doi:10.20944/preprints202106.0617.v1

Solid-state hydrogen storage: materials, systems and the relevance of a gender perspective

Erika Michela Dematteis,[a)*] Jussara Barale,[a)] Marta Corno,[a)] Alessandro Sciullo,[b)] Marcello Baricco,[a)] Paola Rizzi[a)]

[a)] Department of Chemistry and NIS - INSTM, University of Turin, Via Pietro Giuria 7, 10125 Torino, Italy

[b)] Department of Culture, Politics and Society, University of Turin, Lungo Dora Siena 100, 10153, Torino, Italy

*Corresponding author

Erika Michela Dematteis

E-mail address: erikamichela.dematteis@unito.it

Keywords: energy transition, hydrogen, hydrogen storage, metal hydride, complex hydride, hydrogen tank, social impact, gender

Abstract

This paper aims at addressing the exploitation of solid-state carriers for hydrogen storage, with attention paid both to the technical aspects, through a wide review of the available integrated systems, and to the social aspects, through a preliminary overview of the connected impacts from a gender perspective.

As for the technical perspective, carriers to be used for solid-state hydrogen storage for various applications can be classified into two classes: metal and complex hydrides. Related crystal structures and corresponding hydrogen sorption properties are reviewed and discussed. Fundamentals of thermodynamics of hydrogen sorption evidences the key role of the enthalpy of reaction, which determines the operating conditions (i.e. temperatures and pressures). In addition, it rules the heat to be removed from the tank during hydrogen absorption and to be delivered to the tank during hydrogen desorption. Suitable values for the enthalpy of hydrogen sorption reaction for operating conditions close to ambient (i.e. room temperature and 1-10 bar of hydrogen) are close to 30 $kJ{\cdot}mol_{H2}^{-1}$. The kinetics of hydrogen sorption reaction is strongly related to the microstructure and to the morphology (i.e. loose powder or pellets) of the carriers. Usually, kinetics of hydrogen sorption reaction is rather fast, and the thermal management of the tank is the rate determining step of the processes.

As for the social perspective, various scenarios for the applications in different socio-economic contexts of solid-state hydrogen storage technologies are described. As it occurs with the exploitation of other renewables innovative technologies, a wide consideration of the social factors connected to these processes is needed to assess the extent to which a specific innovation might produce positive or negative impacts in the recipient socio-economic system and to explore the potential role of the social components and dynamics in fostering the diffusion of the innovation itself. Attention has been addressed to the gender perspective, in view of the enhancement of hydrogen-related energy storage systems, intended both in terms of the role of women in triggering

the exploitation of hydrogen-based storage as well as to the impact of this innovation in their current conditions, at work and in daily life.

Summary

Introduction

According to the analysis performed by the International Energy Association,[1] the electricity consumption per capita increased significantly in last thirty years. At the global level, it changed from 2.06 MWh/capita in 1990 up to 3.26 MWh/capita in 2018, with an increase of 58%. This indicator is very different considering different areas, as evidenced from the comparison of the electricity consumption in 2018 in Europe (3.26 MWh/capita) and in Africa (0.57 MWh/capita).[1] On the other hands, thanks to the significant introduction of renewable energies, the CO_2 production per capita increased much less at the global level (i.e. 14%), changing from 3.88 tCO_2/capita in 1990 to 4.42 tCO_2/capita in 2018. Even in this case, the values are very different comparing data for 2018 in Europe (5.72 tCO_2/capita) and in Africa (0.98 tCO_2/capita).[1] It is worth noting that, considering the values of the same indicator in 1990, a significant decrease has been obtained in Europe (-29%), whereas it increased in Africa (+15%), as it can be observed in **Figure 1**. The decreased CO_2 emission in Europe can be correlated to an increment of renewable energy production over the last 20 years that replaced the production of electricity by non-renewable sources. Though, increased emissions in Africa are mainly related to the increased production of electricity using non-renewable sources, even if a significative increment in renewables electricity production has been implemented moving from 326 GWh produced in 1990 to 28286 GWh in 2018.[1]

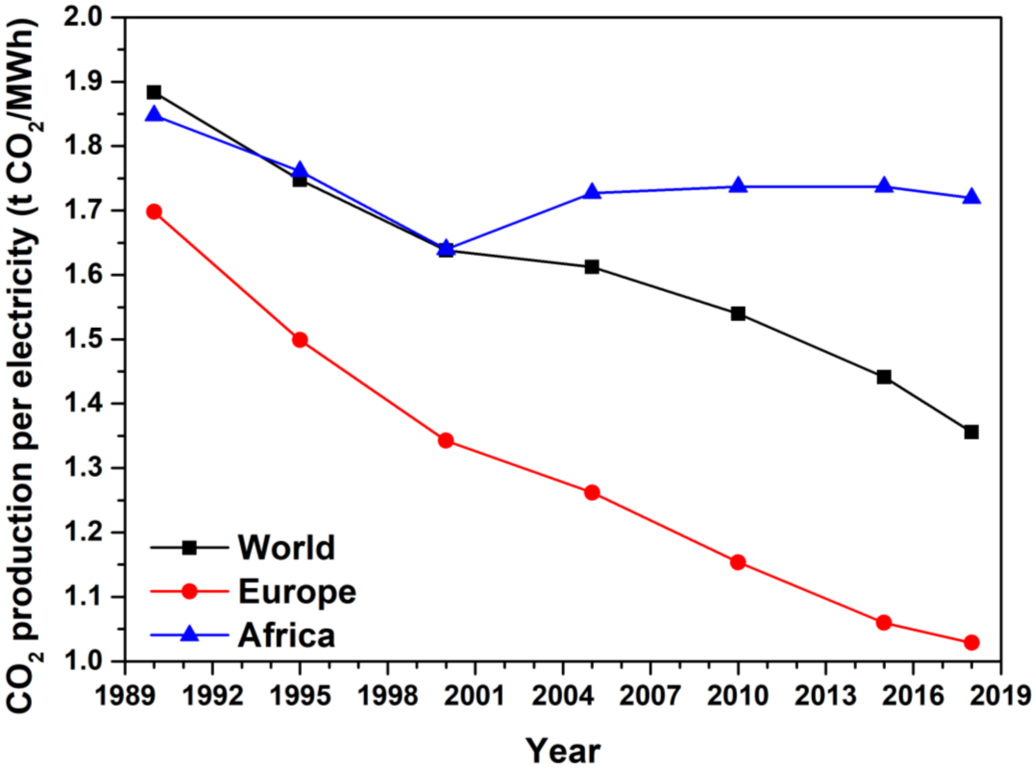

Figure 1 - CO_2 produced per electricity consumed in the World, Europe and Africa.[1]

These trends underline the need of implementation of renewable energy production in areas that can benefit on increased green energy production while decreasing CO_2 emissions. In fact, to get rid of pollution and global temperature increase, it is fundamental to look for alternative to fossil fuels. The Paris Agreement aims at holding the increase in global average temperature below 2 °C above the pre-industrial levels.[2] The Clean Energy for all Europeans Package (CEP) represents the response of the European Union to the Paris Agreement and its purpose is to drive European Union towards a complete de-carbonization within 2050.[3] This ambitious goals provide for: (i) enhancement of efficiency in all energy-consuming applications, especially in the building sector, (ii) enhancement of the security of energetic supply, (iii) help for the integration of renewable energy sources (RES). CEP updates the energetic objectives for 2030 (the Climate and Energy Package of 2009 set the so-called “20-20-20” energy targets) and defines the 2050 goals.

The turning point for renewables exploitation (e.g wind, solar, water..) can be reached only through the efficeint storage of their energy. In fact, renewable energies are highly considered for the distributed production of energy, but their fluctuations in time and geography call for the use of energy storage systems that can deliver energy when needed. The development of good, clean and efficient materials for energy storage is the bottleneck for using only renewable energies, instead of fossil fuels.[4] It is therefore important to design integrated systems at the large scale that allow storing excess energy to meet future demand and utilisation at another place or time. The phasing-out of the fossil fuels cannot be solved by a single technology but must involve the development of different approaches, which could offer economic and environmental benefits and cover any requirements concerning application, cost and footprint, so considering all its life cycle assessment.

At present, the storage facilities that do exist use pumped hydropower,[5] a system that pumps water uphill to a reservoir when excess electricity is available and then lets the water flow downhill through turbines to generate electricity when it is needed. However, it can be only located in very limited areas. Developing new energy storage technologies that are comparable in reliability and cost to pumped hydropower, and that are deployable at any location, could enable the storage of vast amounts of electricity anywhere on the grid worldwide and would enable the increased use of renewable electricity generation while maintaining high reliability in electric supply. A continuous flow of clean energy can be obtained with the development of smart grids connected with different energy storage systems, such as batteries or heat storage systems.

One of the best options for the storage is the production of green hydrogen from water. In fact, electricity excess can be exploited to produce hydrogen to be used in various applications and in different periods, for example in power production to satisfy domestic or multiple users.

For this reason, the paper aims at providing an overview of the opportunities and the challenges to be addressed for the available hydrogen-based solutions to become key technologies and boost energy transition improving energy storage efficiency and smart grids.

Although it is mostly focused on technical aspects, the ambition is to shade a light also on social aspects that the scientific literature (and the experience) suggests always to consider when dealing with innovation processes. It is widely recognized in fact that in order for innovation to be able to produce a systemic change and exploit all its potential, in order for it to 'get out from the niche' and become the normality, it has to be addressed as a socio-technical innovation, that is to consider the many social, economic, regulatory, cultural aspects that characterize the system within which the innovation is expected to spread[183]. Therefore, the ambition is to grasp the impacts of innovation on the wider communities and different social groups (passive perspective) and to take advantage of the social dynamics as a potential catalyser of innovation diffusion and acceptance (active perspective).

Therefore, the paper firstly gives an overview of hydrogen-based technologies for energy storage, considering the social aspects related to the spread of this solutions on the energy transition from a gender perspective. Then, the paper focuses on available materials for solid state hydrogen storage in alloys and inorganic materials and presenting examples of applications of hydrides for hydrogen storage in integrated systems available at the lab-scale (units of kilos of hydrogen stored) and at the industrial scale (tens of kilos of hydrogen stored). Larger amount of hydrogen storage at the large scale (tons of hydrogen) have not been developed at the solid state yet, and examples of large scale storage are mainly realised at the liquid state or as compressed gas in tanks or underground empty cavities for seasonal storage. Finally, some provisional remarks about how the gender persepctive relate to hydrogen-based tecnhologies is provided.

Hydrogen-based solutions for energy storage

The hydrogen cycle from renewables is completely CO_2-free and water is the only by-product.[6] The energy storage can be obtained using hydrogen (H_2) that is a secondary energy vector, which shows several advantages: it can be produced from other primary energy sources, resulting unlimited, it can be stored for a long period of time, and its storage is a key enabling technology for the advancement of hydrogen and fuel cell technologies in applications including stationary power, portable power, and transportation.[7,8] Moreover, the interest of hydrogen as an energy vector is due to its highly exothermic reaction with oxygen to produce only water. Compared to fossil fuels, 1 kg of H_2 has the same energy as 2.4 kg of CH_4 or 2.8 kg of gasoline. This means that hydrogen has a higher energy-to-weight ratio compared to other fuels. On the other hand, for the energy-to-volume ratio, the situation is inverted. Liquid hydrogen has 8.5 MJL^{-1} against 32.6 MJL^{-1} of gasoline.[9] This is a drawback for hydrogen storage, because a much higher volume of hydrogen is required to have the same amount of energy provided by most of fossil fuels. The aim of hydrogen storage research is to overcome this problem, increasing energy density to limit systems volume.

Conventionally, H_2 is stored as compressed gas or liquid. It requires significant energy consumption to reach hyperbaric pressures and cryogenic temperatures, resulting non-economically advantageous. On the contrary, the use of hydrogen carriers is a promising solution, since they allow storing H_2 at low pressure and close to room temperature, achieving large volumetric densities compared to compressed or liquid hydrogen. Considering a generic hydrogenation reaction of an intermetallic compound (M) to form the corresponding hydride (MH): $M + x/2\ H_2 \leftrightarrows MH_x$, the thermodynamic of the equilibrium is characterized by the interrelation between H_2 equilibrium pressure (P_{eq}), its concentration (C) in the carrier and temperature (T), which is described in PCT-diagrams. The P_{eq} is given as a function of temperature by the Van't Hoff equation, $P_{eq}=\Delta H/RT-\Delta S/R$, where ΔH and ΔS are the standard enthalpy and entropy of the reaction, respectively, and R is the gas constant. The kinetic properties of H_2 sorption reactions determine the rate at which a practical handling can be realized in the material. Moreover, handling hydrogen as hydride results to be safer than liquid and compressed gas. In addition, the environmental impact evaluation, through a Life Cycle Analysis (LCA), of the use of solid-state carriers in a tank has demonstrated that the environment impact could be limited with respect to other H_2-storage technologies.[10,11]

The energy produced by a renewable source (e.g. sun and wind) is used to produce H_2 from water through an electrolyser. The gas is then stored in the designed tank using a carrier. A heat storage system allows to collect solar heat, which can be used during the desorption event to release hydrogen from the MH. Finally, the released green H_2 supplies a fuel cell (FC) producing electricity to refill electric vehicles or feed stationary fuel cells for on demand electricity production, in order to meet the needs of end users (either prosumers or energy communities). The flows of hydrogen, heat and electricity during the hydrogen production and use are described in **Figure 2**, **a** and **b**, respectively.

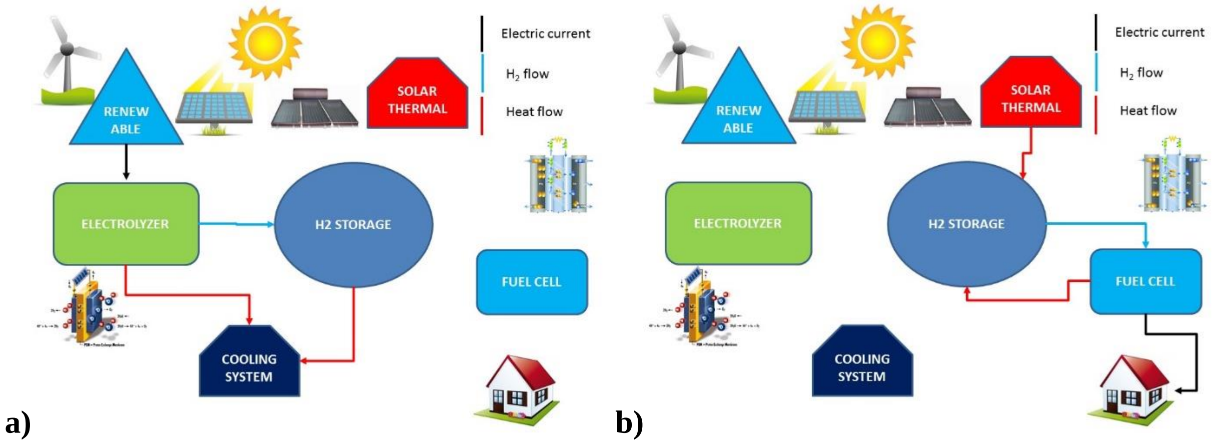

Figure 2 - Flow of hydrogen, heat and electricity during the hydrogen production (a) and use (b).

Considering bottlenecks in energy storage systems, potential technological applications using hydrogen as a carrier in a MH-based system are expected to provide practical operation conditions at pressures below 50 bar and temperatures below 120 °C, including the solar thermal energy contribution to the management of the hydrogen storage system. The main drawback in using MH that operate close to ambient temperature and pressure for hydrogen handling is the gravimetric capacity, being made of transition metals (e.g. 1.3 wt.% hydrogen for $LaNi_5$). Achieving hydrogen capacity close to 2 wt.% at mild pressure and temperature conditions is important also for stationary applications, because it lowers the cost of MH per kg H_2. For these reasons, it is necessary the definition and design of innovative green hydrogen (i.e. produced by non-programmable renewable sources) storage systems, aimed at small-scale users in the civil sector (vehicles, individual houses, condominiums, etc.).

In order to allow an even more intense exploitation of non-programmable renewable sources (sun and wind) in the electricity generation system, it is of fundamental importance to develop distributed generation and end-users must be encouraged to install energy production systems equipped with energy storage thus becoming prosumers.

As for the end users, it is worth to higlight that prosumers (both as individual housholds and collective initiatives, such as energy coop and communities) have been gaining more and more relevance for the past 2 decades as a catalyzer for renewables technologies diffusion mainly triggered by the feed-in-tariffs incentives schemes in many EU countries.[12] Again, a major challenge that prosumers and energy communities have to face for being actually able to satisfy their own energy demand is the discontinuity of power production from RES. Therefore, hydrogen-related storage solution can play a crucial role in fostering their diffusion and development, thus making the national energy system able to exploit the funding and policy opportunities coming from the extraordinary convergence of the emergency funds provided by Next Gen EU and the policy framework resulting from the national transposition of th EU directives on Energy Market and Renewables.[13,14]

Therefore, electricity prosumers and energy communities indeed could be able in the near future to play a central role as an integral part of the electric system, for the spreading of hydrogen technologies and for the overall energy transition by reducing network losses, by encouraging the implementation of innovative technologies and by reducing pollutant emissions and energy import, thanks to energy self-production.

Basic and applied research and knowledge on new class of multifunctional materials will lead the way for the development of such flexible and efficient energy storage, the key to a reliable clean electricity supply as it will be resumed in the present paper, focusing on hydrogen storage technologies and the few examples of integrated solid-state hydrogen storage systems presented so far at the lab-scale and up to the storage of tens kilos of hydrogen (industrial scale).

Social aspects of energy transition: a gender perspective

Climate change is making our world overall less safe for the entire biosphere. Human beings (and human culture and societies) are at risk of being overwhelmed by this global process that they consistently contribute to trigger. Both the increase in the frequency and magnitude of catastrophic events and the negative trends in environmental assets, such as temperature, droughts and pollution might produce economic and social negative impacts, able to affect individuals and social groups, and therefore hamper and challenge the current social order. A changing climate therefore affects any living and human beings, but as for the most delicate natural ecosystems, it is the world's poorest and most vulnerable groups, such as the elderly, migrants, indigenous groups (and women and girls within these groups) who withstand the worst of environmental, economic, and social shocks. The reason why women and girls are more vulnerable to climate change, especially in the developing countries, is often socially constructed with women and girls predominantly responsible for food production, household management, water supply, and energy supply for heating and cooking. As climate change impacts increase, these tasks become more difficult and more time consuming[15–17]. But due to their role in organizing social life, women are at the same time at the forefront of the solutions of many of the societal concerns connected with energy transition. In developing as well as in developed countries, they are early adopters of climate-friendly agriculture and clean energy, and offer solutions and valuable insights into better managing climate risks.[18]

The centrality of women in the transition processes has entered the international policy agenda for sustainability. At the last United Nations Climate Change Conference (UNCCC), governments approved the Gender Action Plan (GAP), recognising the importance of involving men and women equally in climate action for an efficient and equal energy transition that will ensure human rights-based and gender-just implementation in the energy transition.[19] With the GAP, we have entered in a new era in which we must enable women leadership in decision-making at all level of society. By empowering women and girls, we can both address a right issue, and give ourselves a better

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 25 June 2021 doi:10.20944/preprints202106.0617.v1

chance to meet the sustainable development goals and the Paris agreement. In fact, in the 2015 Paris agreement, calls for gender equality and women's empowerment were clearly established.

The energy transition is an essential component of the climate action and there is a high need for the consideration of social aspects and dynamics as a crucial component of the transformation of energy systems. Not only from the passive perspective of the social risks connected to the transition process' impact and the ambition to reduce social problems such as energy security, energy poverty, gender gap but also, and even more, in terms of the relevance that the social factors (culture, values, education...) and dynamics (interaction, solidarity, imitation…) might play in fostering the transition process. Within this social turn in the transition research and policy design, the adoption of a gender perspective to investigate the processes at stake and to promote effective policies although highly underestimated has shown to have a great potential.

First of all, it has been evidenced that effectiveness of energy policies improves when gender is acknowledged, through the optimization of outcomes for all the actors involved in the energy system, as highlighted by some policy design approaches such as women in development, gender in development, transformative approach, intersectional approach and social justice.[20] Women roles in society equips them with an understanding of the cultural and community context, which is useful for introducing behavioural change with regard to energy consumption, starting from the household level.[21,22] Therefore, women empowerment in the energy transition through their enhanced inclusion in energy access and use and through the strengthening of their role in the energy chain and decision making processes, can play a decisive role for addressing the impacts of the sustainable transformation in energy systems on the social, cultural, economic and political contexts they are embedded in.[20] Nonetheless, for this involvement to be effective and sustainable, energy policies have to be properly implemented, allocations of time and resources between genders should be levered to further include women as participants of the entire energy supply chain, in order to support energy planners and consumers in making informed energy choices and to acknowledge and support women's livelihood priorities.[18,20] Taking into account gender roles and relations in energy policies design might trigger a shift towards energy justice in implementing availability, affordability, sustainability, intra- and inter-generational equity and responsibility in the development of energy system infrastructures.[20]

Secondly, when it comes to the already introduced prosumers exploitation, with energy consumers becoming energy producers for their self-consumption and the market, women role can bridge and play as agent of change in the whole energy system. As a matter of fact, women have a high potential in developing and implementing energy solutions locally. This can be mainly related to women different energy dynamics outlooks, decision-making areas, energy needs, responses to crises or coping mechanisms with respect to men, that lead to more inclusive prospective to energy technologies and services that match those dynamics.[20].

Third, the design and implementation of more sustainable ways to produce, distribute and consume energy affect gender equality if women are involved in the process, by hindering stereotypes, levering opportunity and access to education and culture, stimulating energy research to better understand and account for energy transitions, particularly around envisioning a more just transition along political, socio-ecological, economic, technical dimensions, and creating more democratic systems and processes.[23]

Therefore, the transition towards renewable energies, starting from their production till use, seems to be a unique opportunity to foster women empowerment and, the way around, involving women might play a role in fostering the transition process itself. Greater gender equality and equity in energy would result in social impacts that will lead to greater participation to the energy transition, beneficial and efficient management of energy resources at a lower climate impact level, more savings, more free time and lowering workloads. Furthermore, given the competences required to develop hydrogen-based solutions that go far beyond the mere technical-engineering and involve other hard sciences (e.g. chemistry, physics...) where women are relatively more represented, hydrogen can be a leverage for STEM women valorization. And, as a results, this valorization might trigger an increment in women technical skills and employment in technical role (STEM-related activities) . Finally, women role is crucial for spreading the green energy transition through communications at a family and local level, and creating networks and supporting mentorship (up to institutional level and policy making) with a new perspective to engender the energy transition.[24,25]. Summarizing, engendered energy policy might create therefore enabling conditions and opportunities for energy transition in general and, at a lower scale, might facilitate project design and implementation.[26]

As for the hydrogen-related storage solutions, the reciprocal influence between technical and social systems is evident if we consider how important is the general social acceptance of new technologies that should replace energy systems based on fossil fuel, a process that might be supported by women involvement. The social acceptance connected to a fair transition can be performed only including and empowering minorities in the transformative pathways and should include all gender perspectives towards the new energy regime.[27]

As a provisional conclusion, it seems clear that the involvement of women in the energy transition is crucial for the transition itself to be properly and fairly implemented. Because, given their role in organizing social life, women are likely to be more affected than men by the negative and positive impacts of the transition (especially in developing countries) and at the same time they can play as agent of energy transition. A woman’s prospective offers a more comprehensive perception of inequalities and power imbalances in the current energy transition.[28] As women take on more leadership roles can lead to addressing climate change by promoting a transition to renewable energy, redistributing power, with more balanced community and public control in the energy sector benefits and risks, and prioritize equity and justice with community ownership and distributed governance.[29]

Hydrides for energy storage

As introduced, the bottleneck towards an affordable and efficient storage of RES through hydrogen is related to the development of high-density hydrogen storage and integrated systems.

Hydrogen may be stored in pure metals or in inorganic compounds, forming metal and complex hydrides. In some cases, hydrogen is uptaken and released in solid solutions (e.g. ZrV_2), without changing the crystal structure of the compound, but only increasing the lattice parameters. On the contrary, some pure elements (e.g. Mg) and intermetallic compounds (e.g. $LaNi_5$) form a hydride phase upon hydrogen absorption.[30,31]

In the following a brief introduction on selected materials for solid-state hydrogen storage will be reported (i.e. pure metals, intemetallic compounds, complex hydrides) to introduce and discuss realised tanks or integrated system applications, that will be describe in the last section.

Pure metals

Considering pure metals, MgH_2 is an excellent material due to its high hydrogen storage capacity (i.e. volumetric H_2 density about 130 kg H_2 m^{-3} and gravimetric H_2 density around 7.6 wt.%).[32] According to available thermodynamic databases (ΔH = -75 kJ/mol_{H2} and ΔS = -130 $J/mol_{H2}/K$),[33] the equilibrium dehydrogenation temperature is high, around 297 °C under 1 bar of H_2 and the ab/desorption kinetics is undesirably slow. The presence of nanostructured materials, prepared by ball milling (BM), rapid solidification, sputtering and inert gas condensation, may have significant effects on the thermodynamics and kinetics of the hydrogenation/dehydrogenation reaction.

A number of techniques have been applied to improve the ab/desorption kinetics of MgH_2, for example by ball milling with different additives, e.g. transition metals (TM) and transition metal oxides (TMO).[34] Typically, 3d transition metals can play a catalytic role in hydrogen chemisorption, due to their d-electrons.[35] Moreover, transition metals may reduce the nucleation barrier, speeding up the formation of hydrides.[36] In addition, they were shown to affect the desorption kinetics, decreasing the activation energy for hydrogen sorption in MgH_2.[36] However, they do not change significantly the thermodynamic properties of MgH_2. A summary of Mg additives used to improve hydrogen sorption properties has been discussed by Baran *et al.*[37].

Another promising elemental metal hydride is aluminium hydride (AlH_3),[38] characterized by a theoretical gravimetric H_2 density of 10.1 wt.%. Hydrogen is bonded relatively weakly to Al and the enthalpy of dehydrogenation is close to 7 kJ mol $_{H2}^{-1}$, which imply a hydrogen release at ambient temperature. However, its dehydrogenation reaction is practically irreversible, because aluminium hydride cannot be formed by the direct reaction of aluminium metal and gaseous hydrogen, even at very high pressures. So, for real applications as hydrogen storage material, it is necessary to identify a reasonable route to regenerate it from aluminium.

Other hydrides of pure metals are characterized by extreme conditions for hydrogen sorption reactions (e.g. Li) or by very high costs (e.g. Pd).

Intermetallic compounds

A huge number of metal hydrides has been investigated,[39] and particularly interesting for hydrogen storage are hydrides based on intermetallic compounds A_2B, AB, AB_2 and AB_5. *A* is an element which forms stable hydrides (AH_x), like transition metals of the left side of the periodic table or a rare earth metal. On the contrary, *B* elements form unstable hydrides (BH_y), like transition metals of the right side of the periodic table. In this way the resulting hydride $A_mB_nH_z$ will have intermediate properties of the AH_x and BH_y.[33] The hydrides formed are called metallic hydrides, since the interaction between hydrogen and metals is based on metallic bond, with hydrogen that occupies interstitial sites. The number of available interstitial sites depend on the crystal structure of the compound, and they can be located in octahedral (O) and tetrahedral (T) interstitial sites in fcc-, hcp- and bcc-type structures. Examples of composition for intermetallic compounds of interest for H_2 storage are reported in **Table 1**.[33]

Table 1 – Examples of intermetallic hydrides for solid-state hydrogen storage.

Composition	***A***	***B***	***Compounds***
A_2B	Mg, Zr	Ni, Fe, Co	Mg_2Ni, Mg_2Co, Zr_2Fe
AB	Ti, Zr	Ni, Fe	TiNi, TiFe, ZrNi
AB_2	Zr, Ti, Y, La	V, Cr, Mn, Fe, Ni	$LaNi_2$, YNi_2, YMn_2, $ZrCr_2$, $ZrMn_2$, ZrV_2, $TiMn_2$
AB_3	La, Y, Mg	Ni, Co	$LaCo_3$, YNi_3, $LaMn_2Ni_9$
AB_5	Ca, La, Rare Earth	Ni, Cu, Co, Pt, Fe	$CaNi_5$, $LaNi_5$, $CeNi_5$, $LaCu_5$, $LaPt_5$, $LaFe_5$

AB compounds

ZrNi was the first hydride-forming compound discovered to display reversible hydrogen properties.[40] From that point, a huge variety of AB compounds has been studied, in particular Ti- and Zr- based. The most known AB compound for hydrogen storage application is the TiFe and its modifications, obtained by substituting Ti or Fe with other metals.[41] TiFe has a high potential for widespread use, since it stores H_2 at low pressure and temperature (e.g. 30-70 °C and 10-20 bar) and has a good cycle stability at low pressure.[42,43] Moreover, it is cheap, not toxic and raw materials are abundant.

TiFe Pressure-Composition-Temperature (PCT) diagram displays two consequent plateaux, related to the formation of the two hydrides (i.e. TiFeH and $TiFeH_2$). The cycle stability of the monohydride is good and it is reported around 0.6 H/M,[43] while the dihydride has a slope which increases with increasing cycles, negatively impacting on capacities and performances in real applications. A drawback of TiFe is its hard activation, which usually requires thermal cycling between room temperature and high temperatures (e.g. 400 °C) and/or high hydrogen pressures (≈ 100 bar),[43] resulting difficult and costly to be used in real applications. Different strategies have been investigated to overcome this problem, but also to tailor H_2 sorption properties. In this regard, Dematteis et al. recently reviewed the substitutional effects on hydrogenation properties of TiFe in ref.[41]. Another example of production and tailoring of intermetallics are mechanical treatments. A recent work by Bellosta von Colbe *et al.*[44] presents the industrial scale-up of a ball milling production of a Ti(Fe,Mn) alloy. The alloy after the synthesis does not require activation and display good cycle stability, compared to a commercial one prepared with melting techniques. Mnsubsituted TiFe-alloys (Ti(Fe_xMn_{1-x}) have been reported to display easy activation, no changes in gravimetric capacity until x = 0.70 and decreased plateau pressure, compared to TiFe, thanks to the increase in cell dimension due to the Mn substitution.[45] Even quaternary alloys can manifest improved hydrogenation properties, as in the case of Mn- and Cu-substitutions in $TiFe_{0.9}$.[46] It has been shown that Mn and Cu increase TiFe lattice parameter, decreasing the 1st plateau pressure. Cu stabilizes the monohydride, while it destabilizes the dihydride. Mn and Cu improve activation process in mild conditions, suggesting that Mn and Cu substituted TiFe alloys are good candidates for large-scale H_2 storage at low pressures.

AB_2 compounds

AB_2 compounds for hydrogen storage include usually Ti and/or Zr as A-type element, while B is a transition metal. Rare earth metals could also form AB_2 compounds, but because of their high cost, these compounds are not economically competitive compared to conventional ones.[47] AB_2 compounds have a crystal structure of Laves-phases. Three Laves phases are observed, i.e. a hexagonal $MgZn_2$-type (C14), cubic $MgCu_2$-type (C15) and hexagonal $MgNi_2$-type (C36).[48] Thanks to this type of structures, AB_2 compounds have the advantage to show high H_2 gravimetric capacity (up to about 2 H_2 wt.%). They also have a fast kinetics in absorption and desorption and show easy activation.[49] However, they do not show high resistance to gas impurities, because of possible reactions with constituent elements. Most of the applications based on AB_2 compounds are linked to mobile sector, and most of the composition are based on $TiMn_{2,}$[50] which has the hexagonal C14 Laves phase structure of $MgZn_2$. PCT curves of $TiMn_2$ are markedly sloped and the gravimetric capacity progressively decreases while cycling.[51] Moreover, $TiMn_2$-substitued alloys allow to decrease the plateau pressure of $TiMn_2$, which otherwise would not be suitable for hydrogen storage applications. In general, Zr substitutes Ti, while other transition metals are used for Mn substitutions. Relating to substituted element and hydrogen soprtion properties, it can be noticed that Cr, V, Zr and Ti-rich compositions helps in decreasing the hysteresis gap, Cu and Cr flatten the plateau pressure and Zr, V, Cr, Ni, and Fe act on equilibrium pressure.[49] Thanks to substitution of both Ti and Mn, a huge number of hydrides with high gravimetric capacity has been realized, with a wide range of thermodynamic properties.

AB_5 compounds

AB_5 compounds involves rare earth metals and transition metals and the most representative composition is $LaNi_5$,[52] which displays fast activation, high reversibility at low temperatures, fast kinetics, good resistance to gas impurities and quite good cycling stability.[39,47] Thanks to their excellent hydrogen sorption properties, AB_5 compounds are widely used for hydrogen storage applications, but they are based on Critical Raw Materials (i.e. rare earths).[53,54]

$LaNi_5$ has a hexagonal $CaCu_5$-type structure, space group *P6/mmm*, with a cell parameter *a* of 5.0615 Å and *c* of 3.9794 Å.[55] Upon hydrogenation, it forms $LaNi_5H_x$ hydrides (with x reported between $5<x<7$). $LaNi_5$ has a hydrogen volumetric capacity of 115 kgH_2m^{-3} and a maximum gravimetric capacity of 1.5 H_2 wt.%.,[56] PCT-curves display flat plateau and hysteresis is limited.[57] Activation is easy and fast and usually involves cycle of hydrogenation and dehydrogenation with pressures and temperatures lower than 100 bar and 100 °C, respectively.

Gravimetric capacity can be preserved upon cycling with the partial substitution of La with Ca, Ce, and Mm (Misch metal), and the partial substitution of Ni with Zn, Al. Both La and Ni can be substituted, generating a huge variety of hydrides. Example of La substitutes are Mm, Ce, Ca, Zr, Y, while of Ni are Fe, Al, Sn, Mn, Cr, Co, Cu. In general, substitution of B sites tends to decrease equilibrium pressure, while substitutions of A site increases it.[58] Substitutions helps also in limiting problems of degradations while cycling, linked to disproportionation, in which Ni tends to precipitate decreasing the H_2 storage capacity.[59] Substitution of Ni improves thermal resistance and helps in decreasing the degradation while cycling. Sharma *et al.*[60] found particularly interesting the Al, Co and Mn substitutions, which allow the formation of hydrides with a wide range of thermodynamic properties. Al decreases sensitively equilibrium pressure and increases cycle stability, forming stable hydrides. Increasing the Al content, the equilibrium pressure, and the gravimetric capacity decrease with temperature. A careful study on the effect of Al-substitutions in

$LaNi_5$ on thermodynamics of the hydrogen sorption reaction has been reported.[61] The possible sources of sloping plateaux have been described considering possible paraequilibrium effects.

Similar effects on the equilibrium pressure and cycle stability are detected for $LaNi_{5-x}Sn_x$ systems. Alloys with $0.2<x<0.4$ are particularly interesting for their fast absorption.[62] Increasing the amount of Sn, kinetics in absorption increases, decreasing that in desorption.

Concerning substitution of La, Ce tends to increase the equilibrium pressure.[63] In particular, a plateau pressure increase has been observed increasing the amount of Ce, resulting suitable for high-pressure hydrogen applications. Indeed, it is reported that for $CeNi_5$, no hydrogenation reaction occurs up to 10 MPa.[47] Ce also contributes in stabilizing the hydride while cycling, and the stabilization increases with Ce content.[63]

Complex Hydrides

Recently, attention has been focused on complex hydrides, which are interesting because of their light weight and their high number of hydrogen atoms per metal atom.[64] In general, they present a wide variety of compositions, and, as a result, the hydrogen storage properties may vary significantly. Complex hydrides can be described by the general chemical formula $A_xB_yH_z$. The A elements are mainly light elements of the first and second groups of the periodic table, which forms the cation. The B element could be aluminium, boron, nitrogen or a transition-metal, which, bonded to hydrogen, forms the anion. Examples are given by alanates $M(AlH_4)_n$, borohydrides $M(BH_4)_n$, amides $M(NH_2)_n$ and imides $M(NH)_n$, with M = Li, Na, K, Mg, Ca and n=1, 2. The complex hydrides anions present very attractive hydrogen storage properties for mobile and portable applications, especially if they are combined with a low-atomic-weight cations, such as Li, Na, or Mg.

As an example, another strategy to taylor thermodynamic stability of MgH_2 is to synthetize new storage materials that results in the formation of complex metal hydrides, instead of using the transition metal as additive (MgH_2-TM),[33] such as in the case of MgH_2 mixed with Ni to form Mg_2NiH_4, with a theoretical hydrogen content equal to 3.6 wt.%. Combining Mg with TMs, forming ternary, $Mg_2TM_xH_y$, (e.g. Mg_2NiH_4)[65] or quaternary, $Mg_2TM_xTM'_{1-x}H_y$ (e.g. $Mg_2(FeH_6)_x(CoH_5)_{(1-x)}$ with $0.1 \leq x < \leq 0.9$)[66] hydrides, in which TM-H forms complex anions $[TMH_y]^{n-}$, stabilized by Mg cations, Mg^{2+}. The so-called Reactive Hydride Composites (RHC), for example, allows mixtures of metal hydrides and borohydride to release hydrogen in a reversible manner under moderate temperature and hydrogen pressure conditions.[67]

These complex metal hydrides typically have higher hydrogen gravimetric storage capacities and volumetric densities than metal hydrides. A maximum value of 150 kg m^{-3} has been reported for Mg_2FeH_6 and $Al(BH_4)_3$. The gravimetric density is also larger than that found in metal hydrides (e.g. from 5.5 wt.% for Mg_2FeH_6 and Mg_3MnH_7, up to 18 wt.% for $LiBH_4$).[64]

Low-weight complex hydrides include alanates $[AlH_4]^-$, amides $[NH_2]^-$, imides $[NH_4]^-$, and borohydrides $[BH_4]^-$. However, they have issues with poor reversibility and high stability, decomposing only at elevated temperatures.

Nevertheless, owing to their multi-functionality and fine compositional tailoring, complex hydrides have been considered for a vast variety of energy storage applications such as solid-state hydrogen storage, solid-state electrolyte, thermal energy storage, catalysis.[68–74] In the following, a brief description on selected complex hydrides classes will be reported (i.e. alanates, borohydrides, amides and imides) to introduce and discuss the realised applications, that will be describe in the last section.

Alanates

Alanates are composed of a complex anion $[AlH_4]^-$ or $[AlH_6]^{3-}$ and respective cation, which are salt-like, insulating materials. Depending on the metal cation, theoretical gravimetric capacity are equal to 10.5 wt.% for $LiAlH_4$, 5.5 wt.% for $NaAlH_4$, 5.7 wt.% for $KAlH_4$, 9.3 wt.% for $Mg(AlH_4)_2$.[75] The usable capacity however can differ significantly, depending on the thermodynamics of the material and working conditions. Alanates desorb hydrogen through chemical decomposition, the process begins with melting of the hydride, followed by the formation of an intermediate trialkali metal hexahydroaluminate (M_3AlH_6).[76]

Their decomposition temperature can be reduced to room temperature using metal catalysts, such as Ti or Ce.[77,78] Kinetics, thermodynamic and cycling properties of alanates can be tailored through the variation of particle sizes, addition of catalysts (dopants) and doping procedures, as in the case of $NaAlH_4$ (3.7 wt.%) and Ti-doped $NaAlH_4$ (3.0 wt.%).[77–79] Catalysed system involving sodium alanate has been considered from a long time. Sandrock *et al*. studied two materials: one mechanically milled with the liquid alkoxides $Ti(OBu^n)_4$ and $Zr(OPr^i)_4$ and one milled with dry $TiCl_3$ as catalyst precursors.[80] The alkoxide-catalysed materials had low reversible capacities and released hydrocarbon impurities during discharge, which is avoided in the case of $TiCl_3$ catalysis.[80] Besides Ti and Ce doping, or more generally metal halides doping, C-based materials (i.e. pure carbon, carbon nanotubes, nanofibres, graphitic nanofibres, single- and multi-walled carbon nanotubes) have been tested as catalysts, as well as La_2O_3.[75]

Borohydrides

Borohydrides are inorganic ionic compounds suitable for hydrogen storage in the solid state and they are a multifunctional class of materials that may also be used as fast ion conductors for new types of batteries, for gas adsorption or CO_2 capture and recycling.[69] They may also have optical, electronic and magnetic properties and can be used as reducing agents in organic synthetic chemistry. [69] Since they contain a large amount of hydrogen, they are promising materials as neutron shield from ionizing radiation such as high energy electrons and protons in the space.[32] The most promising ones contain light alkali or alkali-earth metal cation ionically bonded to the complex borohydride anion (BH_4^-).[69]

For their rich chemistry and tuneable properties in relation to their structures and interactions in mixtures, the attention of the latest research focused on the synthesis and characterization of new borohydrides.[69,73] A large variety of crystal structure characterize borohydrides, which shows also a tendency to form polymorphs as a function of temperature or pressure.

The theoretical hydrogen content of $LiBH_4$ is 18.5 wt.%, i.e. the highest among metal borohydrides, while it is equal to 10.7 wt.% for $NaBH_4$, 7.5 wt.% for KBH_4, 14.9 wt.% for $Mg(BH_4)_2$ and 11.6

wt.% for $Ca(BH_4)_2$. Observed values are usually lower, depending on the experimental conditions.[81] Generally high temperatures are required to determine their pressure composition temperature isotherm in an experimental feasible pressure range. Borohydrides decomposition process involved the intermediate formation of the binary metal hydride and elemental boron, or, due to kinetics, the formation of closoboranes ($M_xB_{10}H_{10}$, $M_xB_{12}H_{12}$), which limit the reversibility of the process. Thermodynamic and kinetic of hydrogen release and uptake reaction in borohydrides can be tailored by adding a catalyst, doping or mixing. Since borohydrides show high hydrogen content, the research focus on studying their thermodynamics and hydrogen release properties.[69,82–84] The first group metal borohydrides have shown the highest hydrogen content, but also high thermodynamic stability and slow kinetics in hydrogen release and uptake.[85] The second group metal borohydrides show low temperatures of decomposition and release of hydrogen and, when observed, the melting of mixture turns into dark brown colour instead of transparent liquid, because of decomposition before melting.[86–88]

The kinetic and thermodynamic limitations of these compounds has to be addressed and different approaches have been described in the literature to improve them.[67,89] For instance, the melt infiltration of eutectic mixtures of borohydrides into mesoporous carbon scaffolds improves the kinetic and reversibility of hydrogen release.[90–97] Moreover, low melting mixtures of complex hydrides have been studied recently as ionic liquids, aiming to provide fast and convenient re-fuelling of hydrogen in fuel cell vehicles.[98,99] The use of eutectic mixtures is strongly related to the stability of the liquid phase, therefore the characterization of their thermodynamic properties is of fundamental importance.[90,100,101] Recently, a systematic study of hydrogen release in pure and eutectic mixtures of borohydrides was reported by Paskevicius *et al*.[86].

Among many tailoring routes, cation and anion substitution in borohydrides has been demonstrated to provide solid solutions,[102–111] i.e. cationic or anionic fully disordered structures, as well as hydrogen-fluorine exchange which improved the hydrogen desorption reactions.[111–114] On the other hand, by mixing different light-metals borohydrides, the formation of bimetallic and trimetallic compounds, i.e. cationic or anionic fully ordered structures, were evidenced. New applications of bimetallic compounds have recently been suggested.[69]

Amides and Imides

Amides and imides of alkali and alkaline-earth metals in combination with metal hydrides have the potential to meet the needs of on-board hydrogen storage. Lithium amide-imide can form a solid solution that plays a functional role in the hydrogen storage reactions. A recent review by Garroni *et al*. has been published recently and will be resumed hereafter.[115]

Li_3N was reported to reversibly store more than 9 wt.% of hydrogen in a two-step process that includes the formation of lithium imide firstly and then lithium amide. Even if pure lithium amide ($LiNH_2$) decomposes above 300 °C releasing hydrogen and ammonia gas during the decomposition, mixtures of lithium amide and lithium hydride improve the thermodynamic of hydrogen release, achieving a reversible capacity of 6.5 wt.% and a releasing temperature lower than 300 °C.[115] The tailoring of particles size by ball milling or the addition of catalyst such as $TiCl_3$ are effective strategies to improve kinetics of hydrogen release and to suppress ammonia release during decomposition.

Reactive Hydrides Composites (RHC)

As introduced for N-containing systems, another way to tailor and improve hydrogen storage in complex hydrides is the formulation of mixtures which enables reversible and kinetically/thermodynamically favourable hydrogen desorption/absorption.[67] The so-called Reactive Hydride Composites (RHC) are a mixture of complex hydrides (mainly borohydrides or amide/imide) with metal hydrides, that can reversibly release and uptake hydrogen under moderate conditions of temperature and pressure. This strategy offers the advantage of improved reversibility and of high gravimetric storage capacity.[81]

Besides the addition of LiH to amide or imide systems, the addition of other hydrides, elements or compounds have been investigated, showing improved dehydrogenation rate with the addition of MgH_2, CaH_2, TiH_2, Si, graphite, Ti- and B-based nitrides and suppressed ammonia release.[115]

For example, mixtures of lithium amide ($LiNH_2$) and imide (Li_2NH) with Li- or Mg-halides evidenced the formation of new phases with improved hydrogen storage properties. The new phases are able to desorb hydrogen between 150 °C and 200 °C, with no release of ammonia gas, and they can be rehydrogenated under 90 bar and 300 °C. These composites system, however, still suffer of poor cycling properties.[115]

Borohydrides in mixtures with amides enhance both thermodynamics and kinetics. However, they have limited reversible capacity. Just in case of lithium, combination of amide and borohydrides guarantees high gravimetric capacity at reasonable temperature (10 wt.% at 350 °C for $2LiNH_2$:$1LiBH_4$).[115]

When the Li-Mg-N-H system is considered, a significant reduction in desorption enthalpy is evidenced caused by the formation of a reactive mixture that produced $Mg(NH_2)_2$. The system can form different bimetallic amides that can be rehydrogenated in mild conditions. The $1LiNH_2$:$0.7MgH_2$ mixture has been reported to be fully reversible and desorbs/absorbs 3.6 wt.% at 175 °C.[115] Faster kinetics and no ammonia release can be reached by mixing magnesium amide with lithium borohydride and LiH/KH, leading to a reversible gravimetric capacity of 5 wt.% at 140/100 °C respectively.[115]

Considering Na-based composites, their decomposition temperature remains still too high for practical applications (around 400 °C) and/or they suffer of low gravimetric capacity.[115] These complex mixed systems revealed rich and variegated structural properties and tuneable thermodynamics and kinetics. However, their properties are still far for practical applications, and more studies should focus on the definition of local structures, ion mobility and kinetic constrains during dehydrogenation.

Few examples have been tested in lab-scale tank, and main research efforts investigated combination between different complex hydrides (evidencing the formation of bimetallic compounds, or eutectic melting) of complex hydrides and metal halides playing with cation and anion substitutions. Recent review reported RHC involving alanates, borohydrides, metal hydrides and metal halides mixtures.[64,69,81,116]

Applications of hydrides for hydrogen storage

Looking forward applications of the above-mentioned materials for solid state hydrogen storage in integrated energy systems, the thermodynamic modelling of materials and systems is essential to define and tailor hydrogenation properties and their stability as a function of temperature and pressure in the direction of defining their thermo-fluido-dynamic behaviour. In the following, an overview of modelling approaches will be resumed and hydride-based integrated systems available at both the lab-scale (storing a hydrogen amount lower than 1 kg) and at the industrial scale (storing a hydrogen amount higher than 1 kg) will be presented.

Modelling of hydride-based integrated systems

A full picture of the thermodynamic properties of a system can be obtained by the CALPHAD approach.[117] The goal of CALPHAD assessments is to obtain a description of the dependence of the free energy of all phases on temperature, pressure and composition. The interaction parameters can be obtained with a least square procedure, starting from experimental values of existing phase diagrams and thermodynamic data (**Figure 3**).

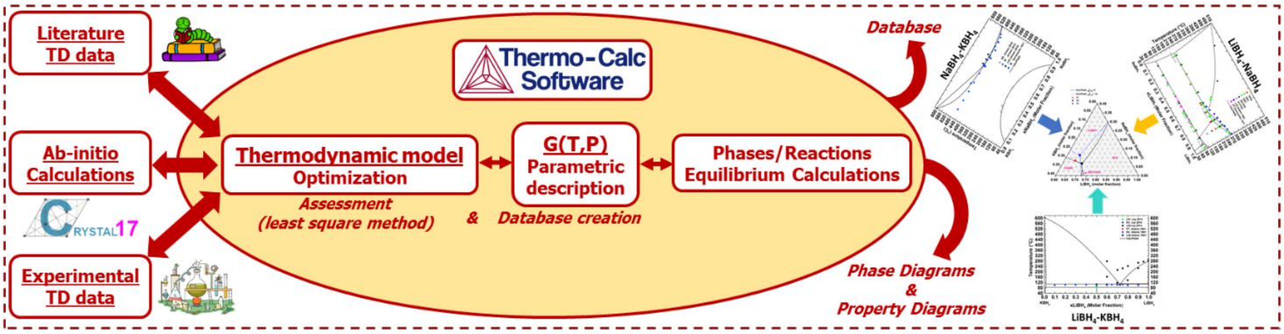

Figure 3 – Flowchart of the assessment procedure by the CALPHAD method.

As a consequence, all the thermodynamic functions of the various phases can be derived by optimising the input data. The analytical description of the temperature dependence of free energy, enthalpy, entropy and specific heat is given by parametric expressions and the composition dependence could be described analytically by suitable models. The excess Gibbs energy of a binary solution phase is often described in terms of Redlich-Kister polynomials. For higher order solutions, several interpolation approaches have been suggested and, if necessary, high order interaction parameters can be introduced. The Gibbs free energy of a pure compound is usually described on the basis of an enthalpy and entropy of formation.

The base of the CALPHAD method is the availability of thermochemical data related to the investigated systems. In absence of experimental information, the output of various thermodynamic or quantum mechanical models can be used.[118] In particular, an estimation of the energy of formation of a compound can be obtained by ab-initio modelling. In this perspective, calculations have been performed on hydrides with the CRYSTAL program, in its 2009,[119] 2014[120] and current 2017[121,122] versions. The CRYSTAL software performs ab-initio calculations of the ground state energy, energy gradient, electronic wave function and properties (electronic, vibrational, thermodynamic, elastic) of periodic systems. Hartree-Fock (HF) or Kohn-Sham Hamiltonians, following Density Functional Theory (DFT), are used. CALPHAD assessments of various systems have been carried out in the recent years for systems of interest for hydrogen storage. In particular, the suggested approach including a combination of CALPHAD and ab-initio modelling has been recently applied to a number of complex hydride systems.

For example, the thermodynamic properties of $LiBH_4$–$NaBH_4$, $LiBH_4$–KBH_4, and $NaBH_4$–KBH_4 binary systems have been investigated and the assessed binary systems have shown good agreement with experimental data (**Figure 3**).[123] Ab-initio results provided the enthalpy of mixing for the solid solutions on both the lithium- and sodium-rich side. Moreover, a full investigation of the ternary system $LiBH_4$–$NaBH_4$-KBH_4 have been carried out.[124] As for divalent complex borohydrides, calcium[105] and magnesium[102] borohydrides have been also investigated with the

CALPHAD and ab-initio modelling, particularly aiming at the study of halogenation as an alternative for destabilizing them, by changing their bond strength. Concerning the effect on nanostructuration in the decomposition of another complex borohydride, i.e. $Ca(BH_4)_2$, very recent ab-initio simulations of thin films have been able to highlight the advantages of nanozing thermodynamics of hydrogen release from metal borohydrides for energy storage applications.[125] Furthermore, the design of a tank for hydrogen storage in the solid state requires, together with the selection and modelling of materials with specific properties, the development of suitable control of the hydrogenation and dehydrogenation processes. The goal of modelling is to combine the thermodynamic/kinetic properties of the selected materials with a proper design of the tank. To achieve short refuelling times in a metal hydride storage tank and appropriate release of hydrogen for coupling to a fuel cell system, it is first necessary to understand the details of the hydrogen charging dynamics in the hydride bed. Hydrogen storage in a hydride vessel results to be a complex problem, since heat and mass transfer, fluido-dynamics and chemical reaction are not independent processes. Therefore, the detailed physical and chemical processes in the storage bed in relation to heat and mass transfer, chemical reaction and fluid flow are translated into a heterogeneous model, which is solved with the help of Computational Fluid Dynamics (CFD) simulation software. The implementation of the tank geometry into the program code can be used as a design tool for solid state hydrogen storage tanks. The key point for the tank design is the use of coupling of hydrogen storage materials with different intrinsic properties, aimed at an internal management of thermal effects during hydrogen charging and discharging. Usually, metal hydrides have a low thermal conductivity, of the order of 0.3 to 1 $Wm^{-1}K^{-1}$,[126] and in many cases heat transfer is the rate-limiting step in storage systems. So, experimental data in combination with numerical methods become necessary to understand the mechanism of heat transfer in the bed in order to improve the design and the efficiency of heat exchangers.

Hydrogen absorption and desorption phenomena are modelled through the solution of differential equations governing process such as mass balance of hydrogen and metal, momentum and energy equations. When the values of all parameters are not available in the literature, the model must be validated by comparing the results of calculations with the data obtained from experiments of hydrogen absorption and desorption. As an example, the value of some critical parameters, such as heat transfer coefficient and effective thermal conductivity, have been estimated for the $LaNi_{4.8}Al_{0.2}$ powder on the basis of experimental data.[127] The geometry used in modelling is shown in **Figure 4-a** and represents a longitudinal section with two subdomains (one for the porous media and one for the free space), which is sorrounded by an isothermal bath.

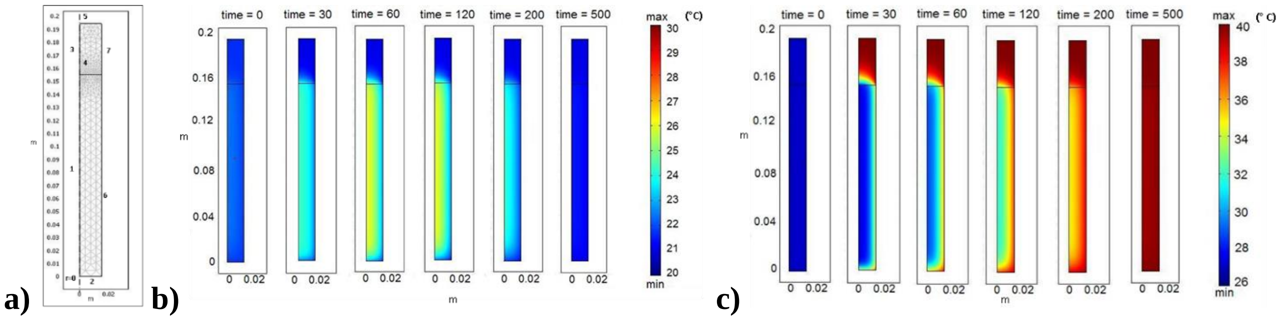

Figure 4 – (a) Schematic view of the domain with unstructured mesh used in the simulation. Temperature distribution in the bed during hydrogen absorption (b) and desorption (c) processes at different times (in seconds).

Once all the parameters have been set,[127] it was possible to obtain the time-space evolution of temperature, as shown in **Figure 4-b** and **Figure 4-c** for the hydrogen absorption and desorption process, respectively. In **Figure 4-b**, the temperature into the vessel increases in the first 60 s until to reach 25 °C due to the exothermic hydrogen absorption reaction. Later, the temperature of the vessel reaches the equilibrium temperature of the bath. In **Figure 4-c**, the temperature into the vessel decreases in the first 30 s due to endothermic hydrogen desorption reaction. As the external bath is fixed at 40 °C, after 30 s the temperature increases until it reaches the equilibrium. As a result, a full description of thermo-fluido-dynamic processes during hydrogen absorption and desorption became available.

Hydride-based systems available at lab-scale

In 2019, Bellosta von Colbe *et al*. reviewed metal hydride-based storage systems for stationary and mobile applications, mainly available at the lab-scale and presenting technology's future perspectives.[128]

Previously, in 2017, Lototskyy *et al*. summarized integrated system realized in the past years, reporting some examples of tanks based on solid-state hydrogen storage materials to be coupled with a Fuel Cells system at the lab-scale.[50] Most of them are based on intermetallic compounds and are demonstrative, prototype or simulated devices.[50] Reported materials used are mainly based on AB_2 ($(TiZr)(Mn,Fe,V)_2$-type) and AB_5 ($LaNi_5$- type) intermetallic compounds, which are preferred thanks to their low pressure and temperature working conditions, despite their low gravimetric capacity. Few systems used MgH_2 or other carriers, including mixtures of hydrides.

Even less examples and studies have been reported in the literature regarding complex hydride-based system for solid-state hydrogen storage at the lab-scale. Usually very limited amount of hydrogen (grams) were successfully and reversibly stored and demonstrated as resumed hereafter.[129]

Utz *et al*. tested and cycled 98 g of Ce-doped $NaAlH_4$ in a lab-scale tank ensuring fast kinetic and a good gravimetric capacity of 4 wt.% at 120 °C upon 36 cycles.[130] Another 0.3 kg of Ce-modified sodium alanates tank has been realized and tested over 25 cycles, working between 1-100 bar and 30-168 °C it reached a capacity as high as 3.7 wt.%.[131] An overall system description was presented by Pfeifer *et al*., consisting in 4 parallel tanks with 0.5 kg of Ce-doped $NaAlH_4$ in each, coupled with a 1 kW H_2-consumption High Temperature Proton-Exchange Membrane Fuel Cells (HT-PEM FC), a pre-heater system and a pump.[132] A cumulative output of 0.8 kWh was reached in a test run at 120 °C, where full material discharging was possible.[132]

Usually, in operating condition only the first reaction of decomposition can be exploit at 160 °C, as in the case of Weiss-Ungethüm *et al*. system.[133] In their study, they successfully coupled an HT-

PEM FC with a 0.3 kg tank of Ce-doped $NaAlH_4$, reversibly storing hydrogen for a capacity equal to 2.24 wt.%, and generating an electrical energy of 660 Wh.[133]

An aluminium alloy tank containing 1.9 kg of Na_3AlH_6 doped with 4 mol% of $TiCl_3$ and 8 mol% of activated carbon has been characterized upon 15 cycles by Urbanczyk *et al*.[134] The tank operates under 25 bar in absorption and can release 38 g of hydrogen during desorption, for a gravimetric hydrogen density of 2.0 wt.%.[134] Mosher *et al*. built a 3 kg and 20 kg $TiCl_3$–doped $NaAlH_4$ tank reaching a material capacity in large scale production of about 1 wt.%.[135,136] Furthermore, a lab-scale tank using Ti-doped Na_3AlH_6 synthetized by ball milling was able to store 3.6 g of hydrogen (gravimetric capacity equal to 1.7 wt.%) at 177 °C and 25 bar.[137] The same group developed another prototype tank based on sodium alanates, with a gravimetric reversible density of 2.24 wt.% coupled with a HT-PEM FC stack with an output power of 260 W_{el}. The operating temperature range of the stack was 120-190 °C.[138]

A small sodium alanate tank (30 g) has been build and tested by Na Ranong *et al*. simulating the scale up to 8 kg alanate-tank for the STORHY project, together with a preliminary study to scale it up to store 5 kg of hydrogen for mobile applications.[139] The STORHY project (2004-2008)[140] developed a high-capacity complex hydrides sodium alanate tank, with a reached capacity of 4.5 wt.%. The tank could be successfully cycled and charged up to 80% in less than 10 min.[141] Later on, the NESSHY project (2006-2010) developed a sodium alanates tank (doped with $TiCl_3$ and $AlCl_3$) with improved gravimetric and volumetric capacity for a total amount of 0.2 kg of hydrogen stored.[142] Sandia and General Motors have successfully designed, fabricated, and experimentally operated and optimized a vehicle-scale hydrogen storage demonstration system using sodium alanates.[143] The demonstration system module design and the system control strategies were enabled by experiment-based, computational simulations that included heat and mass transfer coupled with chemical kinetics.[143]

From a perspective of industrial applications, a lab-scale tank has been tested using 98 g of $Mg(NH_2)_2$-2LiH-0.07KOH reactive composite as hydrogen storage media.[144,145] The tank ran under 60 bar in absorption and at 180-250 °C, the heat management of the system is of fundamental importance for efficient hydrogen delivery and storage.[146]

Beside their use as solid-state hydrogen storage materials, borohydrides can be exploited in Direct Borohydride Fuel Cells (DBFC), very promising system for portable applications,[147] where hydrogen is generated by hydrolysis of complex hydrides. Usually, a DBFC employs an alkaline solution of sodium borohydride ($NaBH_4$) as fuel and oxygen or hydrogen peroxide as oxidant. Recent developments in DBFC research have been reviewed in ref.[148]. However, such technology is at an infant stage of development, with a strong need of improvement in materials and in lowering their cost. Kim *et al*. described a system that combines PEM FC and a reactor for $NaBH_4$ hydrolysis as hydrogen generator. The PEM FC consumed approximately 1.2 L/min of hydrogen to generate the electric power of 100 W.[149] Main research on tank and system integration exploiting borohydrides in hydrolysis reaction have been reviewed by Ley *et al*. together with the description of other developed tank based on thermolysis for hydrogen generation mostly involving sodium alanates and reactive hydride composites mixtures.[129] Hydrolysis of borohydride has been also considered for one-shot hydrogen production on demand, it is however still restricted to niche and limited applications.[150,151]

Hydride-based systems available at industrial scale

Metal hydrides are known since late 1970s as low risk option to store hydrogen.[128] Intermetallic compounds are usually commercialized in form of powder, which is usually obtained by the crash of ingots prepared by melting techniques. In order to improve thermal conductivity, some producers provide powders aggregated by suitable binders in form of pellets. Usually, metal hydrides powders can be handled in air until their hydrogenation/activation. For industrial scale hydrogen storage applications (i.e. units of kilos of hydrogen and even more) metal hydride powders are produced at a ton level. Hydrogen storage systems based on hydrides are available in the market, even if real applications are still limited. Some examples will be briefly described in the following.

Applications for mobility are limited by the low gravimetric density of metal hydrides. Nevertheless, when an increased weight is a benefit for the application, hydrogen storage by metal hydrides become an added value. On the contrary, for mobile applications on roads (i.e. automotive, heavy-duty, trains), compressed gas is preferred for the hydrogen storage.

An important heavy mobile application is forklift.[128] An AB_2 alloy ($(Ti,Zr)(Fe,Cr,Mn,Ni)_2$ with a Ti:Zr atomic ratio of approximately 0.65:0.35) was developed to work at room temperature and pressure <10 bar. The storage system consists of twenty metal hydride containers for a final weight of approximately 200 kg of metal powder. Each container delivers about 7.5 Nl/min and supplies a PEM FC of about 10 kW.

Maritime sector is interested in limit pollutants emission to face climate change and the use of fuel cell supplied by H_2 have found high potential in the last years. Van Biert et al. recently reviewed fuel cell systems for maritime applications, including hydrogen as a promising energy carrier to be exploited.[152] A special focus on hydrogen storage media at the solid state for submarine applications has been review by Fiori et al.[153]. Many other reviews describe the development of fuel cell vessels and potential of hydrogen for maritime and submarine applications.[154–158] Hydrogen fuelled submarines have about 300 kW FC and the storage system is based on an AB_2 alloy, which works between 20 and 50 °C.[128] Another example of application in the maritime sector is for the AB_2 alloy $(Ti_{0.93}Zr_{0.05})(Mn_{0.73}V_{0.22}Fe_{0.04})_2$ used for the canal boat Ross Barlow, in UK,[159] where eight cylinders containing about 30 kg of metal hydride powder each were used and 4 kg of H_2 were stored and used to supply a 1 kW PEM FC, which allows 10 h of operation.

Stationary applications are mainly referring to the volumetric density rather than to the gravimetric density of the hydrogen carrier. In particular, the final footprint per weight of stored hydrogen becomes the key performance to be considered. Most of the integrated system are based on AB_5 compounds, such as $LaNi_5$ and $LaNi_5$-based alloys. As an example, an automated hydrogen-based auxiliary power unit was developed by Doucet et al.[160], with a storage capacity of about 1 Nm^3, to be used by a PEM FC of 1 kW. A stationary system commercially available based on an AB_5

intermetallic compound is the H2ONE developed in Japan and commercialized by Toshiba.[161] Systems are scaled to be easily installed anywhere, with a H_2 storage capacity of ≈ 150 Nm^3 per module. An example of stationary application, based on a commercial $LaNi_{4.8}Al_{0.2}$ alloy, was developed by Rizzi et al.[162]. The hydrogen tank worked at 60 °C and it was integrated with a 1 kW PEM FC. A scheme of the developed tank is reported in **Figure 5-a**, while a general view of the developed system is reported in **Figure 5-b**.

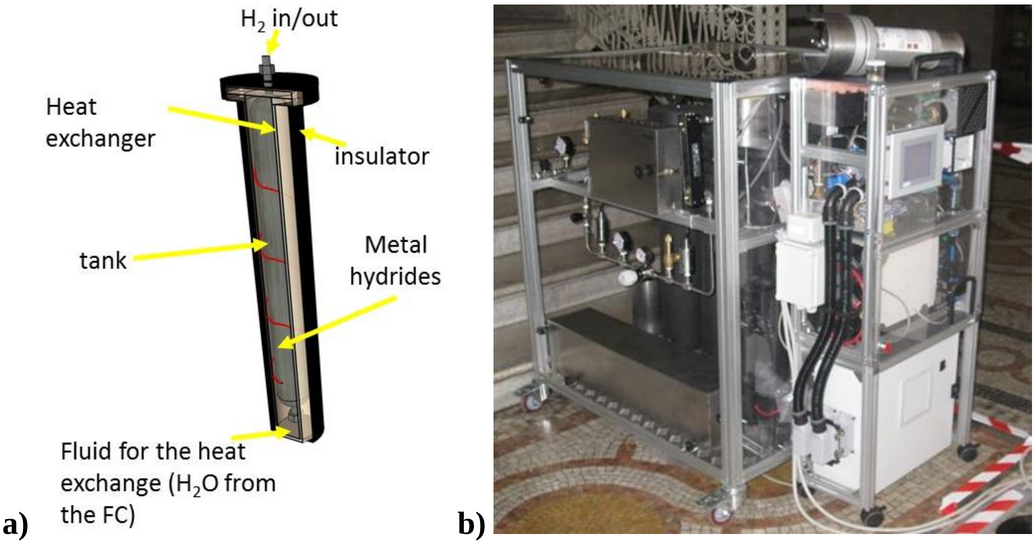

Figure 5 - Stationary application of hydrogen storage using $LaNi_{4.8}Al_{0.2}$ as carrier. (a) Schematic view of the hydrogen tank; (b) General view of the developed system. Details available in Rizzi *et al.*[162].

A hydrogen storage system based on a AB intermetallic (i.e. Ti(FeMn)) alloy was developed in South Tyrolean Alps by GKN,[163] with a system providing energy for a house, which has no access to the grid. At the Brookhaven National Laboratory, engineering-scale tests were performed in the ‘70s and a large TiFe-based system prototype was developed.[164–167] A final optimised tank stored 6 kg hydrogen using 405 kg of TiFe for the storage of off-peak electricity in an integrated system that combined an electrolyser, hydrogen tank and a fuel cell.[168] In the framework of the European project HyCARE, supported by FCH-JU, a hydrogen storage system based on AB alloys is planned.[169,170] The aim of the project is to store ≈50 kg of H_2 integrating the storage tank with an electrolyser upstream and a fuel cell downstream to produce energy for the grid (stationary application). The tank is based on an innovative concept that links hydrogen and heat storage for stationary storage of excess renewable energy.

Mg-based systems are working at high temperatures (e.g. 360 °C) and 0.1 MPa. As an example, the McStore system from McPhy (France) is based on a standard configuration containing 12 cylinders containing about 90 Nm^3 (i.e. 8 kg) of H_2. A demonstration has been developed in the frame of the INGRID project, using about 750 kg of H_2-carrier.[171]

Complex hydrides are only available at the lab-scale from mainstream chemical seller. They have been mainly investigated at the lab-scale, with high purity grade, for research purposes. Applicative-oriented projects, however, have demonstrated their scale up. As an example, a scaled-up system was built and tested by Johnson *et al.*, storing 3 kg of hydrogen in modified-$NaAlH_4$.[172]

For on-board vehicular applications, sodium and lithium alanates are particularly effective, since they have high gravimetric capacities and they can release hydrogen at temperatures lower than 200 °C, ideal to be coupled with HT-PEM FC. Within the SSH2S (Fuel Cell Coupled Solid State Hydrogen Storage Tank) project (2011-2015), a demonstration solid-state hydrogen tank has been realized,[173] to supply for 2 h a 1 kW HT-PEM FC stack as Auxiliary Power Unit (APU) for a light duty vehicle. The optimized hydrogen storage material has been synthetized by ball milling.[174] It is a amide-hydride composite that contains $2LiNH_2$-$1.1MgH_2$-$0.1LiBH_4$-3 wt.% $ZrCoH_3$ coupled with $LaNi_{4.3}Al_{0.4}Mn_{0.3}$, and it can release reversibly, at 150 °C, 4.5 wt.% of hydrogen in 300 min under 0.1 MPa, forming $Li_2MgN_2H_2$, together with some residual $ZrCoH_3$.[175–177] The tank has a gravimetric hydrogen storage density of 2.45 wt.% H_2 (volumetric storage capacity of 10 g l^{-1}), releasing hydrogen at 170 °C.[177,178] An overview of the developed tank is reported in **Figure 6**. The storage tank consisted of three concentric tubes and the hydrogen carrier was based on a mixed lithium amide/magnesium hydride system, coupled with an intermetallic compound.[177] The system was planned to supply a 1 kW HT-PEM FC stack for 2 h. The developed hydrogen tank is reported in **Figure 6-a**. The complete storage system combined twelve vessels in parallel (**Figure 6-b**) and a general view of the integrated APU system is reported in **Figure 6-c**.

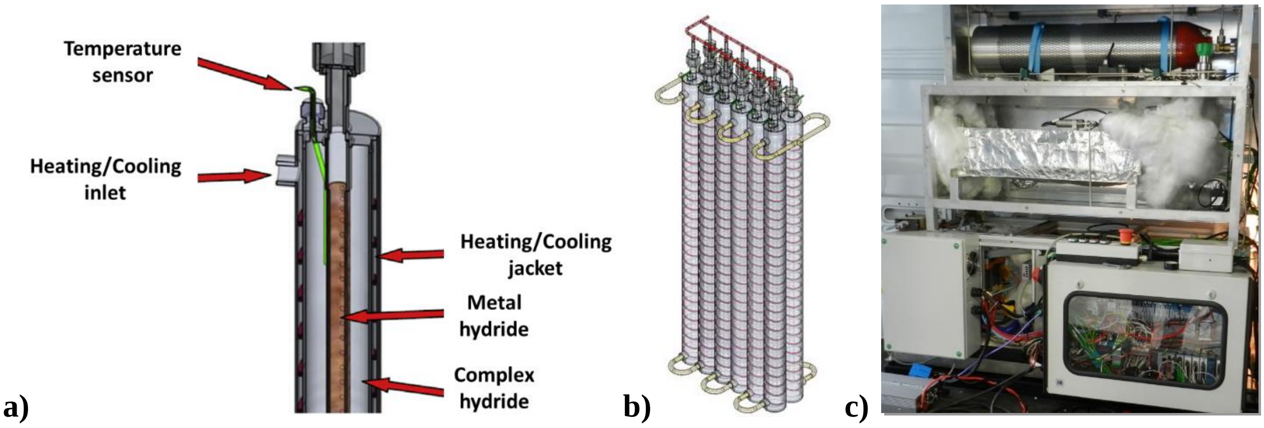

Figure 6 - Solid-state hydrogen tank, coupled with a HT-PEM FC to be used as Auxiliary Power Unit (APU) using a complex hydride as carrier. (a) Scheme of single vessel implementing the double storage materials concept (combi-tank); (b) assembly of twelve vessels in parallel to form the complete storage system; and (c) general view of the developed system. Details available in Baricco *et al.*[177].

The development of the tank has been followed by a study involving a Life Cycle Assessment (LCA),[10] which demonstrated that, when the electricity consumption for hydrogen gas compression is included into the analysis, a solid-state hydrogen storage tank has similar greenhouse gas emissions and primary energy demand than those of type III and IV gas tanks.[10]

Discussion

Metal hydrides allow to store H_2 at low temperature (e.g. even close to room temperature) and at low pressures (e.g. < 50 bar), being easily integrated with low pressure electrolyser upstream and/or fuel cell downstream. A drawback is their low gravimetric capacity, (< 2 wt.%), which implies higher amount of alloys compared to high gravimetric capacity hydrides, such as complex ones, to reach the same amount of H_2 stored. Nevertheless, easier design thanks to low temperature and pressure conditions are allowed, compared to complex hydrides, which usually require high temperatures. Intermetallic compounds are particularly interesting in stationary applications,[128] in which there are not limitation on system weight, and in heavy mobile applications, like forklift[179] or submarine.[153] Finally, concerning the volumetric capacity, it is of the order of 110 kgH_2m^{-3} (i.e. higher than liquid H_2). Complex hydrides can store high gravimetric amount of hydrogen, however their working conditions for reversible storage requires either high temperature or high pressure. Their synthesis has been demonstrated at the lab-scale by ball milling or wet-chemistry, processes which can be scaled-up. On the other hand, their synthesis is still mainly related to research purposes and their cost still remains rather high. Furthermore, since complex hydrides are sensible to moisture, especially water and oxygen, their manipulation and use should be performed under inert atmosphere, to ensure safe handling and usage.

In order to estimate possible applications of solid-state hydrogen storage for energy communities, different scenarios have been considered. As a starting point, the green hydrogen production by water electrolysis is considered. Taking as a reference the production of 1 kg of hydrogen and an energy consumption for hydrogen production of 50 kWh/kg H_2, the time for production can be estimated as a function of the power of an alakalyne elctrolyzer. Results are reported in **Figure 7-a** and they show a significant decrease of production time up to about 6 kW, which allows the production of 3 kg H_2 per day. Similarly, the running time of a PEM FC with 1 kg of H_2 can be estimated as a funcion of power, as reported in **Figure 7-b**. In this case, an hydrogen consumption of 0.075 kg H_2 per electric kWh has been considered, which implies an FC efficiency of about 50%. It turns out that, with a 3 kW PEM FC, a one day running time would be possible with about 3 kg H_2.

In order to estimate a possible supply for energy communities, electric consumptions obtained in 2018 have been considered[1] and days per capita of electric supply are reported as a function of the amount of hydrogen available (**Figure 8**).

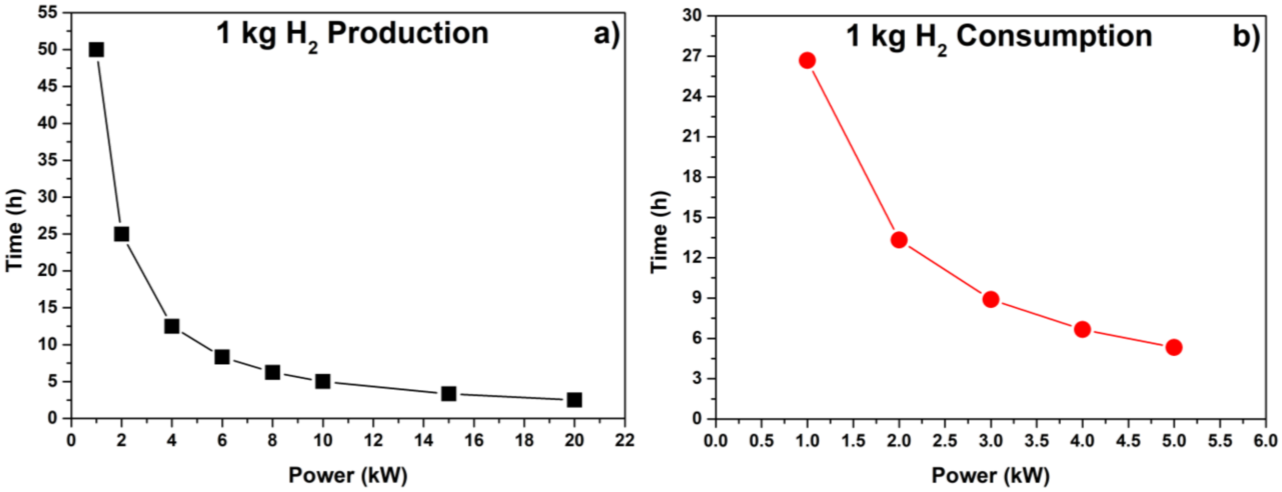

Figure 7 - Time for the (a) production by an electrolyzer and the (b) consumption by a fuel cell of 1 kg H_2 as a function of power of the equipment.

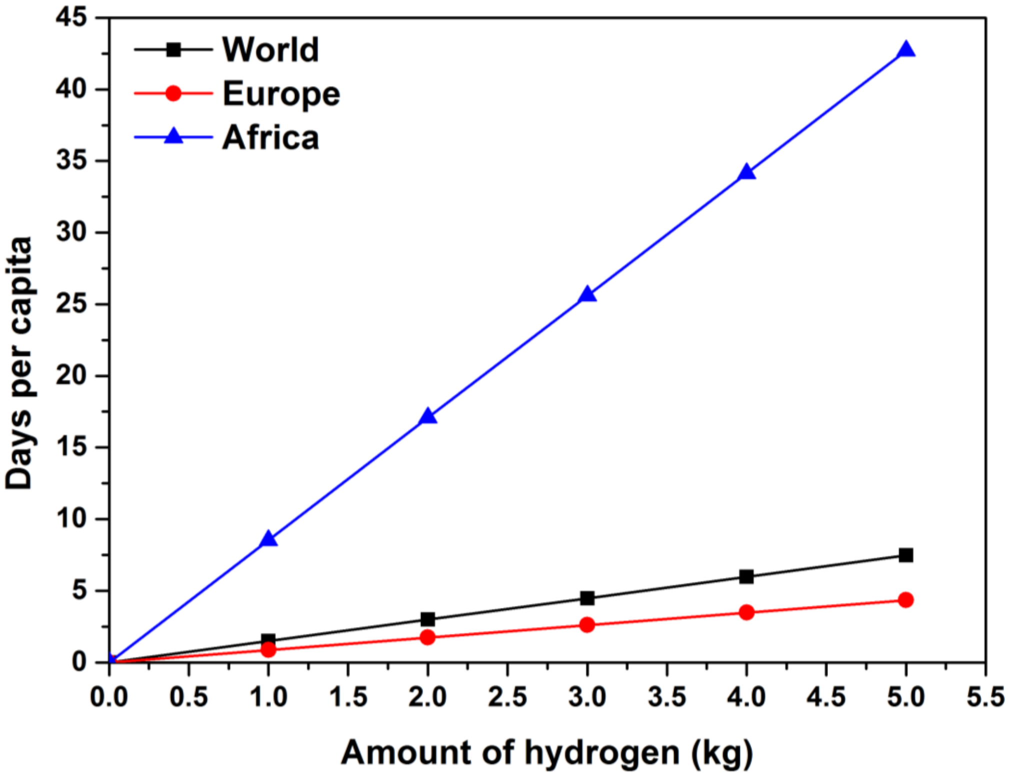

Figure 8 - Days of electric supply per capita as a function of the amount of hydrogen available, considering different social environments.

It turns out that, with 5 kg of H_2 available, a family of 4 persons can be fully supplied for 1 day in Europe, whereas the same amount of hydrogen can supply nowdays the same family in Africa for about 10 days. If a usable amount of 1.3 wt.% in the temperature and pressure ranges of the metal hydride storage system is considered, the storage of 5 kg H_2 would need abot 385 kg of powder. This would occupy only 0.071 m^3 with a metal hydride showing a volumetric density of 100 kgH_2/m^3, considering a bulk-to-powder ratio of 0.7. Of course, the real volume of the system would increase due to the need of a piping, valves and thermal managements. Finally, considering a price of 50 €/kg for the selected powder, a total cost of less than 20.000 € would be necessary for the active materials, which would increase because of auxiliaries. A scale up of the storage of renewable energies by hydrogen using metal hydrides would benefit significantly from the cost reduction due to the increased quantity of powder, mainting a reduced footprint of the system, coupled with safe conditions, linked to the low pressure and temperature involved in the technology.

Hydrogen technologies, especially for the stationary storage of energy, can be coupled with renewables sources to produce and store green energy thus allowing for a crucial step beyond towards the overcoming of the discontinuity in the provision of electricity from RES. From the social perspective, this innovation might represent a huge shift as well for encouraging local communities and families to become prosumers and could also be a leverage for making the energy transition an opportunity for women conditions enhancement. A recent study on prosumers' energy practice in households in Norway and United Kingdom in fact evidenced that the introduction of energy production and use influence everyday routines and lifestyle. [180] The implementation of a storage system based on hydrogen within an integrated energy system enables new organization of in-house tasks due to the improved control in the distribution of smart energy use. H_2-based storage solutions might therefore positively impact the condition of women, to date still the most responsible in managing chores at home. On the one hand, these solutions might increase women free time and their autonomy in managing the daily scheduling, on the other they might trigger the shift to a more gender balanced chores distribution in an ungendered house space.

From the gender perspective, the dark side of the H_2 development as reported by the study,[180] is the role of males in the decision and adoption of renewable energy system and in their maintenance.[180] This process, nowadays, is still men-skewed due to the requirement of more technical skills, and, as a result of an historical but still persistent trend, is characterized by a highly unbalanced distribution of STEM competencies.[180] Given this evidence, the goal must be to increase women involvement in the process as bearers of expert knowledge and therefore able to steer the decision making process. A goal and an ambition are that the H_2-based technologies development might help in fulfilling through two main dynamics/strategies. First, and at present, by collecting women present STEM skills that are relevant for H_2-based solutions. More than other RES technologies H_2-based need the mere technical-engineering skills to be complemented by other knowledge (e.g. chemistry and physics) where the female component is relatively more represented. Secondly, and in the mid-term, the inclusion of STEM women in H_2 development might play as a driving force for steering women educational and professional careers towards the STEM fields.

In conclusion, H_2 might positively impact women both as a trigger for a more balanced distribution of daily activities connected to the family and house management, and as a trigger for enhancing the role of women in the decision process towards the adoption of H_2 solutions through the enhancement of their STEM skills.

The implementation of a storage system based on hydrogen within an integrated energy system would enable new organisational in-house tasks leaving more freedom in the use of smart energy and empowering women implementing their free time and developing an ungendered house space towards a balanced division of household tasks and maintenances. Furthermore, climate change impact will affect differently the north and the south of the world, the vulnerability of women during the energy transition should be considered to protect these population and supporting the unique values and virtues of women, to foster the energy transition locally and to lead towards an increased women's responsibility and communication role in the energy market.[181]

Conclusions

Intermetallic compounds are good candidates for safe H_2-carrier systems in the storage of renewable energies, thanks to their low working temperature and pressure. Thermodynamic and kinetic properties of metal hydrides allow simple and suitable design for solid-state hydrogen tanks.

AB_2 compounds have found a high interest for mobility applications, but also AB_5–based systems are under developments. Although the use of novel hydrogen storage media such as complex hydrides could be advantageous, their integration into hydrogen storage tanks need further assessment in scaled up systems under real operating conditions. Thermal exchange remains the main issue in the system management.

Hydrogen tanks based on solid-state materials are already available in the marked, but limited applications have been demonstrated. Because of the main properties of the hydrogen carriers (i.e. gravimetric and volumetric H_2 density), large weights and volumes must be considered for the tank system, if the request for stored hydrogen is high. The limited market strongly limits the availability and increases the cost of metal powders for hydrogen storage.

In conclusion, hydrides can provide a technical suitable solution for the storage of renewable energies and therefore can play a relevant role in fostering the transition towards an energy system characterized by a wide adoption of renewables technologies. But it is now recognized, both in the research and the policy fields, that technical aspects are only part of the solutions and the social aspects have been gaining relevance in the past decades as crucial components for investigating the transition pathways (e.g. the long lasting socio-technical transition approach)[182–184] and to design effective policies for their implementation. For a technical innovation to be properly developed and diffused and to be adequately accepted and adopted by the users (ultimately, the citizens) attention has to be paid to the social, economic and cultural context within which the innovation should be embedded, to better design the innovation itself, to minimize the negative impacts and to maximise the potential benefits. Among the many social aspects and dynamics that would deserve to be considered, this paper focused on the promotion of a gender perspective as a driver for more innovative and inclusive solutions in the clean energy transition and in the hydrogen-based solution exploitation. Given their role in the organization of social life and in fostering innovative solutions, both in the developing and developed countries, even though different mechanisms, women inclusion in the development of hydrogen-related technologies will provide a more comprehensive view on the exploitation of its storage potential in the overall reorganization of the daily and working life and, the way around, it might trigger to an actual empowerment of women through an increase of their talent and skills (i.e. share in STEM) and their involvement in the energy chain decision making. A process that has the potential to result in a safer, more affordable, sustainable and inclusive clean energy future.

Acknowledgements

The project leading to this publication has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826352, HyCARE project. The JU receives support from the European Union's Horizon 2020 research, Hydrogen Europe, Hydrogen Europe Research innovation programme and Italy, France, Germany, Norway, which are all thankfully acknowledged.

References

1. https://www.iea.org/data-and-statistics.
2. Paris Agreement - Report of the Conference of the Parties on its twenty-first session, FCCC/CP/2015/10/Add.1. **2015**.
3. Clean energy for all Europeans - European Commission, Directorate General for Energy. **2019**, doi:10.2833/9937.
4. Armaroli, N.; Balzani, V. The Future of Energy Supply: Challenges and Opportunities. *Angew. Chemie Int. Ed.* **2007**, *46*, 52–66, doi:10.1002/anie.200602373.
5. Rehman, S.; Al-Hadhrami, L.M.; Alam, M.M. Pumped hydro energy storage system: A technological review. *Renew. Sustain. Energy Rev.* **2015**, *44*, 586–598, doi:10.1016/j.rser.2014.12.040.
6. Møller, K.T.; Jensen, T.R.; Akiba, E.; Li, H.-W. Hydrogen - A sustainable energy carrier. *Prog. Nat. Sci. Mater. Int.* **2017**, *27*, 34–40, doi:10.1016/j.pnsc.2016.12.014.
7. Armaroli, N.; Balzani, V. The Hydrogen Issue. *ChemSusChem* **2011**, *4*, 21–36, doi:10.1002/cssc.201000182.
8. Lai, Q.; Paskevicius, M.; Sheppard, D.A.; Buckley, C.E.; Thornton, A.W.; Hill, M.R.; Gu, Q.; Mao, J.; Huang, Z.; Liu, H.K.; et al. Hydrogen Storage Materials for Mobile and Stationary Applications: Current State of the Art. *ChemSusChem* **2015**, *8*, 2789–2825, doi:10.1002/cssc.201500231.
9. Ball, M.; Wietschel, M. The future of hydrogen – opportunities and challenges. *Int. J. Hydrogen Energy* **2009**, *34*, 615–627, doi:10.1016/j.ijhydene.2008.11.014.
10. Agostini, A.; Belmonte, N.; Masala, A.; Hu, J.; Rizzi, P.; Fichtner, M.; Moretto, P.; Luetto, C.; Sgroi, M.; Baricco, M. Role of hydrogen tanks in the life cycle assessment of fuel cell-based auxiliary power units. *Appl. Energy* **2018**, *215*, 1–12, doi:10.1016/j.apenergy.2018.01.095.
11. Belmonte, N.; Girgenti, V.; Florian, P.; Peano, C.; Luetto, C.; Rizzi, P.; Baricco, M. A comparison of energy storage from renewable sources through batteries and fuel cells: A case study in Turin, Italy. *Int. J. Hydrogen Energy* **2016**, *41*, 21427–21438, doi:10.1016/j.ijhydene.2016.07.260.
12. Wierling, A.; Zeiss, J.P.; Lupi, V.; Candelise, C.; Sciullo, A.; Schwanitz, V.J. The Contribution of Energy Communities to the Upscaling of Photovoltaics in Germany and Italy. *Energies* **2021**, *14*, 2258, doi:10.3390/en14082258.
13. Directive (EU) 2019/944 on common rules for the internal market for electricity.
14. Directive (EU) 2018/2001 on the promotion of the use of energy from renewable sources.
15. Hopkins, M. Human development revisited: A new UNDP report. *World Dev.* **1991**, *19*, 1469–1473, doi:10.1016/0305-750X(91)90089-Z.
16. Gender and Climate Change - Thematic Issue Briefs and Training Modules (accessed July 2018) Available online: http://www.undp.org/content/undp/en/home/librarypage/womens-empowerment/gender-and-climate-change.html.
17. Arora-Jonsson, S. Virtue and vulnerability: Discourses on women, gender and climate change. *Glob. Environ. Chang.* **2011**, *21*, 744–751, doi:10.1016/j.gloenvcha.2011.01.005.
18. Wong, S. Can Climate Finance Contribute to Gender Equity in Developing Countries? *J. Int. Dev.* **2016**, *28*, 428–444, doi:10.1002/jid.3212.
19. COP24 Women Gender Constituency - Key Demands. *www.womengenderclimate.org* **2021**.
20. Feenstra, M.; Özerol, G. Energy justice as a search light for gender-energy nexus: Towards a conceptual framework. *Renew. Sustain. Energy Rev.* **2021**, *138*, 110668, doi:10.1016/j.rser.2020.110668.
21. Shankar, A. Strategically engaging women in clean energy solutions for sustainable development and health. *Glob. Sustain. Dev. Rep. Br.* **2015**.
22. Carlsson-Kanyama, A.; Lindén, A.-L. Energy efficiency in residences—Challenges for women and men in the North. *Energy Policy* **2007**, *35*, 2163–2172, doi:10.1016/j.enpol.2006.06.018.
23. Cannon, C.E.B.; Chu, E.K. Gender, sexuality, and feminist critiques in energy research: A review and call for transversal thinking. *Energy Res. Soc. Sci.* **2021**, *75*, 102005, doi:10.1016/j.erss.2021.102005.
24. International Renewable Energy Agency *Renewable Energy: A Gender Perspective*; 2019; ISBN 9789292600983.
25. Sartori, S. Further steps are needed to endure a gender-just energy transition. **2020**.
26. Clancy, J.S.; Mohlakoana, N. Gender audits: An approach to engendering energy policy in Nepal, Kenya and Senegal. *Energy Res. Soc. Sci.* **2020**, *62*, 101378, doi:10.1016/j.erss.2019.101378.
27. Lieu, J.; Sorman, A.H.; Johnson, O.W.; Virla, L.D.; Resurrección, B.P. Three sides to every story: Gender perspectives in energy transition pathways in Canada, Kenya and Spain. *Energy Res. Soc. Sci.* **2020**, *68*, 101550, doi:10.1016/j.erss.2020.101550.
28. Mang-Benza, C. Many shades of pink in the energy transition: Seeing women in energy extraction, production, distribution, and consumption. *Energy Res. Soc. Sci.* **2021**, *73*, 101901, doi:10.1016/j.erss.2020.101901.
29. Allen, E.; Lyons, H.; Stephens, J.C. Women's leadership in renewable transformation, energy justice and

energy democracy: Redistributing power. *Energy Res. Soc. Sci.* **2019**, *57*, 101233, doi:10.1016/j.erss.2019.101233.
30. Bannenberg, L.J.; Heere, M.; Benzidi, H.; Montero, J.; Dematteis, E.M.; Suwarno, S.; Jaroń, T.; Winny, M.; Orłowski, P.A.; Wegner, W.; et al. Metal (boro-) hydrides for high energy density storage and relevant emerging technologies. *Int. J. Hydrogen Energy* **2020**, *45*, 33687–33730, doi:10.1016/j.ijhydene.2020.08.119.
31. El Kharbachi, A.; Dematteis, E.M.; Shinzato, K.; Stevenson, S.C.; Bannenberg, L.J.; Heere, M.; Zlotea, C.; Szilágyi, P.Á.; Bonnet, J.-P.; Grochala, W.; et al. Metal Hydrides and Related Materials. Energy Carriers for Novel Hydrogen and Electrochemical Storage. *J. Phys. Chem. C* **2020**, *124*, 7599–7607, doi:10.1021/acs.jpcc.0c01806.
32. Yartys, V.A.; Lototskyy, M.V.; Akiba, E.; Albert, R.; Antonov, V.E.; Ares, J.R.; Baricco, M.; Bourgeois, N.; Buckley, C.E.; Bellosta von Colbe, J.M.; et al. Magnesium based materials for hydrogen based energy storage: Past, present and future. *Int. J. Hydrogen Energy* **2019**, *44*, 7809–7859, doi:10.1016/j.ijhydene.2018.12.212.
33. Dornheim, M. Thermodynamics of Metal Hydrides: Tailoring Reaction Enthalpies of Hydrogen Storage Materials. In *Thermodynamics - Interaction Studies - Solids, Liquids and Gases*; InTech, 2011; Vol. Dr. Juan C, pp. 891–918 ISBN 978-953-307-563-1.
34. Cheng, F.; Tao, Z.; Liang, J.; Chen, J. Efficient hydrogen storage with the combination of lightweight Mg/MgH2 and nanostructures. *Chem. Commun.* **2012**, *48*, 7334, doi:10.1039/c2cc30740e.
35. Vegge, T.; Hedegaard-Jensen, L.S.; Bonde, J.; Munter, T.R.; Nørskov, J.K. Trends in hydride formation energies for magnesium-3d transition metal alloys. *J. Alloys Compd.* **2005**, *386*, 1–7, doi:10.1016/j.jallcom.2004.03.143.
36. Liang, G.; Huot, J.; Boily, S.; Van Neste, A.; Schulz, R. Catalytic effect of transition metals on hydrogen sorption in nanocrystalline ball milled MgH2–Tm (Tm=Ti, V, Mn, Fe and Ni) systems. *J. Alloys Compd.* **1999**, *292*, 247–252, doi:10.1016/S0925-8388(99)00442-9.
37. Baran, A.; Polański, M. Magnesium-Based Materials for Hydrogen Storage—A Scope Review. *Materials (Basel).* **2020**, *13*, 3993, doi:10.3390/ma13183993.
38. Graetz, J.; Reilly, J.J.; Yartys, V.A.; Maehlen, J.P.; Bulychev, B.M.; Antonov, V.E.; Tarasov, B.P.; Gabis, I.E. Aluminum hydride as a hydrogen and energy storage material: Past, present and future. *J. Alloys Compd.* **2011**, *509*, S517–S528, doi:10.1016/j.jallcom.2010.11.115.
39. *Hydrogen Technology*; Léon, A., Ed.; Green Energy and Technology; Springer Berlin Heidelberg: Berlin, Heidelberg, 2008; ISBN 978-3-540-79027-3.
40. Cuevas, F.; Burzo, E. *Hydrogen Storage Materials*; Burzo, E., Ed.; ed. Berlin.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2018; ISBN 978-3-662-54259-0.
41. Dematteis, E.M.; Berti, N.; Cuevas, F.; Latroche, M.; Baricco, M. Substitutional effects in TiFe for hydrogen storage: a comprehensive review. *Mater. Adv.* **2021**, *2*, 2524–2560, doi:10.1039/D1MA00101A.
42. Sujan, G.K.; Pan, Z.; Li, H.; Liang, D.; Alam, N. An overview on TiFe intermetallic for solid-state hydrogen storage: microstructure, hydrogenation and fabrication processes. *Crit. Rev. Solid State Mater. Sci.* **2019**, 1–18, doi:10.1080/10408436.2019.1652143.
43. Reilly, J.J.; Wiswall, R.H. Formation and properties of iron titanium hydride. *Inorg. Chem.* **1974**, *13*, 218–222, doi:10.1021/ic50131a042.
44. Bellosta von Colbe, J.M.; Puszkiel, J.; Capurso, G.; Franz, A.; Benz, H.U.; Zoz, H.; Klassen, T.; Dornheim, M. Scale-up of milling in a 100 L device for processing of TiFeMn alloy for hydrogen storage applications: Procedure and characterization. *Int. J. Hydrogen Energy* **2019**, *44*, 29282–29290, doi:10.1016/j.ijhydene.2019.01.174.
45. Dematteis, E.M.; Dreistadt, D.M.; Capurso, G.; Jepsen, J.; Cuevas, F.; Latroche, M. Fundamental hydrogen storage properties of TiFe-alloy with partial substitution of Fe by Ti and Mn. *J. Alloys Compd.* **2021**, *874*, 159925, doi:10.1016/j.jallcom.2021.159925.
46. Dematteis, E.M.; Cuevas, F.; Latroche, M. Hydrogen storage properties of Mn and Cu for Fe substitution in TiFe0.9 intermetallic compound. *J. Alloys Compd.* **2021**, *851*, 156075, doi:10.1016/j.jallcom.2020.156075.
47. Rusman, N.A.A.; Dahari, M. A review on the current progress of metal hydrides material for solid-state hydrogen storage applications. *Int. J. Hydrogen Energy* **2016**, *41*, 12108–12126, doi:10.1016/j.ijhydene.2016.05.244.
48. Stein, F.; Palm, M.; Sauthoff, G. Structure and stability of Laves phases. Part I. Critical assessment of factors controlling Laves phase stability. *Intermetallics* **2004**, *12*, 713–720, doi:10.1016/j.intermet.2004.02.010.
49. Liu, B.-H.; Kim, D.-M.; Lee, K.-Y.; Lee, J.-Y. Hydrogen storage properties of TiMn2-based alloys. *J. Alloys Compd.* **1996**, *240*, 214–218, doi:10.1016/0925-8388(96)02245-1.
50. Lototskyy, M. V.; Tolj, I.; Pickering, L.; Sita, C.; Barbir, F.; Yartys, V. The use of metal hydrides in fuel cell applications. *Prog. Nat. Sci. Mater. Int.* **2017**, *27*, 3–20, doi:10.1016/j.pnsc.2017.01.008.
51. Semboshi, S.; Masahashi, N.; Hanada, S. Degradation of hydrogen absorbing capacity in cyclically hydrogenated TiMn2. *Acta Mater.* **2001**, *49*, 927–935, doi:10.1016/S1359-6454(00)00371-2.
52. Joubert, J.-M.; Paul-Boncour, V.; Cuevas, F.; Zhang, J.; Latroche, M. LaNi5 related AB5 compounds: Structure, properties and applications. *J. Alloys Compd.* **2021**, *862*, 158163, doi:10.1016/j.jallcom.2020.158163.

53. Commission's communication on the 2017 list of Critical raw Materials for the EU. *COM* **2017**, *490*.
54. EU Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability. Communication from the commission to the European parliament, the council, the European Economic and Social Committee and the committee of the regions. *COM* **2020**, *474*.
55. Liang, G.; Huot, J.; Schulz, R. Hydrogen storage properties of the mechanically alloyed LaNi5-based materials. *J. Alloys Compd.* **2001**, *320*, 133–139, doi:10.1016/S0925-8388(01)00929-X.
56. Read, C.; Petrovic, J.; Ordaz, G.; Satyapal, S. The DOE National Hydrogen Storage Project: Recent Progress in On-Board Vehicular Hydrogen Storage. *MRS Proc.* **2005**, *885*, 0885-A05-01, doi:10.1557/PROC-0885-A05-01.
57. An, X.H.; Gu, Q.F.; Zhang, J.Y.; Chen, S.L.; Yu, X.B.; Li, Q. Experimental investigation and thermodynamic reassessment of La–Ni and LaNi5–H systems. *Calphad* **2013**, *40*, 48–55, doi:10.1016/j.calphad.2012.12.002.
58. Chen, J.; Dou, S.X.; Liu, H.K. Effect of partial substitution of La with Ce, Pr and Nd on the properties of LaNi5-based alloy electrodes. *J. Power Sources* **1996**, *63*, 267–270, doi:10.1016/S0378-7753(96)02461-5.
59. Suzuki, K.; Ishikawa, K.; Aoki, K. Degradation of LaNi5 and LaNi4.7Al0.3 Hydrogen-Absorbing Alloys by Cycling. *Mater. Trans. JIM* **2000**, *41*, 581–584, doi:10.2320/matertrans1989.41.581.
60. Sharma, V.K.; Anil Kumar, E. Effect of measurement parameters on thermodynamic properties of La-based metal hydrides. *Int. J. Hydrogen Energy* **2014**, *39*, 5888–5898, doi:10.1016/j.ijhydene.2014.01.174.
61. Pinatel, E.R.; Palumbo, M.; Massimino, F.; Rizzi, P.; Baricco, M. Hydrogen sorption in the LaNi5-xAlx-H system ($0 \leq x \leq 1$). *Intermetallics* **2015**, *62*, 7–16, doi:10.1016/j.intermet.2015.03.002.
62. Borzone, E.M.; Baruj, A.; Blanco, M.V.; Meyer, G.O. Dynamic measurements of hydrogen reaction with LaNi5−xSnx alloys. *Int. J. Hydrogen Energy* **2013**, *38*, 7335–7343, doi:10.1016/j.ijhydene.2013.04.035.
63. Odysseos, M.; De Rango, P.; Christodoulou, C.N.; Hlil, E.K.; Steriotis, T.; Karagiorgis, G.; Charalambopoulou, G.; Papapanagiotou, T.; Ampoumogli, A.; Psycharis, V.; et al. The effect of compositional changes on the structural and hydrogen storage properties of (La–Ce)Ni5 type intermetallics towards compounds suitable for metal hydride hydrogen compression. *J. Alloys Compd.* **2013**, *580*, S268–S270, doi:10.1016/j.jallcom.2013.01.057.
64. Milanese, C.; Jensen, T.R.; Hauback, B.C.; Pistidda, C.; Dornheim, M.; Yang, H.; Lombardo, L.; Zuettel, A.; Filinchuk, Y.; Ngene, P.; et al. Complex hydrides for energy storage. *Int. J. Hydrogen Energy* **2019**, *44*, 7860–7874, doi:10.1016/j.ijhydene.2018.11.208.
65. Reilly, J.J.; Wiswall, R.H. Reaction of hydrogen with alloys of magnesium and nickel and the formation of Mg2NiH4. *Inorg. Chem.* **1968**, *7*, 2254–2256, doi:10.1021/ic50069a016.
66. Barale, J.; Deledda, S.; Dematteis, E.M.; Sørby, M.H.; Baricco, M.; Hauback, B.C. Synthesis and characterization of Magnesium-Iron-Cobalt complex hydrides. *Sci. Rep.* **2020**, *10*, 9000, doi:10.1038/s41598-020-65774-8.
67. Rude, L.H.; Nielsen, T.K.; Ravnsbaek, D.B.; Bösenberg, U.; Ley, M.B.; Richter, B.; Arnbjerg, L.M.; Dornheim, M.; Filinchuk, Y.; Besenbacher, F.; et al. Tailoring properties of borohydrides for hydrogen storage: A review. *Phys. status solidi* **2011**, *208*, 1754–1773, doi:10.1002/pssa.201001214.
68. He, T.; Cao, H.; Chen, P. Complex Hydrides for Energy Storage, Conversion, and Utilization. *Adv. Mater.* **2019**, *31*, 1902757, doi:10.1002/adma.201902757.
69. Paskevicius, M.; Jepsen, L.H.; Schouwink, P.; Černý, R.; Ravnsbæk, D.B.; Filinchuk, Y.; Dornheim, M.; Besenbacher, F.; Jensen, T.R. Metal borohydrides and derivatives – synthesis, structure and properties. *Chem. Soc. Rev.* **2017**, *46*, 1565–1634, doi:10.1039/C6CS00705H.
70. Ley, M.B.; Jepsen, L.H.; Lee, Y.-S.; Cho, Y.W.; Bellosta von Colbe, J.M.; Dornheim, M.; Rokni, M.; Jensen, J.O.; Sloth, M.; Filinchuk, Y.; et al. Complex hydrides for hydrogen storage – new perspectives. *Mater. Today* **2014**, *17*, 122–128, doi:10.1016/j.mattod.2014.02.013.
71. Jepsen, L.H.; Ley, M.B.; Lee, Y.-S.; Cho, Y.W.; Dornheim, M.; Jensen, J.O.; Filinchuk, Y.; Jørgensen, J.E.; Besenbacher, F.; Jensen, T.R. Boron–nitrogen based hydrides and reactive composites for hydrogen storage. *Mater. Today* **2014**, *17*, 129–135, doi:10.1016/j.mattod.2014.02.015.
72. Li, H.-W.; Yan, Y.; Orimo, S.; Züttel, A.; Jensen, C.M. Recent Progress in Metal Borohydrides for Hydrogen Storage. *Energies* **2011**, *4*, 185–214, doi:10.3390/en4010185.
73. Callini, E.; Atakli, Z.Ö.K.; Hauback, B.C.; Orimo, S.; Jensen, C.; Dornheim, M.; Grant, D.; Cho, Y.W.; Chen, P.; Hjörvarsson, B.; et al. Complex and liquid hydrides for energy storage. *Appl. Phys. A* **2016**, *122*, 353, doi:10.1007/s00339-016-9881-5.
74. Sakintunaa, B.; Lamari-Darkrimb, F.; Hirscher, M. Metal hydride materials for solid hydrogen storage: A review. *Int. J. Hydrogen Energy* **2007**, *32*, 1121–1140, doi:10.1016/j.ijhydene.2006.11.022.
75. Milanese, C.; Garroni, S.; Gennari, F.; Marini, A.; Klassen, T.; Dornheim, M.; Pistidda, C. Solid State Hydrogen Storage in Alanates and Alanate-Based Compounds: A Review. *Metals (Basel).* **2018**, *8*, 567, doi:10.3390/met8080567.
76. Mamatha, M.; Weidenthaler, C.; Pommerin, A.; Felderhoff, M.; Schüth, F. Comparative studies of the decomposition of alanates followed by in situ XRD and DSC methods. *J. Alloys Compd.* **2006**, *416*, 303–314, doi:10.1016/j.jallcom.2005.09.004.
77. Bogdanović, B.; Brand, R.A.; Marjanović, A.; Schwickardi, M.; Tölle, J. Metal-doped sodium aluminium

hydrides as potential new hydrogen storage materials. *J. Alloys Compd.* **2000**, *302*, 36–58, doi:10.1016/S0925-8388(99)00663-5.

78. Liu, Y.; Ren, Z.; Zhang, X.; Jian, N.; Yang, Y.; Gao, M.; Pan, H. Development of Catalyst-Enhanced Sodium Alanate as an Advanced Hydrogen-Storage Material for Mobile Applications. *Energy Technol.* **2018**, *6*, 487–500, doi:10.1002/ente.201700517.
79. Gross, K.J.; Thomas, G.J.; Jensen, C.M. Catalyzed alanates for hydrogen storage. *J. Alloys Compd.* **2002**, *330–332*, 683–690, doi:10.1016/S0925-8388(01)01586-9.
80. Sandrock, G.; Gross, K.; Thomas, G.; Jensen, C.; Meeker, D.; Takara, S. Engineering considerations in the use of catalyzed sodium alanates for hydrogen storage. *J. Alloys Compd.* **2002**, *330–332*, 696–701, doi:10.1016/S0925-8388(01)01505-5.
81. Puszkiel, J.; Garroni, S.; Milanese, C.; Gennari, F.; Klassen, T.; Dornheim, M.; Pistidda, C. Tetrahydroborates: Development and Potential as Hydrogen Storage Medium. *Inorganics* **2017**, *5*, 74, doi:10.3390/inorganics5040074.
82. Züttel, A. Materials for hydrogen storage. *Mater. Today* **2003**, *6*, 24–33, doi:10.1016/S1369-7021(03)00922-2.
83. Nakamori, Y.; Miwa, K.; Ninomiya, A.; Li, H.; Ohba, N.; Towata, S.; Züttel, A.; Orimo, S. Correlation between thermodynamical stabilities of metal borohydrides and cation electronegativites: First-principles calculations and experiments. *Phys. Rev. B* **2006**, *74*, 045126, doi:10.1103/PhysRevB.74.045126.
84. Orimo, S.-I.; Nakamori, Y.; Ohba, N.; Miwa, K.; Aoki, M.; Towata, S.; Züttel, A. Experimental studies on intermediate compound of LiBH4. *Appl. Phys. Lett.* **2006**, *89*, 021920, doi:10.1063/1.2221880.
85. Züttel, A.; Borgschulte, A.; Orimo, S.-I. Tetrahydroborates as new hydrogen storage materials. *Scr. Mater.* **2007**, *56*, 823–828, doi:10.1016/j.scriptamat.2007.01.010.
86. Paskevicius, M.; Ley, M.B.; Sheppard, D.A.; Jensen, T.R.; Buckley, C.E. Eutectic melting in metal borohydrides. *Phys. Chem. Chem. Phys.* **2013**, *15*, 19774, doi:10.1039/c3cp53920b.
87. Roedern, E.; Jensen, T.R. Thermal Decomposition of Mn(BH4)2–M(BH4)x and Mn(BH4)2–MHx Composites with M = Li, Na, Mg, and Ca. *J. Phys. Chem. C* **2014**, *118*, 23567–23574, doi:10.1021/jp507770g.
88. Ley, M.; Roedern, E.; Thygesen, P.; Jensen, T. Melting Behavior and Thermolysis of NaBH4−Mg(BH4)2 and NaBH4−Ca(BH4)2 Composites. *Energies* **2015**, *8*, 2701–2713, doi:10.3390/en8042701.
89. Nickels, E.A.; Jones, M.O.; David, W.I.F.; Johnson, S.R.; Lowton, R.L.; Sommariva, M.; Edwards, P.P. Tuning the Decomposition Temperature in Complex Hydrides: Synthesis of a Mixed Alkali Metal Borohydride. *Angew. Chemie Int. Ed.* **2008**, *47*, 2817–2819, doi:10.1002/anie.200704949.
90. Liu, X.; Peaslee, D.; Sheehan, T.P.; Majzoub, E.H. Decomposition Behavior of Eutectic LiBH 4 –Mg(BH 4) 2 and Its Confinement Effects in Ordered Nanoporous Carbon. *J. Phys. Chem. C* **2014**, *118*, 27265–27271, doi:10.1021/jp509708t.
91. Lee, H.-S.; Lee, Y.-S.; Suh, J.-Y.; Kim, M.; Yu, J.-S.; Cho, Y.W. Enhanced Desorption and Absorption Properties of Eutectic LiBH4–Ca(BH4)2 Infiltrated into Mesoporous Carbon. *J. Phys. Chem. C* **2011**, *115*, 20027–20035, doi:10.1021/jp206000h.
92. Javadian, P.; Sheppard, D.A.; Buckley, C.E.; Jensen, T.R. Hydrogen storage properties of nanoconfined LiBH4–Ca(BH4)2. *Nano Energy* **2015**, *11*, 96–103, doi:10.1016/j.nanoen.2014.09.035.
93. Gosalawit-Utke, R.; Nielsen, T.K.; Saldan, I.; Laipple, D.; Cerenius, Y.; Jensen, T.R.; Klassen, T.; Dornheim, M. Nanoconfined 2LiBH4–MgH2 Prepared by Direct Melt Infiltration into Nanoporous Materials. *J. Phys. Chem. C* **2011**, *115*, 10903–10910, doi:10.1021/jp2021903.
94. Vajo, J.J. Influence of nano-confinement on the thermodynamics and dehydrogenation kinetics of metal hydrides. *Curr. Opin. Solid State Mater. Sci.* **2011**, *15*, 52–61, doi:10.1016/j.cossms.2010.11.001.
95. Roedern, E.; Hansen, B.R.S.; Ley, M.B.; Jensen, T.R. Effect of Eutectic Melting, Reactive Hydride Composites, and Nanoconfinement on Decomposition and Reversibility of LiBH4–KBH4. *J. Phys. Chem. C* **2015**, *119*, 25818–25825, doi:10.1021/acs.jpcc.5b09228.
96. Javadian, P.; Sheppard, D.A.; Buckley, C.E.; Jensen, T.R. Hydrogen storage properties of nanoconfined LiBH4–Ca(BH4)2. *Nano Energy* **2015**, *11*, 96–103, doi:10.1016/j.nanoen.2014.09.035.
97. Javadian, P.; Jensen, T.R. Enhanced hydrogen reversibility of nanoconfined LiBH4–Mg(BH4)2. *Int. J. Hydrogen Energy* **2014**, *39*, 9871–9876, doi:10.1016/j.ijhydene.2014.03.007.
98. Doroodian, A.; Dengler, J.E.; Genest, A.; Rösch, N.; Rieger, B. Methylguanidinium Borohydride: An Ionic-Liquid-Based Hydrogen-Storage Material. *Angew. Chemie Int. Ed.* **2010**, *49*, 1871–1873, doi:10.1002/anie.200905359.
99. Li, S.; Gao, H.; Shreeve, J.M. Borohydride Ionic Liquids and Borane/Ionic-Liquid Solutions as Hypergolic Fuels with Superior Low Ignition-Delay Times. *Angew. Chemie Int. Ed.* **2014**, *53*, 2969–2972, doi:10.1002/anie.201309044.
100. Li, H.-W.; Orimo, S.; Nakamori, Y.; Miwa, K.; Ohba, N.; Towata, S.; Züttel, A. Materials designing of metal borohydrides: Viewpoints from thermodynamical stabilities. *J. Alloys Compd.* **2007**, *446–447*, 315–318, doi:10.1016/j.jallcom.2007.02.156.
101. Ley, M.B.; Roedern, E.; Jensen, T.R. Eutectic melting of LiBH4–KBH4. *Phys. Chem. Chem. Phys.* **2014**, *16*, 24194–24199, doi:10.1039/C4CP03207A.

102. Hino, S.; Fonneløp, J.E.; Corno, M.; Zavorotynska, O.; Damin, A.; Richter, B.; Baricco, M.; Jensen, T.R.; Sørby, M.H.; Hauback, B.C. Halide Substitution in Magnesium Borohydride. *J. Phys. Chem. C* **2012**, *116*, 12482–12488, doi:10.1021/jp303123q.
103. Rude, L.H.; Groppo, E.; Arnbjerg, L.M.; Ravnsbæk, D.B.; Malmkjær, R.A.; Filinchuk, Y.; Baricco, M.; Besenbacher, F.; Jensen, T.R. Iodide substitution in lithium borohydride, LiBH4–LiI. *J. Alloys Compd.* **2011**, *509*, 8299–8305, doi:10.1016/j.jallcom.2011.05.031.
104. Olsen, J.E.; Karen, P.; Sørby, M.H.; Hauback, B.C. Effect of chloride substitution on the order–disorder transition in NaBH4 and Na11BD4. *J. Alloys Compd.* **2014**, *587*, 374–379, doi:10.1016/j.jallcom.2013.10.171.
105. Grove, H.; Rude, L.H.; Jensen, T.R.; Corno, M.; Ugliengo, P.; Baricco, M.; Sørby, M.H.; Hauback, B.C. Halide substitution in Ca(BH 4) 2. *RSC Adv.* **2014**, *4*, 4736–4742, doi:10.1039/C3RA46226A.
106. Rude, L.H.; Filinchuk, Y.; Sørby, M.H.; Hauback, B.C.; Besenbacher, F.; Jensen, T.R. Anion Substitution in Ca(BH4)2−CaI2: Synthesis, Structure and Stability of Three New Compounds. *J. Phys. Chem. C* **2011**, *115*, 7768–7777, doi:10.1021/jp111473d.
107. Ravnsbæk, D.B.; Rude, L.H.; Jensen, T.R. Chloride substitution in sodium borohydride. *J. Solid State Chem.* **2011**, *184*, 1858–1866, doi:10.1016/j.jssc.2011.05.030.
108. Rude, L.H.; Zavorotynska, O.; Arnbjerg, L.M.; Ravnsbæk, D.B.; Malmkjær, R.A.; Grove, H.; Hauback, B.C.; Baricco, M.; Filinchuk, Y.; Besenbacher, F.; et al. Bromide substitution in lithium borohydride, LiBH4–LiBr. *Int. J. Hydrogen Energy* **2011**, *36*, 15664–15672, doi:10.1016/j.ijhydene.2011.08.087.
109. Arnbjerg, L.M.; Ravnsbæk, D.B.; Filinchuk, Y.; Vang, R.T.; Cerenius, Y.; Besenbacher, F.; Jørgensen, J.-E.; Jakobsen, H.J.; Jensen, T.R. Structure and Dynamics for LiBH4−LiCl Solid Solutions. *Chem. Mater.* **2009**, *21*, 5772–5782, doi:10.1021/cm902013k.
110. Zavorotynska, O.; Corno, M.; Pinatel, E.; Rude, L.H.; Ugliengo, P.; Jensen, T.R.; Baricco, M. Theoretical and Experimental Study of LiBH4-LiCl Solid Solution. *Crystals* **2012**, *2*, 144–158, doi:10.3390/cryst2010144.
111. Pinatel, E.R.; Corno, M.; Ugliengo, P.; Baricco, M. Effects of metastability on hydrogen sorption in fluorine substituted hydrides. *J. Alloys Compd.* **2014**, *615*, S706–S710, doi:10.1016/j.jallcom.2014.01.028.
112. Corno, M.; Pinatel, E.; Ugliengo, P.; Baricco, M. A computational study on the effect of fluorine substitution in LiBH4. *J. Alloys Compd.* **2011**, *509*, S679–S683, doi:10.1016/j.jallcom.2010.10.005.
113. Rude, L.H.; Filsø, U.; D'Anna, V.; Spyratou, A.; Richter, B.; Hino, S.; Zavorotynska, O.; Baricco, M.; Sørby, M.H.; Hauback, B.C.; et al. Hydrogen–fluorine exchange in NaBH4–NaBF4. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18185, doi:10.1039/c3cp52815d.
114. Richter, B.; Ravnsbæk, D.B.; Sharma, M.; Spyratou, A.; Hagemann, H.; Jensen, T.R. Fluoride substitution in LiBH4; destabilization and decomposition. *Phys. Chem. Chem. Phys.* **2017**, *19*, 30157–30165, doi:10.1039/C7CP05565J.
115. Garroni, S.; Santoru, A.; Cao, H.; Dornheim, M.; Klassen, T.; Milanese, C.; Gennari, F.; Pistidda, C. Recent Progress and New Perspectives on Metal Amide and Imide Systems for Solid-State Hydrogen Storage. *Energies* **2018**, *11*, 1027, doi:10.3390/en11051027.
116. Hirscher, M.; Yartys, V.A.; Baricco, M.; Bellosta von Colbe, J.; Blanchard, D.; Bowman, R.C.; Broom, D.P.; Buckley, C.E.; Chang, F.; Chen, P.; et al. Materials for hydrogen-based energy storage – past, recent progress and future outlook. *J. Alloys Compd.* **2020**, *827*, 153548, doi:10.1016/j.jallcom.2019.153548.
117. Saunders, N.; Miodownik, A.P. *CALPHAD (calculation of phase diagrams): a comprehensive guide. Vol. 1.*; Elsevier, 1998;
118. Turchi, P.E.A.; Abrikosov, I.A.; Burton, B.; Fries, S.G.; Grimvall, G.; Kaufman, L.; Korzhavyi, P.; Rao Manga, V.; Ohno, M.; Pisch, A.; et al. Interface between quantum-mechanical-based approaches, experiments, and CALPHAD methodology. *Calphad* **2007**, *31*, 4–27, doi:10.1016/j.calphad.2006.02.009.
119. Dovesi, R.; Orlando, R.; Civalleri, B.; Roetti, C.; Saunders, V.R.; Zicovich-Wilson, C.M. CRYSTAL: a computational tool for the ab initio study of the electronic properties of crystals. *Zeitschrift für Krist. - Cryst. Mater.* **2005**, *220*, doi:10.1524/zkri.220.5.571.65065.
120. Dovesi, R.; Orlando, R.; Erba, A.; Zicovich-Wilson, C.M.; Civalleri, B.; Casassa, S.; Maschio, L.; Ferrabone, M.; De La Pierre, M.; D'Arco, P.; et al. CRYSTAL14: A Program for the Ab Initio Investigation of Crystalline Solids. *Int. J. Quantum Chem.* **2014**, *114*, 1287–1317, doi:10.1002/qua.24658.
121. Dovesi, R.; Saunders, V.R.; Roetti, C.; Orlando, R.; Zicovich-Wilson, C.M.; Pascale, F.; Civalleri, B.; Doll, K.; Harrison, N.M.; Bush, I.J.; et al. CRYSTAL17 User's Manual. *Univ. di Torino Torino, Italy* **2017**.
122. Dovesi, R.; Erba, A.; Orlando, R.; Zicovich-Wilson, C.M.; Civalleri, B.; Maschio, L.; Rérat, M.; Casassa, S.; Baima, J.; Salustro, S.; et al. Quantum-mechanical condensed matter simulations with CRYSTAL. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, *8*, e1360, doi:10.1002/wcms.1360.
123. Dematteis, E.M.; Roedern, E.; Pinatel, E.R.; Corno, M.; Jensen, T.R.; Baricco, M. A thermodynamic investigation of the LiBH4–NaBH4 system. *RSC Adv.* **2016**, *6*, 60101–60108, doi:10.1039/C6RA09301A.
124. Dematteis, E.M.; Pinatel, E.R.; Corno, M.; Jensen, T.R.; Baricco, M. Phase diagrams of the LiBH4–NaBH4–KBH4 system. *Phys. Chem. Chem. Phys.* **2017**, *19*, 25071–25079, doi:10.1039/C7CP03816J.
125. Albanese, E.; Corno, M.; Baricco, M.; Civalleri, B. Simulation of nanosizing effects in the decomposition of Ca(BH4)2 through atomistic thin film models. *Res. Chem. Intermed.* **2021**, *47*, 345–356, doi:10.1007/s11164-

020-04326-1.
126. Kim, K.J.; Montoya, B.; Razani, A.; Lee, K.-H. Metal hydride compacts of improved thermal conductivity. *Int. J. Hydrogen Energy* **2001**, *26*, 609–613, doi:10.1016/S0360-3199(00)00115-4.
127. Baldissin, D.; Urgnani, J.; Palumbo, M.; Gagliano, S.; Baricco, M. Thermofluidodynamic modelling of hydrogen absorption and desorption in a LaNi4.8Al0.2 hydride bed. *Present. MH2008 Int. Symp. Met. Syst. Reykjavik, Icel.* **2008**, *23-28 June*.
128. Bellosta von Colbe, J.; Ares, J.-R.; Barale, J.; Baricco, M.; Buckley, C.; Capurso, G.; Gallandat, N.; Grant, D.M.; Guzik, M.N.; Jacob, I.; et al. Application of hydrides in hydrogen storage and compression: Achievements, outlook and perspectives. *Int. J. Hydrogen Energy* **2019**, *44*, 7780–7808, doi:10.1016/j.ijhydene.2019.01.104.
129. Ley, M.; Meggouh, M.; Moury, R.; Peinecke, K.; Felderhoff, M. Development of Hydrogen Storage Tank Systems Based on Complex Metal Hydrides. *Materials (Basel).* **2015**, *8*, 5891–5921, doi:10.3390/ma8095280.
130. Utz, I.; Linder, M.; Schmidt, N.; Hu, J.J.; Fichtner, M.; Wörner, A. Experimental study of powder bed behavior of sodium alanate in a lab-scale H2 storage tank with flow-through mode. *Int. J. Hydrogen Energy* **2012**, *37*, 7645–7653, doi:10.1016/j.ijhydene.2012.02.016.
131. Utz, I.; Schmidt, N.; Wörner, A.; Hu, J.J.; Zabara, O.; Fichtner, M. Experimental results of an air-cooled lab-scale H2 storage tank based on sodium alanate. *Int. J. Hydrogen Energy* **2011**, *36*, 3556–3565, doi:10.1016/j.ijhydene.2010.12.057.
132. Pfeifer, P.; Wall, C.; Jensen, O.; Hahn, H.; Fichtner, M. Thermal coupling of a high temperature PEM fuel cell with a complex hydride tank. *Int. J. Hydrogen Energy* **2009**, *34*, 3457–3466, doi:10.1016/j.ijhydene.2009.02.041.
133. Weiss-Ungethüm, J.; Bürger, I.; Schmidt, N.; Linder, M.; Kallo, J. Experimental investigation of a liquid cooled high temperature proton exchange membrane (HT-PEM) fuel cell coupled to a sodium alanate tank. *Int. J. Hydrogen Energy* **2014**, *39*, 5931–5941, doi:10.1016/j.ijhydene.2014.01.127.
134. Urbanczyk, R.; Peinecke, K.; Meggouh, M.; Minne, P.; Peil, S.; Bathen, D.; Felderhoff, M. Design and operation of an aluminium alloy tank using doped Na3AlH6 in kg scale for hydrogen storage. *J. Power Sources* **2016**, *324*, 589–597, doi:10.1016/j.jpowsour.2016.05.102.
135. Daniel A. Mosher; Xia Tang; Ronald J. Brown; Sarah Arsenault; Salvatore Saitta; Bruce L. Laube; Robert H. Dold; Donald L. Anton *High Density Hydrogen Storage System Demonstration Using NaAlH4 Based Complex Compound Hydrides*; Golden, CO (United States), 2007;
136. Mosher, D.A.; Arsenault, S.; Tang, X.; Anton, D.L. Design, fabrication and testing of NaAlH4 based hydrogen storage systems. *J. Alloys Compd.* **2007**, *446–447*, 707–712, doi:10.1016/j.jallcom.2007.01.042.
137. Urbanczyk, R.; Peinecke, K.; Felderhoff, M.; Hauschild, K.; Kersten, W.; Peil, S.; Bathen, D. Aluminium alloy based hydrogen storage tank operated with sodium aluminium hexahydride Na3AlH6. *Int. J. Hydrogen Energy* **2014**, *39*, 17118–17128, doi:10.1016/j.ijhydene.2014.08.101.
138. Urbanczyk, R.; Peil, S.; Bathen, D.; Heßke, C.; Burfeind, J.; Hauschild, K.; Felderhoff, M.; Schüth, F. HT-PEM Fuel Cell System with Integrated Complex Metal Hydride Storage Tank. *Fuel Cells* **2011**, *11*, 911–920, doi:10.1002/fuce.201100012.
139. Na Ranong, C.; Höhne, M.; Franzen, J.; Hapke, J.; Fieg, G.; Dornheim, M.; Eigen, N.; Bellosta von Colbe, J.M.; Metz, O. Concept, Design and Manufacture of a Prototype Hydrogen Storage Tank Based on Sodium Alanate. *Chem. Eng. Technol.* **2009**, *32*, 1154–1163, doi:10.1002/ceat.200900095.
140. Wellnitz, J. Hydrogen storage systems for automotive applications: project StorHy. *Int. J. Sustain. Des.* **2008**, *1*, 93, doi:10.1504/IJSDES.2008.017059.
141. Bellosta von Colbe, J.M.; Metz, O.; Lozano, G.A.; Pranzas, P.K.; Schmitz, H.W.; Beckmann, F.; Schreyer, A.; Klassen, T.; Dornheim, M. Behavior of scaled-up sodium alanate hydrogen storage tanks during sorption. *Int. J. Hydrogen Energy* **2012**, *37*, 2807–2811, doi:10.1016/j.ijhydene.2011.03.153.
142. Bellosta von Colbe, J.M.; Lozano, G.; Metz, O.; Bücherl, T.; Bormann, R.; Klassen, T.; Dornheim, M. Design, sorption behaviour and energy management in a sodium alanate-based lightweight hydrogen storage tank. *Int. J. Hydrogen Energy* **2015**, *40*, 2984–2988, doi:10.1016/j.ijhydene.2015.01.013.
143. Johnson, T.A.; Kanouff, M.P.; Dedrick, D.E.; Evans, G.H.; Jorgensen, S.W. Model-based design of an automotive-scale, metal hydride hydrogen storage system. *Int. J. Hydrogen Energy* **2012**, *37*, 2835–2849, doi:10.1016/j.ijhydene.2011.05.030.
144. Yan, M.; Sun, F.; Liu, X.; Ye, J.; Wang, S.; Jiang, L. Effects of graphite content and compaction pressure on hydrogen desorption properties of Mg(NH2)2–2LiH based tank. *J. Alloys Compd.* **2015**, *628*, 63–67, doi:10.1016/j.jallcom.2014.12.173.
145. Yan, M.Y.; Sun, F.; Liu, X.P.; Ye, J.H.; Yuan, H.P.; Wang, S.M.; Jiang, L.J. Experimental study on hydrogen storage properties of Li–Mg–N–H based tank. *J. Alloys Compd.* **2014**, *603*, 19–22, doi:10.1016/j.jallcom.2014.03.054.
146. Lohstroh, W.; Fichtner, M.; Breitung, W. Complex hydrides as solid storage materials: First safety tests. *Int. J. Hydrogen Energy* **2009**, *34*, 5981–5985, doi:10.1016/j.ijhydene.2009.01.030.
147. Wee, J.-H. Which type of fuel cell is more competitive for portable application: Direct methanol fuel cells or

direct borohydride fuel cells? *J. Power Sources* **2006**, *161*, 1–10, doi:10.1016/j.jpowsour.2006.07.032.
148. Ma, J.; Choudhury, N.A.; Sahai, Y. A comprehensive review of direct borohydride fuel cells. *Renew. Sustain. Energy Rev.* **2010**, *14*, 183–199, doi:10.1016/j.rser.2009.08.002.
149. Kim, J.; Kim, T. Compact PEM fuel cell system combined with all-in-one hydrogen generator using chemical hydride as a hydrogen source. *Appl. Energy* **2015**, *160*, 945–953, doi:10.1016/j.apenergy.2015.03.084.
150. Liu, B.H.; Li, Z.P. A review: Hydrogen generation from borohydride hydrolysis reaction. *J. Power Sources* **2009**, *187*, 527–534, doi:10.1016/j.jpowsour.2008.11.032.
151. Demirci, U.B.; Akdim, O.; Andrieux, J.; Hannauer, J.; Chamoun, R.; Miele, P. Sodium Borohydride Hydrolysis as Hydrogen Generator: Issues, State of the Art and Applicability Upstream from a Fuel Cell. *Fuel Cells* **2010**, *10*, 335–350, doi:10.1002/fuce.200800171.
152. van Biert, L.; Godjevac, M.; Visser, K.; Aravind, P.V. A review of fuel cell systems for maritime applications. *J. Power Sources* **2016**, *327*, 345–364, doi:10.1016/j.jpowsour.2016.07.007.
153. Fiori, C.; Dell’Era, A.; Zuccari, F.; Santiangeli, A.; D’Orazio, A.; Orecchini, F. Hydrides for submarine applications: Overview and identification of optimal alloys for air independent propulsion maximization. *Int. J. Hydrogen Energy* **2015**, *40*, 11879–11889, doi:10.1016/j.ijhydene.2015.02.105.
154. Ghosh, P.C.; Vasudeva, U. Analysis of 3000T class submarines equipped with polymer electrolyte fuel cells. *Energy* **2011**, *36*, 3138–3147, doi:10.1016/j.energy.2011.03.003.
155. Bicer, Y.; Dincer, I. Clean fuel options with hydrogen for sea transportation: A life cycle approach. *Int. J. Hydrogen Energy* **2018**, *43*, 1179–1193, doi:10.1016/j.ijhydene.2017.10.157.
156. Weydahl, H.; Gilljam, M.; Lian, T.; Johannessen, T.C.; Holm, S.I.; Hasvold, J.Ø. Fuel cell systems for long-endurance autonomous underwater vehicles – challenges and benefits. *Int. J. Hydrogen Energy* **2020**, *45*, 5543–5553, doi:10.1016/j.ijhydene.2019.05.035.
157. Sattler, G. Fuel cells going on-board. *J. Power Sources* **2000**, *86*, 61–67, doi:10.1016/S0378-7753(99)00414-0.
158. Swider-Lyons, K.; Deitz, D. Hydrogen Fuel Cells for Unmanned Undersea Vehicle Propulsion. *ECS Trans.* **2016**, *75*, 479–489, doi:10.1149/07514.0479ecst.
159. Bevan, A.I.; Züttel, A.; Book, D.; Harris, I.R. Performance of a metal hydride store on the “Ross Barlow” hydrogen powered canal boat. *Faraday Discuss.* **2011**, *151*, 353, doi:10.1039/c0fd00025f.
160. Doucet, G.; Etiévant, C.; Puyenchet, C.; Grigoriev, S.; Millet, P. Hydrogen-based PEM auxiliary power unit. *Int. J. Hydrogen Energy* **2009**, *34*, 4983–4989, doi:10.1016/j.ijhydene.2008.12.029.
161. www.toshiba-energy.com.
162. Rizzi, P.; Pinatel, E.; Luetto, C.; Florian, P.; Graizzaro, A.; Gagliano, S.; Baricco, M. Integration of a PEM fuel cell with a metal hydride tank for stationary applications. *J. Alloys Compd.* **2015**, *645*, S338–S342, doi:10.1016/j.jallcom.2014.12.145.
163. www.gknpm.com.
164. Beaufrere, A.H.; Salzano, F.J.; Isler, R.J.; Yu, W.S. Hydrogen storage via iron-titanium for a 26 MW(e) peaking electric plant. *Int. J. Hydrogen Energy* **1976**, *1*, 307–319, doi:10.1016/0360-3199(76)90025-2.
165. Strickland, G.; Yu, W.S. *Some rate and modeling studies on the use of iron-titanium hydride as an energy storage medium for electric utility companies*; Upton, NY (United States), 1977;
166. Strickland, G.; Milau, J.; Rosso, M. *Some observations on the effects of the volumetric expansion of iron-titanium hydride on vessels built at BNL*; Upton, NY (United States), 1977;
167. Beaufrere, A.; Yeo, R.S.; Srinivasan, S.; McElroy, J.; Hart, G. Hydrogen-halogen energy storage system for electric utility applications. *Conf. 12. Intersoc. energy Convers. Eng. Conf. Washington, Dist. Columbia, United States Am. (USA), 28 Aug 1977* **1977**.
168. Veziroglu, T.N. *Hydrogen Energy*; Veziroğlu, T.N., Ed.; Springer US: Boston, MA, 1975; ISBN 978-1-4684-2609-0.
169. HyCARE project Available online: www.hycare-project.eu.
170. HyCARE focuses on large-scale, solid-state hydrogen storage. *Fuel Cells Bull.* **2019**, *2019*, 11, doi:10.1016/S1464-2859(19)30068-9.
171. McPhy INGRID project Available online: https://mcphy.com/en/achievements/ingrid.
172. Johnson, T.A.; Jorgensen, S.W.; Dedrick, D.E. Performance of a full-scale hydrogen-storage tank based on complex hydrides. *Faraday Discuss.* **2011**, *151*, 327, doi:10.1039/c0fd00017e.
173. Bürger, I.; Komogowski, L.; Linder, M. Advanced reactor concept for complex hydrides: Hydrogen absorption from room temperature. *Int. J. Hydrogen Energy* **2014**, *39*, 7030–7041, doi:10.1016/j.ijhydene.2014.02.070.
174. Hu, J.; Fichtner, M.; Baricco, M. Preparation of Li-Mg-N-H hydrogen storage materials for an auxiliary power unit. *Int. J. Hydrogen Energy* **2017**, *42*, 17144–17148, doi:10.1016/j.ijhydene.2017.06.021.
175. Hu, J.; Pohl, A.; Wang, S.; Rothe, J.; Fichtner, M. Additive Effects of LiBH 4 and ZrCoH3 on the Hydrogen Sorption of the Li-Mg-N-H Hydrogen Storage System. *J. Phys. Chem. C* **2012**, *116*, 20246–20253, doi:10.1021/jp307775d.
176. Zhang, X.; Li, Z.; Lv, F.; Li, H.; Mi, J.; Wang, S.; Liu, X.; Jiang, L. Improved hydrogen storage performance of the LiNH2–MgH2–LiBH4 system by addition of ZrCo hydride. *Int. J. Hydrogen Energy* **2010**, *35*, 7809–7814, doi:10.1016/j.ijhydene.2010.05.095.

177. Baricco, M.; Bang, M.; Fichtner, M.; Hauback, B.; Linder, M.; Luetto, C.; Moretto, P.; Sgroi, M. SSH2S: Hydrogen storage in complex hydrides for an auxiliary power unit based on high temperature proton exchange membrane fuel cells. *J. Power Sources* **2017**, *342*, 853–860, doi:10.1016/j.jpowsour.2016.12.107.
178. Bürger, I.; Hu, J.J.; Vitillo, J.G.; Kalantzopoulos, G.N.; Deledda, S.; Fichtner, M.; Baricco, M.; Linder, M. Material properties and empirical rate equations for hydrogen sorption reactions in 2 LiNH2–1.1 MgH2–0.1 LiBH4–3 wt.% ZrCoH3. *Int. J. Hydrogen Energy* **2014**, *39*, 8283–8292, doi:10.1016/j.ijhydene.2014.02.120.
179. Lototskyy, M. V.; Tolj, I.; Davids, M.W.; Klochko, Y. V.; Parsons, A.; Swanepoel, D.; Ehlers, R.; Louw, G.; van der Westhuizen, B.; Smith, F.; et al. Metal hydride hydrogen storage and supply systems for electric forklift with low-temperature proton exchange membrane fuel cell power module. *Int. J. Hydrogen Energy* **2016**, *41*, 13831–13842, doi:10.1016/j.ijhydene.2016.01.148.
180. Standal, K.; Talevi, M.; Westskog, H. Engaging men and women in energy production in Norway and the United Kingdom: The significance of social practices and gender relations. *Energy Res. Soc. Sci.* **2020**, *60*, 101338, doi:10.1016/j.erss.2019.101338.
181. Arora-Jonsson, S. Virtue and vulnerability: Discourses on women, gender and climate change. *Glob. Environ. Chang.* **2011**, *21*, 744–751, doi:10.1016/j.gloenvcha.2011.01.005.
182. Geels, F.W.; Schot, J. Typology of sociotechnical transition pathways. *Res. Policy* **2007**, *36*, 399–417, doi:10.1016/j.respol.2007.01.003.
183. Geels, F.W. Socio-technical transitions to sustainability: a review of criticisms and elaborations of the Multi-Level Perspective. *Curr. Opin. Environ. Sustain.* **2019**, *39*, 187–201, doi:10.1016/j.cosust.2019.06.009.
184. Geels, F.W. Technological transitions as evolutionary reconfiguration processes: a multi-level perspective and a case-study. *Res. Policy* **2002**, *31*, 1257–1274, doi:10.1016/S0048-7333(02)00062-8.