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A review of the potential of hydrogen carriers for zero emission, low signature ship propulsion systems

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Synopsis

Increasing pressure on the reduction or elimination of the use of fossil fuels in shipping requires the application of new maritime fuel alternatives. Green and circular produced hydrogen as a maritime fuel in fuel cell systems offers a great solution for these concerns. A fuel cell system has a zero emission performance, solid state silent process cycle, graceful degradation and no single point of failure. From a naval perspective, these characteristics very much support operational requirements like a silent propulsion and very low thermal and acoustic signatures as well as the possibility of an air independent system. Storage of hydrogen, however, is an issue. Traditional hydrogen storage in gas or liquefied aggregation has low volumetric density, low flame point, fire and explosion risks and transport challenges. The aim of this literature review is to investigate several hydrogen carriers and evaluate their characteristics on maritime and naval performance. This includes their volumetric and gravimetric density, dehydrogenation process, safety, logistic availability and handling. Over 15 different (types of) hydrogen carriers have been researched. Borohydrides, specifically sodium borohydride appeared to have several advantages, but still has issues with its hydrogenation process and handling due to it being a solid. The liquid organic hydrogen carrier dibenzyl toluene, on the other hand, does not meet the required energy density, but does have favourable additional properties, such as easy hydrogenation and good handling. Both of these are also subject of current research and development: For example, Hydrogenious LOHC Maritime AS, in combination with Østensjø Rederi, is working on a megawatt application for maritime, which should be finished in 2025. The Dutch government funds the SH2IPDRIVE project and the European Interreg North West Europe organization funds the H2SHIPS research project to analyse the shipboard use of these hydrogen carriers and to establish the design and engineering optimization opportunities.

Keywords: Hydrogen, hydrogen carriers, Solid hydrogen carriers, Liquid hydrogen carriers, Maritime transportation

1 Introduction

Shipping worldwide is a large business, emitting about 2% of CO₂-emissions overall (IEA, 2021). Shipping is currently not on track to reach the desired 50% reduction of greenhouse gas (GHG) emissions by 2050 (IEA, 2021). Also, climate change is only one of the reasons for this desired reduction. With the use of Heavy Fuel Oil (HFO) and Marine Diesel Oil (MDO) other emissions, such as SO_x and NO_x, are emitted as well during combustion (IMO, 2019). Currently, SO_x emissions are already regulated. It is likely that NO_x and soot emissions will be regulated soon as well, especially in urban areas. This all means that it is very important for the shipping industry to transition towards a zero emission way of transport (IMO, 2019).

The automotive industry is a front runner in this respect. There are already many cars and busses with zero emissions. The solution of the automotive industry is the Li-ion battery. These batteries are not the solution for the shipping industry, due to the low gravimetric and volumetric energy density of batteries; for a container ship sailing with a certain operational profile, about 45% of the weight and 16% of the volume of the cargo hold would have to be used by the batteries for the ship to be able to comply with the operational profile (McKinlay et al., 2020). When fueled with HFO this is only 2% of the weight and less than 2% of the volume of the cargo hold (McKinlay et al., 2020). This means that other alternatives have to be found.

There are a few demands to which these new future fuels have to comply:

- Safe (from toxic and fire hazard perspective)

Authors' Biographies

Erin van Rheenen is a PhD-candidate at the TU Delft, Faculty Mechanical, Maritime and Materials Technology. Originally a mechanical engineer and nuclear fusion physicist, she is currently working on the integration of hydrogen carriers on ships, within the SH2IPDRIVE project.

Johan Padding is professor of Complex Fluid Processing at TU Delft. He specializes in multiscale modelling of multiphase flows, mesoscale transport phenomena, soft matter, rheology, and heterogeneous catalysis, with a focus on scale-up of fluidised beds, spray dryers, crystallisers, and (electro)chemical reactors.

Chris Slootweg is associate professor of sustainable chemistry at the University of Amsterdam. The mission of his laboratory is to educate students at the intersection of fundamental physical organic chemistry, main-group chemistry and circular chemistry.

Klaas Visser (RADM Marine Engineering ret) is Associate Professor Marine Engineering at the Faculty Mechanical, Maritime and Materials Technology, Delft University of Technology, the Netherlands, since 2013. His research topics include Hybrid Ship Configurations, Alternative maritime zero carbon fuels, Maritime System Integration and Autonomous Ships. Before 2013, Klaas Visser served in the Royal Netherlands Navy, with an operational focus on submarines.

- Zero emission (GHG, hazardous pollutants)
- High volumetric and gravimetric energy density
- Good logistic availability and easy handling

One of the most promising alternative future fuels are hydrogen based future fuels, especially in combination with fuel cells. Hydrogen has the advantage that it is zero-emission when used in combination with fuel cells (van Biert et al., 2016). When using a PEM fuel cell, less noise and vibrations are produced compared to an internal combustion engine (van Biert et al., 2016; Inal and Deniz, 2020). Additional advantages are modularity, causing gradual degradation, economic, efficient (40-60%), silent and operation at low temperatures (338 to 358 K) (van Biert et al., 2016; McKinlay et al., 2020). Silent operation, very low acoustic and thermal signatures as well as low maintenance requirements very much support the applicability in naval systems.

Therefore, this paper will focus on the application of hydrogen onboard a ship. The main issue is the hydrogen storage. This is difficult, as storage at ambient conditions results in extremely large tanks and is thus not viable. Hydrogen can be stored in several ways, such as pressurizing (70 MPa) or liquefying (20 K) it to enhance the volumetric energy density (Rivard et al., 2019). Storing hydrogen this way does not reach the set goals of gravimetric (9 MJ/kg or 7.5 wt% of hydrogen) and volumetric (8.4 MJ/L) energy density (Rivard et al., 2019; U.S. Department of Energy, 2015).

There are also other ways to store hydrogen, namely by storing it inside other substances, for example by chemical bonding or physical adsorption (Moradi and Groth, 2019). In order to comply with the zero emission target, it is important that the fuel can be made without emitting harmful substances.

The aim of this literature review paper is to give an overview of the many ways to store hydrogen in hydrogen carriers, viable for the shipping industry in general and naval engineering in particular. An overview of different types of hydrogen carriers will be given. For some viable hydrogen carriers the effective energy density will be discussed, in order to have a good comparison to the current fuels used. Also, several state-of-the-art industrial examples will be discussed.

2 Classification of Hydrogen carriers

The storage of hydrogen in general can be split into different ways of storage methods. The exact definition of the storage methods is under debate (Durbin and Malardier-Jugroot, 2013; U.S. Department of Energy, 2015; Abe et al., 2019; Kojima, 2019; Bellosta von Colbe et al., 2019; Tarasov et al., 2021). Most of the time hydrogen storage is defined as storing hydrogen as a chemical hydride or using physical sorption (material based storage) (Durbin and Malardier-Jugroot, 2013; Abe et al., 2019). A point of discussion here is the definition of chemical hydrides and physical storage. Some authors define metal hydrides as hydrogen connected to metals, in all sorts of forms (Durbin and Malardier-Jugroot, 2013), whereas other authors see it as hydrogen bonded into metals, making it behave similar to physical sorption storage (Abe et al., 2019). In this literature review, metal hydrides will be defined as part of material-based solid hydrogen carriers. The term chemical hydrides, even though extensively used, will be avoided due to its vagueness (Abe et al., 2019; Moradi and Groth, 2019; Tarasov et al., 2021; Nguyen and Shabani, 2021; Malleswararao et al., 2022).

These types of discussions is the reason that in this literature review, a classification as based on figure 1 is proposed. Hydrogen storage is defined as either material or physical-based, with physical-based being the storage of pure hydrogen. Material-based storage is split up into liquid and solid material-based storage. This is more of an engineering approach, as liquid and solid storage methods require different handling. Metal hydrides can now be a part of solid storage, together with complex hydrides and physical adsorption methods. The MOFs used for physical adsorption are also solid materials. Next to handling, the material classification also provides groups of storage with similar dehydrogenation processes and gravimetric energy density storage. From an engineering overview, these materials can be treated in similar ways for both storage, hydrogenation and dehydrogenation. The hydrogen carriers will be reviewed on the demands that are placed by the shipping industry and will include safety, emissions, volumetric and gravimetric energy density, ease and speed of generation of hydrogen from carrier and recyclability of the carrier. The US Department of Energy (DOE) has defined a goal for both the gravimetric and volumetric energy density, stating that it should be at least 7.5wt% of hydrogen per kg of the carrier and 2.3kWh/L for light duty vehicles (U.S. Department of Energy, 2015). This goal will be taken as a guideline in this paper.

3 Solid hydrogen carriers

Solid hydrogen carriers are materials that are in solid state when storing the hydrogen. This does not necessarily mean that they have to be at solid state at ambient conditions, an example is ice XVII, which requires specific temperature and pressure to exist in that state (del Rosso et al., 2017). It is considered good practice to keep solid hydrogen storage away from water (Hoecke et al., 2021).

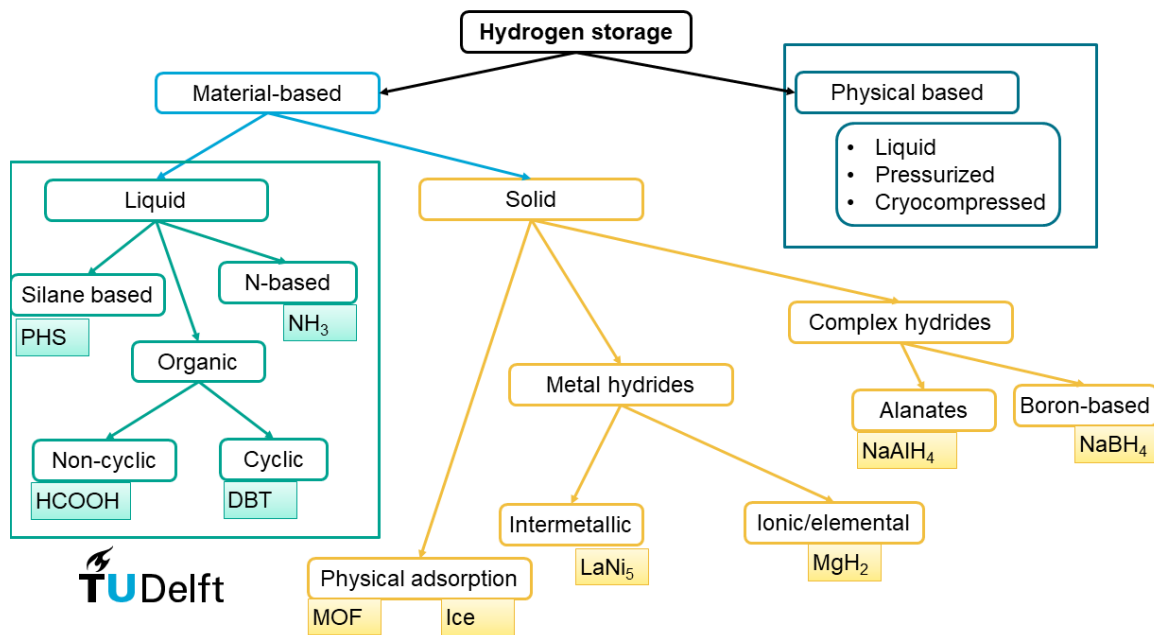


Figure 1: Proposed classification of hydrogen carriers for engineering purposes, including examples

3.1 Physical adsorption

Some materials can be used to store hydrogen inside their structure, without splitting the H-H chemical bond, resulting in no free H atoms present (Moradi and Groth, 2019). This is called physical sorption. The main structures able to adsorb hydrogen physically will be discussed in this section.

3.1.1 Metal organic frameworks

Metal organic frameworks, also known as MOFs, are crystalline structures that are able to adsorb hydrogen in their voids (Shet et al., 2021). MOFs are mostly defined as physical sorption storage and pose a very promising way of storing hydrogen (Moradi and Groth, 2019). MOFs have a large structural diversity and thus, dependent on the application, different MOFs can be used (Langmi et al., 2014). MOFs usually have high porosity (to store the hydrogen inside their voids) and a high surface area (Langmi et al., 2014; Rivard et al., 2019). Research focuses on both cryogenic as well as MOFs that store hydrogen at room temperature and ambient pressures (Langmi et al., 2014). A great advantage of MOFs is their fast release and adsorption of hydrogen, which is usually a matter of only seconds (Langmi et al., 2014; Rivard et al., 2019). The storage of hydrogen inside MOFs is reversible, however after multiple cycles the amount of hydrogen that can be stored inside the MOF can drop substantially (Langmi et al., 2014; Rivard et al., 2019). In order for MOFs to become a suitable option for hydrogen storage, a lot of research is still needed, as current solutions are not practical and hard to scale up (Langmi et al., 2014; Rivard et al., 2019).

3.1.2 Metal decorated structures

Structures such as silicon clusters or honeycomb borophene are capable of storing hydrogen as well, in a very similar way to MOFs (Habibi et al., 2021; Jaiswal et al., 2022). The working principle is very similar to that of MOFs, as these structure also adsorb molecular hydrogen without changing their structures (Habibi et al., 2021; Jaiswal et al., 2022). When alkali metals are added to these structures they can store up to 18 wt% of hydrogen at 100 K and 6000 kPa for a silicon lithium structure (Jaiswal et al., 2022). When borophene oxide is bonded with the metal lithium, a gravimetric density of 8.3 wt% can be reached at 100 K (Habibi et al., 2021). However, at room temperature and low pressure (300 kPa) the hydrogen storage is greatly reduced, to a maximum of 5.5 wt% (Jaiswal et al., 2022). A similar phenomenon applies to the borophene honeycomb structure, although the difference there is smaller, as at room temperature and relatively low pressures (about 3000 kPa) still 5.2 wt% of hydrogen can be stored (Habibi et al., 2021). The volumetric energy density is not mentioned in the papers by Habibi et al. (2021) and Jaiswal et al. (2022). In order for both of these types of storage to become a solution to the hydrogen storage issue, a lot more research has to be done on the exact nature of the structures and how to enhance the hydrogen storage at room temperature and relatively low pressures.

3.1.3 Nanostructures

Nanostructures are not a material by itself, but an example of physical storage. Nanostructures are usually made of carbon (Durbin and Malardier-Jugroot, 2013; Zuttel et al., 2002). There are several types of nanostructures (Durbin and Malardier-Jugroot, 2013). Nanomaterials can, amongst others, be based on carbon, silicon carbide, boron and boron nitride (Froudakis, 2011; Durbin and Malardier-Jugroot, 2013). The storage principle behind these materials is the same, but the properties are different (Durbin and Malardier-Jugroot, 2013). Carbon nanostructures are the most researched type of nanomaterials, usually they are designed as nanotubes (Froudakis, 2011). It is not entirely clear how much these materials can store as several results are not reproducible (Froudakis, 2011; Durbin and Malardier-Jugroot, 2013). Nanomaterials started with activated carbon, which can hold only about 3.2 wt% hydrogen at 18900 kPa and room temperatures (Durbin and Malardier-Jugroot, 2013). Studies have shown that it is not possible to reach the DOE limit using carbon nanotubes at room temperature (Froudakis, 2011). Like MOFs, at lower temperature these carbon nanostructures are much more effective, storing 8wt% hydrogen at 77 K (Durbin and Malardier-Jugroot, 2013). Refuelling is extremely hard, as it is hard to add hydrogen to these type of structures (Durbin and Malardier-Jugroot, 2013). Additionally, release of hydrogen is very slow, with half of the release in an hour and complete hydrogen release in over 200 h (Zuttel et al., 2002). Another issue is the collapse of nanotubes during dehydrogenation, as well as fracture and strain which influence the size of the tubes that can be used (Durbin and Malardier-Jugroot, 2013). As the carbon nanotubes will not reach the target, other types of nanotubes have been researched (Froudakis, 2011). These were still insufficient in reaching the energy density target (Froudakis, 2011). There is a lot of research into nanostructures, both carbon as well as non-carbon (Durbin and Malardier-Jugroot, 2013).

3.1.4 Ice

Another way of storing hydrogen is in clathrates (Durbin and Malardier-Jugroot, 2013). A common clathrate is ice, which can store hydrogen inside its lattice. The official name of this clathrate is clathrate hydrate (Durbin and Malardier-Jugroot, 2013). The amount of hydrogen stored in a clathrate depends on the pressure and temperature; usually high pressures are required (del Rosso et al., 2017; Durbin and Malardier-Jugroot, 2013). In ice, depending on the pressure, between 5.2 and 12.9 wt% of hydrogen can be stored, at a volume of 1.5 to 3.5 kWh/kg, reaching the target set by the DOE (Durbin and Malardier-Jugroot, 2013; U.S. Department of Energy, 2015; Liu et al., 2019). In order to store higher wt% of hydrogen, however, enormous amounts of pressure are required (at least 700MPa) (Durbin and Malardier-Jugroot, 2013). The main advantages of storing hydrogen in ice is that the required storage material (water) is cheap and the storage is extremely safe: it has low environmental impact and is self-extinguishing (Durbin and Malardier-Jugroot, 2013). The main issue is the high pressures and low temperatures required (Durbin and Malardier-Jugroot, 2013; del Rosso et al., 2017). For example, to store 4 wt% of hydrogen, a pressure of 4000 kPa and a temperature of 114 K is required (del Rosso et al., 2017). The storage can be improved by using promoters (Florusse et al., 2004). When adding a second component, in the case of Florusse tetrahydrofuran (THF), the hydrogen can be stored at lower pressure and ambient temperatures (Florusse et al., 2004). It is thought that, by adding THF, 4wt% of hydrogen can be stored inside the ice, at about 297 K and 5000 kPa (Florusse et al., 2004). The main issue of storing hydrogen in ice, with or without a promotor, is the low storage amount. Studies have not shown storage capacities higher than 5wt% of hydrogen, which is significantly below the target.

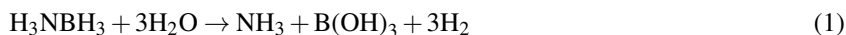
3.2 Complex hydride - Boranes/Borohydrides

Boranes and borohydrides are molecules that have either a BH_3 or BH_4 part (Demirci, 2020). The most common borohydrides are sodium and lithium borohydride, although potassium borohydride is also well researched (Laversenne et al., 2008; Durbin and Malardier-Jugroot, 2013). Boranes and borohydrides are promising storage materials due to their high hydrogen content, of up to 18 wt% (Umegaki et al., 2009). They are usually safe to store as well (Demirci and Miele, 2009). Borohydrides and boranes can release hydrogen in multiple ways, however the two main reaction paths are thermolysis and hydrolysis. Hydrogen release through thermolysis is done by heating the borohydride or borane. The temperatures required to release the hydrogen, however, are extremely high: 953 K for lithium borohydride and 807 K for sodium borohydride (Martelli et al., 2010; Durbin and Malardier-Jugroot, 2013; Rivard et al., 2019). As this is not a practical way of releasing hydrogen, this will not be looked into further. More promising is the release of hydrogen through hydrolysis. Both boranes as well as borohydrides react with water, producing hydrogen and borate (Umegaki et al., 2009), which has a great advantage in shipping, as the ship actually sails in the reactant for the hydrogen production. The reaction is spontaneous and exothermic (Umegaki et al., 2009; Kojima, 2019). The reaction rate depends on the temperature and the catalyst used (Laversenne et al., 2008; Kojima, 2019; Hoecke et al., 2021). Because of the nature of the reaction, both the hydrogen stored in the borane/borohydride as well as the hydrogen inside the water is released, resulting in good gravimetric and energy densities of up to 36 wt% for lithium borohydride. However, in practise only half of the hydrogen is released due to

clogging, which is why lithium borohydride will not be taken into account here (Li et al., 2011). Ammonia borane, sodium and potassium borohydride will be discussed as promising hydrogen carriers.

3.2.1 Ammonia borane

Ammonia borane is a very much researched borane (Demirci, 2020). Ammonia borane has a very high hydrogen content of 19.6 wt% (Akbayrak and Özkar, 2018; Demirci, 2020; Wu et al., 2020). Ammonia borane can be used as an anodic fuel, but also as a hydrogen carrier. Hydrogen can be released from ammonia borane using hydrolysis, pyrolysis and alcoholysis (Wu et al., 2020). Hydrolysis is thought to be the best process, as it requires a mild temperature and no additional fuel (Wu et al., 2020). The amount of hydrogen released by hydrolysis is limited. One source cites 7.8 wt% (Lang et al., 2020), while another says that only 5.8 wt% is released (Shimabayashi and Fujita, 2020). At this moment there is no catalyst that is both active and long-lived (Akbayrak and Özkar, 2018). The hydrolysis reaction of ammonia borane is as follows (Stephens et al., 2007):

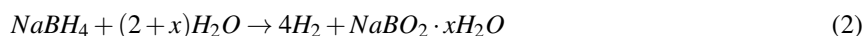


There is also another reaction noted, in which the borate and ammonia react and become ions (Lang et al., 2020). It can be seen from reaction 1 that there are two main products, a borate and ammonia. For a PEM fuel cell, which is assumed in this review, ammonia is very difficult. It is, however, a hydrogen carrier and will be discussed in further detail in section 4.3. In the case of ammonia borane there are a few options for the use of ammonia. The ammonia can be stored on board and taken home, it can be cracked and used inside a fuel cell, or it can be burned in an internal combustion engine together with hydrogen (McKinlay et al., 2020). This is however outside of the scope of this literature review.

Additionally, regeneration of ammonia borane is very difficult, due to the B-O bonds that are formed during dehydrogenation (Lang et al., 2020). This also makes this process extremely costly (Demirci, 2020). So while ammonia borane has an extremely high hydrogen content, in practice this is not the case.

3.2.2 NaBH₄

NaBH₄ can store up to 10.7 wt% of hydrogen in theory (Kojima, 2019). NaBH₄ releases its hydrogen at moderate temperatures (298-333 K) with high hydrogen purity and good control (Ouyang et al., 2018; Abdelhamid, 2021). The release of hydrogen is done using hydrolysis, which is a spontaneous, exothermic, albeit slow, reaction (Rivarolo et al., 2018). The speed of the reaction can be enhanced by using catalysts, which are very well researched (Abdelhamid, 2021). There are many catalysts available, but ruthenium is used mostly (Abdelhamid, 2021). Currently there is also interest in Pd/carbon dots, as these can be easily recycled, as well as cobalt based catalysts as they show good reaction kinetics (Abdelhamid, 2021). The main aim of the catalysts is to enhance the reaction activity, not to reduce the temperature as the reaction happens at low temperatures already (Abdelhamid, 2021). The hydrolysis reaction of NaBH₄ is as follows:



where x is either 2 or 4, depending on the reaction (Demirci et al., 2010). On a ship water does not have to be brought along, but can be purified onboard and recycled from hydrogen-fed fuel cells. This means that twice as much hydrogen is produced as is carried inside NaBH₄. The spent fuel, NaBO₂, however, has to be brought back as well, which is almost 3 times heavier than the original fuel (Demirci et al., 2010). Regenerating this spent fuel is much under debate, according to some it is simple (Abdelhamid, 2021), whereas others say it is very expensive (Ouyang et al., 2018; Lang et al., 2020) or even that there is no evidence at all of its working principle (Rivarolo et al., 2018). This is currently under active research at TUDelft and University of Amsterdam, where they are studying the use of a ball mill and magnesium for the rehydrogenation.

3.2.3 KBH₄

Some sources have mentioned KBH₄ as an alternative for NaBH₄ (LaVersenne and Bonnetot, 2005; Laversenne et al., 2008; Saka and Balbay, 2018). It has very similar properties to NaBH₄, it stores about 7.4 wt% of hydrogen theoretically and releases it by hydrolysis, releasing the hydrogen from water as well (Laversenne et al., 2008). The main arguments to use KBH₄ is that the spent fuel stores less water molecules and is easier to handle (Laversenne et al., 2008). KBH₄ reacts with water to form KBO₂·4/3H₂O, whereas NaBH₄ usually has either 2 or 4 water molecules after hydrolysis (Laversenne et al., 2008). When heated above 408 K the KBO₂ hydrate loses a water molecule, resulting in only KBO₂·1/3 H₂O. At a similar temperature, NaBH₄ still stores 1 water molecule. This means that their spent fuels have a very similar weight, with molar masses of 83 and 87u respectively. The regeneration and storage process of KBH₄ is slightly different from NaBH₄, making KBH₄ an interesting carrier as well.

3.3 Complex hydride - Alanates

Complex hydrides such as NaAlH_4 and LiAlH_4 are named as promising candidates for hydrogen storage (Xueping and Shenglin, 2009). Complex hydrides that are formed with aluminum are also named alanates (Xueping and Shenglin, 2009). Alanates are able to store more than 5wt% of hydrogen (Xueping and Shenglin, 2009). Alanates usually react violently with water (Kojima, 2019). Their decomposition temperatures, however, are still rather high and can be in multiple steps (Sazelee and Ismail, 2021). The first step (which does not necessarily release all hydrogen) is usually between 383 and 573 K (Sazelee and Ismail, 2021). Both LiAlH_4 and NaAlH_4 are available and cheap (Sazelee and Ismail, 2021; Ali and Ismail, 2021).

3.3.1 LiAlH_4

Lithium aluminium hydride (LiAlH_4) has been mentioned as a promising storage material for hydrogen (Wang et al., 2017). It stores up to 10.6wt% of hydrogen (Xueping and Shenglin, 2009; Wang et al., 2017). The dehydrogenation temperature depends on the way of storage and the catalysts used. Dehydrogenation of LiAlH_4 usually happens in three steps. During the first step 5.3wt% of hydrogen is released at about 423 K, resulting in 3H_2 , Li_3AlH_6 and 2Al (Xueping and Shenglin, 2009; Sazelee and Ismail, 2021). During the second and third step 2.6 wt% per step are released, with in between reaction products LiH and Al . These react and form, as the final product (next to the hydrogen) LiAl (Xueping and Shenglin, 2009). The multiple steps occur because each step requires a higher temperature for the substance to decompose (Xueping and Shenglin, 2009). The dehydrogenation temperature can be reduced when using doping, however the main issue is that it also results in a much lower storage availability of hydrogen (Xueping and Shenglin, 2009). An example is doping the LiAlH_4 with TiN (Li et al., 2013). This results in a release of about 7.1 wt% at a temperature of 403 K (Li et al., 2013). Another way of lowering the dehydrogenation temperature is using nanoconfined LiAlH_4 , which will decrease the temperature of the first step to about 408 K (instead of 423-473 K) and the complete dehydrogenation at 573 K (instead of 373-723 K) (Wang et al., 2017). Using only the first step results in a rest product (Li_3AlH_6) which is practically impossible to regenerate (Wang et al., 2017). Next to dehydrogenation, there are also rehydrogenation issues (Xueping and Shenglin, 2009; Wang et al., 2017; Sazelee and Ismail, 2021). The current technology reaches the desired goal of 7.5wt% of hydrogen release, even though only the first two steps are practically applicable as the third step requires a too high temperature (Li et al., 2013; Wang et al., 2017). However, the weak reversibility and bad desorption kinetics, make LiAlH_4 at this moment not a good candidate for hydrogen storage aboard a ship.

3.3.2 NaAlH_4

Sodium aluminium hydride (NaAlH_4) is closely related to lithium aluminium hydride. It has a lower hydrogen weight percentage of only 7.41 wt% and a higher decomposition temperature (483 K) than LiAlH_4 (Sazelee and Ismail, 2021). It also has a higher decomposition temperature (Sazelee and Ismail, 2021). Another issue for NaAlH_4 is the poor reversibility (Ali and Ismail, 2021). Similar to LiAlH_4 the hydrogen is released in three steps, all requiring higher temperatures for decomposition than the previous step (Ali and Ismail, 2021). The reaction products are also similar: after the first step Na_3AlH_6 and Al are created. Na_3AlH_6 decomposes at 533 K to NaH and Al , next to 1.9 wt% of hydrogen. Another 1.9 wt% of hydrogen is released in the third step, where NaH is decomposed into Na and hydrogen at 708 K (Ali and Ismail, 2021). So only the third step is significantly different from the process with lithium aluminium hydride (Sazelee and Ismail, 2021). The dehydrogenation temperature can be lowered by using catalysts and doping (Ali and Ismail, 2021). Doping with TiN , for example, results in a lower dehydrogenation temperature for the first two steps, resulting in 5.2% release of hydrogen, as well as a faster release than without doping (5.2wt% in 10h, instead of 2 wt%) (Ali and Ismail, 2021). The release is still at temperatures between 403 and 458 K (Ali and Ismail, 2021). According to Ali and Ismail (2021) a lot of work still needs to be done before NaAlH_4 can be considered a realistic option for hydrogen storage. Key points are reducing operating temperatures and pressures, enhancing kinetics and understanding dopants (Ali and Ismail, 2021).

3.4 Metal hydrides

In this literature review metal hydrides are split into two types: Ionic or elemental hydrides and intermetallic hydrides. Elemental hydrides such as LiH and MgH_2 have similar properties. They store relative high amounts of hydrogen (i.e. MgH_2 stores 7.6 wt% (Møller et al., 2017)) and require rather high dehydrogenation temperatures (Møller et al., 2017; Hoecke et al., 2021). Hydrogen is stored in metal hydrides inside the structure, by occupying interstitial sites in the metal (Møller et al., 2017).

3.4.1 Elemental hydrides

Elemental hydrides consist of an element combined with hydrogen. Examples of these are magnesium hydride and lithium hydride (Møller et al., 2017). For example, lithium hydride is a material with a theoretically good hydrogen storage capacity as it can store up to 12 wt% of hydrogen (Wang et al., 2016). However, LiH will

not be considered here further, as it requires very high temperatures of about 973 K to release the hydrogen (Wang et al., 2016; Hoecke et al., 2021). Additionally, lithium hydride reacts violently with water, making it rather dangerous (Kojima, 2019). When combining LiH with nanoconfinement, release temperatures of 473 K have been reported, but then only 1.9 wt% of the hydrogen was released, which does not come close to the goal (Wang et al., 2016). This, however, is a promising technology if more hydrogen can be released that way. MgH_2 is also often considered, as it is more stable, safer and has lower release temperatures than LiH (Salman et al., 2022). MgH_2 can store about 7.6 wt% of hydrogen (Hoecke et al., 2021; Salman et al., 2022). It again has a rather high decomposition temperature (573 K) and it is hard to completely hydrogenate magnesium, as it is a surface reaction (Hoecke et al., 2021). This can all be tackled by using catalysts, resulting in better hydrogenation (Hoecke et al., 2021). The dehydrogenation process, however, seems to have a minimum temperature of 523 K (Tarasov et al., 2021). When additives are used, this can be lowered to about 323 K, but additives also reduce the weight percentage of hydrogen that can be stored (Muthukumar et al., 2018; Tarasov et al., 2022).

3.4.2 Intermetallic metal hydrides

Metal hydrides can be grouped depending on the type of materials used. Usually they consist of one or more A atoms (usually a rare-earth or alkaline-earth metal) and B atoms (typically a transition metal) (Abe et al., 2019). Combined, these form the following combinations: AB_5 , AB_2 , AB and A_2B types of metal hydrides (Abe et al., 2019; Moradi and Groth, 2019; Tarasov et al., 2021; Nguyen and Shabani, 2021). Typical intermetallic metal hydrides are $\text{LaNi}_5\text{H}_{6.7}$, Ti-Zr alloys (such as $\text{Ti}_{0.93}\text{Zr}_{0.05}\text{Mn}_{0.73}\text{V}_{0.22}\text{Fe}_{0.04}$)₂, Sn_2Co , Ti-Fe alloys ($\text{FeTiH}_{0.95}$) (Durbin and Malardier-Jugroot, 2013; Abe et al., 2019; Hoecke et al., 2021). The main issue of metal hydrides is their very low gravimetric energy density; usually only a few wt% (Durbin and Malardier-Jugroot, 2013; Abe et al., 2019; McKinlay et al., 2020). For example, $\text{LaNi}_5\text{H}_{6.7}$ only stores 1.4 wt% (Abe et al., 2019). They have good operating conditions (Durbin and Malardier-Jugroot, 2013; Abe et al., 2019). However, their high weight makes them unsuitable for shipping (McKinlay et al., 2020). Metal hydrides are much more suitable for land-based hydrogen storage (Abe et al., 2019). A case study was performed, in which metal hydrides were looked at as effective hydrogen carriers onboard a ship; for the specific case this would result in 40% of the total storage mass taken by metal hydrides to provide the required amount of energy (McKinlay et al., 2020).

4 Liquid hydrogen carriers

Liquid hydrogen carriers offer a way of storing hydrogen in a liquid. It can also be that they have to be at low temperature or moderate to high pressures to keep them in liquid form, as they would be a gas at ambient temperatures (such as ammonia).

4.1 Organic hydrogen carriers

Organic hydrogen carriers are here defined as all carbon based carriers. Within the carbon-based liquid hydrogen carriers, some suggest that there are two types: the cyclic and acyclic carriers (Zheng et al., 2021). Acyclic carriers are substances like formic acid and methanol, whereas cyclic carriers are carriers like dibenzyl toluene. The main difference is the chemical structure: cyclic carriers are usually aromatic molecules that store hydrogen in their double bonds (Hoecke et al., 2021). They are not combusted, but hydrogen is released using heat (Hoecke et al., 2021). The main difference with the acyclic carriers is that these carriers are not aromatic, but consist of much less molecules. When hydrogen is released from them, CO_2 is always released (Hoecke et al., 2021; Zheng et al., 2021). In this review, the organic hydrogen carriers will be split up in those that emit CO_2 (in section 4.1.1) and those that do not (in section 4.1.2). The latter will be referred to as LOHC (Liquid Organic Hydrogen Carriers) from now on. This division has been done before, by Hoecke et al. (2021) amongst others.

4.1.1 CO_2 -based carriers

CO_2 based carriers are a way of storing hydrogen chemically. CO_2 based carriers that are being researched at the moment are mainly formic acid and methanol (Zheng et al., 2021; Hoecke et al., 2021). The main advantage of these two hydrogen carriers is that they have been researched extensively, especially methanol (Zheng et al., 2021). Both are made from hydrogenation of CO_2 or bio-based, thus theoretically reducing the amount of CO_2 in the air. However, after dehydrogenation CO_2 is released again (Hoecke et al., 2021; Zheng et al., 2021). Thus, this makes these hydrogen carriers CO_2 neutral at best. CO_2 is not available as a feedstock on an industrial scale (Hoecke et al., 2021). Rough calculations show that current yearly production of methanol (70 million tons) could be produced using the CO_2 captured yearly (111 million tons) (Borisut and Nuchitprasittichai, 2019; Global CCS Institute, 2021). When methanol is used as fuel by the shipping industry, however, much more methanol will need to be produced. Additionally, CO_2 capture and storage onboard ships would be challenging, although research projects have started to look at how this could be done (Hoecke et al., 2021). As mentioned previously, the aim is to have a zero-emission ship. Without CO_2 capture onboard, the ship is no longer zero-emission. Even if green produced or bio-based fuel is used, the ship can be carbon-neutral, not zero-emission.

4.1.2 Liquid organic hydrogen carriers

Liquid Organic Hydrogen Carriers (LOHCs) are materials that store hydrogen by storing it in their double bonds (Niermann et al., 2019; Chiefari and Hornung, 2021). In this section only cyclic LOHCs will be discussed, which are mostly cycloalkanes (Makepeace et al., 2019). These are able to store about 5 to 8 wt% of hydrogen, depending on the type of LOHC (Makepeace et al., 2019). Generally speaking they are safe and easy to handle as they are similar to oils at ambient conditions, resulting in no need for extra infrastructure (Makepeace et al., 2019; Chiefari and Hornung, 2021). The main issue of LOHCs, however, is the release of hydrogen, which is an endothermic reaction. It also requires rather high temperatures of over 420 K (Makepeace et al., 2019; Niermann et al., 2019). There is an abundance of LOHCs, although mainly toluene (TOL) and its pair methylcyclohexane, N-ethylcarbazole (NEC) and its pair dodecahydro-N-ethylcarbazole and dibenzyltoluene (DBT) and H18-DBT are considered (Makepeace et al., 2019; Niermann et al., 2019; Hoecke et al., 2021). Of these, toluene is often left out due to its carcinogenicity, low flashpoint (277 K) and low boiling point (384 K), even though it is the simplest molecule considered (Hoecke et al., 2021). The other two are researched and reviewed a lot (Hoecke et al., 2021). NEC is thought to be one of the most promising candidates as an LOHC (Lang et al., 2020). NEC has a dehydrogenation temperature of 453-523 K and stores about 5.8 wt% of hydrogen in theory (Niermann et al., 2019). This is 5.2 wt% in practice (Niermann et al., 2019). Complete dehydrogenation can be achieved at only 453 K (Niermann et al., 2019). The dehydrogenation temperature of NEC can be reduced to only 423 K when using iridium complexes as catalysts, but this does not result in complete dehydrogenation (Lang et al., 2020). It has a TRL (Technology Readiness Level) of only 3 on a scale of 1-9 and is very hard to get (Niermann et al., 2019; Hoecke et al., 2021). Additionally, it is solid at room temperature, resulting in more difficulty in bunkering and handling for a ship (Hoecke et al., 2021).

DBT is more promising (Hoecke et al., 2021). It has a storage capacity of about 6 wt% in reality (theoretically 6.2 wt%) (Niermann et al., 2019). It is cheap, stable during dehydrogenation and has a very high TRL level of 9 (Niermann et al., 2019). Additionally, it is less toxic than NEC and much more widely available (Niermann et al., 2019; Hoecke et al., 2021). DBT has a dehydrogenation temperature of 583 K when using Pd/C catalyst (Niermann et al., 2019). This can be reduced to only 543 K, but then only 58% of the hydrogen is released (Sekine and Higo, 2021). It is thought that platine could be a better catalyst for DBT (Lang et al., 2020; Rao and Yoon, 2020; Sekine and Higo, 2021).

Finding a catalyst that reduces the temperature, whilst still recovering all the hydrogen stored is a challenging task and the subject of current research for many LOHCs (Niermann et al., 2019; Lang et al., 2020; Rao and Yoon, 2020; Sekine and Higo, 2021; Zheng et al., 2021).

4.2 Silanes

Silanes are inorganic compounds formed from silicon and hydrogen. It is possible to produce hydrogen from (organo)silanes (Brunel, 2017). Different organosilanes have different properties and Brunel (2017) has specified a few that can be potentially used for hydrogen storage. Organosilanes react with water in the presence of catalysts to form hydrogen (Brunel, 2017). Both catalyst and byproduct (silicon dioxide) are recoverable and recyclable (Brunel, 2017). The recycling process is done commercially and requires high pressures (Atkins et al., 2010). An example as mentioned by Brunel (2017) is silane gas (SiH_4), which can carry up to 12.5 wt% of hydrogen. Unfortunately, silane gas is also highly flammable (Brunel, 2017). Other examples are polyhydrosiloxane (PHS) and pentasilane (Si_5H_{12}), which are both very promising alternatives for hydrogen storage (Brunel, 2017). PHS has a volumetric energy density of 10 MJ/L and pentasilane of 20 MJ/L (Brunel, 2017). The gravimetric energy density of pentasilane is 7.9 wt%, whereas the gravimetric energy density of polyhydrosiloxane is less than 4 wt% (Brunel, 2017).

4.3 Ammonia

Ammonia is a key nutrient and recently also a much researched hydrogen carrier and is often thought to be one of the most promising new (marine) fuels (Kojima, 2019; McKinlay et al., 2020; Aziz et al., 2020; Al-Enazi et al., 2021; Hoecke et al., 2021). Even though ammonia can be used in a direct SOFC (Solid Oxide Fuel Cell) fuel cell or directly burned in an engine, this paper will only look at its use in a PEM fuel cell, for reasons mentioned previously (McKinlay et al., 2020). Ammonia is a chemical with a hydrogen content of 17.6 wt% (Rivard et al., 2019). It is gas at ambient pressure and temperature, but becomes liquid at slightly lower temperatures (263 K) or slightly elevated pressures (1000 kPa) (McKinlay et al., 2020). It is usually stored that way. Ammonia is a well established substance, its production process is very well known and currently at industrial scale, due to its use as fertiliser (Rivard et al., 2019; Aziz et al., 2020; McKinlay et al., 2020). This also makes it a relatively cheap solution (Aziz et al., 2020). Ammonia has good hydrogen carrier properties overall, except for its high toxicity and corrosiveness (McKinlay et al., 2020). The toxicity is usually an issue; it was one of the reasons for the DOE to stop funding ammonia research (Makepeace et al., 2019; Kojima, 2019; Aziz et al., 2020; Hoecke et al., 2021).

Another reason was the difficulty of decomposing ammonia into hydrogen and nitrogen (Makepeace et al., 2019). Releasing the hydrogen from ammonia is a difficult and energy consuming process, as it is an endothermic process that has to happen at temperatures well above 673 K (Makepeace et al., 2019; Aziz et al., 2020; Lee et al., 2021; Lucentini et al., 2021). The decomposition of ammonia is a well-known process and there is a lot of research into the catalysts used for this (Lucentini et al., 2021). Cracking uses a lot of energy, depending on the source 13 to 26% of the total lower heating value of the hydrogen produced (Wijayanta et al., 2019; Lee et al., 2021). This so-called cracking process has to be done very well, as PEM fuel cells are very sensitive to ammonia poisoning (Kojima, 2019). Other fuel cells, such as SOFCs are more tolerant to hydrogen from ammonia (van Biert et al., 2016). So, even though ammonia has some good properties, due to the difficulty of cracking and the high toxicity it will not be taken into account further in this paper.

5 Overview of relevant hydrogen carriers

Figure 2 shows a graphical overview of the energy density of the discussed hydrogen carriers. Only metal decorated structures (discussed in section 3.1.2) are not taken into account in this figure, as their volumetric energy density could not be found. The red line is the DOE target, so everything that is to the right and above of this line has reached the target. Figure 3 shows a zoomed in version of figure 2. As shown in figures 2 and 3, only a few hydrogen carriers have theoretical energy densities that are able to reach the goal set by the DOE. This is only the theoretical (chemical) value, without packaging factors or tank weight. When packaging factors and tank weight are included, the volumetric and gravimetric densities only go down (Kranenburg et al., 2020).

Next to the volumetric and energy densities of the carriers, there are several other criteria to evaluate the carriers on. Table 1 shows the hydrogen carriers and their main properties. From the table it can be seen that the TRL level at this moment and the safety, handling and storage are a main issue for many of the different hydrogen carriers. In order for a hydrogen carrier to be useful onboard, the safety, handling and storage of the carrier should be at reasonable temperatures and pressures to avoid phenomena such as boil-off. Additionally, having storage at near ambient conditions reduces the energy required for storage and thus enhances the efficiency. A similar criteria can be used for the dehydrogenation process. When the dehydrogenation process requires (extremely) high temperatures and/or pressures, this greatly reduces the onboard efficiency, effectively reducing the energy density. In the end there are a certain set of hydrogen carriers that have the possibility of usage on ships. All carriers with a low TRL level at this moment have been disregarded in this literature review, as there is insufficient research to be found on the implementation of these carriers. Additionally, substances that react violently with water or that have difficult dehydrogenation processes are not taken into account either. The rehydrogenation process for such compounds as borohydrides, which is considered difficult, is not seen as a deal-breaker due to the amount of research currently going on. In short, this leaves the LOHC DBT (despite the rather high temperature for dehydrogenation), the borohydrides NaBH_4 and KBH_4 as well as ammoniaborane for further investigation in this paper.

6 Effective energy density of the carriers

As mentioned previously, based on figure 2 a certain amount of hydrogen carriers are chosen as they are promising. These will be discussed here in more detail. These are thus NaBH_4 , KBH_4 , ammoniaborane and DBT. In order to evaluate these carriers, a switch has to be made from theoretical values (such as in figure 2) to more realistic values. This is also what the US DOE goal is based on: values including packing factor and required other materials (Wu et al., 2020). For example, for liquid hydrogen the tanks have to be taken into account, as these weigh a lot and thus reduce the gravimetric energy density (Rivard et al., 2019; Kranenburg et al., 2020). For liquid hydrogen the values as given by Rivard et al. (2019) have been used.

The LOHC DBT does not have issues with a packing factor, as it is very similar to diesel which also does not need any packing factors or additional space requirements (Kranenburg et al., 2020). However, in order to release hydrogen from DBT, about 28 to 35 % of the LHV (Lower Heating Value) of hydrogen stored is required (Lee et al., 2021). This has to be taken into account as it lowers the effective volumetric and gravimetric energy density. For the borohydrides the main issue is the fact that the spent fuel (SF) weighs more and takes up more volume than the initial fuel. Equation 2 shows the possible reaction products. Usually the spent fuel is $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ (Laversenne et al., 2008; Demirci et al., 2010), although it can also be a mixture of $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$. Both spent fuels are heavier and take up more volume. For 1kg (0.93L) of NaBH_4 2.7kg and 1.4L is required to store the spent fuel (in case it is $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$) (Demirci et al., 2010). For KBH_4 a similar issue occurs. This is because during the reaction a metaborate hydrate is formed, which is always heavier than a borohydride.

Reaction 1 shows the hydrolysis reaction of ammoniaborane. It can be seen that there are two products, besides hydrogen: ammonia and borate. Two cases are chosen here, one in which it is assumed that a fuel cell (for example an SOFC) can also use the ammonia. This will enhance the energy density. However, not all fuel cells can use ammonia (directly), so there is a second scenario chosen in which the ammonia has to be stored onboard as well.

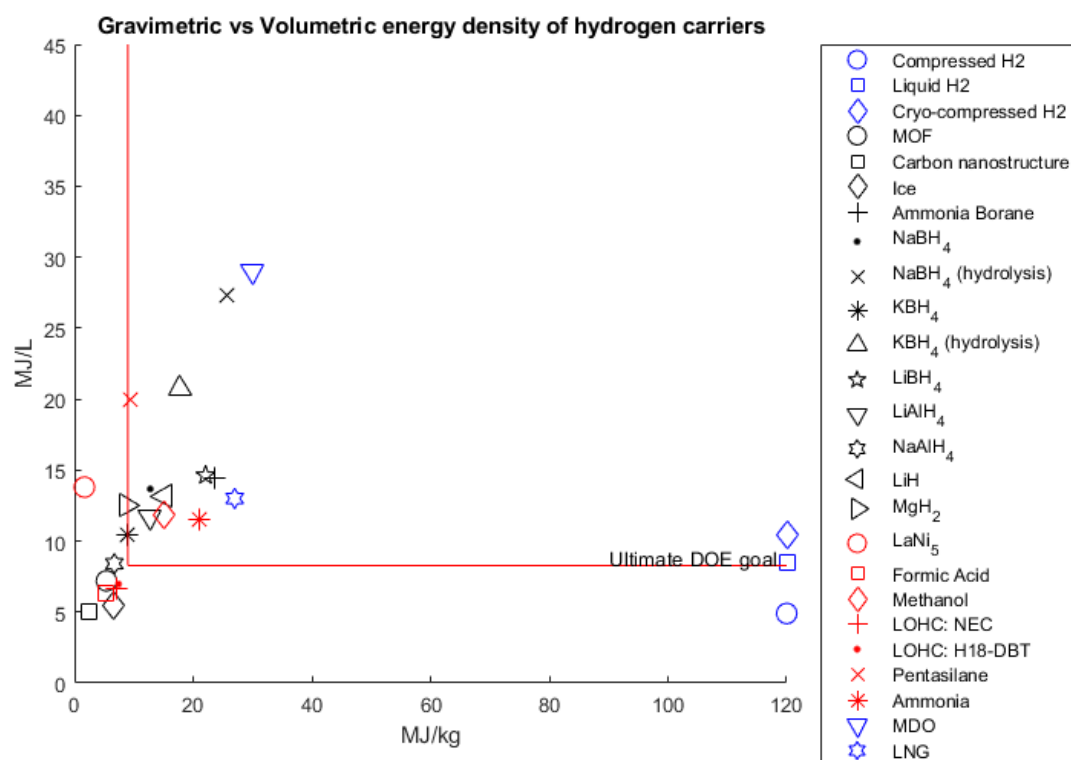


Figure 2: Gravimetric and volumetric energy density of different hydrogen carriers

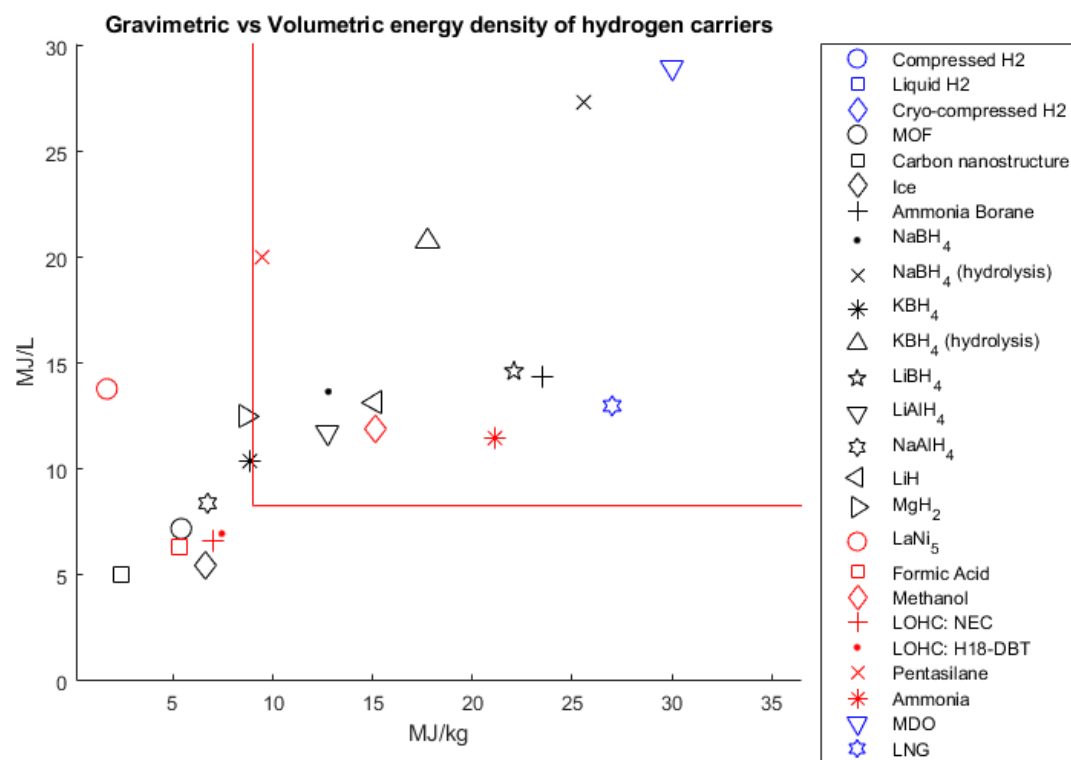


Figure 3: Gravimetric and volumetric energy density of different hydrogen carriers, zoomed in

Table 1: Overview of the chosen hydrogen carriers, their main properties and main problems. Due to the similarity in properties, LaNi₅ is chosen as an example for metal hydrides. Additionally, hydrogen carriers that produce CO₂ are omitted from this table.

	wt%	TRL	Safety, handling, storage	Dehydrogenation	Recycling
MOF	2.5-4.5	Medium	High pressure, low temperature	Fast dehydrogenation	Only limited amount of cycles possible
MDS	5.2	Low	High pressure	Between room temperature and 373 K needed	Possible
Nanostructures	2-7.3	Low	High pressure	Slow and can self-collapse after dehydrogenation	Risk of self-collapse, difficult recycling
Ice	5.5	Low	High pressure, low temperature, low pressure and room temperature possible using THF	Easy and fast	Good
AmmoniaBorane	19.6	Medium	Stable, benign, exposure to water not ideal	Moderate conditions for hydrolysis, but only releases 7.8 wt%. Also, NH ₃ is an issue	Difficult due to B-O bonds
NaBH ₄	10.6	High	Store away from water, relatively safe	Exothermic, water required, fast when catalyst used	Difficult due to B-O bonds
KBH ₄	7.6	High	Store away from water, relatively safe	Exothermic, water required, fast when catalyst used	Difficult due to B-O bonds
LiBH ₄	18.4	Medium	Store away from water, relatively safe	Only 50% release with hydrolysis, due to clogging	Difficult
LiAlH ₄	10.6	Low	Violent reaction with water	486 K without doping, 408 K with TiN doping	Irreversible under moderate conditions, but possible
NaAlH ₄	5.6	Low/Medium	Violent reaction with water	458-708 K, 3 stage process. TiN reduces temperature, 5wt% release	High temperature required, when using Ti doping possible
LiH	12.6	Low/Medium	Very violent reaction with water	Very high temperatures required (>973 K)	Possible
LaNi ₅	1.4	High	Generally considered safe	Endothermic, low temperature (293-353 K)	Possible
NEC	5.8	Low	Biodegradable, easy handling	Endothermic, 423-543 K	Easy process
DBT	6.9	High	Low flammable, low toxic, easy handling	Endothermic, 573 K	Easy process
Pentasilane	7.9	Low	Liquid, non-toxic	Easy, fast and high quality	Possible
NH ₃	17.6	Medium	Toxic, flammable, corrosive, clouds can travel far	Endothermic, cracking required at 673 K	Not possible

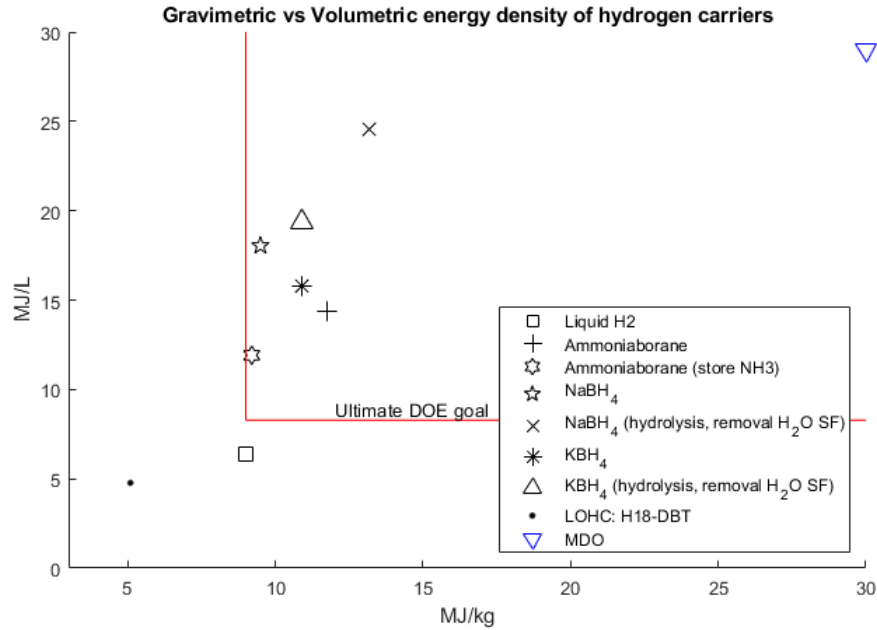


Figure 4: Effective gravimetric and volumetric energy density of selected hydrogen carriers including packing, spent fuel weight, dehydrogenation energy losses and other influencing factors

This is disadvantageous and lowers the energy density. Ammonia, however, still reaches the goals, even if NH₃ has to be stored onboard. It is assumed in this scenario that ammonia is stored onboard in its liquid form, the energy required to reach this liquid form is not taken into account.

Figure 4 gives an overview of the hydrogen carriers with their evaluated volumetric and gravimetric energy densities. It can be seen that for all three boron based hydrogen carriers there are two values plotted. This is because the additional hydrates connected to the spent fuel NaBH₄ and KBH₄ can be removed (Laversenne et al., 2008). The result is a lighter spent fuel and thus a higher gravimetric energy density of the entire system. It does, however, come with a penalty, as dehydration also costs energy (Laversenne et al., 2008). Additionally there is discussion and research on the effect of the spent fuel composition on the rehydrogenation process (Chen et al., 2017; Zhong et al., 2017; Nunes et al., 2021). This is why there are two results, one with removal of the water molecules taken into account and one in which the spent fuel is NaBO₂·2H₂O. Figure 4 shows clearly that the hydrogen carriers have much lower energy densities on average when taking packing factor and spent fuel into account. Still, the combined characteristics in energy density, safety and low toxicity could make them a superior solution for hydrogen storage onboard of ships. For LOHC's this would require an adequate operational profile of the ship and available waste heat for the hydrolysis reaction. For NaBH₄ and KBH₄ this would be enhanced if extraction processes are available to reduce weight and volume of the spent fuel.

7 Ongoing hydrogen carrier projects and their naval relevance

There are several ongoing hydrogen carrier projects. Some have been going on for quite some time (Sattler, 1998), whereas others are very recent. Most current state of the art research is focused on liquid or pressurized hydrogen. The authors are aware of the following projects that seem to be relevant for naval engineering purposes:

- TKMS: Air independent propulsion system for U212 submarines, with metal hydrides as hydrogen storage (Bellosta von Colbe et al., 2019)
- India: air independent propulsion system for naval submarines, using sodium borohydride as hydrogen storage (Bana, 2017)
- H2SHIPS interreg NWE project. Port of Amsterdam demonstrator research ship Neo Orbis. Sodium borohydride as hydrogen storage (Interreg North-West Europe, 2022)
- Ostensjo/Hydrogenious: application for shipping on a megawatt scale using a LOHC as fuel for the propulsion system (Hydrogenious, 2021)

- Netherlands: SH2IPDRIVE project focussing on four types of maritime hydrogen storage: liquid, pressurized, LOHC and sodium borohydride, including the building of seagoing modular demonstrators (Economic Development Board, 2021)
- United Kingdom: Ross Barlow canal boat, with hydrogen storage using LaNi₅ (Bevan et al., 2011)
- South Korea: Sodium Borohydride for unmanned areal vehicles (Kim, 2014)
- France: organosilane for long term storage and onboard applications (HYSILABS, 2022)

8 Conclusion

The combination of hydrogen and fuel cells is interesting from a naval perspective due to the silent propulsion, low thermal and acoustic signatures, low maintenance requirements and possibility of air independence. The main issue is the storage of hydrogen. This paper has given an overview of several potential hydrogen carriers and their relevant characteristics, such as gravimetric and volumetric energy density, safety, storage and handling, technology readiness level and dehydrogenation and rehydrogenation process. State of the art research shows that LOHCs and borohydrides offer good potential, due to their safety, high technology readiness levels, good safety and well known dehydrogenation process. This could contribute significantly towards required naval operational characteristics in terms of enhanced survivability, silent operation and low acoustic and thermal signatures. Several projects are now at hand to further develop and show this potential.

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