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Hydrogen carriers for zero-emission ship propulsion using PEM fuel cells: an evaluation

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ABSTRACT

Green hydrogen combined with PEM fuel cell systems is a viable option to meet the demand for alternative maritime fuels. However, hydrogen storage faces challenges, including low volumetric density, fire and explosion risks and transport challenges. We assessed over fifteen hydrogen carriers based on their maritime performance characteristics to determine their suitability for shipboard use. Evaluation criteria included energy density, locally zero-emission, circularity of process, safety, dehydrogenation process, logistic availability and handling. Thus, excluding ammonia and methanol because of these constraints, we found that borohydrides, liquid organic hydrogen carriers and ammoniaborane are the most promising hydrogen carriers to use on ships with PEM fuel cells. Borohydrides, specifically sodium borohydride, have high energy densities but face regeneration issues. The liquid organic hydrogen carrier dibenzyltoluene has a lower energy density but exhibits easy hydrogenation and good handling. Given varying operational demands, we developed a framework to assess the suitability of hydrogen carriers for use in different ship categories. Evaluating the three types of hydrogen carriers, using our framework and considering current practices, shows that these are viable options for almost all ship types. Thus, we have identified three types of hydrogen carriers, which should be the focus of future research.

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1. Introduction

As the shipping sector is not on track to reach its sustainability goals, there is a need for research on alternative power sources (International Energy Agency 2021). Batteries are not a viable solution for the shipping industry, due to their low gravimetric and volumetric energy density; for example, a container ship would need to use about 45% of the weight and 16% of the volume of the cargo hold by the batteries for the ship to be able to comply with its original operational profile (McKinlay et al. 2020). This means that other alternatives have to be found.

List of abbreviations

BT	Benzyltoluene
DBT	Dibenzyltoluene
DOE	Department of Energy
HFO	Heavy Fuel Oil
LOHC	Liquid Organic Hydrogen Carrier
MDO	Marine Diesel Oil
MOF	Metal Organic Framework
NEC	N-ethyl carbazole
PEM	Proton Exchange Membrane
SOFC	Solid Oxide Fuel Cell
TRL	Technology Readiness Level

These alternative future fuels should meet specific requirements and criteria.:

- Safe (from a toxicity and fire hazard perspective)

- Zero emission (GHG and hazardous pollutants)
- High volumetric and gravimetric energy density
- Good logistic availability and easy handling
- Regenerative or circular produced – not one time use only

The U.S. Department of Energy has set a goal for energy density, and even though this goal is set mainly for lightweight vehicles, it is used more generally to discuss the viability of hydrogen storage methods (Durbin and Malardier-Jugroot 2013; Rivard et al. 2019; Zheng et al. 2021). The goal is to reach an energy density of 9 MJ/kg and 8.4 MJ/L for the entire system (US Department of Energy 2015; Rivard et al. 2019). As gravimetric energy density is often expressed in weight percentage or wt%, the minimum weight percentage of hydrogen in a molecule should be 7.5 wt%. The gravimetric energy is then calculated by multiplying the weight percentage with the lower heating value of hydrogen (120 MJ/kg). This is still excluding the rest of the system, meaning that 7.5 wt% is a lower limit that should always be reached, as the rest of the system will only decrease the energy density.

Currently, the shipping sector looks mainly at alternatives like hydrogen, ammonia and methanol, as well as batteries (International Energy Agency 2021). Of these alternatives (excluding batteries), hydrogen itself is the only one that is completely zero-emission when used in combination with fuel cells (Van Biert et al. 2016). Also, 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 high electrical efficiency (40–60%), silence, operation at low temperatures (338–358 K) and modularity, causing gradual degradation (Van Biert et al. 2016; McKinlay et al. 2020).

Therefore, this paper focuses on the application of hydrogen combined with PEM fuel cells for ship applications. As storing pure hydrogen, even if pressurised or liquified, may not reach the volumetric energy density targets, we will also consider other options, called hydrogen carriers (Rivard et al. 2019). Hydrogen carriers store hydrogen in their structure, for example by chemical bonding or physical adsorption (Moradi and Groth 2019). To comply with the zero-emission target, it is important that hydrogen can be extracted without emitting harmful substances and that the original hydrogen carrier can be reused.

These hydrogen carriers have been researched before, however never specifically for use on ships, despite the additional characteristics that ships add, such as volume limitations and the need for autonomy. Current research either focuses on detailed descriptions of hydrogen carriers but with a different goal, such as storage with undefined purpose (Møller et al. 2017; Niermann et al. 2019; Kojima 2019; Abe et al. 2019; Lee et al. 2021; Zheng et al. 2021) or storage for mobility (Durbin and Malardier-Jugroot 2013; Bellosta von Colbe et al. 2019; Rivard et al. 2019). With regards to the shipping sector, either more conventional alternative fuels, such as pure hydrogen, ammonia or methanol and one or two types of hydrogen carriers are researched (McKinlay et al. 2020; Van Kranenburg et al. 2020; Hoecke et al. 2021) or only one or two types of hydrogen carriers (Gilbert et al. 2018; Preuster et al. 2018; Düll et al. 2022).

This paper aims to contribute to current research by first classifying the different hydrogen carriers based on their engineering characteristics. Then, we evaluate the hydrogen carriers on their viability in the shipping sector. For some viable hydrogen carriers, the effective energy density will be discussed and compared to the current fuels used. Additionally, a framework is developed to evaluate the application of hydrogen carriers for different ship types and ship operations, and discuss the challenges that still remain. This framework is then used to assess the suitability of certain promising hydrogen carriers for different ship types. Finally, in Section 8, several state-of-the-art industrial and scientific examples are discussed. With this paper we aim to provide an overview of the hydrogen carriers that merit investment as alternative fuels to reduce greenhouse gas emissions in the shipping industry.

2. Classification of hydrogen carriers

The storage of hydrogen in general can be split into different methods. The exact definition of the storage methods is under debate (Durbin and Malardier-Jugroot 2013; US Department of Energy 2015; Abe et al. 2019; Kojima 2019; Bellosta von Colbe et al. 2019; Tarasov et al. 2021). Often 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), however, what is meant precisely by these terms can be different per author (Durbin and Malardier-Jugroot 2013; US Department of Energy 2015; Abe et al. 2019; Kojima 2019; Bellosta von Colbe et al. 2019; Tarasov et al. 2021). Additionally, 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 similarly to physical sorption storage (Abe et al. 2019). In this 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 ambiguity (Abe et al. 2019; Moradi and Groth 2019; Tarasov et al. 2021; Nguyen and Shabani 2021; Malleswararao et al. 2022).

These types of discussions are the reason that in this review, a classification 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. Such an engineering approach is required to address existing challenges. Metal hydrides can now be a part of solid storage, together with complex hydrides and physical adsorption methods. Next to handling, the material classification also provides groups of storage with similar dehydrogenation processes and gravimetric energy density storage. From an engineering point of view, these materials can be treated in similar ways for both storage, hydrogenation and dehydrogenation. The overall properties of these groups are discussed in the following subsections.

2.1. Liquid carriers

Liquid hydrogen carriers are carriers that are usually stored as liquid. Both the hydrogenated and dehydrogenated version of the hydrogen carrier has to be liquid to be considered in this category. They do not necessarily have to be a liquid at ambient conditions, as some gases such as ammonia require only slight modifications from ambient conditions to become liquid, which is why they are usually stored as a liquid. The main advantages of liquids are the use of current infrastructure and material handling, especially if the liquid carriers have similar toxicity to diesel. Generally speaking, storage is easier because liquids do not require set shapes.

2.1.1. Silane based

Silanes are inorganic compounds formed from silicon and hydrogen. It is possible to produce hydrogen from organosilanes, hydroxysilanes and (poly)silanes (Mitsudome et al. 2016; Brunel 2017; Kumar and Leitao 2020). Dehydrogenation is usually through hydrolysis and is exothermic, but still requires a catalyst (Brunel 2017). Organosilanes generally have a low boiling point and are gas state at atmospheric conditions, making them generally less safe (Han et al. 2011). The vapour pressure decreases with increased chain lengths (Brunel 2017), so larger molecules are more likely to be liquid. More complex organosilanes, such as polymethylhydrosiloxane (PMHS) have higher boiling points but also lower hydrogen weight percentages, of only 3.7–4.6 wt% (Han et al. 2011; Mitsudome et al. 2016), whilst silane gas (SiH_4) 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, whereas PMHS, the more complicated molecule, only has a volumetric energy density of 2 MJ/L (Brunel 2017). The hydrogen weight percentage of pentasilane is 7.9 wt%, whereas that of PHS is less than 4 wt% (Brunel 2017). Even though silanes are generally easy to handle and not toxic (Shimabayashi and Fujita 2020), public research on the use of polysilanes and organosilanes is limited (Brunel 2017; Kumar and Leitao 2020). However, there is currently a company, called Hysilabs, investigating and patenting the use of silanes, mainly organosilanes, as a hydrogen carrier. The use of silanes in this practical application will be discussed in Section 8.

2.1.2. Non-cyclic organic (CO_2 -based) carriers

Hydrogen can be stored chemically in non-cyclic organic molecules such as methanol or formic acid (Hoecke et al. 2021; Zheng et al. 2021; Pawelczyk et al. 2022). Such compounds can potentially be produced from CO_2 . Rather than using a chemical dehydrogenation step, most of them can be used directly in engine systems (Hoecke et al. 2021). However, if they are used in PEM fuel cells, they have to be split. They can be used directly in other fuel cell systems,

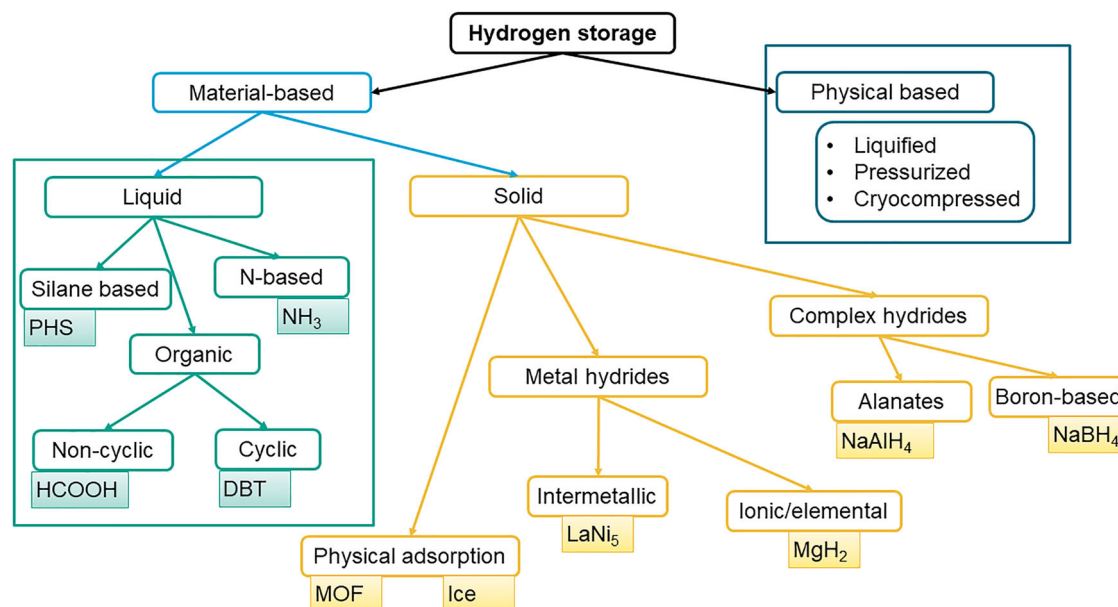


Figure 1. Proposed classification of hydrogen carriers for engineering purposes, including examples.

but at present these have low performance and low TRL (Van Biert et al. 2016). CO₂ and hydrogen are products of the splitting and separation of these two gasses is required because CO₂ is poisonous for (especially low temperature) fuel cells (Van Biert et al. 2016). As 90% of hydrogen (in 2016) was made using steam reforming, the separation process is highly researched (Shimonosono et al. 2016). Generally, pressure swing adsorption or cryogenic distillation are used, which require high amounts of energy and are expensive (Shimonosono et al. 2016; Salim and Ho 2018). Selective membranes to separate CO₂ and hydrogen are currently under research, as these are less costly and energy-intensive (Shimonosono et al. 2016; Salim and Ho 2018). On the other hand, an advantage of the CO₂-based hydrogen carriers is that they have been researched extensively, especially methanol (Zheng et al. 2021). However, as they emit CO₂ upon chemical dehydrogenation or combustion, they are only carbon neutral if green hydrogen and atmospheric CO₂ are used for their production (Pawelczyk et al. 2022). Thus, only the complete cycle is potentially carbon neutral, while there are still local emissions. These local emissions can only be avoided by onboard CO₂ capture, which is not expected to be developed at the required scale (Hoecke et al. 2021). Additionally, CO₂ 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).

2.1.3. Cyclic organic

Cyclic organic carriers are usually aromatic molecules that store hydrogen in their double bonds (Hoecke et al. 2021). Unlike non-cyclic organic hydrogen carriers, cyclic organic not only dehydrogenate but can also hydrogenate, that is, take up hydrogen, making them completely circular (Niermann et al. 2019; Hoecke et al. 2021). The cyclic organic hydrogen carriers are often referred to as LOHCs (liquid organic hydrogen carriers), which is the term also used in this review paper (Niermann et al. 2019; Hoecke et al. 2021; Zheng et al. 2021). Most of these LOHCs are cycloalkanes (Makepeace et al. 2019). LOHCs can usually store about 5 to 8 wt% of hydrogen (Makepeace et al. 2019) and are generally safe and easy to handle, due to their oil-like physical properties (Makepeace et al. 2019; Niermann et al. 2019; Chiefari and Hornung 2021). However, the release of hydrogen is through an endothermic reaction, requiring

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 its pair 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 (Niermann et al. 2019; Hoecke et al. 2021). Additionally, the company Hydrogenious is currently focussing on benzyltoluene and its counter pair perhydrobenzyltoluene, instead of dibenzyltoluene (Hydrogenious 2023). For all LOHCs, a major challenge is to find a catalyst that reduces the temperature for both dehydrogenation and hydrogenation, while still having high conversion rates (Niermann et al. 2019; Lang et al. 2020; Rao and Yoon 2020; Sekine and Higo 2021; Zheng et al. 2021).

2.1.4. N-based (Amines)

Amines are saturated nitrogen hydrides (Moss et al. 1995). Of these, ammonia is the most well-known. It is also the only amine that is in gas form at ambient conditions, as amines with higher molecular weights are in the liquid form (Motta et al. 2021). Amines generally have a high energy density because of the relatively low weight of the nitrogen atom compared to metals (Motta et al. 2021). However, as amines are generally explosive and often toxic, they pose safety concerns (Motta et al. 2021; National Center for Biotechnology Information 2023a, 2023c). Because of the decreasing energy density for larger molecules, the lack of safety and the elaborate energy research into ammonia as a hydrogen carrier, only ammonia will be discussed further here.

2.2. Solid carriers

There are a large variety of solids that can store hydrogen. Despite the large variety, it is always considered good practice to keep solid hydrogen storage away from water (Hoecke et al. 2021). Compared to current, liquid, fuels, new or different infrastructures may be required to refuel ships when solid hydrogen carriers are used.

2.2.1. Physical adsorption

Physical adsorption is defined as storing hydrogen without the splitting of the H–H bond (Moradi and Groth 2019). There are many different mechanisms that can store hydrogen this way, but usually, the hydrogen is stored inside the molecule itself (Langmi et al. 2014). Generally speaking, physical adsorption processes are hard to scale up and require either high pressures or extreme temperatures to get sufficiently (C 5 wt%) high energy density (Durbin and Malardier-Jugroot 2013; Rivard et al. 2019). Reversibility is a general issue (Langmi et al. 2014; Rivard et al. 2019). Substances that can physically adsorb hydrogen well generally have high porosity and large specific surface area (Langmi et al. 2014; Rivard et al. 2019). Despite the drawbacks, several physical adsorption substances will be discussed in further detail, as there is a large variety of them and they are well-researched and cannot be left out of an overview of hydrogen carriers.

2.2.2. Metal hydrides

There are two types of metal hydrides, intermetallic and ionic metal hydrides. Of the metal hydrides, ionic metal hydrides exhibit an average gravimetric energy density (up to 8 wt% or 9.6 MJ/kg), and a high volumetric energy density. Intermetallic metal hydrides, on the other hand, have a poor gravimetric energy density, with a maximum of 2 wt% or 2.4 MJ/kg (Zuttel et al. 2002; Bellosta von Colbe et al. 2019). Desorption of hydrogen occurs at extreme temperatures (Bellosta von Colbe et al. 2019; Rivard et al. 2019) and the reversibility of the process is under debate and thus requires more attention (Bellosta von Colbe et al. 2019; Durbin and Malardier-Jugroot 2013). Because metal hydrides have been used on ships before (Bevan et al. 2011; Bellosta von Colbe et al. 2019), they have a high technology readiness level and will thus be discussed in further detail.

2.2.3. Boron-based complex hydrides

Boranes and borohydrides are molecules that have either a BH_3 or BH_4 moiety (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). The regeneration of boron-based complex hydrides is currently a major challenge, as the B–O bonds formed during dehydrogenation are hard to split (Lang et al. 2020). Borohydrides and boranes release hydrogen in multiple ways, but the two main reaction paths are thermolysis and hydrolysis. Hydrogen release through thermolysis is done by heating the borohydride or borane. However, the temperatures required to release the hydrogen 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 discussed further in this review.

More promising is the release of hydrogen through hydrolysis. Both boranes and 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 needed for hydrogen production. The reaction is exothermic and can happen spontaneously, although for high conversion rates catalysts or acids are necessary (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 originating from the water is released. This results in an effective hydrogen storage capacity of up to 36 wt%

based on the weight of the borohydride, excluding the weight of water (Laversenne et al. 2008).

2.2.4. Alanates

Even though alanates have the possibility to store up to 10.6 wt% of hydrogen, most of them are not able to store more than 5 wt%, which means they do not have very high capacities (Xueping and Shenglin 2009; Rivard et al. 2019; Liu et al. 2023). The thermal release of hydrogen from alanates is endothermic and usually happens in multiple steps, with the first step requiring temperatures of 383–573 K (Rivard et al. 2019; Sazelee and Ismail 2021). The last desorption step takes place at higher temperatures, which depends on the alanate and may be too high for practical applications (Milanese et al. 2018). Doping can reduce this high dehydrogenation temperature, but always comes at a cost of less hydrogen storage (Xueping and Shenglin 2009; Wang et al. 2017; Sazelee and Ismail 2021). Doping also appears to be required for dehydrogenation (Wang et al. 2017; Milanese et al. 2018; Ali and Ismail 2021; Sazelee and Ismail 2021), except for KAlH_4 , which is reversible at relatively low temperatures and pressures, but there is only little research about this alanate (Milanese et al. 2018). Additionally, alanates usually react violently with water and are classified as dangerous (Suárez-Alcántara et al. 2019), even though they are said to be stable (Kojima 2019).

3. Detailed descriptions of specific hydrogen carriers

In this section, certain hydrogen carriers that are generally considered to be relevant are discussed. 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 the carrier, and recyclability of the carrier (circularity). The US Department of Energy (DOE) has defined a goal for both the gravimetric and volumetric energy density of the entire hydrogen carrier system, including the tank and other subsystems. This goal is set at a minimum of 7.5 wt% of hydrogen per kg of the carrier (9 MJ/kg) and 2.3 kWh/L for light-duty vehicles (US Department of Energy 2015). This goal will be taken as a guideline in this paper.

3.1. Liquid hydrogen carriers

3.1.1. Dibenzyltoluene and benzyltoluene

Dibenzyltoluene (DBT) is a promising LOHC, with a real-life storage capacity of about 6 wt% (theoretically 6.2 wt%) (Niermann et al. 2019; Hoecke et al. 2021). It is cheap, stable during dehydrogenation and has a very high TRL (Technology Readiness Level) (Niermann et al. 2019). Additionally, it is not very toxic and 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 543 K, but then only 58% of the hydrogen is released (Sekine and Higo 2021). It is thought that platinum could be a better catalyst for DBT (Lang et al. 2020; Rao and Yoon 2020; Sekine and Higo 2021). The high dehydrogenation temperature is a point of concern for DBT. Another disadvantage of DBT is its high viscosity (Kwak et al. 2021; Rüde et al. 2022). As a result, benzyltoluene (BT) is currently considered to be a good alternative for DBT. BT has very similar properties, but a much lower viscosity and a higher level of dehydrogenation under similar circumstances (Kwak et al. 2021; Rüde et al. 2022). However, BT has disadvantages as well, of which the low boiling point of only 538 K (at ambient pressure) is the most problematic (Kwak et al. 2021). This low boiling point means that during the dehydrogenation gas by-products are formed, which is undesirable (Kwak et al. 2021). Thus, DBT with its high energy density, good availability and easy handling

is often regarded as one of the most promising LOHCs (Niermann et al. 2019).

3.1.2. *N-ethylcarbazole*

N-ethyl carbazole (NEC) is also thought to be one of the most promising LOHCs (Lang et al. 2020). NEC has a dehydrogenation temperature of 453–523 K and stores about 5.8 wt% of hydrogen in theory, 5.2 wt% in practice (Niermann et al. 2019). Complete dehydrogenation can be achieved already from 453 K (Niermann et al. 2019). The dehydrogenation temperature of NEC can be reduced to 423 K when using iridium complexes as catalysts, but this does not result in complete dehydrogenation (Lang et al. 2020). It has a TRL of only 3 on a scale of 1–9 and is not widely available (Niermann et al. 2019; Hoecke et al. 2021). Additionally, the hydrogenated form is solid at room temperature, requiring either innovative handling solutions or continuous heating for the substance to remain liquid. Both options will result in additional cost and likely less efficient operations (Hoecke et al. 2021).

3.1.3. *Methanol*

Methanol is a low-toxic alcohol, which is liquid at ambient conditions and stores 12.6 wt% of hydrogen (Hoecke et al. 2021). Due to its inertness, it can be stored in the double hull of a ship (Hoecke et al. 2021). Another main advantage of methanol is that it is commercially available, making it cost-attractive (Zheng et al. 2021). However, methanol will pose safety challenges, as it has a low flash-point and is dangerous to inhale or digest, resulting in the requirement of safety measures (Hoecke et al. 2021). Just like formic acid, methanol releases CO₂ when dehydrogenated. Methanol can be used directly in combustion engines and direct methanol fuel cells but needs to be reformed and purified when used in combination with a PEM fuel cell (Van Biert et al. 2016; Hoecke et al. 2021). Additionally, similar to formic acid, the emission of CO₂ means that having a ship that does not emit any CO₂ can only be achieved by using carbon capturing onboard, reducing the overall energy density of the system. If only circular production is desired, carbon capturing on land is sufficient (Hoecke et al. 2021). Thus, even though methanol is a very interesting hydrogen carrier, it will not be reviewed further in this review paper, as the main goal here is to have a fuel onboard which does not produce emissions.

3.1.4. *Formic acid*

Formic acid (HCOOH) is a semi-non-toxic acid, which is liquid at ambient conditions (Zheng et al. 2021). It is highly corrosive (Hoecke et al. 2021). It stores hydrogen at about 4.4 wt% (Hoecke et al. 2021; Zheng et al. 2021). Formic acid is made from the hydrogenation of CO₂, which is theoretically 100% effective (Hoecke et al. 2021; Zheng et al. 2021). It decomposes at about 373 K. At decomposition, it either forms CO₂ and H₂ or CO and H₂O (Zheng et al. 2021). The latter process is not desirable. As mentioned before, having a zero-emission ship running on formic acid is extremely difficult, which, combined with its relatively low gravimetric energy density, means that formic acid will not be considered further in this review paper.

3.2. *Physical adsorption*

There exists a multitude of substances that are capable of physically adsorbing hydrogen, and we will focus on four specific types due to their unique and compelling characteristics. Metal-Organic Frameworks (MOFs), with their broad range of structural diversity, are suitable for a wide range of applications. Metal-decorated structures show great promise due to their high hydrogen uptake capacity. Nanostructures were previously considered interesting but have become a controversy in hydrogen storage research

(Froudakis 2011). Finally, ice is also of interest because of the sustainable way of storing hydrogen in water.

3.2.1. *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 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 are usually highly porous (to store the hydrogen inside their voids) and have a high specific surface area (Langmi et al. 2014; Rivard et al. 2019). The conditions at which MOFs store hydrogen ranges from cryogenic temperatures to room temperatures and ambient pressures (Langmi et al. 2014). A great advantage of MOFs is their fast release and adsorption of hydrogen, which is usually in the scale of 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). Additionally, a lot of light elements such as Li, Na and Mg cannot be used for MOFs as they are susceptible to hydrolysis, resulting in violent reactions with water (Durbin and Malardier-Jugroot 2013; Kojima 2019; Hoecke et al. 2021). The amount of hydrogen that can be stored in MOFs is also generally an issue. MOFs at room temperature are only able to store about 1wt% of hydrogen if they are at 20 bar (Langmi et al. 2014; Rivard et al. 2019). In order for MOFs to store higher quantities of hydrogen, they have to be at very low temperatures and high pressures (Langmi et al. 2014; Rivard et al. 2019). The hydrogen uptake of MOFs is proportional to the pressure (Shet et al. 2021). The relationship between temperature and storage capacity is different, as physisorption decreases at higher temperatures (Shet et al. 2021). At room temperature, using iron MOFs 6 wt% at 101 bar was reported (Durbin and Malardier-Jugroot 2013), whereas at 77 K and 70 bar, for example, NU-100 can store up to 16 wt% of hydrogen (which reaches the DOE target of 7.5 wt%) (Farha et al. 2010). Keeping the MOFs at such low temperatures and high pressures is very costly and energy-consuming, even though MOFs generally have extremely low thermal conductivity (Rivard et al. 2019).

3.2.2. *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 metal decorated structures also adsorb molecular hydrogen physically (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.

3.2.3. Nanostructures

Nanostructures are not materials, but a way of physical storage. Nanostructures are usually made of carbon (Zuttel et al. 2002; Durbin and Malardier-Jugroot 2013). 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 hydrogen 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 18,900 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 temperatures (Froudakis 2011). Like MOFs, at lower temperature these carbon nanostructures are more effective, with storage of up to 8 wt% hydrogen at 77 K (Durbin and Malardier-Jugroot 2013). Regeneration is complicated, as it is difficult to add hydrogen to these types of structures (Durbin and Malardier-Jugroot 2013). Additionally, the dehydrogenation process is slow, with a 50% hydrogen release taking an hour and complete hydrogen release taking over 200 h (Zuttel et al. 2002). An additional 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 based and non-carbon based (Durbin and Malardier-Jugroot 2013).

3.2.4. 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; high pressures are required to store larger amounts of hydrogen (Durbin and Malardier-Jugroot 2013; Del Rosso et al. 2017). Depending on the pressure, between 5.2 and 12.9 wt% of hydrogen can be stored in ice. The volumetric energy density is then 1.5–3.5 kWh/kg, reaching the target set by the DOE (Durbin and Malardier-Jugroot 2013; US Department of Energy 2015; Liu et al. 2019). In order to store higher weight percentages of hydrogen, however, enormous amounts of pressure are required (at least 700 MPa) (Durbin and Malardier-Jugroot 2013). The main advantages of storing hydrogen in ice are the required storage material (water) is cheap and the safety of the storage: it has a low environmental impact and is self-extinguishing (Durbin and Malardier-Jugroot 2013). However, the high pressure and low temperature required form a major complication (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, such as tetrahydrofuran (THF), the hydrogen can be stored at lower pressure and ambient temperatures (Florusse et al. 2004). It is thought that by adding THE,

4 wt% 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, remains the low energy densities. Studies have not shown hydrogen storage capacities beyond 5wt%, which is significantly below the target.

3.3. Metal hydrides

In this review, metal hydrides are split into two types: ionic or elemental hydrides and intermetallic hydrides. Elemental hydrides consist of an element combined with hydrogen. Examples of these are magnesium hydride and lithium hydride (Møller et al. 2017). 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).

3.3.1. LiH and mgH_2

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 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 of the DOE (Wang et al. 2016). This, however, is a promising technology if more hydrogen can be released.

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 require 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).

3.3.2. Intermetallic metal hydrides

Intermetallic metal hydrides can be grouped according to the type of material. 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 $LaNi_5H_{6.7}$, Ti–Zr alloys (such as $Ti_{0.93}Zr_{0.05}Mn_{0.73}V_{0.22}Fe_{0.04}$)₂, Sn_2Co , Ti–Fe alloys ($FeTiH_{0.95}$) (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, $LaNi_5H_{6.7}$ only stores 1.4 wt% hydrogen (Abe et al. 2019). Metal hydrides generally have favourable operating conditions, as they do store and release hydrogen at temperatures in the range of 298 to 353 K and do not need elevated pressures with their equilibrium pressures of 1 to 10 bar (Durbin and Malardier-Jugroot 2013; Abe et al. 2019). However, their high weight makes them unsuitable for shipping (McKinlay et al. 2020).

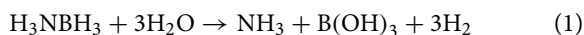
Metal hydrides are much more suitable for land-based hydrogen storage (Abe et al. 2019). A case study was performed, in which metal hydrides were looked at as effective hydrogen carriers onboard a ship; for the specific case this would result in 40% of the total storage mass taken by metal hydrides to provide the required amount of energy (McKinlay et al. 2020).

3.4. Complex hydrides

Complex hydrides such as NaAlH_4 and NaBH_4 are named as promising candidates for hydrogen storage (Xueping and Shenglin 2009). Complex hydrides that are formed with aluminium are also named alanes (Xueping and Shenglin 2009), those formed with boron are named borohydrides. Both LiAlH_4 and NaAlH_4 are available and cheap (Ali and Ismail 2021; Sazelee and Ismail 2021).

3.4.1. Ammonia borane

Ammonia borane is a very much researched borane (Demirci 2020). Ammonia borane has a very high hydrogen content of 19.6 wt% (Akbarak and Özkaz 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 (Akbarak and Özkaz 2018). The hydrolysis reaction of ammonia borane is as follows (Stephens et al. 2007):



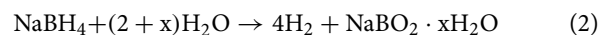
There is also another reaction noted, in which the borate and ammonia react and become ions (Lang et al. 2020). It can be seen from reaction 1 that there are two main products, a borate and ammonia. For a PEM fuel cell, which is assumed in this review, ammonia is very difficult. It is, however, a hydrogen carrier and will be discussed in further detail in Section 3.5. 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 back to shore; 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 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, it may be hard to use in practical applications.

3.4.2. NaBH_4

NaBH_4 can store up to 10.7 wt% of hydrogen in theory (Kojima 2019). NaBH_4 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 or acids, both of 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 NaBH_4 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 NaBH_4 . The spent fuel, NaBO_2 , however, has to be brought back as well, which is 2.7 to 3.6 times heavier than the original fuel, depending on the hydrogenation of the spent 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). However, it is most likely difficult for the same reason as regeneration of ammonia borane is difficult, due to the B–O bonds that are formed during dehydrogenation (Lang et al. 2020). The dehydrogenation is currently under active research at TUDelft and University of Amsterdam (SH2IPDRIVE 2023).

3.4.3. KBH_4

Some sources have mentioned KBH_4 as an alternative for NaBH_4 (LaVersenne and Bonnetot 2005; Laversenne et al. 2008; Saka and Balbay 2018). It has very similar properties to NaBH_4 , 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 KBH_4 is that the spent fuel stores less water molecules and is easier to handle, as it reacts less strongly with water (Laversenne et al. 2008). KBH_4 reacts with water to form $\text{KBO}_2 \cdot 4/3\text{H}_2\text{O}$, whereas NaBH_4 usually has either 2 or 4 water molecules after hydrolysis (Laversenne et al. 2008). When heated above 408 K the KBO_2 hydrate loses a water molecule, resulting in only $\text{KBO}_2 \cdot 1/3\text{H}_2\text{O}$. At a similar temperature, NaBH_4 still stores 1 water molecule. This means that the spent fuels have a very similar weight, with molar masses of 83 and 87u respectively. The regeneration process of KBO_2 back to KBH_4 is very similar to that of NaBH_4 . However, depending on the process, KBH_4 has an advantage. If ball-milling is used, anhydrous borate is desired (Düll et al. 2022). The energy required to get an anhydrous borate costs less energy and only comprises of two steps (compared to 4 steps for NaBH_4) and is thus advantageous (Laversenne et al. 2008). Thus, KBH_4 has some advantages considering storage and perhaps regeneration as well, but the overall energy density of KBH_4 is much lower than that of NaBH_4 .

3.4.4. 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, Qiu et al. 2013). This results in a release

of about 7.1 wt% at a temperature of 403 K (Li, Qiu 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 residual 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 7.5 wt% of hydrogen release, even though only the first two steps are practically applicable as the third step requires a too high temperature (Li, Qiu 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.

3.4.5. NaAlH_4

Sodium aluminium hydride (NaAlH_4) is closely related to lithium aluminium hydride. It has a lower hydrogen weight percentage of 7.41 wt% and a higher decomposition temperature (483 K) than LiAlH_4 (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). Additionally, all three steps are slow (Møller et al. 2017; Rivard et al. 2019). 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. Keypoints are reducing operating temperatures and pressures, enhancing kinetics and understanding dopants (Ali and Ismail 2021).

3.5. 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 energy-consuming process of decomposing ammonia into hydrogen and nitrogen (Makepeace et al. 2019). Since this research is focused exclusively on the PEMFC and not on other energy conversion technologies like internal combustion engines or SOFCs that can utilise ammonia, the process of cracking becomes indispensable (McKinlay et al. 2020). Cracking of ammonia is energy-consuming due to its endothermic nature and high temperature (higher than 673 K) requirements (Makepeace et al. 2019; Aziz et al. 2020; Lee et al. 2021; Lucentini et al. 2021). Because ammonia has a high energy density, research focuses on lowering the energy consumption by using catalysts (Makepeace et al. 2019; 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 13–26% of the total lower heating value of the hydrogen produced (Wijayanta et al. 2019; Lee et al. 2021). The 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 a high energy density and is widely available, due to the complex and energy consuming cracking (required for use in a PEM fuel cell) and the high toxicity, it will not be taken into account further in this paper.

4. Evaluation of hydrogen carriers

This section aims to evaluate the hydrogen carriers on characteristics relevant for shipping purposes. It starts with the pure, theoretical energy densities, without packing factors or tanks, despite the lower limit of the DOE including these factors. If this lower limit is not reached without taking these factors into account, it will not be reached regardless, which is why only theoretical energy densities are taken into account here. Next other characteristics, such as TRL, dehydrogenation, safety and handling are evaluated.

4.1. Energy density

Figure 2 shows a graphical overview of the pure theoretical energy density of the discussed groups of hydrogen carriers. Only metal decorated structures (discussed in Section 3.2.2) are not taken into account in this figure, as their volumetric energy density could not be found. As the red lines indicate the DOE targets, everything above and to the right of these lines can theoretically reach the targets. 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 figure shows 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 (Van Kranenburg et al. 2020).

4.2. Overview of relevant characteristics for shipping purposes

Next to the volumetric and energy densities of the carriers, there are several other criteria to evaluate the carriers. The main relevant parameters which are relevant for shipping purposes are given in Table 1, including reasoning and limits. For safety, handling and storage, flashpoints are taken into account, however low flashpoints do not necessarily limit application onboard, as there are already guidelines for low flashpoint fuels.

Table 2 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

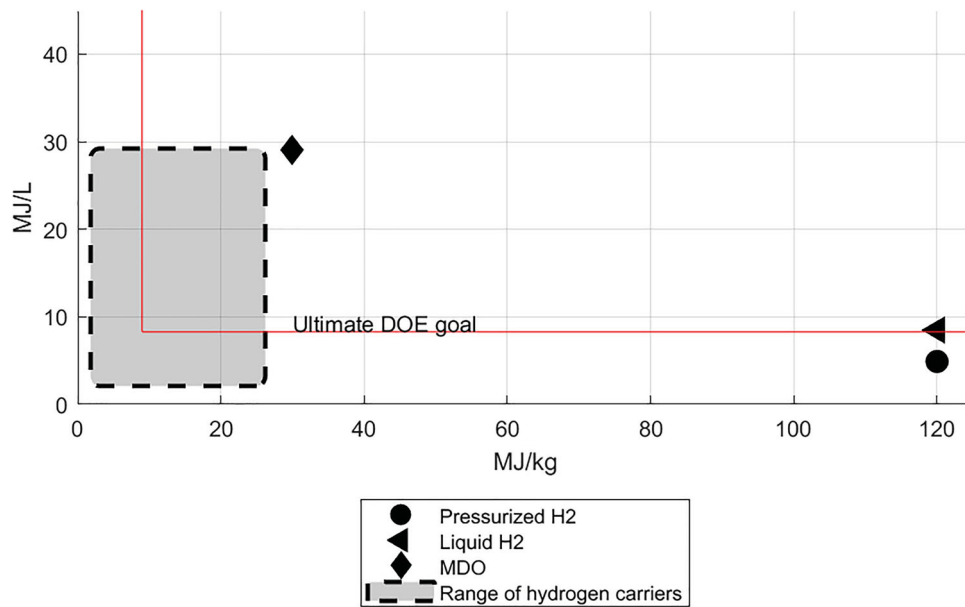


Figure 2. Theoretical gravimetric and volumetric energy density range of hydrogen carriers, liquid and pressurised hydrogen and diesel, with the red line representing the DOE target of 9 MJ/kg and 8.28 MJ/L for lightweight vehicles.

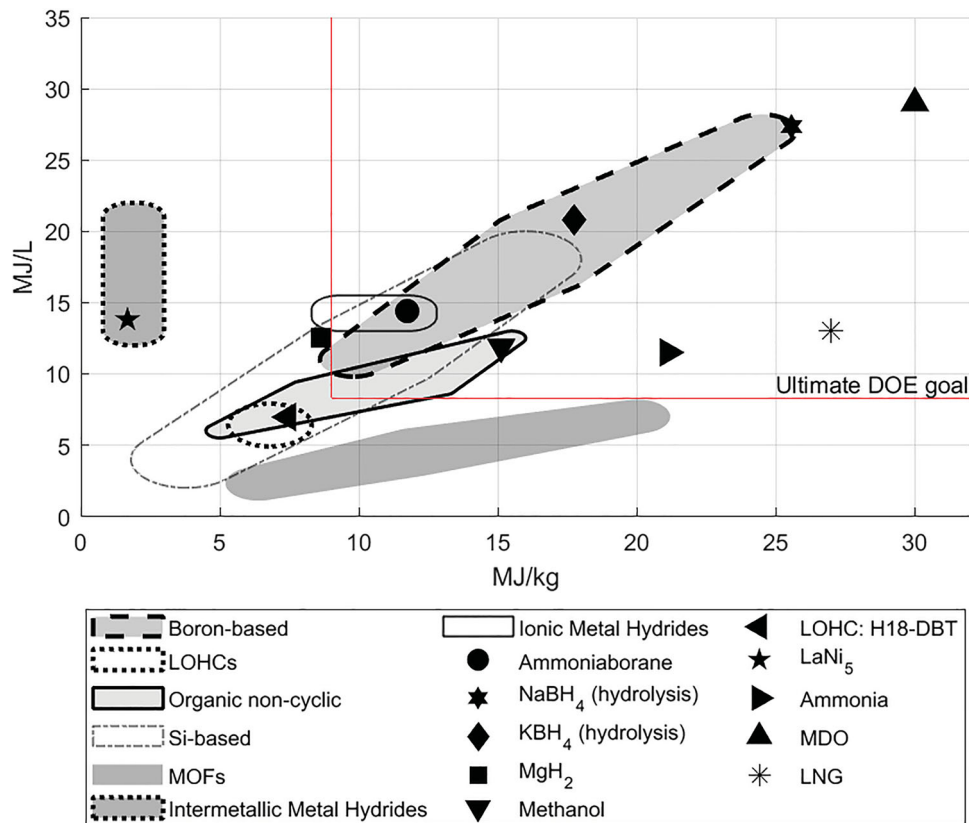


Figure 3. Theoretical gravimetric and volumetric energy density of different groups of hydrogen carriers, with the red line representing the DOE target of 9 MJ/kg and 8.28 MJ/L for lightweight vehicles. Physical-based hydrogen storage is left out because otherwise, details are not visible due to the high theoretical gravimetric energy density of liquid and pressurised hydrogen.

the different hydrogen carriers. 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 efficiency. 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 is a set of hydrogen carriers that may be interesting for usage on ships in general, likely without there being a single solution that fits all ship types and operations. All carriers with a low

Table 1. Relevant characteristics to judge hydrogen carriers for shipping purposes.

	Relevance for shipping purposes	Limiting metrics
Gravimetric and volumetric energy density	Define the required storage capacity	At least 9 MJ/kg and 8.28 MJ/L
Technology Readiness Level	Estimate the timeline for technology implementation	Higher than 4 (research stage only)
Safety, handling and storage	Defines the measurements needed for onboard application	No species that either combust spontaneously (very low flashpoint) or that react violently with substances that cannot be avoided onboard a ship, such as (humid) air. Toxic gasses are also unwanted, as in case of a leak, these may spread easily through the ship. Substances that require high pressures (over 10MPa) for storage are also unwanted, because of additional explosion risks. Similarly, risk of freeze burns limits application of substances that need cryogenic temperatures (lower than 77 K).
Dehydrogenation	The dehydrogenation process onboard should be relatively fast, to enable load following and not release extremely high temperatures, as this will result in high energy requirements and thus reduction of energy density. Dehydrogenation should produce restproducts that can safely be stored on board and regenerated on land	Release temperatures lower than 620 K Possibility of 100% release
Recycling	Recycling should be possible and energy efficient	No metrics, usually mentioned as either possible, theoretically possible or not possible

TRL level at this moment have been disregarded in this 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 (on-shore) rehydrogenation process for compounds such 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.

5. Effective energy density of interesting hydrogen carriers

In the previous section, a set of promising hydrogen carriers have been identified based on their theoretical energy densities and other basic properties. These hydrogen carriers are NaBH_4 , KBH_4 , ammoniaborane and DBT. To thoroughly evaluate these hydrogen carriers, a switch has to be made from theoretical values to realistic energy density values. This is also what the US DOE goal is based on: values including packing factor and required other materials (Wu et al. 2020). The effective energy density is based on the following three parameters: the properties of the material itself, the tanks that are required and the extra equipment required to release the hydrogen. The aim of this section is to give an overview of what is already known about the effective energy density of promising hydrogen carriers for each of the three parameters and to identify where additional research is required.

5.1. Challenging material properties for application

Material properties, such as the state of matter and the density of both the fuel and the spent fuel influence the energy density. As DBT is a liquid, the density and viscosity depend on temperature. Especially the viscosity is important for DBT as it influences the pumping power. As DBT has a very high viscosity, pumping at normal temperatures may not be feasible and preheating of the tanks may be required. However, in the shipping industry, this is a common practice, as HFO needs to be preheated before pumping is possible (Ampah et al. 2022). However, preheating costs energy and thus lowers the overall energy density of the hydrogen carrier, by up to 7% as estimated by Lee et al. (2021).

For the borohydrides and ammoniaborane the exact composition of the solid defines the bulk packing density and thus the energy density. The rougher the particles, the less densely packed the substance becomes. The exact differences between the bulk density and the material density depend on the material but can be as low as 25–35% of the material density (Carson and Pittenger 1998). Thus, the exact composition and state of the solids onboard will highly influence the overall energy density. This does not only apply to the fuel, but even more to the spent fuel. Equation 2 shows a potential dehydrogenation process of NaBH_4 . The form of the spent fuel depends on the temperature and can be NaBO_2 , $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$. All these spent fuels are heavier and take up more volume compared to the original NaBH_4 . For example, 1 kg (0.93L) of NaBH_4 produces 2.7 kg and 1.4L if $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ is produced (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.

For ammoniaborane, there is an additional complication as ammonia is released during the hydrolysis. Ammonia cannot be used in its pure form in fuel cells, it has to be cracked first, which costs between 33% and 95% of the total energy inside ammonia (Lee et al. 2021). However, ammonia can also be used as a fuel inside an internal combustion engine. There is a lot of research on use of ammonia as a power source, see for example (Valera-Medina et al. 2018). Further research is needed to determine the optimal utilisation of the released mixture from ammonia borane to evaluate the overall energy density onboard ships.

5.2. Tanks

The size and especially the shape and thickness of the walls of the tanks are determined by safety measures. The additional amount of material due to tanks is called the packing factor (Van Kranenburg

Table 2. Overview of the chosen hydrogen carriers, their main properties and main problems.

	MJ/L	MJ/kg	TRL	Safety, handling and storage	Dehydrogenation	Recycling
MOF	5.4	7.2	4-6	Low temperature (77 K) Solid	Fast	Limited amount of cycles possible
MDS	2.4	5	< 4	Low temperature (100 K) Solid	293 K-373 K	Possible
Nanostructures	6.2-8.76	N.A.	< 4	High pressures (> 15MPa), Low temperature (77 K) Solid	Slow, can self-collapse	Risk of self-collapse, complex recycling
Ice	6.6	5.5	< 4	High pressure (> 700MPa) Low temperature (\approx 114 K) Solid	Fast, high quality	Possible
Ammonia borane	23.5	14.4	4-6	Stable, preferably store away from water, solid	Byproduct NH_3 , exothermic, water required. Only releases 7.8wt% hydrogen, rest ammonia	Possible, but energy intensive
NaBH_4^*	12.8	13.7	4-8	Store away from water, solid	Exothermic, water required, catalyst needed	Possible, but energy intensive
KBH_4^*	8.9	10.4	4-8	Store away from water, solid	Exothermic, water required, catalyst needed	Possible, but energy intensive
LiBH_4	22.1	14.6	4-6	Store away from water, solid	Only 50% release during hydrolysis	Possible
LiAlH_4	12.7	11.7	< 4	Violent reaction with water (occurs with humid air already) Solid	486 K without doping 408 K with doping	Not possible under moderate conditions
NaAlH_4	6.7	8.4	3-6	Violent reaction with water (occurs with humid air already) Solid	High temperatures (up to 708 K), 3 stage process Only 5wt% release	Possible, but energy intensive
LiH	15.1	13.2	3-6	Violent reaction with water (occurs with humid air already) Solid	High temperatures required (> 973 K)	Possible
LaNi_5	1.7	13.8	7-9	Generally considered safe, solid	Endothermic, Ambient to moderate conditions (293-353 K)	Possible
NEC	7.0	6.6	< 4	Generally considered safe, liquid	Endothermic, 423-353 K	Possible
DBT	8.3	7	7-9	Generally considered safe, liquid	Endothermic, 573 K	Possible
Pentasilane	9.5	20	< 4	Generally considered safe, liquid	Fast, high quality	Possible
NH_3	21.1	11.5	4-8	Toxic gas	Cracking required at high temperatures (673 K)	Not directly possible
Methanol	15.1	11.9	4-8	Low flashpoint fuel	Byproduct CO_2	Not directly possible without onboard CO_2 capturing
Formic acid capturing	5.3	6.4	3-6	Generally considered safe, liquid	Required product hard to get	Not directly possible without onboard CO_2
Liquid hydrogen	120	N.A.	7-9	Gas at ambient conditions, flammable	Not applicable	Not possible

Note: Due to the similarity in properties, LaNi_5 is chosen as an example for metal hydrides. Highlighted cells indicate inadequate values. Borohydrides indicated with a *, have theoretical values only, without added hydrogen from hydrolysis.

et al. 2020). The packing factor of the hydrogen carriers is relatively easy to determine. DBT does not have a packing factor, as it is very similar to HFO and can thus be stored in standard HFO tanks. For the borohydrides and ammoniaborane, it currently appears that they do not react with moisture in the air, as long as the temperature stays below approximately 30C (Murtomaa et al. 1999; Li, Yu et al. 2013). Additional research here is needed to see whether the air in the storage tanks of borohydrides stays below this threshold and whether no hydrogen is released at all because otherwise, countermeasures have to be taken to avoid preliminary release of hydrogen.

5.3. Additional equipment related to hydrogen carriers

To release the hydrogen from hydrogen carriers, specialised equipment is necessary. The amount of components and their size depends on the process, which in its turn depends on the hydrogen carrier. As most of the promising hydrogen carriers are still in laboratory phase, upscaling to industrial size is required, which is difficult but necessary to be able to calculate both the energy but also the power density of the hydrogen carriers. We believe the size of the equipment depends on the required power, the dehydrogenation process

and possible pre- and post-treatment. Whether the dehydrogenation process is exothermic or endothermic determines whether cooling or heating is required. The exact amount of energy necessary or produced during the dehydrogenation and the heat integration also determines the size of the additional heating or cooling equipment. The possible pre- and post-treatment is closely related to the material properties of the hydrogen carrier.

As mentioned in the first subsection, DBT might need pre-heating as pre-treatment and purifying of the hydrogen as post-treatment. On the other hand, the borohydrides and ammoniaborane likely require mixing with water as pre-treatment and crystallisation of spent fuel as post-treatment. These additional treatments will require additional components, which will take up space and thus reduce the overall energy and power density of the system.

5.4. Initial calculations of effective energy density

With the current knowledge, we can make an initial attempt at computing the effective energy density. For liquid hydrogen, this data is taken from literature (Rivard et al. 2019).

For the hydrogen carriers, the calculations are based on the following assumptions. For NaBH_4 and KBH_4 the spent fuel is taken into account. Depending on the operating conditions of the reactor and process this spent fuel is between 1.7 and 3.3 (NaBH_4) or 1.5 and 2 (KBH_4) times heavier than the original fuel. Thus, instead of using the weight and volume of the original fuel, we calculated the energy density using the spent fuel, as the weight and size of the spent fuel determines the amount of fuel that can be brought on the ship. Under the operating conditions on the ship, the spent fuels are most likely to be $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{KBO}_2 \cdot 1/3\text{H}_2\text{O}$. The hydrate (water) part can be removed at a cost of approximately 50 kJ/mol H_2 that should be removed for NaBH_4 (Laversenne et al. 2008), thus resulting in 100 kJ per mol NaBH_4 energy loss. For KBH_4 this is a total of 59 kJ/mol for the first mol and 19 kJ for the 0.3 H_2O that should be removed (Laversenne et al. 2008). This energy cost is subtracted from the overall contained energy per molecule to calculate the energy density of the borohydrides with the non dehydrated spent fuel. Thus, an estimate on the effectiveness of removing the hydrate can be made, as there is discussion and research on the effect of the spent fuel composition on the regeneration process (Chen et al. 2017; Zhong et al. 2017; Nunes et al. 2021).

Ammonia borane does not form a hydrated spent fuel, but it does produce additional ammonia. We have calculated the spent fuel as either B(OH)_3 part with and without ammonia. With ammonia means that the ammonia is stored onboard as well, without ammonia means that ammonia is either cracked (and used in the PEM fuel cell), or used for other onboard processes. In this 'use ammonia' case, however, we have assumed that the ammonia does not add to the overall energy density because of the large difference in estimation of the energy costs related to cracking of ammonia (ranging from 95% to 33% of total energy available) (Lee et al. 2021).

For DBT an average loss of 31% as calculated by Lee et al. (2021) is used to calculate the overall energy density. Here the weight and volume of the spent fuel is not taken into account. The spent fuel is lighter than the fuel and the density does not differ much (Niermann et al. 2019).

The calculated energy densities of the hydrogen carriers as well as of liquid hydrogen are visible in Figure 4. Figure 4 shows clearly that the hydrogen carriers have much lower energy densities than diesel when the known factors such as the energy required for dehydrogenation or weight of spent fuel are taken into account, especially as additional things like packing factors have not been taken into account yet for the hydrogen carriers.

6. Assessment of suitability of hydrogen carriers for different ship types

We developed a framework to assess the suitability of hydrogen carriers for different ship types and ship operations. Table 3 gives an overview of this framework and the ship types we considered.

The first of the different ship types we considered are inland cargo ships, travelling up and down rivers, canals and other inland ship corridors, with intermediate bunkering facilities along the corridor. Because these are inland ships, they do not have a large amount of volume available for fuel. Due to the characteristics of inland ship corridors, inland ships are likely to travel through densely populated areas, resulting in the need for a fuel that is safe for the environment and the general public in the surrounding areas. As they do not always travel the same river or have the same destination, they are generally a bit flexible in their destination.

Ships that also travel parts across the sea, along the coastline, are short sea ships. These ships can travel large distances, from Africa

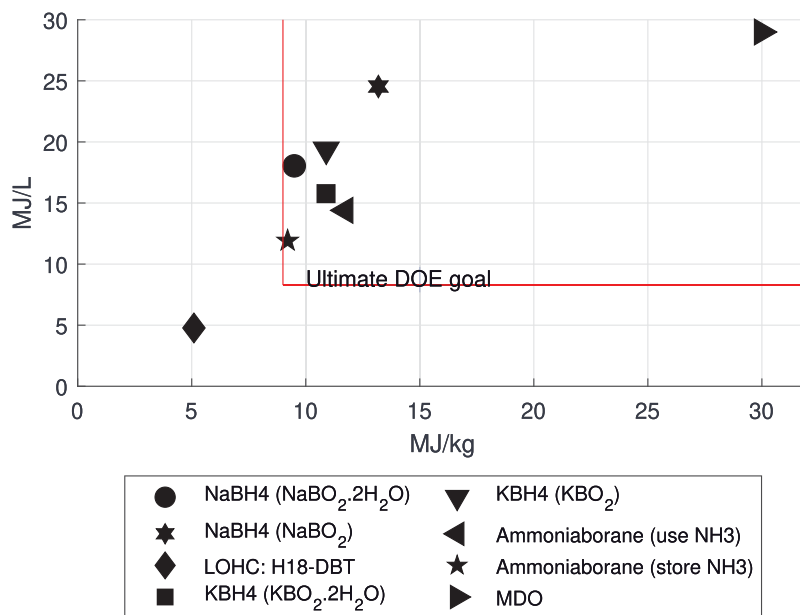


Figure 4. Effective gravimetric and volumetric energy density of selected hydrogen carriers including packing, spent fuel weight, dehydrogenation energy losses and other influencing factors.

Table 3. Framework to evaluate the application of hydrogen carriers for ship types and ship operations.

	Inland	Short sea	Seagoing	Dredging	Workboats (tugs)	Fishing vessels	Ferries	Naval
Required range	–	+	++	+	–	+	+	+++
Volume available for fuel and process plant	+	++	+++	–	---	0	0	+
Safety requirements relative to stakeholders and environment	+++	++	+	++	++	++	++++	+
Bunker flexibility requirement	++	++	++	++	--	--	--	+++

to the Baltic Sea. Because they are bigger and sail longer distances compared to inland ships, they require more propulsion power and energy storage. Therefore, they have a larger volume available for fuel. The safety requirements for detonation and toxicity are more manageable, as they are less likely to travel through densely populated areas and have a higher educated crew, that is able to respond better to incidents. Finally, just like the inland ships, they do not always have the same destination, even though a lot of short sea (and inland) ships that sail in line services with standard destinations.

The largest types of cargo ships are the ocean-going ships. They have the most volume available for fuel. Again, similar to short sea ships, detonation and toxicity risks are more manageable on these ships because of the size of the ship, the larger free area surrounding the ship and the higher level of education of the crew. However, as these ships stay at sea for longer periods of time, the risks have to be covered. Because of the distances they travel, which depend on the world trade, they have to be flexible in which harbours they go to.

Besides these types of cargo ships, there are special-purpose ships, such as dredgers, workboats, pushboats and fishing vessels. These ships generally do not have large volumes onboard available for fuel. Especially tugs and push boats have extremely little space, but dredgers and fishing vessels have less space than cargo ships. For dredgers, workboats and fishing vessels, similar reasoning for safety as for short sea ships is used, resulting in an 'in-between' level of safety required.

Another type of ship is ferries. These travel a broad distribution of distances, but all have in common that they transport people. This results in high safety requirements. Because of the number of people on board, they have less space for fuel than cargo ships. Ferries generally shuttle between ports and thus have very little flexibility in destinations.

Naval ships are the final type of ship considered. Even though they are generally at sea for long periods of time, they do not have a lot of excess volumes available for fuel. Additional space is preferably used for weaponry and other systems, instead of fuel. Because of the presence of weapon systems and the possibility of attacks on the ship, the safety requirements for the fuel are considered different. Unsafe fuel should not give additional risks, but the crew has a high level of education and is trained to react adequately to possible threats, including fuel-related incidents. Thus, fuels that are not safe enough for ships with passengers, may be used on naval ships. Of course, naval vessels are extremely flexible in their destination, as they travel across the world.

7. Suitability of identified hydrogen carriers for different ship types and ship operations

Based on Table 3 we can evaluate the suitability of the identified hydrogen carriers for different ship types and ship operations. Additionally, we will provide recommendations for further development. Table 4 gives an overview of the relevant parameters to evaluate the suitability of hydrogen carriers for the different ship types. For the hydrogen carriers, we assume that regeneration does not take place locally and definitely not onboard the ship. This assumption is made because of the uneven distribution of renewable energy resources

(Ritchie et al. 2022) and the envisioned size and complexity of regeneration locations, which combines likely results in more centralised regeneration locations.

7.1. Borohydrides

The borohydrides NaBH_4 and KBH_4 have very similar properties. They have a high energy density and can thus provide a high range with a relatively small volume required for storage. However, the size of the reactor and pre/post-treatment equipment required is unclear. Assuming it depends on the power consumption required by the ship, this can make the borohydrides less favourable for ships with high power requirements and low onboard volume available, such as dredgers, push boats and other workboats. Thus, in order to assess whether borohydrides can be used as alternative fuel on these types of ships more research on reactor design is required. For many of the other ship types, such as inland, short sea and seagoing ships, as well as fishing vessels and ferries the borohydrides seem to be suitable to use. For ferries, safety is extremely important. Because of the slow reaction kinetics, especially at relatively low (B 303 K) temperatures (Murtomaa et al. 1999; Li, Yu et al. 2013), no hydrogen gas is expected to be released outside of the controlled environment, making the borohydrides relatively safe. However, borohydrides remain corrosive to human skin (National Center for Biotechnology Information 2023b). For fishing vessels, volume is important with less power requirements than workboats or dredgers. This is why the borohydrides are considered for fishing vessels and less for workboats and dredgers, as the ratio between additional equipment (such as the fuel cell and dehydrogenation reactor) and fuel itself may become less favourable. As it is assumed that regeneration will take place at centralised locations, the borohydrides have to be transported to and from these locations, which is relatively easy due to their powdery structure. Thus, borohydrides can be used in a large variety of locations, providing a high bunkering flexibility. Naval ships are extremely flexible in their destination, but they also occasionally require large amounts of power, while not having large amount of volume available for the fuel and the reactor. This means that more research is required to assess whether borohydrides are suitable for naval vessels. So, additional research in reactor design and regeneration of borohydrides is considered important and generally speaking borohydrides are suitable for inland-, short sea- and seagoing cargo ships, as well as fishing vessels and ferries.

7.2. Ammonia borane

Ammonia borane (AB) is very similar to the borohydrides, but it has a much higher energy density and is less safe due to ammonia gas released during dehydrogenation. However, AB does not react spontaneously with water, so it can still be used for vessels that sail in areas that are less densely populated (Stephens et al. 2007; Sanyal et al. 2011; Shimbayashi and Fujita 2020). The high energy density makes ammonia borane very suitable for naval and seagoing vessels as there range is important. However, before AB can be used on ships in general, further development is needed to make full use of the energy density of ammonia borane. For internal combustion engines and gas turbines, research on hydrogen and ammonia

Table 4. Relevant parameters of promising hydrogen carriers and liquid hydrogen for application as storage of hydrogen fuel onboard ships.

	Borohydrides	LOHCs	Ammonia borane	Liquid H_2
Range	High	Low	High	Low
Onboard space needed for storage and dehydrogenation	Medium because of mixing tank. Requires specialised equipment for handling due to solid	Medium because of preheating. Onboard handling can use conventional equipment	Medium because of mixing tank. Requires specialised equipment for handling due to solid	Medium, large tank required but no additional dehydrogenation equipment needed
Safety	Medium	High	Low	Low

dual-fuel is needed, whereas for both SOFC and PEMFC ammonia cracking should be researched. Additionally, more research on both the dehydrogenation and hydrogenation of ammoniaborane is needed, the former because of the uncertainty in current literature on the exact process and how much hydrogen is released. Hydrogenation, or regeneration of ammoniaborane, faces similar issues as the borohydrides, as a by-product of regeneration of ammoniaborane appears to be sodiumborohydride. However, because ammoniaborane is a powder just as the borohydrides, it can be transported easily to different destinations and thus does not affect the flexibility of bunkering. For shipping applications besides naval and seagoing vessels, ammoniaborane is not encouraged because of the generation of ammonia. Depending on the region, however, ammoniaborane could be considered for short sea, dredgers, workboats or fishing vessels. These vessels should then have the majority of their operation far away from densely populated areas. For ferries and inland ships ammoniaborane is not suitable as densely populated areas cannot be avoided for these ship types and ferries obviously carry passengers. So, ammoniaborane is a prime interest for usage on naval and seagoing cargo ships, but research into the dehydrogenation, regeneration and conversion processes is required.

7.3. LOHCs

Dibenzyltoluene, but also benzyltoluene and NEC have generally low energy densities, but are easy to handle and extremely safe. This easy handling provides a high flexibility in bunkering locations, as again dehydrogenation is assumed to be a centralised process. This would mean that for ships with flexible destinations and a lower range, LOHCs would be ideal. This would fit with dredging vessels, but research is required on whether the limited available volume onboard is sufficient for the volume required by the LOHC to provide the power and energy the vessel needs. Furthermore, as the dehydrogenation reaction is endotherm, either waste heat or, when not enough waste heat is available, costly hydrogen is needed to release hydrogen from LOHCs. Additionally, the reactor size for LOHC dehydrogenation is unclear and should be researched further to see how the deliverable power and size relate, especially for use on dredging vessels. An advantage that LOHCs have here is that they are fluids and do not need special tanks or transport systems for storage. LOHCs can also be considered for inland shipping and short sea ships, depending on the range and bunkering locations available. Transport of LOHCs is easy and current oil distribution systems can be used for LOHCs as well, opening up the possibility of LOHCs becoming widely available. However, for ships whose operations require large sailing distances, such as seagoing ships and naval ships, or large amounts of power, such as workboats, LOHCs are not suitable as they do not contain enough energy. For ferries and fishing vessels it depends on the range and volume available onboard for the storage and dehydrogenation reactor. The safety of LOHCs is another advantage for use of LOHCs onboard of ferries. So LOHCs have limited suitability for different ship types because of their low energy density. Depending on the exact requirements, they may be suitable for inland, dredgers, short sea, ferries and fishing vessels. Just like with the borohydrides and ammoniaborane, however, more research into the dehydrogenation reactor and specifically its power and size relation is required to assess where are LOHCs are suitable as fuel.

7.4. Liquid hydrogen

Next to the liquid hydrogen carriers, liquid hydrogen is also considered. Liquid hydrogen has a low energy density and requires tanks with a set, suboptimal shape, but when using liquid hydrogen no reactor is used. The tanks make liquid hydrogen harder to transport,

resulting in less bunkering flexibility. However, the absence of a reactor can be advantageous for applications with high power demands, relatively small range and small onboard volume. Thus, liquid hydrogen might be suitable for workboats such as tugs or dredging vessels. These are also the types of vessels where hydrogen carriers may not be suitable. For the other ship types, liquid hydrogen is not considered as an option because of the relatively low safety and many requirements to onboard storage. This makes liquid hydrogen a less attractive option for short sea, seagoing, fishing, naval vessels or ferries. For inland shipping liquid (or pressurised) hydrogen could be considered (and is, see the inland ship *Antonie* (Mandra 2023)), however, we consider borohydrides or LOHCs here as better options because of their higher safety levels.

8. Ongoing hydrogen carrier projects and their maritime relevance

This section gives an overview of ongoing and finished projects that use hydrogen carriers. We also comment on their relevance, potential limitations and future opportunities.

8.1. Metal hydride for the ross barlow channel boat

Metal hydrides, such as the one used in the Ross Barlow Channel boat are very suitable for these kinds of boats; boats that have rather short distances each year (B 1000 km) at low speeds (B 5 km/h). The Ross Barlow Channel Boat is 18 metres long and uses an $MgZn_2$ type metal hydride based on $TiMn_2$ (Bevan et al. 2011). Batteries are insufficient because these boats are not used often enough to avoid discharging (Bevan et al. 2011). As metal hydrides do not discharge over time and are safe, produce pure hydrogen and have a silent and emission-free operation, they have been used in this channel boat (Bevan et al. 2011). However, their practical energy density (B 2%) becomes a problem when larger distances need to be covered. Additionally, because the charging of the boat is slow (taking 2.5 h to store 4 kg of hydrogen), charging very often is not possible (Bevan et al. 2011). So metal hydrides are mainly suitable for boats that do not have to go far and operate too infrequently to use batteries or boats that need a bit more than batteries can deliver. It can be seen mainly as a range extender for boats that would otherwise be using batteries. Thus, for the normal operation of most ships, metal hydrides are insufficient.

8.2. Metal hydrides for air-independent propulsion system for u212 submarines

The U212 and U214 submarines (approximately 1500 tonnes and 56 metres) use a metal hydride system, developed by TKMS, for their air-independent propulsion (Bellosta von Colbe et al. 2019). This system can also be installed during retrofit of older submarines (Bellosta von Colbe et al. 2019). Submarines are one of the largest applications using metal hydrides (Bellosta von Colbe et al. 2019). Just like the Ross Barlow Channel Boat, it was decided that the range of submarines should be larger than that of conventional diesel-electric submarines. The metal hydride based air-independent propulsion system has metal hydrides as a base power source, with batteries supplying peak powers and even recharging when little power is required (Bellosta von Colbe et al. 2019). Because of the difference between submarines and channel boats, the reason behind choosing metal hydrides is different. For the submarines a large range of air-independent propulsion systems was researched and metal hydrides are chosen due to their low volume and relative simplicity. As metal hydrides have such a low hydrogen weight percentage, they had to be positioned in such a way as not to destabilise the submarine (Bellosta

von Colbe et al. 2019). So, metal hydride powered submarines have a larger air-independent range than battery-powered submarines. The range of the metal hydride powered submarine is, however, limited by the weight of the metal hydrides, thus if an even larger range is required, metal hydrides would not be suitable anymore.

8.3. Metal hydrides for hydrogen in hybrid system of Zeus

Zeus (zero emission ultimate ship) is a 25 metres long and 100 tonnes heavy ship with a hybrid power system. It has a diesel-electric generator, a fuel cell and a battery system for its propulsion system (Fincantieri 2023). The hydrogen for the fuel cell is stored in metal hydrides. Again, similar to the previous two uses of metal hydrides, the metal hydrides are used to extend the range the ship can sail, with the batteries supplying peak powers. For longer journeys, the diesel generators will provide the power (Fincantieri 2023). The main difference between submarines and Zeus is the goal of the use of hydrogen. For Zeus, the goal is to be able to sail without any emissions, whereas for U212 submarines it is to stay undetected. However, the outcome is the same type of energy system, with a diesel engine to supply main power for longer journeys and the metal hydride and battery combination to sail for shorter periods of time (of up to 6 hours for the Zeus) (Fincantieri 2023).

8.4. NaBH_4 on submarines in India

An alternative to using metal hydrides for air-independent propulsion is NaBH_4 . The Indian navy is planning to start retrofitting Kalvari-class (67metres, 1600 tonnes) submarines with NaBH_4 as a power source for air-independent propulsion within the upcoming 2 years (Raghuvanshi 2023). Prototypes using sodium borohydrides have been tested and meet design requirements (Raghuvanshi 2023). The main advantage of NaBH_4 over metal hydrides is their higher gravimetric energy density. The volumetric energy density of NaBH_4 is theoretically higher, but in practice, it is more likely to be similar to metal hydrides because of the need for a dehydrogenation reactor. The overall NaBH_4 system is also more complicated to use. As they have a very similar volumetric energy density, only the weight of the hydrogen storage is reduced, which can be promising. Thus, submarines that want to sail larger ranges than practically possible with metal hydrides because of the weight, can possibly use NaBH_4 as a hydrogen carrier. It also opens up more possibilities for the use of hydrogen carriers, besides the current use on submarines, as weight is often an issue.

8.5. H2SHIPS pilot ship Neo Orbis on NaBH_4

An example of the use of NaBH_4 for other ships will be a pilot project of the H2Ships project: the 19.5 metres long Neo Orbis. The Neo Orbis will be an inland port vessel with NaBH_4 as a power source (Interreg North-West Europe 2022). The keel has been laid in January 2023 and the aim is for the ship to be ready by the end of 2023 (Port of Amsterdam 2023). Because of the distances and speeds the Neo Orbis will be sailing, metal hydrides and batteries are not an option. However, similar to the metal hydride system, the NaBH_4 system will also be supplemented with a battery for peak shaving (Interreg North-West Europe 2022). As the Neo Orbis will be operating in the harbour of Amsterdam and its adjacent areas, a safe and emission-free operation is important. This pilot project aims to demonstrate the feasibility of hydrogen in general, but also the use of hydrogen carriers such as NaBH_4 as a safe storage of hydrogen.

8.6. NaBH_4 UAV

For unmanned aerial vehicles (UAV), weight is of utmost importance, which limits the use of lithium batteries (Gang and Kwon 2018; Kwon, Kim et al. 2019). The high energy density combined with the safe handling makes NaBH_4 a promising storage method for UAVs as well (Gang and Kwon 2018; Kwon, Kim et al. 2019). An additional advantage is not having to control the temperature or pressure, which is not the case for pressurised or liquid hydrogen (Gang and Kwon 2018; Kwon, Kim et al. 2019). Because of this, there is quite some research on NaBH_4 as hydrogen supplier for UAVs. Some studies use acids (Kwon, Kim et al. 2019), instead of catalysts, to gain more control and speed up the process. It is also said that use of catalysts may cause an unsteady flow of hydrogen (Kwon, Kang et al. 2019), however other studies do not suggest this (Gang and Kwon 2018). Next to catalysts, to reduce onboard required space, volume exchange tanks have been tested, which remained stable during the flight (Kim 2014). So, the works on using NaBH_4 to store hydrogen is interesting, because of the system integration and volume and weight limitations. Unfortunately, because of the complex and heavy and bulky hydrogen release process, NaBH_4 is not commercially used for hydrogen storage on UAVs (Kim 2014). Thus, additional research into the release mechanism and the dehydrogenation reactor is required.

8.7. SH2IPDRIVE

Contrary to the other projects, which are all rather concrete, the SH2IPDRIVE project is still very much in the research phase regarding hydrogen carriers. Research on hydrogen carriers within SH2IPDRIVE mainly focuses on NaBH_4 , particularly on the dehydrogenation process, regeneration process and handling process of this substance. A second point of research within the hydrogen carrier group is the development of a new LOHC by Voyex (Voyex 2023). The third and final point of research is on the integration of these two hydrogen carriers within ships. Results of the SH2IPDRIVE project are expected in the coming years. The project plan foresees application of borohydride and LOHC technology in a modular unit, to be placed on ships or other platforms.

8.8. Hydrogenious and alma clean power pilot project with LOHC and SOFC system

Hydrogenious is a company that has developed a hydrogen oil, based on benzyl toluene. As hydrogen release from benzyl toluene and other LOHCs is endothermic, they are planning to integrate the LOHC system with a solid oxide fuel cell (Hydrogenious 2023). Alma Clean Power will provide the SOFC. The 100kW integrated system pilot will be tested on board the Edda Ferd, an offshore supply vessel (Hydrogenious 2023). The Edda Ferd is a ship which already has different types of tanks for storage of liquids like marine gas oil, methanol and special products (Østensjø date unknown). This is advantageous for the use of the LOHC onboard, as there is not only liquid tank space available, but also knowledge about other chemical substances than the conventional fuels. This pilot project will be interesting as it makes use of heat integration between an LOHC and SOFC, increasing the efficiency of the total system, which will give relevant data for the effective energy density of LOHCs in combination with SOFCs. Additionally the system will be tested out on the open seas, because the Edda Ferd is an offshore supply vessel. So, the behaviour of the dehydrogenation reactor under the different movements a ship is susceptible to on open seas will most likely provide very relevant information for reactor design.

8.9. HydroSil by hySilabs for long term storage and use on ships

HySilabs has developed the organosilane HydroSil, a liquid, earth friendly molecule which releases hydrogen exothermically (HYSIL-ABS 2023). They promote HydroSil for onboard applications, long-term storage and green hydrogen transportation (HYSILABS 2022). A 15kW release reactor should be finished by the end of this year and they aim for 10 large release systems and charging plants, as well as 100 smaller release systems and one massive charging plant by 20230 (HYSILABS 2023).

8.10. Electriq global

Electriq Global is a company using KBH_4 as a hydrogen carrier. They have already produced a pilot power plant, which demonstrates the use of KBH_4 as a hydrogen supplier for a crane (Sluijters 2022). Electriq Global aims to produce KBH_4 in large quantities starting in 2025 (Sluijters 2022). It is currently unclear where the powder will be used and how it will be regenerated, but using KBH_4 as a hydrogen carrier to fuel a ship is not disregarded.

9. Conclusion

This paper aimed to evaluate hydrogen carriers as an alternative power source for ships. We have done this by first categorising hydrogen carriers based on relevant characteristics such as the dehydrogenation process and reaction, phase of the hydrogen carrier and temperature, pressure and reactivity of the carrier. We also looked into several hydrogen carriers in more detail and discussed features important for circular use on ships, such as gravimetric and volumetric energy density, safety, storage and handling, technology readiness level and dehydrogenation and rehydrogenation process.

We found that LOHCs and borohydrides offer good potential, due to their high energy densities, medium to high technology readiness levels, good safety and well-known dehydrogenation processes. These hydrogen carriers are viable to use on ships. LOHCs can most likely make use of the current infrastructure, whereas borohydrides show energy densities close to diesel.

Our framework shows that these two types of hydrogen carriers are suitable for almost all types of ships, ranging from fishing vessels and ferries to naval and seagoing ships. We have further substantiated this conclusion through an analysis of current state-of-the-art projects, ranging from canal boats to submarines, which shows that borohydrides and LOHCs are being considered as alternative power sources on ships in the industry as well.

So hydrogen carriers, especially borohydrides and LOHCs, are promising and viable options for alternative power sources on ships. However, practical implementation requires further research, particularly in the regeneration of borohydrides and heat integration of LOHCs. Nevertheless, our study highlights the potential of these regenerative, circular, high energy density and zero-emission hydrogen carriers, contributing to the research for alternative power sources for shipping applications.

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Disclosure statement

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