. 6. Crystal structures of selected metal borohydrides highlighting the fascinating structural diversity. (A) The ionic Rock salt structure of NaBH_4 , with averaged H positions shown (B) The porous and partly covalent framework structure of $\gamma\text{-Mg}(\text{BH}_4)_2$ with ~33% open space [189]. (C) The structure of cesium strontium borohydride, $\text{CsSr}(\text{BH}_4)_3$, is highlighting the resemblance to the perovskite structure [202]. (D) The crystal structure of $\beta\text{-KB}_3\text{H}_8$ [230]. The multiplicity of boron illustrates the dynamics of the B_3H_8^- groups in this compound and thus hydrogen has been omitted. Colour code: H: white; B: gray; Mg: light green; Cs: purple; Sr: red; K: dark green. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

degree of covalency and exist as framework structures; for example, rare earth metal borohydrides, $\text{RE}(\text{BH}_4)_3$, with framework structures related to that of $\text{Y}(\text{BH}_4)_3$ [180,186]. This can lead to polymorphism as observed for $\text{M}(\text{BH}_4)_2$, $\text{M} = \text{Mg}$ or Mn , which has both a high pressure polymorph, $\delta\text{-M}(\text{BH}_4)_2$, with high hydrogen densities, and a polymorph with an open zeolite-type structure, $\gamma\text{-M}(\text{BH}_4)_2$; among a total of seven known polymorphs [187–190].

Transition metal borohydrides with electron configurations d^0 , d^5 , or d^{10} are often stable at room temperature, e.g. $\text{Zr}(\text{BH}_4)_4$, $\text{Mn}(\text{BH}_4)_2$, and $\text{Cd}(\text{BH}_4)_2$ [191,192]. Other compounds can be stabilised by ammonia or a coordination solvent to form, for example, $[\text{Fe}(\text{NH}_3)_6](\text{BH}_4)_2$ and $[\text{Co}(\text{NH}_3)_6](\text{BH}_4)_2$ [193,194]. Another approach is to stabilise these compounds as bi-metallic borohydrides, e.g. $\text{LiZn}_2(\text{BH}_4)_5$, which has an interpenetrated framework structure. The structure of $\text{LiZn}_2(\text{BH}_4)_5$ can also be described as being built from anionic complexes, i.e. $[\text{Zn}_2(\text{BH}_4)_5]^-$ [195–197].

Structures consisting of discrete anionic complexes often occur for bi-metallic borohydrides (Fig. 6), as a consequence of the electronegativity difference between the two metals. The most electronegative metals form partly covalent bonds to BH_4^- complexes, usually by edge sharing, e.g. $\text{MSc}(\text{BH}_4)_4$, $\text{M} = \text{Li}$, Na , or K , consisting of $[\text{Sc}(\text{BH}_4)_4]^-$ [198–200]. Known structure types are also adopted by metal borohydrides, e.g. the perovskite structure [201–203]. The structure types formed from the metathesis reaction between LiBH_4 and RECl_3 include $\text{LiRE}(\text{BH}_4)_4$ (CuAuCl₄-type with $\text{RE} = \text{Sc}$, Yb , Lu), $\alpha\text{-RE}(\text{BH}_4)_3$ (distorted ReO_3 -type, $\text{RE} = \text{Y}$, Pr , Sm , Gd , Tb , Dy , Ho , Er , Yb), and $\beta\text{-RE}(\text{BH}_4)_3$ (ReO_3 -type, $\text{RE} = \text{Y}$, Ce , Pr , Sm , Ho , Er , Yb). A small number of trimetallic borohydrides are also known, e.g. $\text{Li}_3\text{MZN}_5(\text{BH}_4)_{15}$, $\text{M} = \text{Mg}$ or Mn [204].

Mixed-cation, mixed-anion borohydrides with ordered structures have also been discovered, such as spinel-type $\text{LiRE}(\text{BH}_4)_3\text{Cl}$ ($\text{RE} = \text{La}$, Ce , Pr , Nd , Sm , Gd) [182,205–214]. This structure contains isolated tetranuclear anionic clusters of $[\text{Ce}_4\text{Cl}_4(\text{BH}_4)_{12}]^{4-}$ charge balanced by Li^+ cations occupying two-thirds of the available positions [215–219]. Another example of double-anion hydrides with ordered structures is $\text{KZn}(\text{BH}_4)\text{Cl}$ [220]; otherwise, anion disorder is more common, as observed for $\text{NaY}(\text{BH}_4)_2\text{Cl}_2$ [221].

The anion substitution of metal borohydrides contributes to the structural diversity, reactivity and changes of properties [172]. Fluorine substitution of the hydride atom in the borohydride complex of alkali metal borohydrides was observed, but unfortunately it was accompanied by release of diborane [222,223]. The heavier halides, Cl^- , Br^- , and I^- , often readily substitute the borohydride complex [224], which in many cases leads to disordered structures or solid solutions [225–229].

4.2. Complex metal aluminium hydrides

The properties of NaAlH_4 and LiAlH_4 continue to be studied to elucidate the process involved in catalytic cycling initiated by titanium and other transition metal containing compounds [231–235]. Advances in instrumentation and sample containment have allowed for *in situ* characterization of these processes using NMR spectroscopy, and X-ray and neutron diffraction. Such studies show that NaAlH_4 formation and decomposition progress via the formation of Na_3AlH_6 [232,233], whereas the solvent-mediated synthesis of LiAlH_4 occurs directly [233,234]. In addition, the titanium additive tends to form a range of $\text{Al}_{1-x}\text{Ti}_x$ phases including Al_3Ti [231,232]. Destabilization of NaAlH_4 has also been studied by the addition of aluminium sulphide and by nano-confinement [236,237].

One of the first intensively studied complex light metal aluminium hydrides of type MAlH_4 was LiAlH_4 , originally considered as a reducing agent [238]. The most explored metal alanate for solid-state hydrogen storage is NaAlH_4 , including its crystalline

dehydrogenation intermediates. A few mol% of Ti catalysts significantly enhances the kinetics of hydrogenation of alanates [239]. More recently, crystal structures of complex aluminium hydrides with large metal cations, i.e. $\text{Eu}(\text{AlH}_4)_2$ and $\text{Sr}(\text{AlH}_4)_2$, as well as that of their intermediate decomposition products EuAlH_5 and SrAlH_5 , were solved [240]. The structure of potassium alanate, KAlH_4 , is also known, but not three of its intermediates [241]. The hydrogen (deuterium) positions in SrAlD_5 could be determined from neutron diffraction data and, based on this, the connectivity of corner-sharing $[\text{AlD}_6]^{3-}$ octahedra was established [242]. CsAlH_4 and RbAlH_4 can be prepared either by ball-milling of salts with NaAlH_4 or LiAlH_4 , or directly by hydrogenation of the metals by ball-milling at elevated hydrogen pressures with small amounts of Ti catalysts [243–245]. Even though the storage capacity of 2.5 wt% H_2 is relatively low, direct synthesis from the metals indicates that both compounds form and decompose reversibly. The decomposition pathway is complex compared to that of the light alkali metal alanates and intermediate structures are difficult to isolate. Transition metal and rare earth aluminium hydrides have been shown to be unstable [246,247]. However, $\text{TaH}_2(\text{AlH}_4)_2$ and $\text{Y}(\text{AlH}_4)_3$ possess a remarkably high stability [248]. Recently it has been shown that, upon heating, $\text{Y}(\text{AlH}_4)_3$ dehydrogenation proceeds via four steps with the first dehydrogenation step being reversible [249]. Only a limited number of unstable complex metal aluminium hydrides have been reported so far and most of their crystal structures still remain unknown. Below Al we find Ga in the periodic table. Ga is more likely to form complex hydrides with the help of electrons from an electropositive counterion. With one electron added, Ga will form a carbon like chemistry, as exemplified by $\text{Rb}_8\text{Ga}_5\text{H}_{15}$ where $\text{Ga}[\text{GaH}_3]_4^{5-}$ forms an entity with a neopentane structure, where carbon has been substituted by gallium [602]. Similar species with hydrocarbon structures are for example $[\text{GaH}_2]_n^{(n-)}$ with a polyethylene structure and $\text{Ga}_3\text{H}_8^{3-}$ with a propane structure [603]. If this property could be transferred to Al, we could expect to make possible a large number of new Al complexes.

4.3. Aluminium based complex hydrides

Aluminium is a cheap and abundant element, having low weight per electron exchanged. The small size and high charge make the Al^{3+} cation highly polarizing and thus complex forming. Three coordinate Al^{3+} in $\text{Al}(\text{BH}_4)_3$ easily converts to four-coordinate complexes upon a reaction with more ionic borohydrides, yielding $\text{M}[\text{Al}(\text{BH}_4)_4]$ composites with very high hydrogen content, where M is an alkali metal or ammonia cation [250–252].

Nitrogen donor atoms compete successfully for the Al^{3+} coordination sites, producing homoleptic $[\text{Al}(\text{en})_3](\text{BH}_4)_3$ [253] or heteroleptic $[\text{Al}(\text{en})(\text{BH}_4)_2][\text{Al}(\text{BH}_4)_4]$ complexes [254], depending on the ratio of Al^{3+} and ethylenediamine (*en*) in the reaction mixtures. The stoichiometry control enables a series of borohydride complexes with nitrogen-containing ligands, similar to ammoniates of Mn and Y borohydrides [149,255–257], of potential interest for hydrogen storage and ion conductivity. The heteroleptic Al complex with ammonia borane (NH_3BH_3 , AB), namely $[\text{Al}(\text{BH}_4)_3(\text{AB})]$ shows an endothermic dehydrogenation to a single decomposition product, identified as $[\text{Al}(\text{BH}_4)_3(\text{HBNH})]_n$ [258]. The coordination of the starting and of the dehydrogenated AB to Al^{3+} allows one to consider the latter as an effective template for a reversible dehydrogenation of the hydride complexes with Al^{3+} [258,259]. Recently, this idea was further explored in a series of complexes between various Al salts and AB-derived RNH_2BH_3 ligands [254]. It was shown that two ABs can be coordinated to a single Al atom, opening a way to materials with a higher H-content.

Ball milling of metal alanates with AB results in Al amidoborane complexes, $\text{M}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$, where the N-donor ligand becomes

anionic and thus shows high affinity to Al^{3+} [260,261]. For $M = \text{Na}$, a partial hydrogen reversibility was reported for the amorphous decomposition products. Ball milling of $\text{LiAl}(\text{NH}_2)_4$ and LiBH_4 resulted in $\text{Li}_2\text{Al}(\text{NH}_2)_4\text{BH}_4$, which was the first reported compound containing both $[\text{Al}(\text{NH}_2)_4]^-$ and BH_4^- anions [262]. Aluminium amidoborane ammoniate complexes have also been reported to form via the reaction of $\text{AlH}_3\text{Et}_2\text{O}$ with ammonia borane ammoniate forming $[\text{Al}(\text{NH}_2\text{BH}_3)_6]^{3-}[\text{Al}(\text{NH}_3)_6]^{3+}$ [263]. This solution based synthesis prevents possible decomposition of the products by avoiding the high-energy impact associated with ball milling.

Despite pure aluminium hydride (AlH_3 , alane) not being classified as a formal complex hydride, complexes of alane have been synthesised with a range of Lewis bases including amines, ethers and phosphines [264–266]. A number of complexes have been recently synthesised and characterised including tetramethylpropylenediamine (TMPDA) alane, trimethylamine alane, and dioxine alane. DFT has been used to predict the stability of other complexes to identify potential for reversible hydrogenation. Many complexes are liquid at or above room temperature and as such may be of interest as liquid hydrogen carriers.

4.4. Thermodynamic predictions

The thermodynamic properties of a complex hydride can be obtained by the CALPHAD approach [267]. The goal is to describe the dependence of the Gibbs Free Energy (GFE) as a function of temperature. The dependence from pressure and composition of their free energy can be neglected because complex hydrides are condensed phases with a fixed stoichiometry. For simple compounds, the temperature dependence of the GFE can be described using the following polynomial expression [268]:

$$G = A + BT + C\ln T + DT^2 + ET^3 + FT^{-1} + \sum_n G_n T^n \quad (1)$$

where parameters $A-G_n$ are optimized on the basis of available experimental data. When thermodynamic data are available at low temperatures, a more complex expression of GFE, based on the Einstein model for the molar heat capacity can be used. In the absence of experimental information, the output of various thermodynamic or quantum mechanical models can be used [269]. An estimation of the energy of formation of a compound can be obtained by ab-initio modelling. If necessary, different sets of parameters can be used to describe GFE in different temperature ranges. A CALPHAD assessment of various complex hydrides has been carried out in recent years. A summary of thermodynamic description of selected complex metal hydrides is reported in Table 1.

4.5. Hydrogen release and uptake

The stability of metal borohydrides based on the observed decomposition temperature, T_{dec} , is correlated to the metal-borohydride coordination via the Pauling electronegativity, see Fig. 7 [172,180,276]. The reaction mechanism for hydrogen release and uptake in complex hydrides has been extensively studied since the discovery of hydrogen desorption and absorption at moderate conditions in Ti-catalyzed NaAlH_4 , as mentioned above [239]. However, analogous reactions for hydrogen release and uptake for metal borohydrides are complex and poorly understood [199]. Bi- and tri-metallic borohydrides usually decompose via formation of more stable mono- or bimetallic borohydrides. Eutectic melting of metal borohydrides may also be involved in their decomposition reactions, for example, in the systems $\text{LiBH}_4\text{-CaBH}_4$ and $\text{LiBH}_4\text{-NaAlH}_4$ [277–284].

The possible effect of additives in metal borohydrides has been extensively studied recently [237,285–293]. Several studies have shown a decrease in temperature for the first desorption of different polymorphs of $\text{Mg}(\text{BH}_4)_2$ by using TM based additives. During absorption, the major kinetic effect has been observed for partly decomposed $\text{Mg}(\text{BH}_4)_2$ at moderate conditions (<12 MPa H_2 and <260 °C).

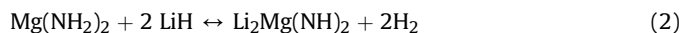
The reversible hydrogenation of metal borohydrides, such as NaBH_4 and $\text{Mg}(\text{BH}_4)_2$, has been studied with additives [285,286,294]. Additives to NaBH_4 reduce the decomposition temperature by at least 85 °C, which allows the event to occur below its melting point, enabling the possibility of rehydrogenation. Following the success of transition metal boride additives on NaBH_4 , these compounds were also added to $\text{Mg}(\text{BH}_4)_2$ in order to enhance the reaction kinetics during hydrogen cycling and to inhibit the formation of $[\text{B}_n\text{H}_n]^{2-}$ ($n = 10, 12$) species. An isotopic exchange study of porous and dense Mg-borohydride with Raman spectroscopy showed that solid state H (D) diffusion is considerably slower than the gas-solid $\text{H} \rightarrow \text{D}$ exchange reaction at the surface and is thus a rate-limiting step for hydrogen sorption in $\text{Mg}(\text{BH}_4)_2$ [295]. These systems have been studied by XRD, X-ray absorption spectroscopy, NMR, and FT-IR [296–300].

Rehydrogenation of the composite $\text{KB}_3\text{H}_8\text{-}2\text{KH}$ ($T = 100\text{--}200$ °C, $p(\text{H}_2) = 380$ bar and $t = 24$ h) reveal formation of higher borates, e.g. $\text{B}_n\text{H}_n^{2-}$, $n = 9, 10$ or 12, and about one-third of the boron as KBH_4 [230]. Rehydrogenation of the *closo*-borate composites $\text{M}_2\text{B}_n\text{H}_n\text{-(}n\text{-}2\text{)MH}$, ($T = 300\text{--}400$ °C, $p(\text{H}_2) = 0.5\text{--}1.0$ kbar and $t = 24$ h) reveal formation of MBH_4 only for the $\text{M}_2\text{B}_{10}\text{H}_{10}$ precursor at the physical conditions applied [301]. Unidentified intermediate compounds were also observed using *in situ* diffraction experiments [296,297,301].

Nano confinement has been shown to have a significant influence on hydrogen release and uptake, and has received significant interest. Volatile complex hydrides such as $\text{Ti}(\text{BH}_4)_3$ have been stabilised by nanoconfinement in MOFs for several months. Upon confinement, the density of the $\text{Ti}(\text{BH}_4)_3$ is twice that of the gaseous material [302]. Nanoconfinement has been used to change the hydrogen release and uptake properties of a range of compounds and composites. The effect is strongest in the first cycle [236,278,279,303–312].

4.6. Reactive hydride composites

While many complex hydrides show very high gravimetric hydrogen storage densities, they suffer from sluggish reaction kinetics and/or unfavourable thermodynamic properties [313]. However a combination of LiNH_2 and LiH showed superior kinetic and thermodynamic properties to the pure hydrides by themselves [314]; followed by systems consisting of a metal hydride and a metal amide or borohydride [315]. More recently, a range of other composites have been discovered [316–322] such as:



as well as MgH_2 and LiBH_4 [323]. With the addition of suitable additives, the latter shows an extremely high reversible gravimetric storage density of around 10 wt%, according to the reaction:



During desorption, the components of the different hydrides react to form a stable compound, by which the total reaction enthalpy is lowered and the kinetics improved. However, in spite of improvements in the thermodynamic and kinetic properties of such high capacity hydrides, the working temperatures of such two

Table 1
Assessed Gibbs Free Energy as a function of temperature (T) for selected complex hydrides. R is the gas constant.

Compound	Phase	Reference system	Gibbs Free Energy (J/mol of f.u.)	T range (K)	Ref.
LiBH ₄	Ortho	Li _{cub} , H _{gas} , B _{rhomb}	-206438.80 + 312.84347*1.5R+3R*T*LN(1-EXP(-312.8434*T ⁻¹))-0.0568714*T ² -3.01186*10 ⁻⁵ *T ³	300–383	[270]
LiBH ₄	Hex	Li _{cub} , H _{gas} , B _{rhomb}	-210953.207 + 328.4978*T-56.52963*T*LN(T)-0.05777964*T ² +4.303902*10 ⁻⁶ *T ³ +766385.13*T ⁻¹	383–551	[270]
LiBH ₄	Liq	Li _{cub} , H _{gas} , B _{rhomb}	-222466.273 + 751.660356*T-124.7*T*LN(T)	551–1000	[270]
Li ₂ B ₁₂ H ₁₂	Cub	Li _{cub} , H _{gas} , B _{rhomb}	-7.833*10 ⁵ +702*T	300–1000	[270]
Li ₂ B ₁₀ H ₁₀	Hex	Li _{cub} , H _{gas} , B _{rhomb}	-3.48*10 ⁵ +480*T	300–1000	[270]
NaBH ₄	Cub	Na _{cub} , H _{gas} , B _{rhomb}	-215396.375 + 362.347799*T-65.62694*T*LN(T)-0.039943205*T ² +2.0758*10 ⁻⁶ *T ³ +82445.5*T ⁻¹	300–600	[271]
NaBH ₄	Cub	Na _{cub} , H _{gas} , B _{rhomb}	-246176.6 + 712.133426*T-116.5235*T*LN(T)-0.00822906*T ² -2.133325*10 ⁻⁷ *T ³ +3283588.5*T ⁻¹	600–900	[271]
NaBH ₄	Cub	Na _{cub} , H _{gas} , B _{rhomb}	-156907.445-242.126185*T+22.42824*T*LN(T)-0.1050230*T ² +1.253794*10 ⁻⁵ *T ³ -7527375*T ⁻¹	900–1000	[271]
NaBH ₄	Liq	NaBH _{4,cub}	+16926-21.756*T	300–505	[271]
NaBH ₄	Liq	Na _{cub} , H _{gas} , B _{rhomb}	-217735 + 693*T-119.233*T*LN(T)	505–1000	[271]
KBH ₄	Cub	K _{cub} , H _{gas} , B _{rhomb}	-293231.57 + 1332.6103*T-226.809*T*LN(T)+.19700505*T ² -5.85629833*10 ⁻⁵ *T ³ +1955620*T ⁻¹	300–600	[271]
KBH ₄	Cub	K _{cub} , H _{gas} , B _{rhomb}	-488023.684 + 3356.66883*T-514.005*T*LN(T)+.3227912*T ² -5.0464016*10 ⁻⁵ *T ³ +2333251*T ⁻¹	600–800	[271]
KBH ₄	Cub	K _{cub} , H _{gas} , B _{rhomb}	-288613.971 + 822.480344*T-134.187*T*LN(T)+.0033015*T ² -3.8573666*10 ⁻⁷ *T ³ +3833085*T ⁻¹	800–1000	[271]
KBH ₄	Liq	KBH _{4,cub}	+19176-21.841*T	300–1000	[271]
LiK(BH ₄) ₂	Ortho	LiBH _{4,cub} , KBH _{4,cub}	-1300 + 3.53*T	300–1000	[271]
α-Mg(BH ₄) ₂	Hex	Mg _{hex} , H _{gas} , B _{rhomb}	-222624.9 + 158.46145*T-35.22138*T*LN(T)-0.035975*T ²	300–1000	[272]
β-Mg(BH ₄) ₂	Ortho	Mg(BH ₄) _{2,hex}	+12954.437-26.4266*T	300–1000	[272]
γ-Mg(BH ₄) ₂	Cubic	Mg(BH ₄) _{2,hex}	+3900	300–1000	[272]
Mg(AlH ₄) ₂	Tetr	Mg _{hex} , H _{gas} , Al _{cub}	-79000 + 386*T	300–1000	[273]
NaMgH ₃	Tetr	Na _{cub} , Mg _{hex} , H _{gas}	-156905.827 + 186.831990*T-33.6064520*T*LN(T)-0.0612717213*T ²	300–1000	[274]
LiNH ₂	Tetr	Li _{cub} , H _{gas} , N _{gas}	-196871.25 + 161.64083*T	300–1000	[275]
Li ₂ (BH ₄) (NH ₂)	Tetr	LiBH ₄ , ortho, LiNH ₂ , tetr	-6600	300–1000	[275]
Li ₄ (BH ₄) (NH ₂) ₃	Cub	LiBH ₄ , ortho, LiNH ₂ , tetr	-13900	300–1000	[275]

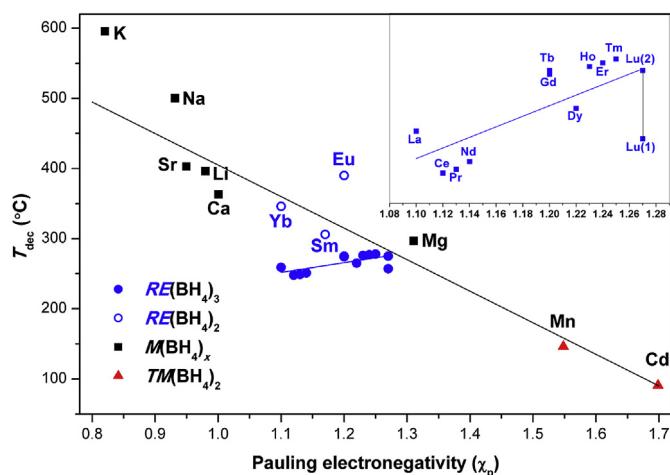


Fig. 7. Comparison of the Pauling electronegativity and the decomposition temperature of complex metal hydrides. Generally, a decreasing decomposition temperature is observed with increasing Pauling electronegativity of the metal. However, the opposite trend is observed for the series of rare-earth metal borohydrides, as further highlighted in the inset [180,276]. Trend lines have been added for clarity.

component reactive hydride systems are significantly above 100 °C. However, recent work showed that by combining the three different hydrides, LiBH₄, Mg(NH₂)₂, and LiH, high capacity complex hydrides can indeed be used for hydrogen storage at temperatures below 100 °C [324]. The influence of LiH and/or LiBH₄ on the hydrogen sorption properties and rehydrogenation has been further investigated for La-, Er- and Pr-based borohydrides [325–327]. For the 3LiBH₄ + Er(BH₄)₃ + 3LiH composite, 3.5 wt% H was desorbed after the third cycle from a maximum of 6 wt% [327].

4.7. New properties

Research efforts during the past two decades have led to the discovery of many new series of hydrides, in some cases with unexpected and fascinating properties [172–174]. Optical properties were discovered for perovskite-type metal borohydrides [201,328].

Rare earth metal borohydrides have magnetic properties which deviate somewhat from the Landé formula for calculation of magnetic moments, suggested to be due to strong coupling of orbitals [180]. Among the rare earth metal borohydrides, RE(BH₄)₃, praseodymium has the most extensive polymorphic chemistry with five polymorphs, denoted as α-, β-, β'-, β''-, and r-Pr(BH₄)₃ [329]. This series of polymorphs appear to be the first example of stepwise negative thermal expansion, which appears to depend on gas atmosphere, e.g. H₂ or Ar.

4.8. Metal closo-borates as solid-state electrolytes

The pursuit of a solid-state electrolyte with high ion conductivity has resulted in the identification of a range of metal closo-borates and their derivatives that show great promise [172,330]. Many closo-borates exhibit a polymorphic structural transition at elevated temperature, which can exhibit structural dynamics such as reorientational disorder of anions and partial occupancy of cations [331,332]. The most promising ion conductors are metal closo-borate derivatives with monovalent anisotropic charge density of the anion, e.g. [CB₁₁H₁₂]⁻ and [CB₉H₁₀]⁻. Impressive ion conductivity is also observed in isotropic metal closo-borates such as [B₁₂Cl₁₂]²⁻, albeit at elevated temperatures [333]. Particular solvated closo-borates have also been shown to melt near 130 °C and display a step-function increase in ion conductivity in the molten state [334]. Thus, complex hydrides have potential applications in electrochemical, as well as hydrogen, storage. Recent progress in electrochemical storage is detailed in Section 9.

5. Intermetallic hydrides. Structure-properties relationship

5.1. Intermetallic hydrides – a short historical overview

Binary metal hydrides are either very stable (LaH₂, YH₂, ZrH₂, TiH₂) releasing hydrogen on heating to several hundred °C (as an example, 800 °C for YH₂) [335], or very unstable requiring application of kbar level of hydrogen pressure to form a hydride in the metal-hydrogen system (NiH, FeH) (as an example, above 5 kBar H₂ for Ni–H system) [336]. Both alternatives are inconvenient for the

practical storage of hydrogen gas. Thus, the discovery of intermetallic hydrides having intermediate stabilities between these two mentioned groups of hydrides opened attractive new possibilities to build practical systems for the storage of hydrogen gas in a form of solid hydride.

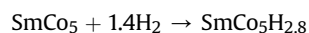
Early works on intermetallic hydrides, which appeared in the 1950s, had already shown that intermetallic compounds containing hydride-forming (Zr) and transition (Ni) metals can reversibly absorb large amounts of hydrogen. Even though the very first examples of such hydrides, ZrNiH and ZrNiH₃, formed by ZrNi intermetallic still appeared to be rather stable, studies showed that the H content in ZrNiH₃ (H/Me = 1.5), was superior to the value reached at the same P-T conditions for the equivalent amounts of two individual metals, Zr and Ni (H/Me = 1.0) [337]. Furthermore, a decrease in the H₂ release temperature by several hundred °C as compared to the binary hydride ZrH₂ was another significant benefit. From a structural viewpoint, the reason for the decreased hydride stability is that the interstitial sites occupied by hydrogen atoms in intermetallic hydrides have mixed chemical surroundings so the hydrogen interacts with both hydride-forming (e.g. Zr) and non-hydride-forming (e.g. Ni) metal atoms in the metal sublattice. Such interactions decrease the stability relative to the pure binary hydride (e.g. ZrH₂). Neutron scattering is recognized as an important tool of choice to directly locate H/D atoms inserted into the metal sublattice, as was demonstrated in 1961 during an investigation of one of the first structures of the ternary hydrides, Th₂AlD₄, which was probed by neutron diffraction and showed that H/D atoms occupy tetrahedral Th₄ sites [338,339].

Nevertheless, these interesting behaviors of ternary hydrides required significant improvements before becoming suitable for practical applications. The discovery of metal hydrides appropriate to conveniently store hydrogen was announced in the late 1960s when intermetallic hydrides of the AB₅ composition with A = Rare Earth metal and B = Ni or Co, including LaNi₅, showed excellent performance as chemical reversible stores of hydrogen gas. In fact, the excellent performance of LaNi₅H_{6.7} as a hydrogen storage material [340,341] was discovered by fortune during systematic studies of SmCo₅ as a high coercivity permanent magnet material at Philips Research Labs in Eindhoven, Netherlands led by Prof. K. H. Jürgen Buschow [342].

It was observed that the coercivity of the SmCo₅ powders significantly decreased when storing the material in open air because of the chemical interaction with water vapour which released hydrogen gas in the following process:



while in a subsequent step a formation of intermetallic hydride SmCo₅H_{2.8} [340]



occurred, causing a decay in coercivity.

A nonmagnetic analogue of SmCo₅ was selected for the study of the hydrogenation process to understand the fundamental aspects of the interactions in the metal-hydrogen system by utilizing NMR, and LaNi₅ was the choice [343].

This resulted in the discovery of excellent features of H storage in LaNi₅ and its analogues as they are able to quickly, in just seconds, form hydrides when the metal alloy is exposed to hydrogen gas and to reversibly release H₂ when lowering the pressure in the system, while reaching high H/Me ratios exceeding 1.0 and high volumetric H capacity surpassing the values for liquid hydrogen. Particularly attractive behaviors were found for LaNi₅H_{6.7} as it was formed at pressures just slightly higher than atmospheric pressure

((PH₂ absorption/PH₂desorption @ 20 °C of 1.83/1.36 atm H₂) and it was able to provide stable hydrogen pressure during hydrogen absorption and desorption at equilibrium conditions [344]. Substitutions on the Ni and La sites to form (La_{1-x}R_x)Ni₄M, where M represents Pd, Co, Fe, Cr, Ag or Cu, and for La_{0.8}R_{0.2}Ni₅ where R represents Nd, Gd, Y and Er, also Th and Zr, significantly changed the thermodynamics of the metal-hydrogen interactions yielding hydrides with a broad range of stabilities, which were significantly different from the characteristics of LaNi₅H_{6.7}.

As the equilibrium pressure of hydrogen for LaNi₅H_{6.7} is close to atmospheric pressure, a natural progression was to use LaNi₅ as a negative electrode and to charge it electrochemically with hydrogen when using an aqueous electrolyte. This has been successfully realized and LaNi₅ showed an electro-chemical capacity of 330–390 mAh/g corresponding to the composition LaNi₅H_{5-6.7} [345–347].

Even though LaNi₅ was found to be unsuitable for use as an electrode in the Ni-Metal Hydride battery because of its corrosion degradation in KOH solution, changing the composition by doping on both La and Ni sites to form La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Si_{0.1} resulted in a drastic improvement of the cycling stability, which was related to decreased stresses in the material because the doping reduced the lattice expansion during the hydrogenation and therefore reduced the corrosion, as it was caused by repeated large expansion and contraction of the lattice [346].

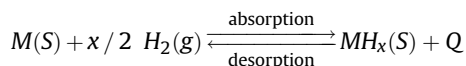
The early stages of the development of intermetallic hydrides received an outstanding contribution from the work performed at Philips Research Laboratories with a leading role of Prof. K. H. J. Buschow who, in addition to the discovery of LaNi₅ and characterization of the basic features of the metal-hydrogen interactions in the (La,R)(Ni,TM)₅ systems and a huge number of novel intermetallic hydrogen absorbing compounds, also developed a fundamental modelling approach allowing explanation and prediction of the formation of the hydrides by using Miedema's rule of reversed stability [348,349]. This was complemented by systematic studies of the interrelations between structure, chemical composition and magnetism of intermetallic hydrides [350].

Studies of magnetism were particularly important as hydrogen appeared as an indispensable medium in the manufacturing of rare earth based permanent magnets, allowing the improvement of magnet performance by obtaining oxygen free powders and/or recycling SmCo₅, Sm₂(Co,FeCu,Zr)₁₇ and NdFeB-type magnets by using a Hydrogen Decrepitation process [351,352] and by using a Hydrogen-Disproportionation-Desorption-Recombination route [353,354].

Finally, for the intermetallics exhibiting a magnetocaloric effect, the cooling efficiency of the alloys can be improved by hydrogenation; indeed, for La(Fe,Si)₁₃ as hydrogen is accommodated in the metal lattice, the critical temperature increases significantly (by 200 K) reaching 450 K for the hydride La(Fe,Si)₁₃H₁. This is accompanied by a parallel increase of the average magnetic moment per Fe during a transformation of La(Fe,Si)₁₃ into its hydride La(Fe,Si)₁₃H₁ as a consequence of a hydrogen-caused volume expansion of 1.5% [352].

5.2. General characteristics of intermetallic hydrides

Metal hydrides are formed via the reversible interaction of a hydride-forming metal/alloy, or intermetallic compound (IMC), with H₂ gas:



where M is an individual metal, or a multicomponent alloy or IMC.

Typical M components include individual metals – for example, rare earths such as La, Ce, Nd or Pr, and elements such as Zr, Ti, Mg, Ca and V – and IMCs, which can include AB_5 (e.g. $LaNi_5$, $CaNi_5$), AB_2 (e.g. $ZrMn_2$, ZrV_2 , $ZrCr_2$), AB (e.g. $TiFe$), and A_2B (e.g. Ti_2Ni , Zr_2Fe) compounds. For a binary IMC, A is typically a hydride-forming element, while B is a transition or non-transition metal/element that does not form a stable hydride under normal conditions.

Hydride formation is normally exothermic, with the amount of heat released being closely related to the host element or compound. In contrast, the reverse process of hydride decomposition is usually endothermic, thus requiring a supply of heat to induce hydrogen desorption. Hydrogen is stored in metal hydrides in atomic form (or as screened protons), so this results in a very high volumetric H capacity, up to 150 g_H/L , to be achieved; more than double the H density in liquid H_2 (70.8 g/L).

Many IMCs rapidly react with hydrogen. At ambient conditions, they also have equilibrium H_2 pressures that are convenient for practical use. Metal hydrides can therefore be used to safely store H_2 , particularly in stationary [355] and portable applications [356]. Furthermore, heat can be stored using metal hydrides [357], such as hydrogen energy systems integrated with solar energy. Another application is metal hydride-based compression of H_2 gas [356], in which heat can be used to boost pressures to several hundred bar [358] (see Section 11).

The hydrogen storage properties of the most extensively studied groups of H storage alloys have been presented in several reviews, which can be consulted for further detailed data on the main classes of hydride-forming compounds, including AB_5 and AB_2 IMCs, and BCC alloys [349,359,360]. Practically achievable reversible H storage capacities of most intermetallic hydrides do not exceed 2 wt% H – for example, 1.5 wt% for AB_5 hydrides, 1.8 wt% for AB_2 , and 2.0 wt% H for BCC alloys. Light metal hydrides, such as MgH_2 and AlH_3 , have therefore been investigated widely for H storage applications. Although these materials have high gravimetric capacities – 7.6 wt% H for MgH_2 and 10.1 wt% H for AlH_3 – they have other drawbacks, such as the high working temperature for MgH_2 [361,362] and the difficulty of directly synthesising AlH_3 , which requires kbar H_2 pressures and high temperatures [363,364].

Generally speaking, recent efforts have aimed at improving the properties of metal hydride systems for practical applications by:

- increasing reversible H storage capacity by modifying the composition of known materials and by studying novel alloys;
- improving the kinetics of hydrogen absorption and desorption – as materials and on a system level – while adopting more convenient conditions for the operation of H energy systems;
- adapting the properties of metal-hydrogen systems by making them better suited for efficient H storage, for electrochemical applications as metal hydride battery anodes, as materials for heat storage, and for use in the compression of H_2 gas.

One interesting example involving MgH_2 is the use of reactive composites of MgH_2 with $LiBH_4$ catalyzed by additives [320]. This decreases the temperature for reversible H_2 desorption and absorption, while achieving a high rate of hydrogenation and H_2 release. FeF_3 was used as a catalyst, producing 5 wt% H_2 at a working temperature of 275 °C for the composite Mg –10 mol% $LiBH_4$ –5 mol% FeF_3 [320].

5.3. Crystal and electronic structures of the intermetallic hydrides

Hydrogen storage properties of IMCs are closely related to their

crystal and electronic structures, and their magnetic properties. Thus, we will briefly review fundamental features of metal-hydrogen systems from these three perspectives.

5.3.1. Structural chemistry

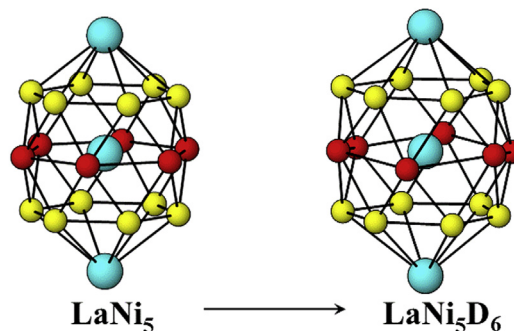
During hydrogen absorption by IMCs, H_2 dissociates at the surface and is stored as atomic H in the metal lattice by filling interstitial sites, most commonly tetrahedral and octahedral. As the number of these sites is higher than the number of metal atoms, H/M ratios exceeding 1, and reaching as high as 3.75, can be achieved in stable metal hydrides, if they have the appropriate chemical composition. This provides a high volumetric density of stored H in the solid state [365,366].

IMCs exhibit a close interrelation between their crystal chemistry and hydrogen sorption behaviour (H storage capacity and stability of the hydrides) allowing alteration and optimization of their H storage performance. Hydrogen accommodation by the metal lattice is typically accompanied by a modest (few percent) change of interatomic metal–metal distances. This results in a much more significant, 10–30%, increase in volume; normalizing this to the number of absorbed hydrogen atoms gives 2.5–3.0 \AA^3 /atom H. As an example, $LaNi_5H_6$ has a volume expansion of 18.9% [365] with two times smaller expansion along the axes of the unit cell, resulting in 7–8% expansion of the interatomic Me–Me distances. This leaves the Me–Me coordination number (CN) in the structure unchanged, as shown in Fig. 8. H atoms enter the interstices, which are available in the virgin intermetallic. Thus, such “isotropic” structures of the hydrides, with nearly even expansion along crystallographically inequivalent directions, are dominated by the Me–Me interactions. Hydrogen–metal interactions appear to be non-directional ones often with simultaneous partial occupancy of various types of positions [367,368].

Three important rules describe the formation of the intermetallic hydrides as related to their structural chemistry:

- structures should contain a significant number of active hydrogenation sites - sites with a high proportion of rare earth metals, Zr, Ti, Mg - that H atoms show a preference to occupy;
- size of a sphere to accommodate H atom in the filled interstices should be at least 0.4 \AA ;

CONVENTIONAL CASE: ISOTROPIC HYDRIDE STRUCTURES



CN for La = 20. Does not change on hydrogenation.

Change of interatomic distances + 7-8 %.

Fig. 8. Changes in a 20-vertex coordination polyhedron of La atom in $LaNi_5$ (hexagonal, $a = 5.0125$; $c = 3.9873$ \AA) during the formation of $LaNi_5H_6$ hydride (hexagonal; $a = 5.426$; $c = 4.269$ \AA).

- (c) the shortest H–H separations between the filled interstices should be at least 1.8–2.1 Å.

Formation of stable hydrides takes place following these rules, as shown in [367,368].

However, this “typical” case does not cover a large group of interesting yet insufficiently studied compounds, the so-called “anisotropic” hydrides [367].

5.3.2. Electronic structures

The stability of the hydrides is linked to their electronic structures. Formation of the hydrides is, in this regard, influenced by:

- chemical interaction between hydrogen and metals resulting in the appearance of new states below the Fermi level of the metal;
- changes in the cohesive energy of the host alloy induced by the expansion of the host structure with H insertion [369].

While (a) results in energy release because of the M–H bonding, (b) needs energy consumption used to achieve deformation of the metal sublattice during the expansion of the metal framework. Their balance defines the stability of the formed metal hydrides.

Interaction of hydrogen with the atoms of the metal sublattice results in various phenomena including modification of the long-range structural order, changes of the magnetic order and the valence state of the constituting metal atoms (most significantly appearing for the rare earth metals, e.g. Ce).

The chemical effect (a) can be influenced by tailoring the position and density of states at the Fermi level, while (b) is an effective way of influencing the formation energy of hydrides. Therefore, to design relatively less stable hydrides (allowing hydrogen to be easily released) one approach is to vary the cohesive energy of the alloys by performing compositional modifications [369].

For LaNi_5H_6 [370], belonging to the AB_5 Haucke phases, one of the first and the most studied group of reversible hydrogen storage alloys, its electronic structure is dominated by the $3d$ -Ni states, which become narrower than in the host structure due to lattice expansion. The structure of LaNi_5H_6 is characterised by a non-directional bonding between the metal sublattice and hydrogen since H atoms show statistical distribution in three types of tetrahedral sites - La_2Ni_2 , LaNi_3 and Ni_4 , with a preference to the La-containing sites. The role of (a) and (b) effects have been illustrated with the investigation of elemental substitutions in the AB_5 phase [371].

More recently, the AB_y stacking structures described by Khan, where $y = (5n + 4)/(n + 2)$ and n is an integer [372], have been a point of interest from both fundamental and application viewpoints [373–375].

Adjusting the y ratio and the A and B chemical composition, with multiple substitutions, where A is usually a RE and B is a TM element, can tune both hydrogen-absorption and magnetic properties of the metal sublattice.

For these hydrides with more complexity, a systematic study has been done for AB_3 and A_2B_7 IMCs. Fig. 9 shows the density of states (DOS) for $\text{Y}_2\text{Ni}_7\text{H}_8$, $\text{La}_2\text{Ni}_7\text{H}_8$ and $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7\text{H}_8$ (La_2Ni_7 with an ordered substitution of La by Mg). The DOSs are characterised by a broad low energy structure extending from about -11 eV to -5 eV corresponding to the bands arising from nickel-hydrogen bonding. The A element contribution to the electronic structure is much more modest despite the larger affinity of A to hydrogen. Interestingly, the La-based hydrides show a continuity of the occupied states in their band structure while $\text{Y}_2\text{Ni}_7\text{H}_8$ shows the presence of well localized electronic states with a band gap around -5 eV [376,377].

This continuity of electronic states is associated with a

simultaneous hydrogen insertion into a large number of interstitial sites, as much as 9 in the case of $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7\text{H}_9$, Fig. 10 [378]. Formation of the structure proceeds via an even expansion of the hexagonal unit cell ($\Delta a/a = 7.4\%$; $\Delta c/c = 9.6\%$; $\Delta V/V = 26.3\%$). However, the expansion is more pronounced for the Laves type AB_2 layer, as detailed in Fig. 10, because of the higher content of H in this layer, $\text{LaMgNi}_4\text{H}_{7.56}$, compared to the AB_5 layers, 4.92 and 5.71 at.H/ LaNi_5 .

For the layered structures composed of AB_5 and AB_2 slabs, AB_3 ($1^*AB_5 + 2^*AB_2$) and A_2B_7 ($1^*AB_5 + 1^*AB_2$), their structural chemistry, electronic structure and metal-hydrogen interactions are described by two principally different mechanisms of interaction. In contrast to the conventional isotropic expansion of the lattice with non-directional Me–H bonding, a totally different type of hydrogen interaction with metals has been observed, characterised and explained for the layered structured based anisotropic hydrides of $AB_3 - \text{CeNi}_3\text{H}_{2.8}$, and $A_2B_7 - \text{Ce}_2\text{Ni}_7\text{H}_{4.6}$ [379–381].

The main features of such an interaction are summarized in Table 2 in comparison with isotropic structures. The formation of directional Ni–H bonding takes place on hydrogenation and proceeds because of the transfer of electronic density from Ce to both Ni and H atoms. Thus, further to a partial negative charge on H, 0.5 to 0.6 e^- , Ni is also carrying a negative charge reaching a maximum value of 0.3 e^- . However, a partial positive charge on Ce is rather low (<1.5) and, obviously, far away from Ce^{3+} or Ce^{4+} configurations. Chains of H–Ni–H–Ni with strong covalent bonding can be found in the structure of $\text{CeNi}_3\text{H}_{2.8}$, Fig. 11, while the strongest Ni–H bonding is observed for H occupying Ni_4 tetrahedra.

Magnetic properties reflect variations in the electronic subsystem and are defined by the electronic structure of the material and will be considered in a separate publication [382].

6. Novel intermetallic hydrides and high entropy alloys

In 2004, a new paradigm of alloying strategy emerged based on the original concept of multi-principal-element alloys (MPEAs), which was initially proposed to develop materials with enhanced mechanical properties [383]. The principle is based on the mixing of elements giving close to equimolar compositions in the systems containing up to five and more elements. This may lead to the formation of simple single-phase solid solutions (body centred cubic-*bcc*, face centred cubic-*fcc* and hexagonal close packed-*hcp*). In each case, there is only one available lattice site to occupy by the

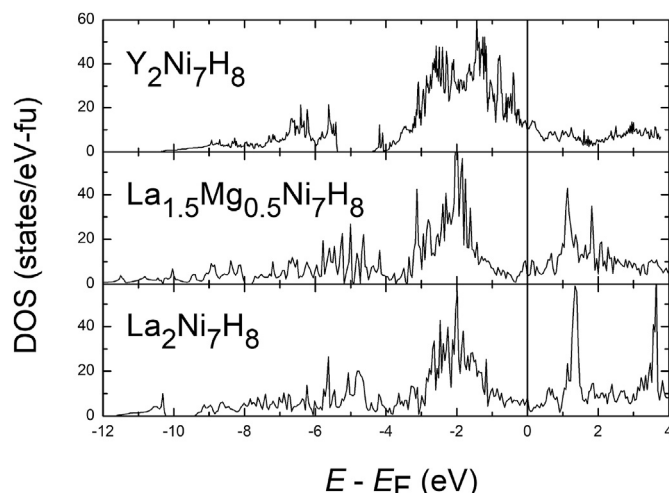


Fig. 9. Density of states for several $A_2B_7\text{H}_8$ hydrides [376,377].

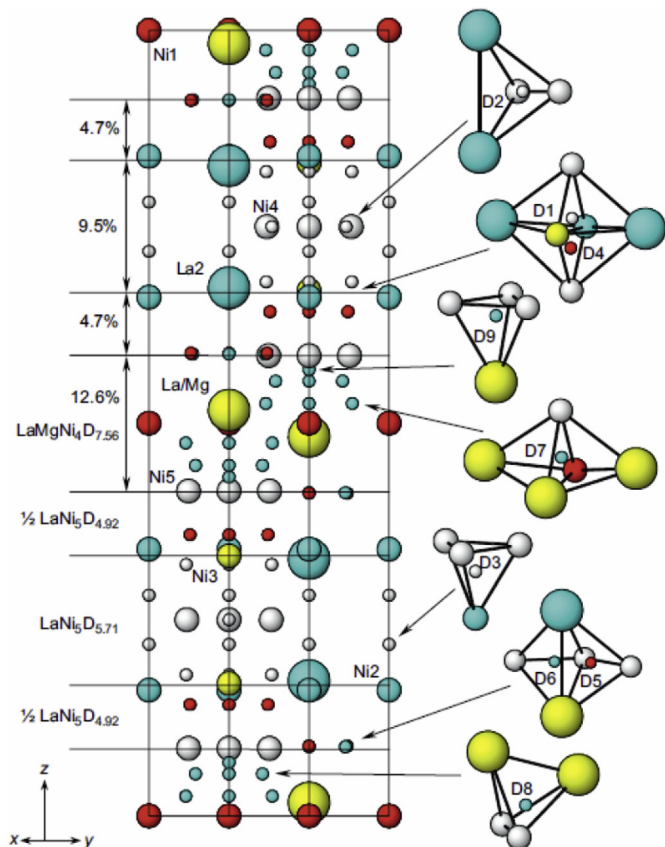


Fig. 10. Hexagonal crystal structure of $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7\text{H}_{9.1}$ with 9 types of occupied by H sites. The H atoms are situated inside the $(\text{La,Mg})_2\text{Ni}_2$, $(\text{La,Mg})\text{Ni}_3$ and Ni_4 tetrahedra; La_2Ni_3 tetragonal pyramids and $(\text{La,Mg})_3\text{Ni}_2$ trigonal bipyramids [378].

different elements over which the elements are randomly distributed. The stability of such phases seems to be based on several chemical and physical characteristics, such as configurational entropy, mixing enthalpy, atomic misfit, valence electron concentration [384]. Among MPEAs, alloys with at least five principal elements with atomic concentrations in the range 5–35% are called high entropy alloys (HEAs) [383,385]. The underlying concept of

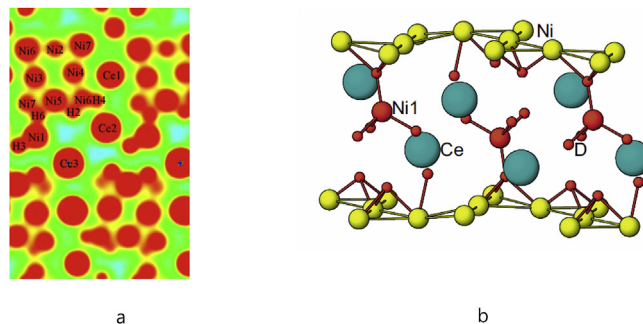


Fig. 11. Crystal and electronic structure of $\text{CeNi}_3\text{H}_{2.8}$. (a) Calculated charge density distributions in the 101 plane. The H—Ni bonds are clearly seen. (b). H—Ni—H—Ni... chains with covalent Ni—H bonding.

“high entropy alloys”, based on the formation of concentrated solutions, is illustrated in Fig. 12. It has been suggested that the high entropy of mixing is the cause of the stabilization of the single-phase solid solutions. It appears that a larger degree of solubility can be achieved in these alloys than what is suggested by the Hume-Rothery rules. Therefore, this alloying concept enables more flexible tuning of the material’s properties.

Due to their multi-principal-element nature, this new class of alloys possesses exciting physical and mechanical properties [384,386]. Among four core effects known for these alloys [384], the development of large lattice strain distortions due to the atomic size mismatch among different component elements is particularly interesting and relevant for hydrogen storage. A quantitative parameter to describe the strained or distorted crystal lattice due to the mixing of many metals with different atomic radii is the lattice distortion, δ [385]. Despite the expected formation of large interstitial sites in MPEAs/HEAs, hydrogen sorption properties are scarcely investigated. Until recently, only a few reports investigated the hydrogen sorption properties of MPEAs/HEAs [387].

Among different classes of MPEAs/HEAs, refractory alloys with *bcc* lattice and related substitutions with lightweight elements have attracted particular interest. ICMPE and Uppsala University proposed the *bcc* alloy TiVZrNbHf as a promising material with improved hydrogen storage performance [388,389]. Hydrogenation of this alloy is a single step reaction (*bcc* \leftrightarrow *bct*) with a storage capacity exceeding the value for the conventional dihydride MH_2

Table 2
Distinguished crystal structure features of typical isotropic - $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7\text{H}_9$ - and anisotropic - $\text{CeNi}_3\text{H}_{2.8}$ - structures.

Type of intermetallic hydride and typical representative References	Expansion mechanism	Interstices filled/H coordination	Metal-H bonding	Electronic structure features
Isotropic $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7\text{H}_9$ [378]	Mostly uniform for AB_5 (CaCu_5) and AB_2 (Laves type) layers. Metal sublattice is a moderately expanded initial structure with linear expansion not exceeding 10 %.	Conventional interstices which are present in the initial intermetallics. Most commonly tetrahedra.	Non-directional M-H bonding while the most electropositive metals (rare earths, Mg) form ions	Continuity of occupied states in the band structure
Anisotropic $\text{CeNi}_3\text{H}_{2.8}$ [379]	Huge differences between the AB_5 and AB_2 layers. AB_5 layers do not expand, even though they undergo a deformation. No H atoms in these layers. AB_2 layer accommodates all H atoms and enormously expands, around 50 %, with all expansion exclusively proceeding along the <i>c</i> -axis. Metal sublattice is totally rebuilt but returns to the initial intermetallic structure upon hydrogen desorption.	New types of coordination for hydrogen (e.g. $A_3B = \text{Ce}_3\text{Ni}$) together with conventional interstitial sites (e.g. $A_2B_2 = \text{Ce}_2\text{Ni}_2$)	Directional Ni—H bonding resulting in covalently bound Ni—H—Ni—H frameworks. Electron density transferred from Ce to both Ni and H.	Distinguished peaks of electron density in the PDOS of H and Ni manifesting a directional Ni—H bonding

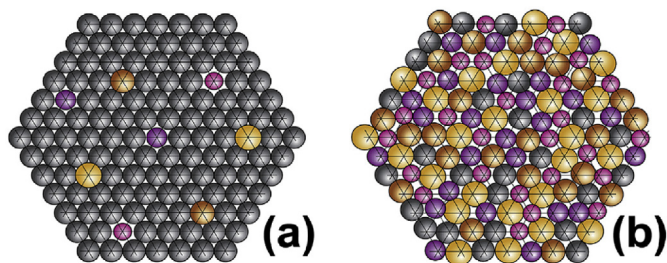


Fig. 12. The effect of atomic size difference on atom position in (a) dilute solution and (b) concentrated solution with no dominant atom species and atom positions deviate from mean lattice position. The variability in atom positions, as illustrated in (b), contributes to an excess configurational entropy [384].

formed by each of the constituting transition metals. Values as high as 2.5 H/M (2.7 wt% H) are comparable to rare-earth metal hydrides ($H/M > 2.3$). Such high hydrogen content, as in TiVZrNbHfH_{2.5}, has never been observed in hydrides based only on transition metals and this implies that hydrogen occupies not only tetrahedral but also the octahedral interstices in the pseudo-fcc lattice. We note, however, that no direct observation confirming a mixed T + O occupancy of the interstitial sites has been provided so far. Certain systems, such as TiVNbTa, TiVZrNb and TiVZrNbHf, have also been observed to phase-separate during hydrogen absorption/desorption cycling [390,391] at the high temperatures often needed to desorb the hydrogen from the hydrides [392–394].

To provide deeper understanding of this behaviour, V in the equimolar TiVZrNbHf alloy has been completely substituted by an isoelectronic element, Ta, resulting in TiZrNbHfTa [393]. Surprisingly, the single-phased bcc TiZrNbHfTa alloy behaves as the conventional bcc materials with two distinct phase transitions during hydrogen absorption: $bcc \leftrightarrow bct \leftrightarrow fcc$, which are associated with a step-by-step formation of the mono- and di-hydrides.

Recently, the hydrogen absorption properties of the Zr-deficient TiVZrNb alloy with a non-equimolar composition have been studied to optimize the synthetic optimization and cycling behaviour [395]. This alloy crystallizes in a single-phase bcc lattice. Hydrogen absorption occurs within a single step, similar to the TiVZrNbHf alloy. The maximum uptake is around 1.75 H/M (2.5 wt% H). The best hydrogen cycling performance was observed for the bct hydride with a similar capacity (1.8 H/M) obtained by reactive ball milling. A stable reversible capacity of around 2.0 wt% H has been observed, which is associated with the absence of disproportionation or irreversible segregation during the hydrogenation.

To explain the different hydrogenation behaviour of different HEAs (either one or two hydrogenation steps) we hypothesize that lattice distortion, δ , plays an important role. It is suggested a larger δ (6.8% for TiVZrNbHf and 6.0% for TiVZrNb) would favour a single-step reaction with hydrogen, whereas a small δ (4.6% for TiZrNbHfTa) would favour a two-step phase transition, as encountered for conventional bcc alloys.

Furthermore, many of the hydrogen storage properties of HEAs are intimately connected to the valence-electron concentration (VEC) of the HEA [391]. Systematic investigation of the hydrogen storage properties for a series of ten HEAs (bcc solid solutions) that are chemically related to the ternary system TiVNb ($VEC = 4.7$) shows that if the $VEC \leq 5.0$, the corresponding metal hydrides form CaF₂-type structures (Fm-3m) following a gas-solid-state reaction. The volumetric expansion of the lattice from the alloy to the hydride increases linearly with the VEC. At the same time, the onset temperature for hydrogen desorption decreases with the VEC. Therefore, it seems that a larger expansion destabilizes the HEA-based metal hydrides and that this effect can be tuned by altering

the VEC.

It can be concluded that the most promising materials for hydrogen storage are bcc MPEAs/HEAs based on refractory metals with $VEC \geq 5.0$ and with large lattice distortion δ and single-phase transformation during hydrogenation. Importantly, due to the magnitude of the number of variations of chemical compositions, this new class of alloys holds promise for the discovery of fascinating multifunctional materials.

For example, based on these insights, TiVCrNbH₈ ($VEC = 5.0$) was identified as a material with suitable thermodynamics for hydrogen storage in the solid state. This HEA-based hydride has a reversible hydrogen storage capacity of 1.96 wt% H at room temperature (RT) and moderate H₂ pressures. Moreover, it is not dependent on any elaborate activation procedure to absorb hydrogen. Thus, the insights provided in [391] might serve as a roadmap towards developing novel bcc HEA-based metal hydrides that are cost-efficient and reversible at RT with higher gravimetric hydrogen capacities.

As a conclusion, the study of hydrogen absorption/desorption properties of this new class of alloys is only at the beginning and holds promise of interesting findings, at least in terms of fundamental knowledge. Large research efforts are needed in the future to attempt to rationalize the behaviour of these alloys towards hydrogen due to the vast number of elemental combinations (in terms of chemical composition, elemental concentration, VEC and lattice distortion).

7. Improved kinetics of hydrogen absorption and desorption and decreasing working temperatures for Mg-containing systems

Using magnesium as a component of H storage alloys or to store hydrogen has a cost benefit, as the commercial price of magnesium metal is < 3 USD/kg. Here we detail recent work on layered structures and nanocomposites.

7.1. Optimization of the hydrogen sorption properties of layered structure AB_x ($A = \text{rare earths}$; $B = \text{transition metal}$; $2 < x < 5$) systems by magnesium substitution

Archetypal intermetallic compounds such as LaNi₅ are able to store 6.7 at. H per formula unit [396]; however, different chemistries offer a wide range of related compositions. Indeed, binary phase diagrams of rare earths (A) and transition metals (B) contain different phases, AB_x ($2 < x < 5$), consisting of a stack of different blocks, $[AB_5]$ and $[AB_2]$. These phases can store larger quantities of hydrogen, but they suffer from poor stability and low reversibility. To overcome these drawbacks, investigation of pseudo-binary or ternary systems adding alkali earths like magnesium is of great interest. Magnesium is a light element with strong hydrogen affinity, inducing a molar mass reduction and thus increased weight capacities, and its substitution has been recently systematically investigated. Examples include La_{3-x}Mg_xNi₉ and (La,Pr,Nd)₂MgNi₉ [397], with an increasing amount of Mg reaching a maximum at LaMg₂Ni₉. Replacement of La by Mg and Pr/Nd has a strong influence on the stability of the hydrides. When the Mg content increases from $x = 0.7$ in La_{2.3}Mg_{0.7}Ni₉ to 2 in LaMg₂Ni₉, equilibrium pressures of hydrogen desorption change by a factor of more than 1000, from 0.011 bar H₂ to 18 bar H₂ at RT, which was reflected also by correspondingly large changes in the enthalpies of hydride formation, from -24 to -40 kJ/(molH₂)⁻¹. Together, Pr/Nd and Mg substitution allow the plateau pressure to be tuned for practical applications (Fig. 13).

Similar beneficial effects were also reported by Ferey et al. [398] in the neighbouring system A₅B₁₉ ($n = 3$) for La₅Ni₁₉. Replacement

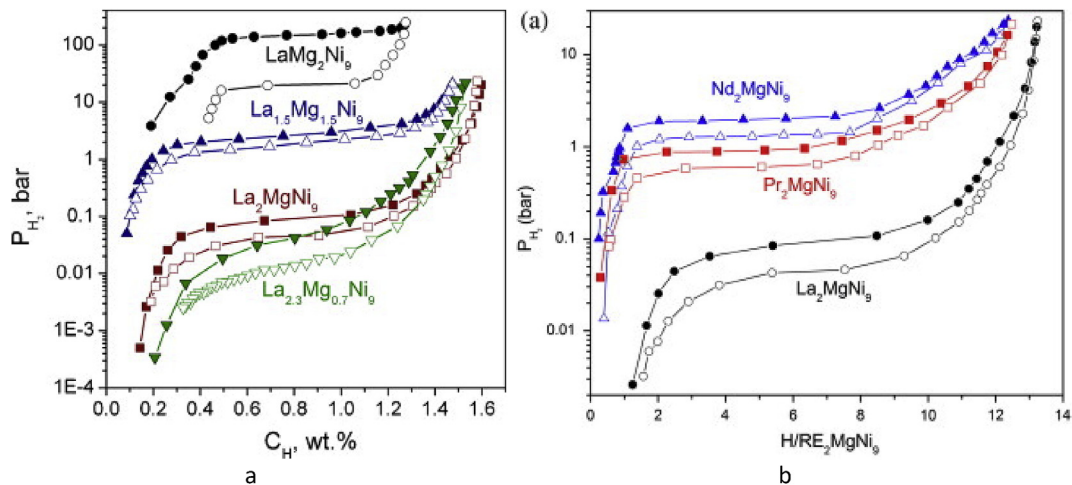


Fig. 13. Evolution of isotherms and equilibrium pressures of H absorption and desorption at room temperature as a function of x for the system $\text{La}_{3-x}\text{Mg}_x\text{Ni}_9$ [460] and RE_2MgNi_9 ($\text{RE} = \text{La, Pr, Nd}$) [463], showing that the optimal performance is reached at $x = 1$.

of La by Mg leads to a reduction of the molecular weight and stabilization of the structure by cell volume reduction, agreeing with recent results of improved behaviour in terms of reversible capacity and the working pressure window. This substitution opens a new route to develop more capacitive materials for hydrogen storage applications.

7.2. Improved kinetics and cycling stability of MgH_2 nanocomposites

To make MgH_2 efficient as a reversible hydrogen store, intensive research has been recently undertaken both to lower its decomposition temperature and to accelerate sorption kinetics [168,361,362,399]. A successful strategy to promote fast reaction kinetics is grounded on the immiscible property of Mg-ETM binary systems (ETM = Early Transition Metal) [362,400–405]. In contrast to Late TMs (e.g. LTM = Fe, Co and Ni) and Zn [406], ETMs such as Ti, V, Zr and Nb do not form any stable intermetallic phases with Mg, nor any ternary Mg-ETM-H compound. Thus, nanostructured composite materials formed by intimate mixtures of MgH_2 and ETMH_x phases can be successfully synthesized by advanced techniques, such as mechanochemistry of elemental metal powders under H_2 gas. MgH_2 - TiH_2 nanocomposites have attracted much attention due to their improved hydrogenation properties [401,402,407,408]. TiH_2 as an additive promotes fast hydrogen uptake in Mg and release from MgH_2 , with reaction rates in the minute range at 300 °C, while ensuring good cycling stability.

From studies on MgH_2 - TiH_2 nanocomposites, the role of TiH_2 as promoter of hydrogen kinetics in Mg/ MgH_2 as well as stabilizer of cycling properties can be summarized as follows:

- TiH_2 acts as a nanostructuring agent during mechanochemical synthesis of the nanocomposite [402]. Short diffusion lengths are required to achieve fast kinetics in Mg;
- TiH_2 acts, at the nanocomposite surface, as a gateway for hydrogen transport to and from the Mg/ MgH_2 matrix. It catalyses surface reactions, while hydrogen diffusion in TiH_2 at 300 °C is fast due to fluorite-type structure of TiH_2 [402,409];
- TiH_2 acts, in the bulk of the nanocomposite, as an inhibitor of Mg grain growth, which is a key property for ensuring cycling stability [410,411]. The close values of cell volume of TiH_2 ($13.2 \text{ cm}^3/\text{mol}$) and Mg ($13.8 \text{ cm}^3/\text{mol}$) allows for effective

interface coupling between these phases [412], which limits grain growth on cycling.

Besides these effects, TiH_2 may also act as a favorable site for MgH_2 nucleation during the absorption process. Further studies will be valuable to evaluate the synergetic effects of TiH_2 and Zr H_2 mixtures as mixed additives in novel MgH_2 - ETMH_x nanocomposite systems.

8. Hydrogen sorption properties of low-dimensional metal hydrides

Many experimental and theoretical studies have investigated hydrogen sorption in low-dimensional materials such as nanoparticles (NPs) and thin films with the aim to understand the mechanistic effects of nanosizing and gain new tools to tailor the hydride properties. Consensus has been reached on topics such as enhanced solubility, interface enthalpy, and enhanced sorption kinetics, while several open questions and unsolved issues remain, for instance strain-induced lowering of desorption enthalpy, interfacial entropy, and enthalpy-entropy correlation [413–416]. Nanosizing is highly effective in enhancing the hydrogen sorption kinetics, while the aspiration to modify the often-unfavourable thermodynamics of hydrogen release is much more difficult to fulfil. We will discuss the fundamental mechanisms that modify the hydrogen sorption properties of low dimensional materials in light of recent progress in this field.

8.1. Surface and interface energetics

The excess free energy associated with surfaces or interfaces in a nanosized system is given by the product $A\gamma$ of the total area A by the specific free energy (surface tension) γ . If its change upon hydriding $\Delta\{A\gamma\} \equiv \{A\gamma\}_{\text{hyd}} - \{A\gamma\}_{\text{met}}$ is positive, the nanomaterial is destabilized compared to the bulk, and vice versa [417]. The free energy change $\Delta\gamma \equiv \gamma_{\text{hyd}} - \gamma_{\text{met}}$ clearly contains enthalpy and entropy terms, i.e. $\Delta\gamma = \Delta h - T\Delta s$. Systematic calculations of Δh for different binary hydrides showed that an enthalpy-driven destabilization is expected for MgH_2 and NaH, whereas VH_2 , TiH_2 , ScH_2 , AlH_3 and LiH would all be stabilised [418]. However, the estimated enthalpy change compared to bulk is only 5 kJ/mol H_2 for Mg NPs with a diameter of 2 nm. For extremely small clusters constituted by less than 10 Mg atoms, the enthalpy change may become more

significant [419,420]. However, these ultra-small cluster sizes have eluded experimental observations until today. Experiments on Mg thin films embedded within TiH_2 layers have demonstrated that $\Delta\{A\gamma\}$ scales inversely with the film thickness, and estimated that $\Delta\gamma = 0.33 \text{ Jm}^{-2}$ [421]. In order to achieve a significant destabilization, a large positive value of $\Delta\gamma$ is required. A higher value of 0.81 Jm^{-2} was reported by replacing TiH_2 with TiAl , a strategy that exploits the strongly different binding energy of Al with Mg and H [422]. Interfacial free energy was also deemed responsible for the destabilization of self-organized MgH_2 clusters within a TiH_2 matrix [423], and of MgH_2 - TiH_2 composite NPs prepared by gas phase condensation [424].

8.2. Enthalpy-entropy correlation

There have been several experimental reports of altered enthalpy and entropy in small NPs due to surface/interface effects [424–428]. In some cases, the enthalpic destabilization was significantly larger than predicted by calculations for the relevant NPs size [425,427]. The puzzling aspect, though, is that the plateau pressure exhibits only small changes (if any) compared to the bulk counterparts. In part, this probably arises from some entropic compensation. On the other hand, an accurate determination of enthalpy and entropy from the slope and intercept of a van't Hoff plot requires the collection of equilibrium data over a wide temperature range, which is often not accessible in nanosized systems. Because of possible statistical phantoms [429], enthalpy-entropy compensation should be invoked with extreme caution to justify the sometimes surprising outcome of data analysis. In nanomaterials, a genuine enthalpy-entropy correlation is expected if $\Delta\{A\gamma\} \propto \Delta\gamma$, in which case systems with different morphologies and/or compositions all attain a plateau pressure equal to the bulk at $T_{\text{comp}} = \Delta h/\Delta s$ [416].

8.3. Elastic clamping

Another source of thermodynamical alteration emerges in mechanically confined nanomaterials, the paradigmatic case being thin films clamped by a rigid substrate. Wagner and Pundt have shown that the attractive H–H interaction energy in Pd thin films is reduced by up to 50% due to substrate-induced stress and microstructural refinement, strongly lowering the critical temperature for the phase separation [430]. The effects of elastic clamping in Mg-based low-dimensional materials have been modelled and experimentally investigated for thin films [431], cores-shell NPs [432] and encapsulated nanodots [433]. The enthalpic destabilization, proportional to the compressive elastic strain in the hydride phase, should attain the remarkably high value of $\approx 15\text{--}20 \text{ kJ/mol H}_2$ in Mg–MgO core-shell NPs or nanodots with diameter of about 50 nm [432,433]. In real life, however, plastic deformation develops due to high stress levels, thereby reducing the magnitude of the effect and increasing the hysteresis between absorption and desorption plateaus [432–436]. For this reason, the exploitation of mechanical constraints to raise the desorption pressure of MgH_2 has not been experimentally successful. Fig. 14 shows that, for Mg nanodots of two different sizes, the desorption pressure is size-independent whereas both the absorption pressure and the hysteresis increase in the smaller nanodots, which are subjected to higher lateral stresses. Nevertheless, the concept remains challenging and open to future developments. For instance, it was recently shown that immiscible Zr nanoclusters within an yttrium thin film induce a stable lattice compression, which increases the hydrogen pressure of $\text{YH}_2 \leftrightarrow \text{YH}_3$ both for absorption and desorption, a signature of true destabilization [437].

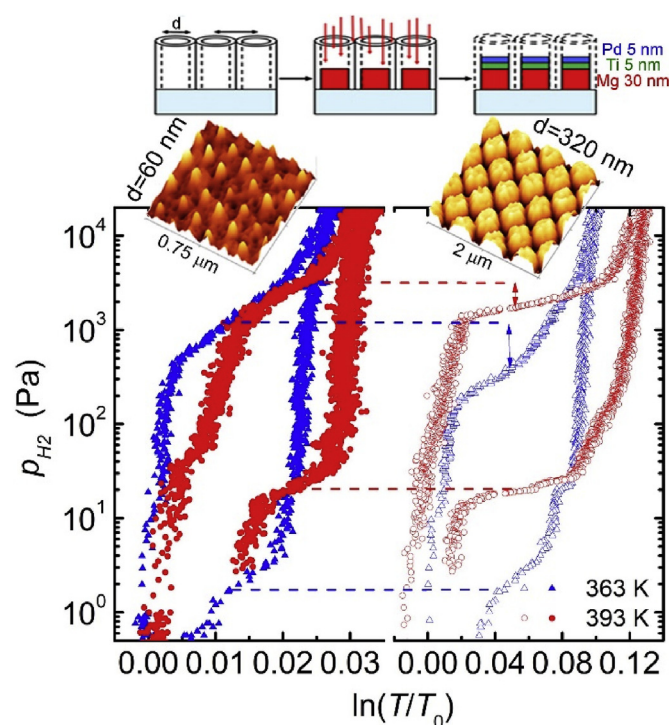


Fig. 14. Size dependent hydrogen properties in Mg(30 nm)/Ti(5 nm)/Pd(5 nm) layered nanodots with diameters of 60 nm (left) and 320 nm (right) obtained by mask-templated deposition [433].

8.4. Nanoconfinement in porous hosts

Through incorporation into porous media or polymer-based host materials, the NPs size of metal hydrides can be stabilised to 5 nm or smaller [306,438–441]. The most effective approaches have been either solution impregnation or melt infiltration using porous carbon materials, such as carbon aerogels, high surface area graphite, and carbon replicas of ordered mesoporous materials [439]. The obtained nanocomposites always display very good sorption kinetics and good cyclic stability because the confining medium reduces coarsening phenomena. The host material may modify the properties of the hydride by a combination of the previously discussed features, in particular mechanical constraints and interfacial free energy. In the case of MgH_2 , however, despite greatly enhanced kinetics, only limited thermodynamic changes (if any) have been observed. A drastic change of the hydrogen-metal interaction appears in Rh NPs supported on a porous carbon host. In contrast to bulk Rh that can form a hydride phase under 4 GPa pressure, the metallic Rh NPs ($\sim 2.3 \text{ nm}$) absorb hydrogen and form a hydride phase at pressures below 0.1 MPa [442].

Beyond porous carbon, other host materials have gained considerable attention. Reduced graphene oxide (rGO) has been proposed as a gas-selective, hydrogen permeable, and atomically thin material suitable for the realization of multi-laminated nanocomposites, in which metal hydride NPs are encapsulated and protected against oxidation [441]. MOFs are also attractive scaffolds because their crystalline structure yields highly defined, monodisperse micropores ($< 2 \text{ nm}$). NaAlH_4 confined in the micropores of a titanium-functionalized Mg-MOF-74 forms clusters of several formula units and can reversibly store hydrogen with minimal loss of capacity [443]. All scaffold materials significantly decrease the overall hydrogen storage capacity by their added weight.

9. Electrochemical storage of energy

9.1. Metallic and complex hydrides as efficient materials for electrochemical storage of energy

Storage of renewable energy is an important issue in the modern energy landscape. Electrochemical storage has shown its capability to provide energy supply for both on-board and stationary applications. Different systems exist from supercapacitors to redox flow batteries. However, the present work focusses on secondary batteries that are already developed in the market, such as alkaline and Li-ion, that suffer from low energy density, high costs and safety issues. Recently, innovative research in the field of complex and metallic hydrides has shown that these materials might bring ground-breaking solutions leading to significant improvement for these electrochemical energy storage devices.

9.1.1. Metallic hydrides as anodes for Ni-MH alkaline batteries

Ni-MH alkaline batteries are widely used for energy storage [444–447] in varied applications from Emergency Lighting Units (ELU) to small portable devices. Despite lower performances compared to Li-ion batteries, they can withstand higher charge currents and are intrinsically safer against overheating issues [448]. Moreover, they are cheaper and can be easily recycled [449]. Therefore, they are now used in most of the hybrid electric vehicles (HEV for Toyota¹ or Honda). Recently, they have been developed for stationary applications. Indeed, Nilar, a Swedish company, has teamed up with the energy company Ferroamp to create an energy management system designed for smart storage and distribution of solar energy. In a pilot project with Nilar, Ferroamp uses Nilar energy storage integrated with a midsize solar power plant to store up to 30 kWh of energy from photovoltaic panels (Fig. 15). An EnergyHub controls the energy storage to support the three-phase grid. When the voltage drops below a certain level, energy storage kicks in to raise the voltage.

This bipolar Ni-MH battery technology is a new approach [450] and the EnergyHub (Fig. 15) provides the necessary energy storage, monitoring and control capability for managing the flow of energy to and from storage, with the expectation of eventually storing up to 200 kWh of energy.

9.1.2. Increasing cycle life of hydride batteries (NiMH) by utilizing gas phase reactions

NiMH chemistry is one of the simplest battery chemistries. Hydrogen atoms are shuttled between the electrodes in the form of water molecules when the battery is cycled. Both electrode reactions are solid state intercalation reactions. When the battery is charged, hydrogen is removed from the Ni(OH)₂ at the Ni-electrode by an OH⁻ ion transforming Ni(OH)₂ into NiOOH and forming a water molecule H₂O. At the MH-electrode another H₂O molecule donates a hydrogen atom inserting into the hydrogen storage alloy, forming another OH⁻ ion. When the battery is discharged, the reactions above are reversed. These simple hydrogen atom transferal reactions can also be manipulated by adding oxygen or hydrogen gas into the battery casing. This opens up possibilities to reset internal electrode balance as well as a controlled way to replenish water to a battery drying out from long time cycling in a way that no other battery chemistry can offer.¹

The surface must contain a passivating layer in order to protect the alloy from excessive corrosion. A passivated surface can be

formed by a controlled oxidation process that slows down the corrosion rate. This is important as corrosion consumes water in the electrolyte leading to an increased internal resistance, which is the main cause of cell failure. The corrosion evolves hydrogen, causing an imbalance between the anode and the cathode. This can lead to a premature internal pressure increase that can accelerate the drying out of cells, if the evolved gases are vented through the safety valve. However, the bipolar design such as in Nilar batteries makes it possible to counteract the aging process of the metal hydride. Adding oxygen causes new water-based electrolyte to form in the battery. This replaces the lost electrolyte and restores the internal electrode balance. With a suitable balance of oxygen and hydrogen, these batteries can reach a superior lifetime and the internal resistance as well as internal cell balance can be restored on old cycled batteries, Fig. 16.

The increased cycle life means that NiMH batteries will be able to store and deliver more energy throughout their lifetime than other industrial battery technologies with reduced cost per kWh. Even though NiMH batteries cannot compete with Li-ion batteries with respect to capacity, they can compete with respect to energy throughput during the lifetime of a system (i.e. battery capacity times cycle life), similar to the success of the even lower capacity Li-titanate (LTO) long cycle life batteries [451].

Current Ni-MH batteries are mainly based on LaNi₅-type materials as anodes. Such materials are effective, but their intrinsic capacity is restricted to 300 mAh.g⁻¹ [446,452–454]. The research approach to improve their energy density is by investigating new materials with larger capacity. One approach is to use stacked-structure phases. These structures are built by stacking along the *c*-axis different subunits with compositions AB₅ and AB₂ (*A*: rare earths and *B*: transition metals). By adding different slabs as *m*AB₅ + 2AB₂, various stoichiometries of the general *A*-*B* phase diagram can be described such as AB₃ (*m* = 1), A₂B₇ (*m* = 2), and A₅B₁₉ (*m* = 3). Costly rare-earths can be partially replaced by additions of magnesium leading to pseudo-binary or ternary systems *A*-Mg-*B* (Fig. 17). Mg substitution has been demonstrated to be effective as it enables a lower molar mass, enhances the structural stability, and stabilizes the equilibrium pressure as well as reducing the overall cost [376,378,455–467].

Furthermore, excellent hydrogen storage performance, including improved cycle life and high electrochemical discharge capacities, attract interest to rare earth-free Zr and Ti based Laves phase intermetallics. Such multicomponent alloys have a variable ratio between Ti and Zr and also contain Ni, Mn, Fe, Co, Ni, and V transition metals together with non-transitional elements, Al and Sn. Depending on the composition, these alloys crystallize with C15 or C14 structures. Further to the structure, properties can be improved by applying a rapid solidification process with the aim of improving the performance of the AB₂-based Laves type alloys as battery anode materials; examples include Ti₁₂Zr_{21.5}V₁₀Cr_{7.5}Mn_{8.1}-Co₈Ni_{32.2}Al_{0.4}Sn_{0.3} as C14 [468] and Ti_{0.15}Zr_{0.85}La_{0.03}-Ni_{1.2}Mn_{0.70}V_{0.12}Fe_{0.12} as C15 [469] predominated alloys. After rapid solidification, both alloys achieved a significant improvement in their discharge capacities and rate performances.

Excellent discharge capacity performance including high reversible storage capacity, together with easy activation, fast charge kinetics, and low polarization, was achieved for two C15 predominated alloys including Ti_{0.15}Zr_{0.85}La_{0.03}Ni_{1.2}Mn_{0.7}V_{0.12}Fe_{0.12} [470] and Ti_{0.2}Zr_{0.8}La_xNi_{1.2}Mn_{0.7}V_{0.12}Fe_{0.12} (*x* = 0.01–0.05) [471]. Both alloys achieved high discharge capacities, 410 mAh/g and 420 mAh/g, respectively. 3 wt% of La was added to both alloys causing an easier activation and an increased capacity because of the catalysing effect of a secondary phase - LaNi intermetallic - on the hydrogenation.

For commercial metal hydride batteries the following range of

¹ The mention of all commercial suppliers in this paper is for clarity and does not imply the recommendation or endorsement of these suppliers by the IEA, NIST or the authors.

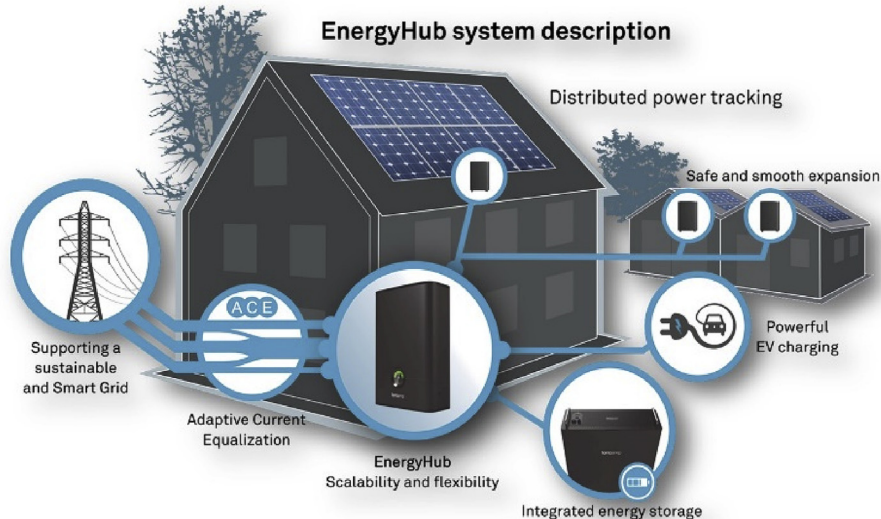


Fig. 15. Schematic of the Ferroamp EnergyHub based on Nilar's bipolar in Sweden (from <http://www.nilar.com/wpcontent/uploads/2017/09/Ferroamp-Customer-Case-NIL17.pdf>).

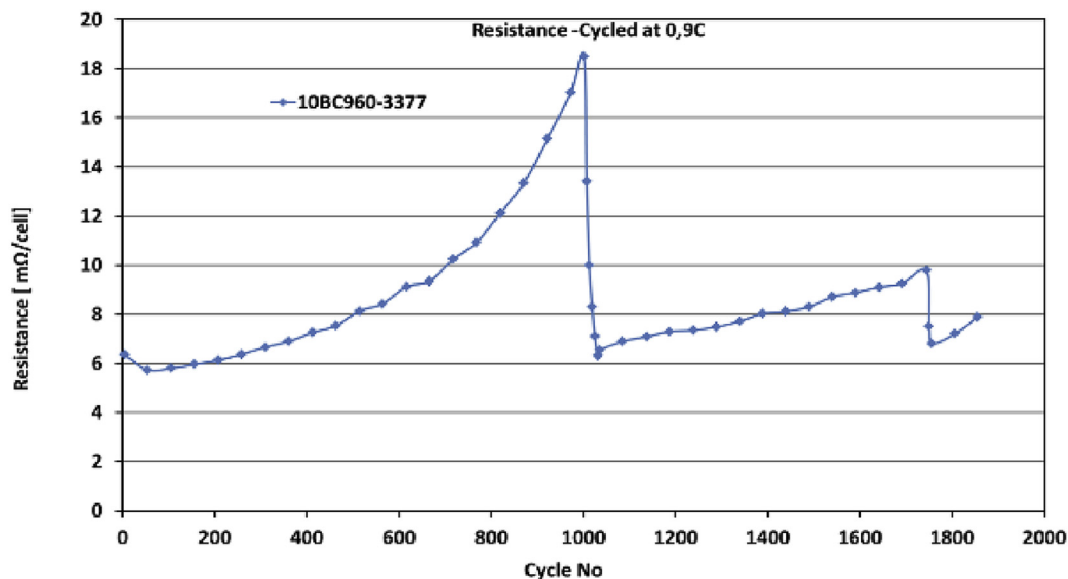


Fig. 16. Internal resistance upon cycling (0.9C rate), with additions of 5 consecutive 3L batches of oxygen gas at cycle 1000, and 2 consecutive 3L O₂ and 3L H₂ batches at cycle 1700 [451].

gravimetric/volumetric energy storage capacities and cycle stabilities is presently reached: 50 to 110 Wh/kg and 150 to 390 Wh/L depending on the materials and technology, with a cycling stability reaching 6000 cycles.

9.2. Metallic hydrides as anodes for Li-ion batteries

Li-ion batteries are dominating the battery market due to their high energy density. Though their capacities are larger than other technologies, such as alkaline batteries (by 50%), demanding applications such as EVs will need much higher energy densities to reach the specifications for long-range vehicles (by a factor of four). All components such as cathodes, electrolytes and anodes are under scrutiny. For anodes, current materials use mainly intercalation/deintercalation reactions while conversion type reactions are an

alternative to develop more capacitive anodes.

Among the possible materials for conversion, metallic hydrides show promise based on their intrinsic properties: low potential, low polarization, high volumetric and weight capacities and low cost [472]. The first evidence of this reaction was provided by Oumellal [450], following the general equation $MH_x + xLi \rightleftharpoons xLiH + M$. From a thermodynamical point of view, the reaction is favorable for electrochemical applications as far as $\Delta G_f(MH_x)/x$ or is greater than $\Delta G_f(LiH)$, opening the opportunity to investigate many hydrides with high capacities [473]. Theoretically, as shown in Fig. 18, such materials might provide volume and weight capacities ten times larger than graphite which is typically used. Indeed, most of the investigated hydrides (MgH₂ [450,473–477], TiH₂ [478,479], composites (Mg,Ti)H₂ [402,480], TiNiH [481], Mg₂MH_x complex hydrides ($M = Fe, Co, Ni$) [482–484], alane [475,485], and alanates

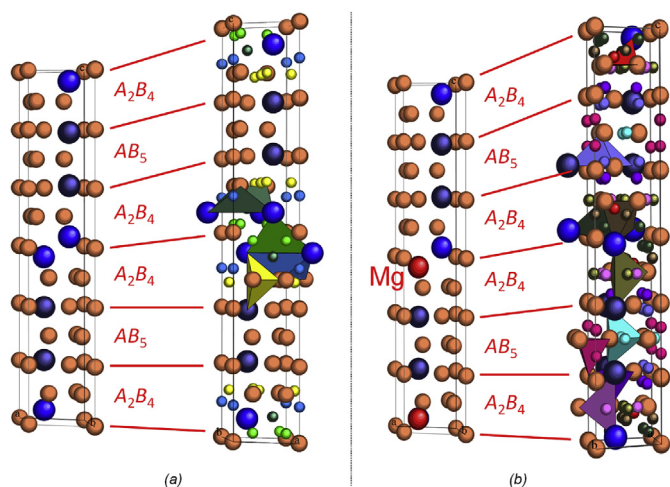


Fig. 17. Comparison of the structural properties of two intermetallics (a) La_2Ni_7 and (b) $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ and their respective deuterides showing the different site occupancies for deuterium (from Refs. [378,458]). Reprinted from Ref. [376], Copyright (2014), with permission from Elsevier.

[485,486]), showed good ability for lithiation.

Despite successful lithiation of these hydrides, reversibility remains an issue for these systems as room temperature experiments show slow kinetics for de-lithiation, limiting the effectiveness of the reaction. Different strategies to improve the reversibility include nanosizing to enhance diffusion paths or the addition of secondary conductive phases such as carbon to improve electronic conductivity. It was demonstrated that increasing the temperature to *c.a.* 120 °C allows good reversibility of the reaction for MgH_2 [487–490], composites $(\text{Mg},\text{Ti})\text{H}_2$ [491], or complex hydride Mg_2FeH_6 [492]. In addition, a recent study made on a thin film of MgH_2 [493] at room temperature shows that the poor reversibility of the hydride conversion reaction is not due to electronic contact losses, neither to low conductivity of the electrode nor to cracks or voids induced by the volume expansion upon cycling, but rather to mass-transport limitations. This agrees with the enhancement of the reversibility observed at higher temperatures. Keeping low-

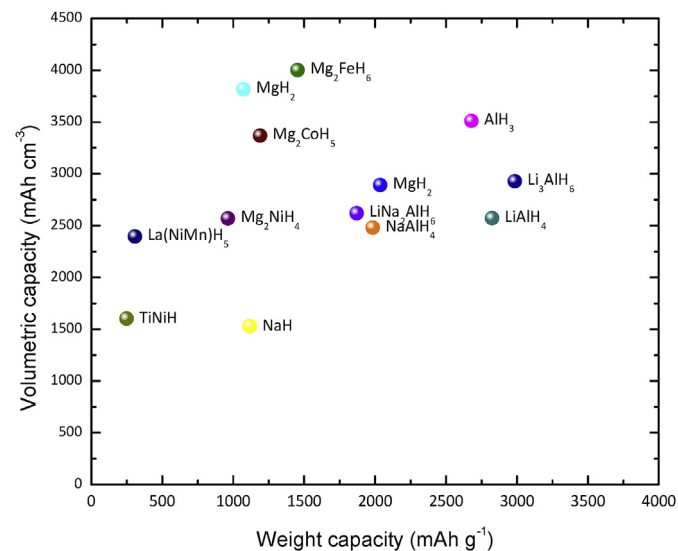


Fig. 18. Calculated capacities (by volume and by weight) for various binary and ternary hydrides using the electrochemical conversion reaction with lithium $\text{MH}_x + x\text{Li} \rightleftharpoons x\text{LiH} + \text{M}$.

dimensional microstructures during electrochemical cycling and utilizing the optimal operating temperature are therefore key to achieving good reversibility and cycling for the use of metal hydrides as efficient conversion anodes in Li-ion batteries.

9.3. Complex hydrides as electrolytes for Li-ion batteries

Solid state electrolytes are a breakthrough in Li-ion technology as they allow to avoid the use of flammable liquid electrolytes while ensuring safer and more powerful batteries by preventing dendrite formation with Li metal. However, obtaining high ionic conductivities in solid materials at room temperature (above $10^{-3} \text{ S cm}^{-1}$), while keeping a low electronic conductivity, remains challenging. Solid electrolytes must present good stabilities in a large range of potential (typically 0–5 V) and should be compatible with the highly reactive materials composing the electrodes.

Complex hydrides were recently found to be interesting materials in this field [494,495]. Indeed, LiBH_4 was reported as a fast ionic conductor for lithium by the group of Matsuo et al. [496,497]. Unfortunately, this compound undergoes a structural transition at 110 °C and only the high temperature hexagonal phase is significantly conductive ($10^{-3} \text{ S cm}^{-1}$) [497]. Various strategies have been developed to lower the transition closer to room temperature. This includes nanoconfinement in scaffold materials such as silica [498,499], partial BH_4^- anion substitution with halides (Cl^- or I^-) [496,500], solid solutions with amides (NH_2^-) [501], and synthesis of rare-earth (RE) chloride compounds $\text{LiRE}(\text{BH}_4)_3\text{Cl}$ [217], leading to some improvement but still one or two orders of magnitude below the required conductivities at RT. This illustrates the potential of other possibilities by modifying both chemistry and nanostructure. In addition, significant ionic conductivities have been also reported with other cations such as Na^+ [502,503] in various *closo*-borate and monocarbo-*closo*-decaborates (Fig. 19) [504], paving the way to many possibilities in the field of solid state ion batteries.

9.4. Full Li-ion batteries made of complex and metallic hydrides

Based on the above reports on the attractive properties of complex and metallic hydrides as solid electrolytes or anodes, several groups have attempted to use them in full cells to demonstrate their ability for developing practical batteries [505]. All attempts were made with LiBH_4 -type electrolytes and with temperatures ranging from 45 to 120 °C. To provide high capacities, most of the investigated batteries were using a metallic lithium anode, coupled with various cathode materials: TiS_2 [504,506–508], sulphur [509–512] and Co or Ti oxides [513]. To our knowledge, only one battery combines the complex hydride LiBH_4 as electrolyte and a metallic hydride as anode ($\text{MgH}_2 + \text{TiH}_2$) [491]. Here, the device was completed with a sulphur cathode. Despite slow kinetics at room temperature, most of the batteries cited above show good cycling behaviour up to hundreds of cycles.

Metallic and complex hydrides have been mainly developed in the past for their capability to reversibly store gaseous H_2 or to serve as anodes in alkaline batteries. Recent research has demonstrated their aptitude to also play a crucial role in Li-ion technology, providing safer solid electrolytes and higher capacitive anodes to face the increasing demand for energy storage. Based on the very rich chemistry of these materials, a large field of research is open to discover new hydride materials that might bring large innovation in this field.

10. Thermal storage using metal hydrides

Thermochemical energy storage materials have higher energy

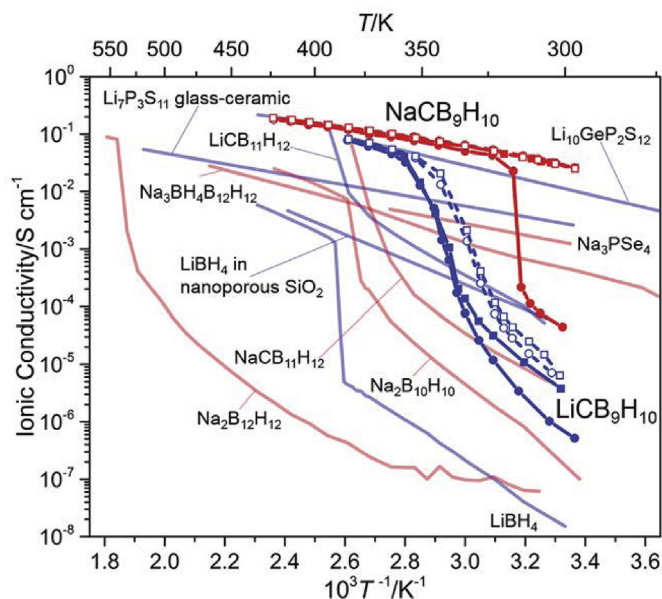


Fig. 19. Comparison of the ionic conductivities (Li^+ or Na^+) as a function of the temperature for various polycrystalline materials, suitable as solid state electrolytes, from Ref. [504].

densities compared to latent and sensible heat storage materials. Metal hydrides have properties such as high enthalpies, reversibility and cycling stability, and this makes them ideal for thermal energy storage applications in the temperature range of $25\text{ }^\circ\text{C}$ – $800\text{ }^\circ\text{C}$ [514]. The heat source can be derived from several sources such as waste heat and concentrated solar thermal (CST).

Solar energy is the most abundant renewable energy resource and therefore logically represents the most important renewable energy resource for the future. The IEA roadmap for solar energy set a target of ca. 22% of global electricity production from solar energy by 2050, with 50% being produced from CST power (CSP) systems. Achieving this target will be possible only if the costs of producing electricity from solar energy are significantly reduced and cost effective energy storage technologies can be developed. A major challenge is to achieve continuous, low-variability power generation from renewable energy sources, for stand-alone applications or for integration with domestic power grids. Solar mirror collection fields can collect thermal energy during the day and run a heat engine to convert it into electricity, but cannot provide power at night. However, if some of the heat is used to remove hydrogen from a metal hydride, the reverse reaction where hydrogen absorbs back into the metal hydride can then occur at night, releasing heat for power generation (Fig. 20). This allows solar energy to provide 24 h power generation. By combining a high temperature metal hydride with a low temperature metal hydride or a compressed gas store, a coupled reversible thermochemical solar energy storage system is created [515,516]. CST coupled to a high and low temperature storage system has the potential to provide a continuous supply of electricity to remote areas around the world.

Recent, focus has widened from being devoted to the development of the metal hydride materials but also to the whole TES system [357,514,517,518]. This includes the containment material for the metal hydride material, which must not only endure temperatures of up to $800\text{ }^\circ\text{C}$, hydrogen pressures of up to 150 bar, but also hydrogen permeation and embrittlement [519]. Thermal management of the system has also been considered including the reduction of heat loss from the system, the heat transfer fluid (HTF) and thermal properties of the metal-hydride bed. Storage of the

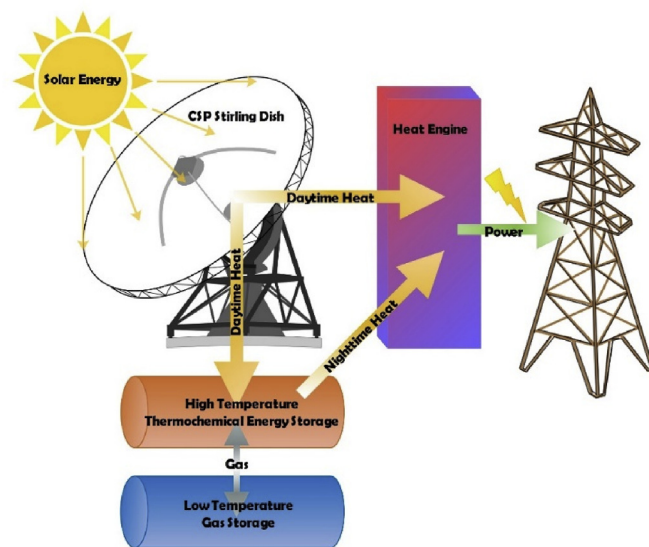


Fig. 20. Depiction of a Stirling dish concentrating solar power plant based on solid-gas thermochemical energy storage. The arrows indicate the heat, gas, and power flow.

hydrogen released by the TES materials during the energy storage regime has been explored with costs simulations being carried out [520–522]. Storage options range from compression of the gas in volumetric containers or salt caverns to compression into low-temperature metal hydrides that are specifically paired to the high temperature metal hydride.

The development of new high temperature metal hydride materials has a vital role to enable maximum efficiency of the CST plant by operating at maximum temperature. A host of compounds have been developed in an effort to increase the operational temperature, while keeping the operating pressures to a minimum. Fluorine substitution for hydrogen has allowed the thermodynamic stabilization of metal hydrides including $\text{Mg}(\text{H}_{1-x}\text{F}_x)_2$, $\text{NaH}_{1-x}\text{F}_x$ and $\text{NaMgH}_{3-x}\text{F}_x$ [521,523–525]. Other potential materials developed as TES materials include $\text{Na}_2\text{Mg}_2\text{NiH}_6$, Mg_2Si , LiBH_4 – $\text{Ca}(\text{BH}_4)_2$, Li – H – Al , Li_2NH and CaAl_2 [153,278,526–528,528–534]. Despite many of these materials having the required thermodynamic stability to operate at temperatures of $>400\text{ }^\circ\text{C}$, reversible hydrogenation and cyclability remain a concern, and as such particle refinement additives were explored [535].

While TES materials have continued to be explored, the construction of prototype TES systems or thermal batteries has also been underway. The materials used for the prototype TES include MgH_2 and NaMgH_3 and over time these materials were scaled up from 19 g of MgH_2 , to 40 g MgH_2 and 150 g NaMgH_3 [536–538]. Each of these prototypes have not only increased in dimension but also operating temperature, with the latter having an upper limit of $480\text{ }^\circ\text{C}$. In addition, thermal management has been tried with the inclusion of a HTF supply line inserted through the powder bed. The super-heated water HTF acts to supply heat during the day cycle to promote the endothermic release of H_2 and the exothermic process at night where H_2 is reabsorbed by the metal powder bed. As stated above, the operating temperature for a thermal storage system should be as high as possible, to operate as efficiently as possible. Since the solar collectors, that are the main source of heat for such systems, already deliver temperatures well in excess of $1000\text{ }^\circ\text{C}$, obtaining suitable temperatures at the beginning of the energy generation chain is not a problem. However, transferring the heat at these high temperatures is problematic and the heat transfer agent needs to be chosen with care.

To maximize steam turbine efficiencies, high temperature thermal stores from 550 to 800 °C are required. However, as mentioned above these higher temperatures put challenges on containment of metal hydride stores and pressure fittings adding significant cost. Therefore, despite the lower steam turbine efficiency, there is still interest in CSP plants that operate at economic hot oil heat transfer fluid temperatures, typically 393 °C. This temperature is the sweet spot for magnesium hydride. Its flat pressure plateau operating at ≈ 12 bar, low hysteresis and low cost of Mg ($\text{€}2/\text{kg}$) makes it attractive. Magnesium hydride's enthalpy of absorption of $\Delta H_{\text{abs}} = -74.06 \pm 0.42 \text{ kJ mol}^{-1} \text{H}_2$ is less than that for the higher temperature candidates, $\Delta H_{\text{abs}}(\text{CaMg-NiH}_4) = -129 \text{ kJ mol}^{-1} \text{H}_2$ and $\Delta H_{\text{abs}}(\text{Ca}_4\text{Mg}_4\text{Fe}_3\text{H}_{22}) = -122 \text{ kJ mol}^{-1} \text{H}_2$ operating at 600 and 800 °C respectively [514]. Higher temperatures are limited for a practical system by not only the increased plateau pressure but excessive sintering of Mg metal powder in its de-hydrogenated state. If the temperature is raised above 420 °C the sintering causes increasing diffusion distances, limiting kinetics. Possible porous structures can be built utilizing lower controlled temperature-pressure cycles. An example is given in Fig. 21.

Often researchers have sought to improve the kinetics of magnesium metal hydride stores by introducing additives such as TiB_2 or Nb_2O_5 during ball milling [535,539–541] or by sputtering [542]. However, it is worth noting that above 380 °C the effect of the catalyst is minimised due to reduction of the oxides by Mg to MgO that would otherwise impede the transport of hydrogen [514,543]. Thus, a more cost-effective pure Mg (without catalysts) can be used as the kinetics are sufficient; provided the simulations and modelling of MH thermal store CSP bed performance and heat transfer is based on reliable and representative kinetic data. A problem remains in that the return oil HTF from the steam turbine is likely to be ≈ 320 °C, thus the entrance to the MH bed will be below 380 °C and suffer from poor kinetics if uncatalyzed, and this must be calculated into the CSP simulations and models.

Another strong influence that needs careful consideration if using Mg is the amount of overpressure the MH bed is subjected to. This can influence both the kinetics and capacity. A simplistic view is to think that an increase in overpressure compared to the bed plateau pressure translates to a subsequent increase in the rate of reaction. However, this is not always the case as beyond a critical overpressure (typically twice the plateau pressure) the overpressure only increases the initial reaction rate but decelerates the remainder of the reaction. One explanation is related to how fast localized regions of MgH_2 form on the surface of each Mg particle and grow together into a single continuous outer layer [544–546].

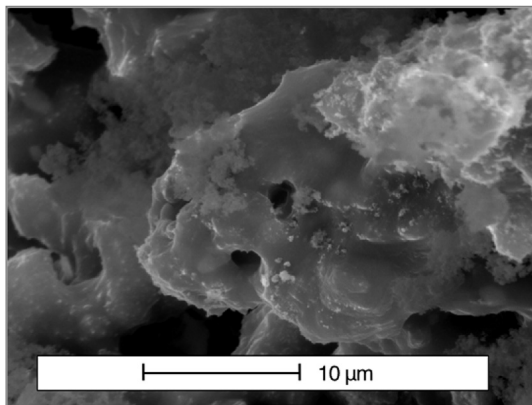


Fig. 21. Example of Porous Mg microstructure produced by partial sintering during cycling at 400 °C.

Further increases in overpressure speed up the formation of MgH_2 reducing the time it takes the outer layer to reach a thickness that will inhibit the penetration of hydrogen into the core of the particle.

At higher temperatures, one material with extremely high cycle stability is Mg_2FeH_6 , working without any degradation over hundreds of cycles. This is derived from a complete separation of Mg and Fe metals during the decomposition and formation of Mg_2FeH_6 during the hydrogenation. The material has a gravimetric hydrogen content of 5.5 wt% and a volumetric hydrogen density of 150 kg m^{-3} . The reaction enthalpy was determined to be $77.4 \text{ kJ mol}^{-1} \text{H}_2$, slightly higher compared to pure MgH_2 with a value of $74 \text{ kJ mol}^{-1} \text{H}_2$. Mg_2FeH_6 can be used for heat storage applications at temperatures up to 550 °C [547]. The high working temperature makes heat transfer more difficult and molten salts must be used instead of thermo oils. This was shown in a demonstration unit with 5 kg of Mg_2FeH_6 as the heat storage material [548,549]. The heat storage unit was constructed as a tube bundle reactor with molten salt as the heat transfer medium flowing partly across and partly parallel to the tubes. During the initial experimental tests heat losses prevent stable conditions during heat storage and heat release, and values of $\approx 60\%$ of the theoretical heat amount could be reached. This corresponds to a heat amount of 1.5 kWh.

At even higher temperatures, for short distances, heat can be transferred via heat pipes using sodium as the heat transfer agent [550]. Although sodium has also been used for longer distance heat transfer in atomic reactors [551], the complexity and safety considerations of pumping a corrosive, pyrophoric liquid metal argue against the economics of the scheme.

Two other heat transfer agent types have been suggested and tried out for heat transfer at high temperatures over distances of up to several hundred meters. One choice is in using supercritical fluids [357,552]. Both supercritical water and supercritical CO_2 are good agents concerning the fact that they boast the density of liquids and therefore also provide relatively high heat capacities and conductivities. Their drawback is the need to keep the fluids in the supercritical state, for which a certain minimum pressure is required. Especially in the case of supercritical water, this requires piping resistant to several tens of bars in pressure, which makes installation more expensive.

The other type of heat transfer agent is a gas. Both helium and air have been considered for this role [357]. Helium has the best heat transfer characteristics at the expense of a considerably higher cost than any other gas. Air is the most economical heat transfer agent, but with significantly worse heat transfer characteristics and therefore needing a higher volume flow to deliver the same performance.

Important for the construction of demonstration units is the measurement of the effective thermal conductivity (ETC) of the heat storage materials, because one drawback could be the low heat transfer capability of packed beds. ETC measurements should be done under working conditions of high temperatures and under hydrogen pressure. For the Mg/ MgH_2 system strong temperature dependency in the dehydrogenated state and a significant influence of hydrogen gas pressure to heat transfer capability at higher temperatures was observed [553]. In addition, the heat transfer in a packed magnesium hydride bed is strongly influenced by repeated hydrogenation and dehydrogenation cycles. The ETC increases by 50% in the dehydrogenated state at ambient pressure and by 10% in the hydrogenated state after 16 and 18 cycles.

Since the systems being considered here are all cost-driven, having an economical heat transfer agent that combines well with the overall concept of the heat storage system is essential to make such systems successful.

11. Hydrogen energy systems – H₂ driven fork lift and metal hydride compressors

Metal hydrides that operate at or around room temperature and provide hydrogen storage capacities close to 2 wt% H (i.e. storage of 1 kg H requires approx. 50 kg of the MH material) can provide compact H₂ storage required for fuel cell driven heavy-duty utility vehicles including material handling units/forklifts where the hydrogen storage system can simultaneously serve as a ballast. Thus, the limited gravimetric hydrogen storage capacity of metallic hydrides, which is frequently considered as a major disadvantage for their use in vehicular hydrogen storage, becomes an advantage in such an application [356,554–558].

Successful integration of metal hydride hydrogen storage in Balance of Plant (BoP) of fuel cell (FC) power modules for electric forklift has been demonstrated by HySA Systems, University of the Western Cape, South Africa. The system concept, Fig. 22, is based on a distributed hybrid hydrogen storage solution [559] where a metal hydride (MH) hydrogen storage tank is connected to a compressed gas hydrogen (CGH₂) tank used as a buffer to dampen H₂ pressure oscillations during the FC stack operation, as well as to provide a sufficient pressure driving force for H₂ absorption in the MH during the short periods of system refuelling. The MH tank is thermally coupled with the FC stack and the BoP components generate heat to balance the endothermic desorption of the MH. In refuelling mode, the heat released during exothermic H₂ absorption in the MH is dissipated into environment.

Fig. 23 shows the first prototype of HySA Systems MH hydrogen storage system integrated with a commercial FC power module (Plug Power, Inc.) installed in a standard 3-ton electric forklift (STILL, GmbH) [556,557]. The MH hydrogen storage extension tank is built as an assembly of 20 MH containers immersed into a water tank. The gas manifold of the tank is connected to the high-pressure side of the buffer gas cylinder of the power module (74 L composite cylinder, CGH₂). Heat management of the MH tank is via a circulating water-glycol mixture driven by a circulation pump (CP), and a radiator–fan (RF) assembly and air-to-liquid heat exchanger. The containers have an optimized MH bed which provides easy activation and fast H₂ charge/discharge. The system has the same hydrogen storage capacity (~19 Nm³ H₂ or 1.7 kg) as the CGH₂ tank charged at $P = 350$ bar, but at a lower H₂ charge pressure (185 bar). The forklift with an FC power module and MH extension tank has been successfully operating at the facilities of an industrial customer (Impala Platinum Ltd, South Africa) since 2015.

A recently developed HySA Systems 15 kW FC power module, which uses a second prototype of the MH hydrogen storage tank

[558], is shown in Fig. 24. Since all the BoP was bespoke, it allowed for flexibility in the integration of the MH tank into the FC system.

The tank uses a C14-AB₂-type MH alloy characterised by a hydrogen storage capacity of about 170 NL/g, a sloping plateau on pressure–composition isotherms (equilibrium H₂ pressure at RT between 5 and 10 bar) and a low absolute value of hydrogenation enthalpy ($\Delta H = -18.5$ kJ/mol H₂, $\Delta S = -78.1$ J/(mol H₂ K)), minimising the heat release during refuelling and relaxing the requirement for the heat supply during H₂ release to the FC stack. The system has 40 MH containers (total H₂ storage capacity about 1.7 kg). Additional features from the initial prototype include: (i) direct integration of the heating/cooling system of MH tank with the FC stack; (ii) counterbalancing by encasing the MH containers in melted-and-solidified lead to reach the required total weight [560], and (iii) a smaller size of the gas buffer (9 L; CGH₂ in Fig. 24) as compared to the first prototype (74 L). Recently performed heavy duty tests (VDI 60/VDI 2198 standard protocol) of the forklift delivered up to 170 NL/min H₂ to the FC stack (average power about 14 kW), at 6–12 bar and by heating at temperatures up to 55 °C. The refuelling time of the MH tank at ambient temperatures - 15 and 20 °C - was between 15 and 20 min². A more stable MH material, as compared to the material used in Ref. [558], enabled the maximum H₂ dispensing pressure to be lowered from 185 to 100–150 bar.

The main advantage of hydrogen storage systems utilizing MH is in a lower hydrogen storage pressure compared to the CGH₂ storage option. According to a recent estimation [561], the replacement of a CGH₂ storage tank with a MH one on-board an FC vehicle allows approx. 38% reduction in the refuelling costs due to a significant reduction in the costs for hydrogen compression.

The on-board MH hydrogen storage systems for forklift applications described above are characterised by an operating H₂ pressure between 30 and 50 bar (plateau pressure at $T = 25$ –50 °C) for the hydrogen storage extension tank (Fig. 23) [557] and between 5 and 20 bar in the same temperature range for the MH tank integrated in HySA Systems forklift power module (Fig. 24) [558]. The higher H₂ refuelling pressures were used only to reduce the refuelling time.

The main material-related problems relevant to future developments of MH hydrogen storage systems on board FC vehicles are associated with the necessity to further decrease the H₂ refuelling pressures while shortening the refuelling time. At the same time, the pressure of hydrogen desorption from the MH at the operating temperature has to be above 1 bar to provide H₂ supply to the FC stack. In doing so, the material engineering, i.e. identification of the composition of a hydrogen storage alloy whose metal–hydrogen thermodynamic characteristics match with the pressure – temperature operating conditions of the application, will be in great demand. An approach establishing empirical correlations between hydrogen equilibrium pressures at different temperatures and elemental composition of C14-AB₂-type alloys [562] has to be developed for this, as well as other classes of hydrogen storage materials, taking into account such properties as hydrogen storage capacity, plateau slope and hysteresis. The issues of accelerating kinetics, particularly for H₂ absorption, lowering hydrogenation enthalpy, and increasing the volumetric hydrogen storage density are also of great importance.

Apart from optimising the composition of the hydrogen storage alloys, reduction of their cost is another challenging problem to be solved in the future. Medium-to-large scale manufacturing of the alloys by induction melting seems to be a viable option. Here, the main problem to be addressed is to inhibit interaction of the melt with the crucible at high temperatures thus minimising

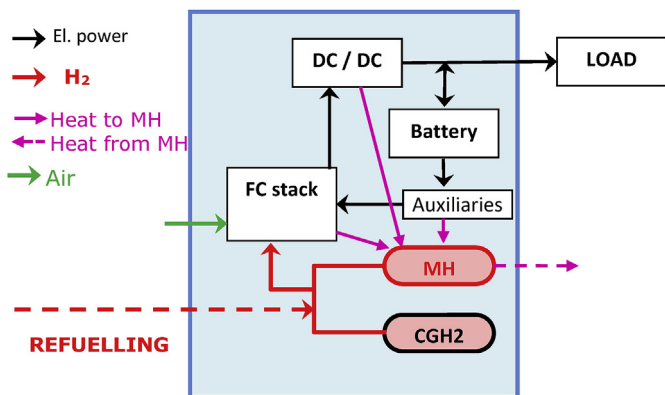


Fig. 22. Hydrogen storage on-board fuel cell powered material handling vehicle: a HySA Systems concept.

² Less than 10 min for 85% H₂ charge.

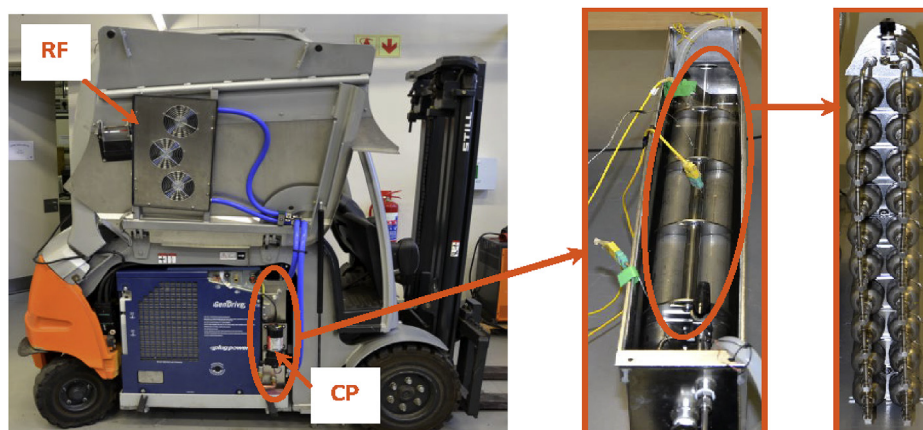


Fig. 23. Left – Electric forklift equipped with fuel cell power module and metal hydride hydrogen storage extension tank (circled). Middle – the MH tank. Right – assembly of MH containers.

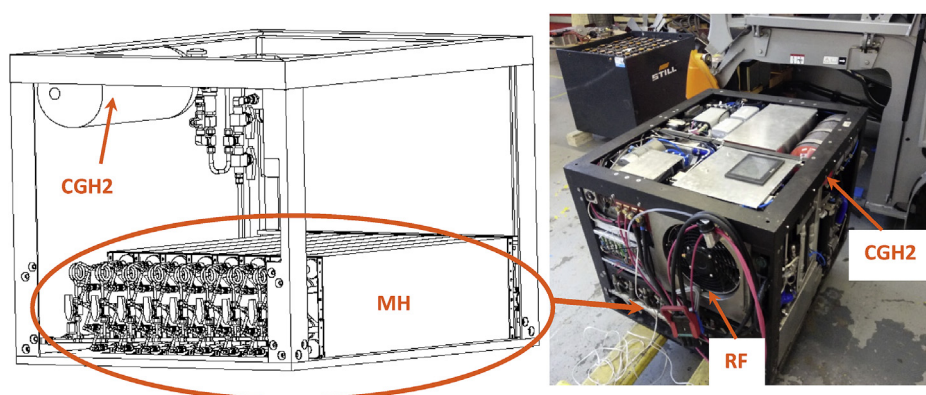


Fig. 24. MH tank with 9L CGH2 buffer cylinder integrated in HySA Systems power module for electric forklift.

contamination of the product and prolonging the crucible service time. Corresponding approaches have been analysed for Ti-containing alloys in a recently published review [563]. Other cost-efficient methods like powder metallurgy [564], hydride combustion synthesis [565], high temperature electrolysis [566], etc., should be considered as well, with the focus on achieving high purity and homogeneity of the final alloy product.

Nearly all current technology demonstrations and commercial FC-powered vehicles store the hydrogen (H_2) fuel as a highly compressed gas up to 875 bar to enable refuelling to 700 bar systems. These pressures are achieved at fuelling stations by compressing H_2 from various initial feed sources at lower pressures [567]. Conventional mechanical compressors contribute approximately half of the station's cost, face reliability issues, and may have insufficient flow rates for a mature FCEV market [561,568,569]. Fatigue associated with their moving parts, including cracking of diaphragms and failure of seals, leads to failures exacerbated by the repeated starts and stops. The conventional lubrication of these compressors with oil is generally unacceptable at hydrogen filling stations due to potential fuel contamination. MH technology offers an excellent alternative to both conventional (mechanical) and the newly developed (i.e., electrochemical, ionic liquid pistons, etc.) methods of hydrogen compression. The advantages of MH compression include simplicity in design and operation, minimal number of moving parts, compactness, safety and reliability, and the possibility to utilize waste industrial heat for the heating of the MH compressor beds [358] offering decreased operational costs.

MH hydrogen compression utilizes a reversible heat-driven interaction of a hydride-forming metal, alloy or intermetallic compound with H_2 gas to form the MH phase and is a most promising candidate for hydrogen energy applications [356,358,570]. Metal hydride hydrogen compressor (MHHC) feasibility has been known with various laboratory experiments and demonstration as well as limited commercial units being offered for a number of years going back to the early 1970s [571].

When the hydride is cycled between a lower temperature (T_L) and a higher temperature (T_H), hydrogen pressure increases from P_L to P_H as illustrated in Fig. 25A. The extent of pressure increase follows the equilibrium of H_2 gas with H atoms within the host metal or alloy in the interstitial hydride phase when the equilibrium H_2 pressure in a plateau region of the pressure–composition isotherm is proportional to the exponent of reciprocal absolute temperature in accordance with the van 't Hoff equation. Accordingly, the pressure increase in an H_2 – MH system significantly exceeds the one taking place during thermal expansion of the gas (Fig. 25B).

The compression ratio, P_H/P_L , is strongly dependent upon the thermodynamic properties (e.g., ΔH and ΔS) for the individual hydride phase, which is restricted by the operating temperature range and structural stabilities of the hydrides [358]. Hence, practical MH compressors use generally two or more consecutive stages with different hydrides [358,570]. Only very few metal hydrides possess the ideal characteristics of broad and flat isotherms with minimal hysteresis between the absorption and desorption

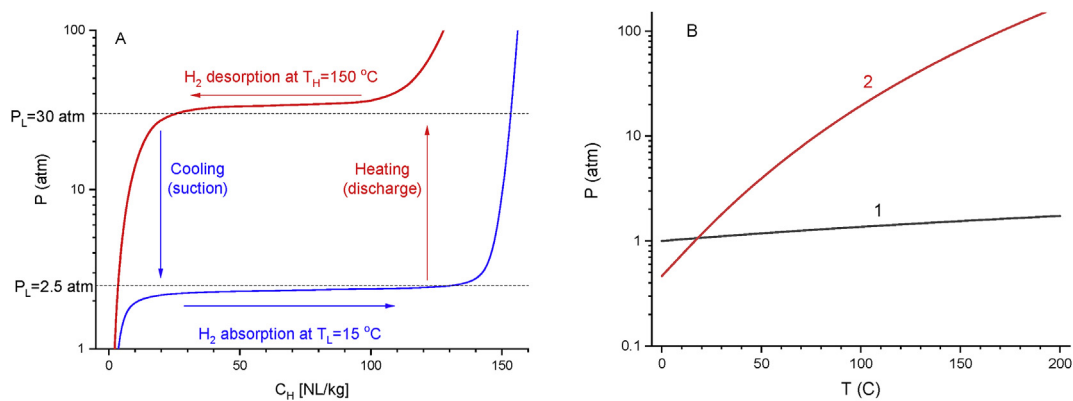


Fig. 25. A – schematic presentation of thermally driven hydrogen compression cycle using metal hydride. B – temperature dependencies of hydrogen pressure in a closed volume (1; thermal expansion) and hydrogen in equilibrium with metal hydride (2; plateau pressure). Both A and B (plot 2) show as an example LaNi_5H_x ($\Delta S^\circ = -110.0 \text{ J mol}^{-1} \text{ H}_2 \text{ K}^{-1}$; $\Delta H = -31.8 \text{ kJ mol}^{-1} \text{ H}_2$).

pressures to allow efficient compression ratios [356,570]. There are usually significant variations in pressure across the plateau (sloping isotherms) as well as several other complications [358,572]. Using the desorption isotherms of the intermetallic alloys $\text{La}_{0.85}\text{Ce}_{0.15}\text{Ni}_5$ (Stage-1) and C14-Laves phase $\text{Ti}_{0.65}\text{Zr}_{0.35}(\text{Mn,Cr,Fe,Ni})_2$ (Stage-2), Yartys et al. [570] showed a two-stage operation achieving a H_2 compression ratio 74.6 from $P_L = 3.5$ bar over the temperature range from 20 to 130 °C. The specific roles and impacts of other factors related to engineering have been described [358,570] to optimize for specific applications. Recent activities are on the materials development [562,573–579], engineering design [574,578,580–589], performance assessments [574,578,589–593], and demonstration [556,578,580,581,584,588] of MH hydrogen compressors over a range of pressures and operating conditions with some publications [578,589,593,594] including the evaluation of their commercialization. A detailed review considering materials, design, system integration aspects and operation of MH compressors with gas-gap heat switches for space applications has been recently published by Bowman [595].

MH compressors are heat engines and their efficiency is low, being limited by Carnot efficiency in a narrow temperature range [358]. Their use is especially beneficial to those applications where efficiency is not critical but safety, reliability and simplicity of operation are; examples include isotope handling, space flight missions, and thermally driven actuators and prototypes [352,557,595]. As stated above, utilization of waste industrial heat for H_2 compression makes large-scale MHCs very promising in industries where this is available. Development of industrial-scale MH compressors is the focus of R&D activities of a number of teams; see Fig. 26 and Table 3.

Apart from proper selection of MH materials with high dissociation pressures [576–578], MHCs have several engineering challenges. In particular, minimising void space to avoid the loss of productivity at high pressure, effective heat exchange between the MH and the heating/cooling fluid, minimising heat losses during periodic heating/cooling of the MH material and H_2 gas containment at operating pressures >500 bar. Effective heat exchange for compressors has been explored with suitable external and internal designs and multiphysics modelling [583,584].

Meeting the challenge of heat management and minimising void space is the focus of a recent prototype MHC system within a US DoE funded project led by Sandia National Laboratories (SNL) [578]. A two-stage prototype MH compressor, providing H_2 compression from 150 to 875 bar with a productivity of 0.15 kg/h using periodic oil heating/cooling in the temperature range from 20



Fig. 26. Top – HYMEHC-10 MHC (HYSTORSYS AS, # 1 in Table 1). Bottom – SAIAMC/UWC MHC (# 3 in Table 3).

to 150 °C, was designed and modelled [578]. Seven alloy candidates for the two stages were selected and test samples were procured for initial volumetric characterization of their hydrogen absorption and desorption behaviour at pressures up to 1000 bar [578]. The AB_2 alloy $\text{TiCrMn}_{0.7}\text{Fe}_{0.2}\text{V}_{0.1}$ was selected for the first-stage hydride to operate from 20 to 150 °C, over a pressure range from a maximum $P_L \sim 150$ bar to $P_H > 450$ bar during desorption. For the second stage, another AB_2 alloy $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{Fe}_{1.6}\text{V}_{0.4}$ was chosen. Based upon its isotherm measurements, this hydride can operate from P_L of >400 bar at a T_L of ~ 20 °C and produce $P_H > 875$ bar at T_H of 150 °C.

All of the components for the prototype hydride beds have been fabricated and a demonstration compressor is currently being assembled at SNL for performance testing scheduled to start during late 2019 in a dedicated high-pressure facility [578]. Stage-1

Table 3
Overview of industrial-scale metal hydride hydrogen compressors developed within last 5 years.

#	Manufacturer (type), country	P_L [bar]	P_H [bar]	Productivity [Nm^3/h]	Number of stages (types of MH material)	T_L [$^\circ\text{C}$]	Cooling medium	T_H [$^\circ\text{C}$]	Heating medium	References
1	HYSTORSYS AS (HYMEHC-10), Norway	10	200	10	2 (1: AB_5 ; 2: AB_2)	15	oil	160	oil	[578, 582]
2	HYSTORSYS AS (HYMEHC-5), Norway	5	200	5	2 (1: AB_5 ; 2: AB_2)	16	oil	200	oil	this work
3	SAIAMC/UWC, South Africa	3	200	5	3 (1,2: AB_5 ; 3: AB_2)	20	water	150	steam	[588]
4	HySA Systems/UWC, South Africa	50	200	up to 13	1 (AB_2)	20	water	130	steam	[556,580,588]
5	HYSTORE Technologies Ltd./Cyprus	7	220	up to 2.5	6 (1: AB_5 ; 2–6: AB_2)	10	water	80	water	[584]
6	Special Design Engineering Bureau in Electrochemistry with Experimental Factory/Russia	2–5	150–160	up to 15	2 (AB_5)	15–20	oil	150–160	oil	[581,591]

contains 25 kg of the low-pressure alloy and stage-2 has 21.7 kg of the high-pressure alloy. Fig. 27 shows design of the MH beds and MH containers. In order to enhance the thermal performance of the compressor design, configurations were numerically examined. The optimal design, which also allowed for filling and assembly of these beds with processed alloy powder in thermally enhanced compacts, was based on internal helical coil design configuration, with minimal free volumes within the hydride filled beds, to increase the pressurization and delivery efficiencies of H_2 desorbed at pressures >800 bar.

Another solution implemented by HySA Systems and its industrial partner, TF Design (South Africa), used a composite MH container (carbon fibre wound stainless steel liner which comprises a MH cartridge) designed for the conditions of hydrogen compression applications (see Fig. 28). This provides H_2 compression from 100 to 500 bar in the temperature range of 20–150 $^\circ\text{C}$ with dynamic performance where the low pressure H_2 absorption/high pressure H_2 desorption completes in 5–10 min [356].

As discussed above, future developments of MH hydrogen compressors will mainly address the problem of achieving high, up to 500–1000 bar, hydrogen pressures with a reasonable productivity when operating over a narrow (20–150 $^\circ\text{C}$) temperature range. Furthermore, the number of hydrogen compression stages should be minimised to avoid a drop in the energy efficiency [358].

Mostly, solution of these problems is related to engineering issues. However, the problems of optimization of MH materials for hydrogen compression are also very important since the engineering solutions are strictly bound to the material's properties.

Generally, future activities in MH materials for hydrogen compression are expected to be similar to the ones for hydrogen storage materials outlined above in this section. They include development of hydride forming alloys (compositions and manufacturing routes) characterised by (i) well-matched operating pressure and temperature ranges, (ii) high reversible hydrogen sorption capacities at the operating pressure–temperature conditions, (iii) minimum plateau slope and hysteresis, (iv) fast kinetics of low-pressure hydrogen absorption and high pressure H_2 desorption. Additional target parameters important for H_2 compression include (v) high cycle stability during the extensive H_2 absorption and desorption implicit with these devices and (vi) minimal volume decrease upon dehydrogenation – the latter property is particularly important for high pressure hydrogen compression by allowing an increase of the MH filling density to minimise “dead space” formation within the MH containers during the hydrogen compression process.

12. Summary and future prospects

This review summarizes the work performed under the umbrella of IEA Hydrogen Task 32 “Hydrogen-based energy storage” during 2013–2018, providing the most up-to-date research results and ideas from leading experts in the field, which is the basis for

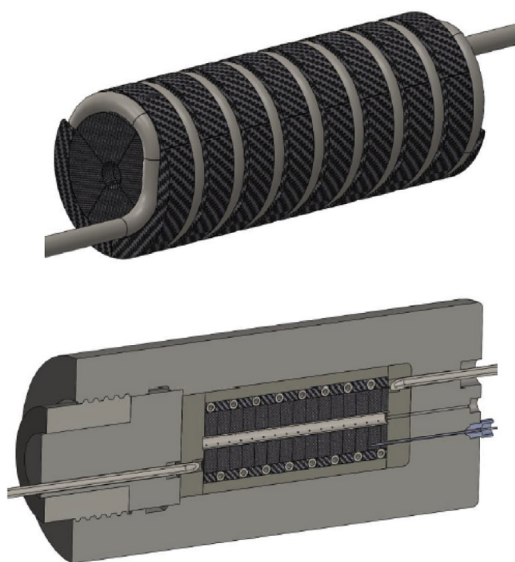


Fig. 27. Design of metal hydride bed and container for up to 875 bar H_2 compression prototype of the Sandia Project (USA) [578]. Pre-compressed pellets consisting of a mixture of MH material with expanded natural graphite (ENG) are loaded in/around the helical coil and gas distribution tube within the Teflon liner.

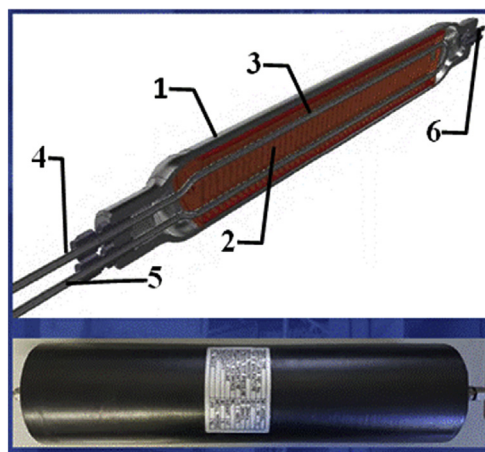


Fig. 28. Composite MH container for 100–500 bar H_2 compression developed by HySA Systems and TF Design (South Africa). Top – stainless steel liner (1) with a finned cartridge (2) filled with powdered mixture of AB_2 -type MH and ENG and equipped with heating/cooling tube (3–5); (6) – H_2 input/output pipeline. Bottom – carbon fibre wound container.

ongoing research and development in this exciting field. Each section gives an insight into the latest results and aspects on research for “hydrogen-based energy storage”.

For many decades, hydrogen interactions with materials and hydrogen storage in solids were mainly of fundamental scientific interest, with some exceptions such as MH batteries at the end of the 1990s. Beginning with the 21st century the need became more urgent to convert individual transportation from internal combustion engines to emission-free FC vehicles. Hydrogen storage research was therefore driven by the goal to find a safe and efficient storage method fulfilling the strict requirements of the automotive industry concerning weight and volume. However, with the ongoing increase in renewable energy replacing more and more fossil fuels power plants, there has been increasing interest in hydrogen for chemical storage and as an energy carrier since 2010.

During this renaissance of hydrogen technologies, the spectrum of areas and topics covered within Task 32 widened compared to previous tasks on hydrogen storage in solids. Totally new areas, e.g. complex hydrides as solid-state electrolytes for novel lithium-ion batteries or heat storage in high-temperature hydrides for solar-thermal plants were initiated by experts in Task 32. Recently, liquid carriers and ammonia came back into focus for hydrogen transport in large quantities over long distances.

For hydrogen storage by physisorption, new framework materials have been developed possessing a high porosity and extremely large inner surface areas. The gravimetric hydrogen storage capacity of these novel frameworks can exceed 15 wt% on a material basis at 77 K and pressures of 50 bar. In the coming years, hydrogen storage in porous materials will focus on improving volumetric and working capacity, operating temperature, and thermal conductivity. The volumetric capacity will be increased by using interpenetrated framework structures that offer more surface area per volume, by compacting powders and preparing monoliths. Increasing the binding energies by tailoring pore volume and chemistry will raise the operating temperature. New materials, including flexible and core-shell MOFs, and porous molecular solids, such as organic cage compounds, will be investigated to optimize working capacity. Thermal conductivity will be improved by designing heat exchangers, such as fins or foams, compaction and mixing with graphite. The aim is a reversible, mobile or stationary energy-storage system with fast kinetics for power-to-hydrogen applications.

Substantial research efforts are being conducted to investigate new approaches towards the chemically based liquid hydrogen carriers. Currently, the two most prominent directions of work are focused on organic liquids containing molecules that can reversibly release and take up hydrogen, and the production of ammonia, which can be transported and stored and later cleaved back to hydrogen and nitrogen.

The chemistry of hydrogen is also very diverse, and hydrogen creates a variety of different types of chemical interactions and bonds, forming compounds with most other elements in the Periodic Table, including new varieties of compounds and solids which have been explored in the past half-decade and described in Section 4. Detailed analysis of intermetallic hydrides reveals their crystal chemistry and electronic, magnetic and hydrogen storage related properties. Sections 9 and 11 demonstrated that use of interstitial hydrides can achieve high volumetric and gravimetric H densities, and that they have excellent performance in MH batteries, in hydrogen stores utilized in hydrogen driven forklifts as well as in hydrogen gas compressors providing output pressures from 100 bar to 800 bar. Recently, alloys consisting of four or five metals have received significant focus as their higher entropy influences hydrogen release and uptake properties as discussed in Section 6. Although their volumetric hydrogen densities are high, the

gravimetric densities are similar to conventional crystalline phases. However, this class of materials has a promising high stability over thousands of cycles of hydrogen release and uptake at moderate conditions, which is a very desirable trait for many applications. Further research efforts are envisaged to identify alloys offering enhanced H capacities exceeding $H/Me = 2$ and revealing the bonding mechanism of the metal-hydrogen interactions.

Magnesium-based materials have been considered for several decades and in the past few years researchers have provided Mg-containing systems with further improved kinetics of hydrogen release and uptake at more moderate working temperatures, which was covered in Section 7. Interestingly, magnesium-based systems are also considered for the concentrated solar thermal energy storage systems described in Section 10. Furthermore, Mg-based materials are utilized commercially for stationary hydrogen storage systems.

Hydrogen also forms covalent bonds to other elements, e.g. boron, aluminum and nitrogen. This behaviour has led to a very large diversity of novel materials with fascinating structures, compositions and physical and chemical properties, denoted complex hydrides. These materials often have both very high gravimetric and volumetric hydrogen densities, but reversible hydrogen release and uptake is very challenging to achieve. However, continuous improvement of the properties of reactive hydride composites has now led to a catalyzed $2LiBH_4$ - MgH_2 composite, which has very promising properties. Higher borate anions, with higher thermal stability, such as closo-borates, have for a long time been considered as unwanted byproducts obtained during dehydrogenation. However, the closo-borates are now being utilized for design and synthesis of novel battery materials, such as electrolytes, owing to their relatively weak coordination to cations and dynamic disorder, which is often observed in high temperature polymorphs. Thus, complex hydrides are shown in Section 9 to have attractive properties for new applications in electrochemical storage as well as hydrogen storage. Recent progress in the design and synthesis of novel materials has opened new routes to solid state batteries and a significant potential for electrochemical energy storage.

Fundamental studies will further focus on nanostructured metal hydrides and will follow the approach described in Section 8. Within the next years, the goal is to achieve an experimental determination of the excess enthalpy and entropy associated with interfaces for a set of magnesium-based nanomaterials with different microstructural scales and compositions, in the search for a material, in which a significant enthalpic destabilization is not counteracted by entropic effects. In addition, we plan to explore the concept of elastic destabilization in nanostructures with an intermediate size range to exploit the power of long-range stress fields. Success in these research areas would promote the development of lightweight hydrides with lower desorption temperature at ambient hydrogen pressure and improved cyclic stability.

After many years of thorough research work and characterization of metal hydrides for heat storage applications, the next step towards commercialization is the up-scaling of these systems for heat storage. The Max-Planck-Institut in Mülheim an der Ruhr recently started a demonstration project together with other partners from academia and industry (IUTA Duisburg, Westphalian University of Applied Sciences, Gelsenkirchen, Martin Busch & Sohn GmbH, Schermbeck). The aim of the project is the storage of 250 kWh heat at a temperature level around 350 °C with an amount of roughly 400 kg of Mg/ MgH_2 . Easy handling of the storage material, a simple storage tank construction with the option for further enlargement and the operation of the system under changing conditions will be demonstrated during the project. Researchers at Western Australia's Curtin University are collaborating with TEXEL

and ITP Thermal for the development of an innovative thermal battery which will be a key component in allowing solar power systems to produce electricity overnight – a breakthrough which could allow solar systems to be used as a viable alternative to fossil fuels in commercial and heavy industries around the world. The research aims to develop new technology to integrate thermo-chemical energy storage via a thermal battery into a dish-Stirling system.

In 2019 the IEA recognized hydrogen as a key part of a clean and secure energy future and presented recommendations on “The Future of Hydrogen” to the G20 in Japan in June [596]. On this exciting pathway to a new, renewable energy economy, the work achieved in Task 32 is continued in Task 40 “Energy storage and conversion based on hydrogen” via eight working groups, focusing on porous materials for hydrogen storage, magnesium- and inter-metallic alloys-based hydrides for energy storage, complex hydrides, ammonia and reversible liquid hydrogen carriers, catalysis, electrochemical storage of energy, hydride-based thermal energy storage, and research and development for hydrogen storage and compression.

In the present paper, we have reviewed the recent assessments on properties of a broad group of hydrogen storage materials, H storage methods and hydrogen-material interactions. Our vision is that for a sustainable energy future, hydrogen will most likely have a prominent status as an energy carrier since it has the highest energy density among all known substances, and can be readily produced from water via several processes including renewable sources [597]. Thus, an energy system based on hydrogen may have just as few steps in the chain as the presently-used methods based on fossil fuels, i.e. production of the energy carrier, storage and transportation and then a variety of possible utilizations. Importantly, hydrogen has the fastest dispersion rate in air [598], which can contribute to the safety aspects of its use in case of a leak with appropriate ventilation considerations.

In conclusion, we have presented different, safe and efficient storage methods for the future energy carrier hydrogen, which are very promising. However, prior to application they still need improvement and optimization requiring further research and development. The ultimate goal is to discover a sustainable replacement for liquid fossil fuels for transportation, for which a U.S. Department of Energy advisory group has indicated that more than 20 properties need to be simultaneously optimized [599]. This is clearly a very challenging task. However, this review reveals that fundamental science and engineering are making headway towards solving this task. Furthermore, new moderate to large scale demonstration projects are underway in 2019. For example, the HyCARE (Hydrogen CArrier for Renewable Energy Storage) project [600] aims at developing a hydrogen storage tank with a 50 kg hydrogen storage capacity through use of a metal hydride by linking hydrogen and heat storage to improve energy efficiency and to reduce the footprint of the complete system. This storage tank will be connected to a 20 kW Proton Exchange Membrane (PEM) electrolyzer as the hydrogen provider and a 10 kW PEM fuel cell as the hydrogen user. While metal hydrides have been utilized for fuel storage on-board submarines for nearly 20 years [356,554], several storage methods were recently assessed for various types of inland maritime vessels [601] and different options were proposed depending upon operating scenarios. Hence, the scope of applications utilizing hydrogen storage in different forms continues to expand.

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.

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