

Technologies of Hydrogen Transportation

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Abstract:

Hydrogen transportation regardless of its state refers to the movement of hydrogen from a production site to end-user(s) or storage facilities. It is a crucial feature of hydrogen economy. Albeit not thoroughly, this paper delves into different aspects, challenges and advancements of hydrogen transportation technologies including gaseous hydrogen transportation, liquid hydrogen transportation and hydrogen carriers transportation. Although technologies scrutinized have been found satisfactory and capable to transport hydrogen, efficiently; to an extent, issues of high cost, safety risks, use of special equipment and impracticalities, to mention a few, are almost features of each technology. Hence, it may be permissible to conclude that safe, cost-effective, efficient, large-scale hydrogen transportation may still be elusive.

Keywords: sustainable, cryogenic, compression, liquefaction, hydrogen carrier.

1. Introduction:

Both the sustainability of traditional energy sources, based on fossil fuels which represent crude oil, natural gas and coal, and their environmental hassle have motivated scientists and engineers both in industry and academia to creatively exploit more efficient energy sources while environmentally cleaner. Renewable energy sources such as solar, wind, geothermal, biomass and different waste, etc., have been an excellent candidate to attain these seemingly paradox tasks. Great results in this regard have been obtained with tremendous positive messages being progressively conveyed in terms of figures of energy efficiency and environment protection. Bearing this in mind, fuel sustainability and renewability as well as environment cleanness may become irrelevant to any relevant debate. Furthermore, opposite to the high cost of initial exploitation of renewable sources for different energy usages, current costs; however, are becoming gradually affordable. Although issues related to the fluctuation of availability of these renewable energy sources have been a nightmare for energy producers via heavily affecting the supply-demand scenarios. It is the ultimate aim of use of renewable sources for energy production and the alike to totally decarbonize such energy applications, although it seems that this is still in its early stages.

Decarbonization of energy and industrial sectors, etc., in part, relies on the use of hydrogen as a potential green clean energy source to better exploit the energy obtained via renewable sources. In addition, hydrogen has also been considered as an energy carrier on its own. In reference to this, the significance of economy of hydrogen has been well-recognized almost worldwide, although few exceptions may apply. To a large extent, hydrogen production, storage and transportation are perhaps the three sides with which a hydrogen triangle can be drawn. According to a recent report concerned with a managerial summary on hydrogen transportation- the key to unlocking the clean hydrogen economy- published in 2021 by ROLAND BERGER, the only management consultancy of European heritage with a strong international footprint, it was emphasized that the investment in clean hydrogen is increasingly continuous as policymakers and private investors are appreciating that both fuel and feedstock are becoming a cornerstone for energy transition as well as decarbonization. So far; however, it seems that a vital cornerstone of hydrogen economy has not been considered as it should, that's cost-efficient, large scale hydrogen transportation from production site(s) to storage facilities or point of end use(s). This is a tricky scenario since hydrogen production plants are often built in cheap remote regions in which renewable sources are abundantly available. However, the demand on hydrogen is highly likely to be a maximal in heavily industrialized regions and perhaps those heavily populated, both of which are likely to be far away from those regions rich with hydrogen. Unless such issues are appropriately addressed, cost-efficient large scale hydrogen may still remain elusive. In fact, high costs of hydrogen transportation further increase its overall costs, putting such a growing sector's commercial viability in a jeopardy. The challenge lies in delivering dependable, large-scale hydrogen transportation while controlling expenses and guaranteeing the clean hydrogen's economic viability [1]. To those purposes, hydrogen transportation has been chosen to be the topic of this review paper. This paper delves, albeit not thoroughly, into different aspects, challenges and advancements of hydrogen transportation technologies including gaseous hydrogen transportation, liquid hydrogen transportation and hydrogen carriers transportation.

2. Technologies of Hydrogen Transportation:

Unless the produced hydrogen is transported, it cannot be available for storage nor for the point of end use(s), e.g., a power generation, refueling station(s) or an industrial facility, etc. Hence, hydrogen transportation is as vital as hydrogen production for hydrogen economy which necessitates that hydrogen is moved from the production site to the point of end use(s) [2]. Among the methods of hydrogen transportation are: gaseous hydrogen transportation, liquid hydrogen transportation and hydrogen carriers transportation. In gaseous hydrogen transportation, be-spoke high-pressure tube trailers or gas cylinders are used to transport gaseous hydrogen that's compressed to a high pressure. In liquid hydrogen transportation, hydrogen is first cooled to cryogenic temperatures to be liquefied at second. In terms of the quantity of hydrogen transported in a given volume, transporting hydrogen in the liquid state ensures more hydrogen is transported than that transported in the gaseous form. Accordingly, transportation of liquid hydrogen is desirable for long distances applications. Furthermore, hydrogen can also be transported using some hydrogen carriers, such as ammonia, metal hydrides or organic liquids, etc., that can absorb (store) and desorb (release) hydrogen on demand at conditions close to ambient temperature and pressure. Compared to gaseous and

liquid hydrogen transportation, hydrogen carriers transportation offers increased simplicity in hydrogen transportation [3-4].

2.1. Gaseous Hydrogen Transportation:

In gaseous hydrogen transportation, be-spoke high-pressure tube trailers/gas cylinders or pipelines are used to transport gaseous hydrogen that's compressed to a high pressure provided that safety measures and related regulations are met [3]. Transportation of hydrogen in the gaseous form is a well-established technology due to its relatively low cost and available infrastructure [4]. In order to reduce the volume of hydrogen transported, via high pressure tube trailers, to promote transportation feasibility, produced hydrogen is compressed to high pressures [5]. To ensure safety and also to reduce the hazard of leakage, this compressed gaseous hydrogen should be stored in pressure storage vessels/cylinders at a hydrogen production site prior to its transportation. Finally, in order to transport gaseous hydrogen, these storage vessels/cylinders are transferred to special high pressure tube trailers that can safely transport hydrogen at high pressures [6]. These trailers are facilitated with several tubes/cylinders, fixed to the chassis of the trailer, to transport compressed gaseous hydrogen to its final destination of storage or for the point of end use(s) either via road, rail or ship in reference to requirements and infrastructure. In order to extract the transported compressed gaseous hydrogen to a storage facility or to the point of end use(s), tube trailers are attached to the hydrogen system of the final destination for power generation, refueling station or an industrial facility, etc. [4].

Likewise, use of pipelines to transport gaseous hydrogen requires mechanical compression of hydrogen to the operating pressure of pipelines ahead of hydrogen injection into the pipeline which is usually covers a long distance. Compression pressures are dictated by the design of the pipeline as well as the destined transportation distance [7]. In a report by Albers and co-workers, it was shown that it might be required to re-compress hydrogen at specific distances through the pipeline in order for hydrogen to be transported to its final destination [1]. Once compressed, hydrogen is ready for injection into the pipeline. Proper monitoring and control are essential in order to ensure safe operation and to preserve sufficient high pressures and flow rates required for gaseous hydrogen transportation. Safe operation requires employment of leak detection system(s) and emergency shutdown system(s) within the transportation pipeline system. Upon arrival to the destination, gaseous hydrogen is withdrawn from the pipeline, although it may require extra compression or pressure regulation to compensate pressure drop usually encounters at the end of a lengthy pipeline [4]. Furthermore, selection of pipeline material is of crucial importance to avoid hydrogen embrittlement [8-10]. Hydrogen embrittlement is a phenomenon that's associated with the use of steel pipeline; in particular, for hydrogen transportation.

Due to its significance, hydrogen embrittlement has been a target of several research work investigations [8-9,11-19]. In fact, hydrogen embrittlement has been with a severe consequences on the infrastructure of hydrogen transportation systems. It has been reported that hydrogen embrittlement is caused by the tendency of hydrogen molecules to react with the steel. The phenomenon of hydrogen embrittlement is a multifaceted occurrence where hydrogen interacts with the metal/metal additives to produce solid solutions, metal hydrides, molecular hydrogen; in addition to, gaseous products, e.g., methane. This interaction can weaken the bonding strength of metal grain boundaries as a result of a reduced plasticity, leading to a brittle

fracture, microscopic cracking or pitting [9]. According to a study by Melaina and others, the occurrence of hydrogen embrittlement largely depends on pressure, purity and moisture content of the stored hydrogen as well as strength level and deformation rate of the pipeline. Surrounding temperature also plays a role in hydrogen embrittlement. Generally, as the pressure is increased, the risk of hydrogen embrittlement would accordingly increase [20]. However, it was reported that such a relationship is assessed on a case-by-case basis in a way that there is no consensus among specialists on all hydrogen embrittlement mechanisms and their interactions [9,14]. Despite this; nevertheless, with the aid of molecular simulations and some cutting-edge technologies, e.g., transmission electron microscopy and atom probe technology, a gradual clarification of the mechanism of hydrogen embrittlement has been made [9].

It is the aim of using certain materials, exploring newer materials, surface alterations, coatings and use of some advanced purification technologies to help mitigate hydrogen embrittlement in order to enhance the overall performance characteristics and durability of hydrogen transportation pipelines. In part, this can be achieved by using materials that highly resist hydrogen embrittlement such as austenitic stainless steel, nickel-based alloys and specific aluminum alloys [21]. Exploring newer materials with a certain microstructure of a unique resistance to hydrogen embrittlement such as high-entropy alloys can also mitigate the severity of the effect of hydrogen embrittlement [22]. Furthermore, use of certain polymeric or composite materials can eradicate the hazard of hydrogen embrittlement [23]. Surface alterations to modify surface properties of the material(s) of pipeline for gaseous hydrogen transportation by means of carbonizing, shot peening and nitriding can help enhance the resistance of pipeline material(s) to hydrogen embrittlement [24]. In addition, use of protective coatings, that act as a barrier that prevents hydrogen diffusion towards the pipeline material(s), e.g., ceramic or metallic materials, reduces the potential of hydrogen embrittlement [25]. Also, it has been reported that presence of certain impurities such as oxygen, water or sulphur in hydrogen may further intensify the occurrence of hydrogen embrittlement. Use of some advanced purification technologies such as membrane separation, pressure swing adsorption or cryogenic distillation can help reduce the presence of such impurities; thus, reducing the hazard of hydrogen embrittlement [26].

Also, as it can be understood, in either mode of gaseous hydrogen transportation (high pressure tube trailers or pipelines), compression of hydrogen gas is an inevitable process. Compression is performed via the use of either mechanical or non-mechanical compressors. Mechanical compressors include: reciprocating piston compressors, diaphragm compressors and centrifugal compressors [5]. On the other hand, non-mechanical compressors, which do not have any moving parts, consist of ionic liquid piston compressors and electrochemical compressors [27]. Reciprocating piston compressors exploit the principle of positive displacement to compress the gas (hydrogen). Hydrogen compression is performed via a piston that continuously moves within the cylinder of the compressor. Whereas centrifugal compressors work to transfer the kinetic energy of a rotating impeller to hydrogen gas which then becomes pressure energy. In diaphragm compressors, risk of contamination as well as leakage is lower as a flexible diaphragm is able to separate the gas (hydrogen) from the hydraulic fluid, although such compressors are usually used for smaller-scale applications due to lower flow rates of the compressed gas obtained [4].

In ionic liquid piston compressors, an ionic liquid is a replacement of the piston in the mechanical reciprocating piston compressor. The ionic liquid which is contactless with the gas

to be compressed (hydrogen) is able to move through an electric or magnetic field to eventually nearly isothermally compresses hydrogen. Away from ionic liquids, electrochemical compressors utilize the principle of electrolysis via proton exchange membrane. Hydrogen gas is compressed once passed through an electrochemical cell for hydrogen electrolysis at different pressures [27]. Further discussion of such compressors can be found in a study carried out by Orlova, et al. for which interested readers are directed to. The study has compared the performance data of mechanical and non-mechanical compressors considering some key factors such as efficiency, deliverable flow rates, pressure capability, cost and the due required maintenance [28]. In another investigation, an overview of the key characteristics of such compressors is given highlighting their advantages and disadvantages [4].

Gaseous hydrogen transportation has been proven efficient. This; in particular, applies to gaseous hydrogen transportation via pipelines. Furthermore, use of pipelines to transport gaseous hydrogen is a well-established and verified technology with an infrastructure already in place, although in certain areas [29]. Most importantly, with gaseous hydrogen transportation in which no additives are used, the purity of hydrogen is maintained. This renders the transported gaseous hydrogen a great candidate for fuel cells applications for which hydrogen of high purity is certainly required [30] to ensure optimum power generation. However, gaseous hydrogen transportation via pipelines; in particular, can be capital-intensive to cover costs of construction and maintenance of the underlying infrastructure [1,29]. Constructing newer pipeline routes or expanding existing ones requires lead times exceeding ten years and is subject to multipart permitting and authorization procedures [1]. Also, at an additional cost, the infrastructure for gaseous hydrogen transportation is susceptible to development and extension with respect to wider adoption of such a technology [4] by those customers located out of pipelines route, for instance. Furthermore, in order for hydrogen pipeline transportation to attain reasonable utilization rates, large amounts of hydrogen are inevitably required [1]. Additionally, energy requirements for hydrogen compression, which is required for hydrogen transportation, are high. Consequently, this could reduce the overall efficiency obtained out of hydrogen as an energy carrier [3]. Furthermore, since gaseous hydrogen in comparison to liquid hydrogen is highly flammable with a low ignition energy, transportation, handling and storage safety issues may arise [31].

2.2. Liquid Hydrogen Transportation:

Although liquid hydrogen transportation and hydrogen liquid storage might be self-expressive and straightforward terms, it might be useful to recap their definitions here to avoid any confusion as they are conceptually highly related to each other [32] and they may be comparable in terms of handling requirements as well as bespoke equipment required [4]. The former refers to the movement of liquid hydrogen provided that sever cooling to extremely low (cryogenic) temperatures is continuously available [3]. The latter; nevertheless, is the action of storing hydrogen in its liquid state in special tanks tailored to preserve certain conditions of pressure and temperature [33]. Recently, the most widely used hydrogen storage methods have been reviewed elsewhere [34]. They both require cryogenic temperatures to preserve hydrogen in the liquid state. Also, for hydrogen transportation and hydrogen storage, use of special insulated tanks is necessary, to keep hydrogen in its liquid form via reducing heat transfer in order to maintain cryogenic temperatures. Furthermore, in both processes in which hydrogen is kept liquid, it is important to firmly adhere to safety regulations and guidelines to avoid

potential accidents that may arise due to the cryogenic nature and possible reactivity of either transported or stored liquid hydrogen. Based on this, it can be concluded that any technological development(s) in one process can be applicable to the other. For instance, current cooling systems, to attain low temperatures, have been efficiently used in hydrogen transportation as well as in hydrogen storage applications. This is also the case with cryogenic refrigeration cycles [35]. Likewise, effective techniques and material(s) of insulation to keep low temperatures of liquid hydrogen in a storage tank can also be effective when used in transportation tankers [36]. This is also applicable to double-walled tanks, multilayer insulation, vacuum-insulated tanks, vacuum insulation panels, cryogenic insulation foams and aerogels [35]. Furthermore, use of composite materials such as carbon-fibre reinforced polymers for both insulation and structural applications in hydrogen transportation and hydrogen storage has been highly effective [37], owing to the low thermal conductivity, high strength and great compatibility with liquid hydrogen of such polymers [38]. Besides, materials suggested as resistant to hydrogen embrittlement have been beneficial for both hydrogen transportation and hydrogen storage systems [39].

Having said that; nevertheless, each application; however, focuses on a different aspect within the hydrogen supply chain as each of them serves a particular objective. Also, there is a unique infrastructure and duration of time for each application. Liquid hydrogen transportation aims to moving hydrogen from the production site(s) to end-user(s) or storage facilities [33], whereas liquid hydrogen storage is concerned with preserving hydrogen for a subsequent use or distribution [3]. Another discrepancy among them is that although both processes require similar special equipment, these equipment; however, are arranged with respect to a different infrastructure in each process [40]. For instance, in transportation of liquid hydrogen, mobile containers (cryogenic tanker trucks, rail or ships) are used to move liquid hydrogen as required between locations. Nevertheless, in the storage of liquid hydrogen, stationary insulated tanks, positioned at production sites, refueling stations or distribution hubs are used to obviously store hydrogen merely. Also, timescales of hydrogen transportation and hydrogen storage also differ. Depending on the distance between production site(s) and final destination, transportation of liquid hydrogen usually requires shorter times than that required for storing liquid hydrogen for extended periods of time [41].

Similar to gaseous hydrogen transportation in which special equipment are used to transport only gaseous hydrogen, in liquid hydrogen transportation, as the name implies, hydrogen can only be transported as a liquid hydrogen only and only by using a special equipment. This requires that gaseous hydrogen is converted into liquid hydrogen prior to its transportation, in nowhere but at the hydrogen production site where it is stored in special tanks. In order to turn gaseous hydrogen into a liquid, it should be subjected to a liquefaction process where it is compressed and that its energy density is boosted for the benefit of its transportation as well as its storage [3-4,42]. In fact, it is the much high volumetric density of liquid hydrogen, compared to that of gaseous hydrogen, is what actually benefits the transportation and storage of the former than those of the latter [4]. In liquefaction, hydrogen also undergoes cryogenic cooling, where temperature may reach to around (20 K) [2-3].

The tanks used for this application are of insulated cryogenic-tank. Obviously, insulation is meant to keep heat transfer from these tanks to the environment as minimal as possible in order to preserve cryogenic temperatures attained [43] following costly energy-intensive liquefaction process [4]. Mainly, liquefied hydrogen can be transported, to where it is meant to be stored or

used, in special cryogenic tankers [44], by road [45], ship or rail subject to certain requirements as well as available infrastructure [4]. These cryogenic tankers can be loaded with liquid hydrogen being stored in cryogenic insulated tanks ready for transportation. In order to maintain the environment of low cryogenic temperatures as well as low pressures of the transported liquid hydrogen, cryogenic tankers are fitted with insulated tanks and pressure-relief valves, respectively [45]. In order to extract the transported liquid hydrogen to a storage facility, cryogenic tankers are attached to the hydrogen system of the final destination [4]. However, for most applications of end use(s), it is required to firstly vaporize and warm this extracted liquid hydrogen to the ambient temperature. Full adherence to relevant regulations and standards; in addition, to proper monitoring and control are essential in order to ensure safe operation and to preserve proper temperature and pressure required for liquid hydrogen transportation. Safe operation requires employment of leak detection system(s) [46] as the case with gaseous hydrogen transportation via pipelines.

Nevertheless, the current technology of liquefaction of gaseous hydrogen; in addition to, the technology of transportation of liquid hydrogen are not optimal. A great deal of effort has been made in order to reduce the cost of energy consumed by a liquefaction process, promote transportation efficiency and to augment the safety of transportation process [3,47]. As it has been shown earlier, in order to liquefy gaseous hydrogen for its transportation, it must; first, be fed to a liquefaction process in which several stages of cooling and compressions are required. This consumes significant amounts of costly energy [4,42], impacting the overall efficiency of liquid hydrogen as an energy carrier [3]. Energy consumption of a typical liquefaction process of hydrogen gas into a liquid state can be reduced by utilizing magnetic refrigeration, thermoacoustic refrigeration or two-stage mixed refrigerant cycles. The first refrigeration relies on the magnetocaloric effect by which the temperature of the material is changed under the influence of variable magnetic fields [48]. The second refrigeration relies on sound waves that generate cooling effects, in the working gas (hydrogen), with the help of pressure oscillations [49]. The third refrigeration relies on the dual effect of two different refrigerants to attain more cooling; thus, increased efficiency of liquefaction of gaseous hydrogen [50]. One further approach to boost process efficiency and to reduce energy consumption of a liquefaction process of hydrogen gas; thus, reduced cost, is to recover and exploit wasted energy developed by the liquefaction process [51].

Furthermore, the technology of transportation of liquid hydrogen by no means can be considered optimal since it requires bespoke cryogenic equipment along with certain expensive while challenging handling procedures [52]. Hence, a great deal of effort has been made in order to promote transportation efficiency and to augment the safety of transportation process. In order to promote transportation efficiency, newer cryogenic tanker insulation has targeted towards finding newer insulation materials, e.g., carbon fibre-reinforced polymers [37], that can further minimize heat transfer from the cryogenic tankers to the environment so as to maintain cryogenic low temperatures essentially required for hydrogen transportation in its liquid state, as mentioned previously. Likewise, use of multilayer-insulations made of thin reflective materials, e.g., metalized films, being away from each other by materials of low thermal conductivity, can also help promote insulation capability [35,53]. Vacuum insulation panels, which are composite insulation materials built from a core material, e.g., silica aerogel/fumed silica, with a vacuum-sealed gas-impermeable barrier, are also useful in this regard [35,54]. In addition, use of lightweight materials such as carbon fibre-reinforced polymers for structural

purposes of cryogenic tankers has also been proposed as a means of reducing the weight and cost of transportation system [37,55]. Use of such polymers for insulation applications in hydrogen transportation offers high strength, low thermal conductivity as well as a great compatibility with liquid hydrogen [38]. Advanced insulated cryogenic storage tanks, instead of cryogenic tankers, fitted on a ship have been proposed for large scale long-distance transportation of liquid hydrogen; in particular [35,44]. Besides, the safety of transportation of liquid hydrogen process can be further augmented through adopting newer pressure relief systems that are more efficiently capable to handle high pressures usually encountered within cryogenic tankers [31]. In addition, it is also of a crucial importance to have heat leakage during transportation of liquid hydrogen as minimal as possible. Otherwise, as heat leaks, liquid hydrogen evaporates, resulting in losses in the form of boil-off gas [35]. Consequently, this may render liquid hydrogen transportation less-cost effective and energy-efficient [4].

2.3 Hydrogen Carriers Transportation:

In addition to transporting hydrogen in its gaseous state or in its liquid state as discussed in the previous two sections; respectively, gaseous hydrogen can be transported using hydrogen carriers. Hydrogen carriers are certain chemical materials/compounds that are capable to store and release hydrogen as demanded [3]. Among the used hydrogen carriers for the purpose of hydrogen transportation are ammonia, liquid organic hydrogen carriers as well as metal hydrides. Of these, metal hydrides have seen wider applications as hydrogen carriers. In this paper; therefore, they are further scrutinized than other hydrogen carriers. Ammonia can be used as a hydrogen carrier via combining hydrogen with nitrogen via Haber-Bosch process using an iron catalyst at a high pressure [56]. Use of liquid organics as hydrogen carriers requires chemically combining hydrogen (hydrogenation) with an appropriate liquid organic carrier compound, e.g., dibenzyltoluene [57-58] or N-ethylcarbazole [57,59] at a high pressure [60]. Dibenzyltoluene represents a liquid organic compound that has been widely used as a hydrogen carrier due to its ease of hydrogenation-dehydrogenation as well as its high gravimetric and volumetric hydrogen storage capacity. Another effective version of dibenzyltoluene is perhydro-dibenzyltoluene, which represents a fully hydrogenated form of dibenzyltoluene, is characterized with a very high hydrogen storage capacity and quite improved thermodynamic properties [4]. Also, it is efficiently capable to release hydrogen if a controlled dehydrogenation control is in place [61]. Likewise, N-ethylcarbazole, which is a heterocyclic organic compound, due to its enhanced hydrogen storage capacities with favorable thermodynamic properties, is also capable to store hydrogen [59] via a reversible hydrogenation-dehydrogenation process. It is also characterized with efficient hydrogen uptake and release [4].

Metal hydrides as hydrogen carriers have been extensively studied [3-4,7,34,62-83]. The synthesis of metal hydrides involves reactions in the gaseous phase, in solution or in solids formed from other hydrides. A number of metal hydrides have been developed via a hydrogenation reaction, in which hydrogen is directly reacted with an elemental metal, intermetallic compounds or as alloy. In a hydrogenation reaction, the temperature typically approaches 827°C at which the adsorption rate of hydrogen is small although fast. The temperature at which the kinetics and capacity of hydrogenation reaction are balanced for the formation of the hydride, it is necessary to cool reaction contents in a hydrogen-rich environment. However, owing to its exothermic nature, a hydrogenation reaction can still

advance despite heat loss due to cooling. If required, it is admissible to use a spark to 'ignite' (overcome the activation barrier) the hydrogenation reaction. With regards to the effect of pressure on a hydrogenation reaction, is that the synthesis of some metal hydrides requires high pressure, while other hydrides do not require a high pressure to form depending on the metal or intermetallic compounds used. In addition, use of high pressures in a hydrogenation reaction is necessary for the stabilization of new phases of metal hydrides with high coordination numbers or high metallic oxidation states. With regards to the effect of temperature on a hydrogenation reaction, lower temperatures negatively affect its kinetics, although low temperatures are with a positive effect on hydrogen storage [65]. Young, K., has found that metal systems with larger unit cell volumes tend to create more stable hydrides. Whereas metal systems with high levels of disorder can exhibit a variety of local cell volumes, i.e., a better storage capacity and adsorption/desorption kinetics [66].

Metal hydride hydrogen storage is relatively new compared to storing hydrogen via other used storage methods, details of which are available elsewhere [34]. Storage of hydrogen by metal hydride(s) for hydrogen carriers is a method to store hydrogen within a solid form. This method is the safest among other methods and with which the highest volumetric hydrogen storage density can be attained [62,65]. Because of their unique capability to absorb and desorb hydrogen, metal hydrides can be utilized to store or release hydrogen (hydrogen carriers) on demand. This capability largely depends on the hydriding conditions. Metal hydrides can be generated if hydrogen molecules and metals, alloys or some intermetallic compounds are combined via chemical bonding. Intermetallic compounds, such as LaNi_5 and Ti-based body-centered cubic alloys such as FeTi alloy, suffer from very low gravimetric hydrogen storage density of 1.28 wt.% and 1.9 wt.%; respectively, due to which their application for hydrogen storage has been limited. Therefore, selected metal and metal alloys materials have been limited to those light metals with a reasonable hydrogen storage density such as Al, B, Be, Li, Mg, Na and Pd [62,67-68], Mg_2Ni , MgN_2 , NaAl, Ti and Ti_2Ni . Other combinations such as are also in use: $\text{LaNi}_{4.7}\text{Sn}_{0.3}$ [70], $\text{MmNi}_{4.6}\text{Fe}_{0.4}$, $\text{MmNi}_{4.6}\text{Al}_{0.4}$ [69], $\text{Nd}(\text{Ni}_{1-x}\text{Cu}_x)(\text{In}_{1-y}\text{Al}_y)$ [70], $\text{LaNi}_{4.96}\text{Al}_{0.04}$, $\text{La}_{1.06}\text{Ni}_{4.96}\text{Al}_{0.04}$ and $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Ti}$ [71] and $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{Ni}$ [72], to mention a few.

Historically, use of metals in this application goes back to 1866 when Graham, T. observed the capability of Pd metal to absorb a large quantity of hydrogen. Later, metal hydrides were also involved in this area following realizing reversible hydrogen absorption and desorption on intermetallic compounds [68]. Among these metal hydrides, metal hydrides based on magnesium (MgH_2) and related alloys are the most promising materials for solid-state hydrogen storage along with the high hydrogen absorption potential, relative affordability and good reversibility [73]. However, in order to ensure the cycle stability of MgH_2 formed, magnesium particles are to be well protected from gaseous impurities such as O, N_2 , CO and CO_2 , as otherwise, they are capable to inhibit or slow down hydrogen absorption [74]. Not far from MgH_2 , $\text{Mg}(\text{BH}_4)_2$ (magnesium borohydride) which is synthesized via combining magnesium with borane in a pressurized hydrogen-rich environment (hydrogenation) [79], has also been used as a hydrogen carrier due to its high gravimetric hydrogen density [4]. Storage of hydrogen via metal/alloy hydride is not a suitable choice for mobile hydrogen transportation applications, but it is a suitable choice for stationary power plants where the heavy weight of the storage material is not a major issue. The volumetric storage density of metal/alloy hydride storage is so high, greater than $100 \text{ kg H}_2/\text{m}^3$ [64]; nevertheless, its gravimetric storage density is quite low

(0.015 kg H₂/kg [76], 0.02-0.06 kg H₂/kg [63], 0.03 kg H₂/kg [64] and 0.07 kg H₂/kg [77]). This can be attributed to the heavy internal structure of the metal/alloy used.

In addition to the gravimetric hydrogen storage density of metal hydrides as hydrogen carriers, the following is also of a significant importance: safe operation while fast kinetics, chemical and thermal stability of the generated metal hydride(s) during multiple cycles of charge/discharge [64,75]. Utmost care should be practiced while handling those metal hydrides comprising heavy alkaline metals as they are tremendously reactive. Also, due to the sensitivity of several metal hydrides, high stability against oxygen/air and moisture should also be a feature of metal hydrides; otherwise, they should be stored under inert atmosphere [65]. Low dissociation temperature with moderate pressure, low heat of dissipation during exothermic formation of the hydride, low heat of formation to reduce the energy required for hydrogen release and low cost of the infrastructure of recycling and charging, are all also important factors. In addition, energy loss during hydrogen charge/discharge should be kept minimal to help limit spontaneous hydrogen release [75].

Once hydrogen is stored in the metal hydride material as discussed above, provided that hydrogen storage process is performed in full at the site of hydrogen production, the process of hydrogen transportation can be initiated. The metal hydride within which hydrogen has been stored can be transported to its final destination of storage or for the point of end use(s) either using trucks, trains or ships in reference to requirements and infrastructure. At the final destination, in order to extract the transported hydrogen from the metal hydride material for its underlying application(s), the latter is heated for the release of the stored hydrogen [78]. Hydrogen-extracted metal hydride materials can be transported back to hydrogen production site to be reloaded with hydrogen, enabling a closed-loop transportation cycle [4].

Use of metal hydrides as hydrogen carriers for hydrogen transportation may be advantageous over gaseous and liquid hydrogen transportation [4]. This can be understood by the higher volumetric and gravimetric energy densities most hydrogen carriers have, enabling a more efficient hydrogen transportation compared to that of gaseous and liquid hydrogen transportation [3]. Furthermore, compared to gaseous and liquid transportation, metal hydrides hydrogen carriers are generally described with a lower flammability and explosion risks, enabling a safer transportation [7]. Also, this increased safety of metal hydrides hydrogen carriers can be attributed to reduced pressure requirements and more compact storage possibilities [4]. Most importantly, they can also help overcome some of the challenges that might face both gaseous and liquid hydrogen transportation, as it is possible to transport hydrogen using these hydrogen carriers, to remote or off-grid locations [80]. It is also might not be required to invest for newer infrastructure since trucks, trains or ships can be used to transport the metal hydride within which hydrogen has been stored to its final destination of storage or for the point of end use(s) [7].

Nevertheless, the storage capacity of some metal hydrides as hydrogen carriers is somewhat limited; mainly due to their low gravimetric storage density (0.015 kg H₂/kg [76], 0.02-0.06 kg H₂/kg [63], 0.03 kg H₂/kg [64] and 0.07 kg H₂/kg [77]). This can be attributed to the heavy internal structure of the metal/alloy used. Another issue with metal hydrides as hydrogen carriers is the ultra-heavy weight of the storage materials for use in mobile application (vehicles), although this renders use of metal hydrides for hydrogen transportation a suitable choice for stationary power plants where the heavy weight of the storage material is not a major issue. Furthermore, as explained earlier, release of hydrogen out of such hydrogen carriers

requires energy and may comprise conversion losses. Consequently, the overall efficiency of hydrogen as an energy carrier may be affected [81]. Overall slow kinetics of hydrogen uptake and release from some metal hydride hydrogen carriers also heavily participates in declining the overall efficiency of this process. Temperature sensitivity of some metal hydrides used as hydrogen carriers is also another obstacle [4]. Another complication of metal hydrides hydrogen carriers systems may arise from the necessity of a specialized equipment for hydrogen storage/release, complex chemical processes [82] and synthesis and handling of complex material(s). One further problem with metal hydrides hydrogen carriers is its high energy requirements. Also, exploring newer materials as hydrogen carriers can be capital-intensive [83]. In terms of the environmental and safety issues associated with the process of storage of hydrogen through metal hydride, are the disposal of spent materials of metals/alloys and those of compressor and storage vessel, while used for storing hydrogen at a high pressure [64].

3. Conclusions:

Albeit not thoroughly, this paper has delved into different aspects, challenges and advancements of hydrogen transportation technologies including gaseous hydrogen transportation, liquid hydrogen transportation and hydrogen carriers transportation. Gaseous hydrogen transportation can be carried out either by special storage vessels/cylinders or through pipelines. Use of pipeline; in particular, for gaseous hydrogen transportation has been proven efficient. Pipeline-transported gaseous hydrogen is highly desirable for fuel cells applications of power generation, owing to its tremendously high purity. However, gaseous hydrogen transportation via pipelines; in particular, can be capital-intensive, energy-consuming and less-safe due to its high flammability. Furthermore, liquid hydrogen transportation also requires high energy requirements for cooling and compression steps. In addition, liquid hydrogen transportation requires bespoke cryogenic equipment along with certain expensive while challenging handling procedures. However, measures to reduce energy requirements as well as to address the expensive challenging handling procedures associated with liquid hydrogen transportation, have been proposed within this paper. Use of high energy to release hydrogen coupled with conversion losses is also reported on metal hydrides as hydrogen carriers. Their low gravimetric storage density, due to the heavy internal structure of the metal/alloy used, may limit their application as hydrogen carriers. Also, their heavy weight has rendered them more used for stationary applications in power plants. Beside, temperature sensitivity of some metal hydrides used as hydrogen carriers, complicated slow chemistry along with the need for complicated equipment are also among other obstacles reported on metal hydrides as hydrogen carriers. Nevertheless, use of metal hydrides as hydrogen carriers for hydrogen transportation may be advantageous over gaseous and liquid hydrogen transportation, due to higher volumetric and gravimetric energy densities most hydrogen carriers have, lower flammability and explosion risks, enabling a safer transportation, reduced pressure requirements and more compact storage possibilities. Beside, use of metal hydrides as hydrogen carriers can also help overcome some of the challenges that might face both gaseous and liquid hydrogen transportation, as it is possible to transport hydrogen to remote or off-grid locations. Despite this; nevertheless, it seems that safe, cost-effective, efficient, large-scale hydrogen transportation may still be elusive. This would certainly hinder a wide- spread distribution of such a hydrogen distribution system, a killer's mistake for decarbonization .

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