A0915

Development of a Hydrogen Metal Hydride Storage Produced by Additive Manufacturing

Tim Röver (1) ◙, Sebastian Roth (1) ◙, Tom Hoffmann (1), Lars Baetcke (2), Dirk Herzog (3)

(1) Hamburg University of Technology (TUHH), Institute of Laser and Systems Technologies (iLAS), Harburger Schloßstraße 28, 21079 Hamburg/Germany

(2) Institute for Maritime Energy Systems, German Aerospace Center (DLR), 21502 Geesthacht, Germany

(3) Hamburg University of Technology (TUHH), Institute for Industrialization of Smart Materials, Hamburg University of Technology, 21079 Hamburg/Germany

◙These authors contributed equally to this work.

Tel.: +49 40 428 78 50 10
tim.roever@tuhh.de

Abstract

Hydrogen as an energy carrier is attributed considerable importance in reduction of carbon dioxide emissions worldwide and transformation of the current economy to a low-carbon one. Production, storage, transportation and application of hydrogen are the key steps in the life cycles of hydrogen. It is desirable to increase the efficiency in any of these steps as well as enhance functionality of the systems. Hydrogen metal hydride storages (HMHS) can be used to store hydrogen at relatively low pressures while being relatively compact in size. Apart from using them for immobile systems they were also found to be beneficial in hydrogen-powered submarines or hydrogen-powered fork lifts.

Additive manufacturing (AM) offers great potential for the simple and direct production of complex and functional components made of polymers and metals. Due to the freedom of design, AM offers great innovation potential compared to conventional manufacturing processes. In many cases, component designs that exploit the possibilities of AM show higher technical performance or functionality compared to components manufactured by conventional processes.

This work assesses how the freedom of design due to laser powder bed fusion of metals (PBF-LB/M) as an additive manufacturing technique can be utilized for HMHS with better functionality than conventionally manufactured ones. The development of the component design was done using a morphological box. The final design incorporates secondary heat transfer surfaces that are inspired by heat transfer topology optimization. It is made in compact rectangular prism form that is in contrast to conventionally manufactured HMHS which commonly are cylindrical in shape. The design shows great potential for fast loading and customized outer dimensions of the tank to allow for more flexibility in the overall system design.

Introduction

Hydrogen is increasingly being recognized as an important energy carrier in the transition to a low-carbon economy. It has the potential to play a key role in reducing greenhouse gas emissions and mitigating climate change. However, the efficient production, storage, transportation, and application of hydrogen are essential steps for the successful integration of hydrogen into the energy industry. One of the key challenges in the use of hydrogen is its storage, particularly in a compact, safe, and cost-effective manner.

One promising approach to hydrogen storage is through the use of hydrogen metal hydride storages (HMHS). These systems offer several advantages over other storage technologies, such as high volumetric energy density, relatively low operating pressures, and the ability to store hydrogen safely without the need for complex compression or liquefaction systems. Additionally, HMHS can be used in a wide range of applications, from stationary power generation to portable power sources for vehicles and electronics. However, the use of HMHS tanks presents some challenges, including the need for effective heat exchange properties. During the absorption and desorption of hydrogen, heat is generated or absorbed, which can cause temperature fluctuations and affect the performance and safety of the system [1].

Effective heat exchange is essential to maintain the temperature within an acceptable range during the absorption and desorption of hydrogen, prevent thermal stress, and ensure a safe and efficient operation of the HMHS tanks. This allows faster reaction times because temperatures above or below the operating limits can have self-regulating effects on the loading time of a metal hydride tank [2]. However, achieving effective heat exchange in HMHS tanks is challenging due to the combination of need for high thermal conductivity and the requirements for durability and resistance to corrosion. In this context, research is ongoing to explore different approaches for improving the heat exchange properties of HMHS tanks, such as the use of novel materials, coatings, and designs.

This paper aims to contribute to this ongoing research by exploring the potential of additive manufacturing in design and production of HMHS tanks with enhanced heat exchange properties [3] [4]. Additive manufacturing (AM) is a rapidly growing manufacturing technology that offers great potential for the direct production of complex and functional components made of polymers and metals. Due to the freedom of design offered by AM, there is a great potential for innovation compared to conventional manufacturing processes. In many cases, component designs that exploit the possibilities of AM show higher technical performance or functionality compared to components manufactured by conventional processes.

In this paper, we explore the development of a HMHS system using AM. Specifically, we focus on the use of laser powder bed fusion of metals (PBF-LB/M) as an additive manufacturing technique for the direct production of HMHS components with better functionality than conventionally manufactured ones. We use a morphological box to develop the component design and incorporate secondary heat transfer surfaces inspired by heat transfer topology optimization.

1. Scientific Background

There are two types of hydrogen storages: direct and material-based storages. In direct storage, hydrogen is stored as a pure substance, while in material-based storage, it is chemically or physically bound to a carrier material. The goal of both methods is to store hydrogen as efficiently as possible. One way to increase the low density of hydrogen is to increase the pressure or change the state of matter. High volumetric energy density is achieved through either liquid storage or transcritical storage, which requires complex tank technology. In contrast, material-based storage attempts to increase the energy density by binding hydrogen to a material, such as metal hydrides or liquid organic carrier materials. This type of storage requires the connection to the carrier material to be easily established and reversible, as well as a stable repeatability of the process [5].
In a metal hydride hydrogen storage system, hydrogen is not stored as a pure substance, but in metal hydride as storage medium. This has the advantage that hydrogen can be stored close to room temperature and atmospheric pressure, so it does not need to be cooled or kept under high pressure. Since hydrogen is bound in the metal hydride, the risk of leakage is strongly reduced in case of a tank damage. The lower pressure and the fact that the gas cannot escape from the metal hydride without energy input makes this storage option safer than a pressure tank [1]. The absorption of hydrogen in the metal hydride is exothermic, while the desorption is an endothermic reaction. Therefore, energy is released during hydrogen absorption, and energy is required for desorption. The absorption of hydrogen into the metal hydride can be divided into four individual reactions, cf. Figure 1. First, the hydrogen molecule contacts the metal lattice and splits into two hydrogen atoms. In the second step, these atoms diffuse along the grain boundaries into the metal and react with the metal at a free interstitial lattice site, forming metal hydride and releasing heat. As the hydrogen atoms are absorbed into the metal lattice, the metal hydride expands to a maximum of 40% [6].

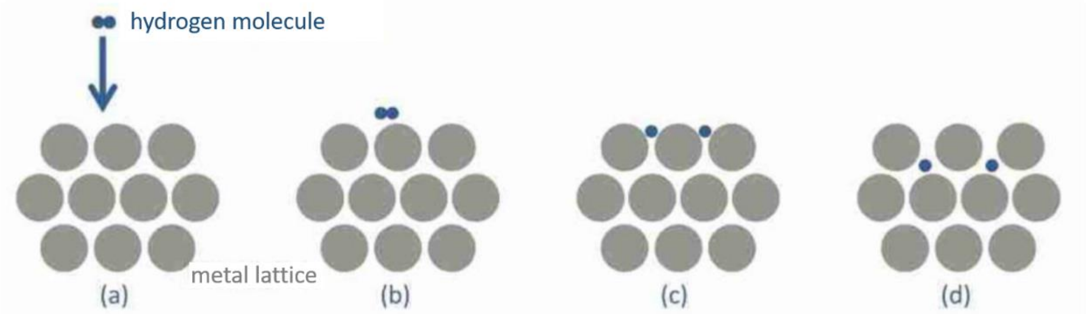

Figure 1: Schematic diagram of the absorption of hydrogen in metal hydride [1]

For the development of a metal hydride tank, it is of great importance to determine the appropriate pressure and corresponding temperature for absorbing the desired amount of hydrogen. To find the optimal operating point, the processes in the metal lattice must be examined more closely: During absorption, hydrogen initially forms the α-phase of the metal hydride with the metal. To store more hydrogen in the metal, the partial pressure is increased proportionally. Once the α-phase is saturated, the β-phase forms at constant pressure and increased hydrogen concentration. This pressure is known as the plateau pressure, cf. Figure 2. To store further hydrogen atoms after conversion into the β-phase of the metal hydride, the pressure must be further increased. Therefore, an operating point is chosen that is just above the plateau pressure, as this achieves the highest efficiency of stored hydrogen in the metal hydride. In addition, the concentration of hydrogen can also be controlled by changing the temperature.

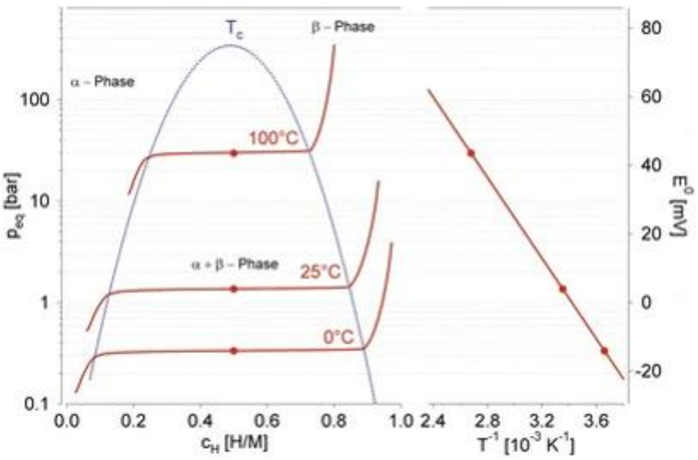

Figure 2: Pressure composition isotherms for the hydrogen absorption in a typical intermetallic compound is shown on the left-hand side*: comprising the solid solution (α-phase), the hydride phase (β-phase) and the region where the two phases coexist. The construction of the Van't Hoff plot is shown on the* right-hand side*. [3]*

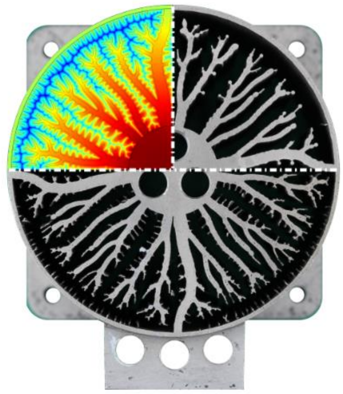

Figure 3: Topology optimized heat exchanger; simulated and additively manufactured metal part. [10]

In general, during the design of a tank, absorption is considered the critical load case since refueling should take as few time as possible [7]. Since absorption is an exothermic process, the temperature in the tank increases. From the pressure concentration temperature diagram (PCT diagram), it can be seen that a higher temperature leads to a higher pressure required to store the same amount of hydrogen. Therefore, cooling a metal hydride tank plays a central role. During desorption, in order to use hydrogen from the tank, energy in the form of heat must first be transferred into the tank. The tanks are usually made out of stainless steel with an internal cooling structure and secondary heat exchanger structures. Each of these components is manufactured separately and then assembled. It is conceivable that integral construction could result in synergistic effects that would increase the overall performance of the tank.

Additive Manufacturing (AM) offers the potential to not only manufacture integral parts but also to optimize each individual structure with regard to its main function. AM is a revolutionary manufacturing process that has gained significant attention in recent years. Unlike traditional subtractive manufacturing methods, AM builds three-dimensional objects layer-by-layer, allowing for unprecedented design freedom and versatility. With its ability to create complex geometries and functional structures, AM has found applications in various industries, including aerospace, automotive, medical, and consumer products, among others.
Through the geometrical freedom offered by AM, it is possible to manufacture function-optimized, compact heat exchangers that can be easily adapted to geometrical boundaries [8] [9]. Lange et al. [10] developed such a heat exchanger that was optimized through a topology optimization process. Topology optimization of heat exchanging structures can be done by defining a design space, material parameters and thermal boundary conditions. Then in an iterative approach an optimization algorithm maximizes the thermal conductivity of the design such that the temperature of the heat dissipating component is minimized. The group has been able to achieve a weight related thermal resistance that outperforms the conventional design by a factor of five. For this study, the design shown in Figure 3 was used to enhance the heat transfer of the designed hydrogen metal hydride tank.

2. Component Design

To generate a design for a hydrogen metal hydride tank, the guidelines outlined in the VDI 2221 [11] were followed. First, a list of requirements for the functions of the hydrogen metal hydride tank was created. From these functions, modules, that fulfill the various requirements, were derived in the second step and summarized in a morphological box for clarity. By combining these modules, partial solutions were developed. A utility analysis was then performed to evaluate the various partial solutions. The design selected through this methodology was finally subjected to finite element analysis (FEA) to verify its ability to withstand the existing mechanical loads.

2.1 Requirement list and modularization

The tank design presented in this paper is intended to be used in a forklift. Some of the requirements presented below are, therefore, fitted to this use case. The first requirement is the need to fully utilize the available space, which cannot be achieved using the conventional cylindrical tank design. To address this, a concept of an angular tank is proposed as it has been observed that round or cylindrical tanks often leave unused space in the overall system.

In addition to the proposed angular design, there are mainly two other geometric requirements: The minimum wall thickness and the maximum feasible overhang when using PBF-LB/M.

The material of the tank must be impermeable to hydrogen and must be resistant to hydrogen embrittlement. A further requirement is that the tank should be compact and lightweight to achieve a high capacity of hydrogen of the tank. This necessitates a thin wall thickness, which should be accompanied by high strength at low density. Finally, the last requirement is that the metal hydride must be filled into the tank under a protective gas atmosphere.

The tank is intended to be used at room temperature, which implies that the chosen metal hydride offers efficient adsorption and desorption properties at room temperature and atmospheric pressure. Furthermore, due to the goal of this work to optimize the heat transfer, a requirement is that the metal hydride should have a high thermal conductivity.

In summary, the successful integration of a metal hydride tank in a forklift requires careful consideration of several design requirements. The proposed angular tank design addresses the need to fully utilize the available space, while the other design considerations ensure optimal performance and safety of the tank.

The Morphological Chart (MC) consists of 5 main functions, for which solutions are developed, refer to Figure 4. The focus was set on functions that can be influenced by AM. The remaining requirements will be considered in the later design process, detached from the Morphological Chart.

The first function examines the possible integration of a cooling jacket that encompasses the outer contour of the tank.

The second module varies the arrangement of cooling channels in the tank, which is an important factor in the cooling performance of the system. The choice of the channel structure depends on various factors, including manufacturing constraints and desired heat dissipation. The leaf structure is a commonly used method where larger channels are divided into smaller channels to be then recombined into large channels again. This structure enables uniform cooling of the entire tank.

Morphological Chart

Hydrogen storage of a metal hydrid tank manufactured by laser powder bed fusion

Functions ↓		Elements							
		1	2	3	4	5	6	7	8
1	cooling jacket	existent	non existent						
2	cooling channels	leaf structure	axial	radial	zigzag	spiral	grid	from jacket to core	no cooling channels
3	heat exchanger	metal foam	adding substance to the metal hydrid	fins	tree-like structure	honeycomb	grid	no heat exchanger	
4	reinforcement	reinforcements outside	braces inside the tank	in the cooling jacket	no reinforcement				
5	splitting the tank	one big tank	single housing, several tanks inside	several small tanks					

Figure 4: Morphological Chart with the different functions and the elements that are used for design creation

Axial channels run longitudinally in the tank and are arranged axially in circular tanks and parallel to the longer side surfaces in rectangular tanks. Radial channels, on the other hand, run perpendicular to the longitudinal direction, which leads to a shorter residence time of the cooling water in the tank and thus contributes to more effective heat dissipation. The zigzag arrangement increases the distance that the water travels in the tank, which also can lead to better heat dissipation. The spiral is another way to improve heat dissipation, where channels wind in one or more spirals in the tank, similar to a double helix.

The mesh structure consists of many small channels that are interconnected and penetrate the entire tank. Although the channel thickness is reduced, this structure enables uniform distribution of cooling water in the tank. With the "From Jacket to Core" arrangement, a cooling jacket is connected to the channels leading into the tank. This method is particularly effective for large tanks. Finally, there is the possibility of completely eliminating cooling channels and instead using other cooling methods, such as external cooling.

The heat exchanger was identified as the third module and is used to transfer heat out of the metal hydride. This is an essential function due to the low thermal conductivity of metal hydrides, making heat dissipation challenging. Several solutions have been developed to control the heat transfer in the metal hydride tank as this is one of the key parameters [3]. One possible solution is to insert metal foams into the tank, typically made of aluminum, nickel, or copper, which significantly increases the thermal conductivity. Metal foams have a large surface area, providing direct contact with the metal hydride [3]. Another approach involves adding another substance with significantly higher thermal conductivity, such as copper or graphite, to the metal hydride. This mixture is either directly filled into the tank or compressed into pellets [12] [13]. Thin metal sheets called fins or ribs can also be inserted into the tank to provide a large surface area for contact with the metal hydride. A material that can conduct heat well is used to create the fins. A tree-like structure is another possible solution that penetrates deeply into the metal hydride. The structure begins with a large trunk and becomes increasingly delicate, with smaller branches attached. This approach ensures that more material is present in the heat exchanger where it is needed to transfer heat [10]. Another solution is to use a honeycomb geometry inspired by the biomimetic forms of a bee's honeycomb. This structure is widely used, for example, in sandwich structures, providing a larger surface area in comparison to a circle [10]. By dividing the metal hydride into small individual cells, the heat that needs to be dissipated can be precisely determined, and the required amount of material and cell size can be calculated. This structure is called

a grid, and it can also be designed to absorb the compressive forces [10]. Finally, it is also possible to not use a heat exchanger at all.
The fourth module varies the reinforcements of the tank, which are needed to withstand the mechanical loads that are present. One possible solution is to reinforce the outer wall of the tank through additional struts or material accumulations. Additionally, reinforcement can also be achieved through struts inside the tank, which can better compensate for pressure loads. It is also possible to insert additional reinforcements between the inner and outer walls of a cooling jacket. This would allow for a thinner inner wall, which would in turn result in an increase in heat transfer to the coolant. Omitting additional reinforcements is also conceivable, which is why this case was also included in the morphological chart.
The last module considers the division of a large tank into smaller individual tanks. This results in a larger surface area of the metal hydride in contact, which in turn has a positive effect on heat transfer. Additionally, dividing the tank into multiple smaller tanks can be beneficial as it can reduce the mechanical loads due to the pressure load. Possible approaches include the use of a large tank, division into smaller tanks integrated into a housing, or the use of multiple individual tanks.

With the help of the MC, seven different tank versions were analyzed in depth and rated with the help of an evaluation matrix (EM). This method helps to objectify the evaluation. The criteria for the EM are the heat transfer, the amount of metal hydride inside the tank and the integrability of the solution in the overall system. By the application of weighting factors, a criterium can be prioritized. The evaluation of the tank versions resulted in the tank version that is presented in section 3 to be the most promising. The design composition, a principle sketch as well as the evaluation through the EM are provided as additional content by Röver et al. [14].

3. Results

The final solution selected through the MK consists of a cooling jacket surrounding the tank. Additionally, reinforcement ribs will be integrated into the cooling jacket to enhance the mechanical strength of the tank. The heat transfer within the tank is achieved through an axial arrangement of cooling channels and the utilization of topology-optimized tree structures. Furthermore, the entire metal hydride powder is intended to be stored in a single tank without division. This particular design variant is primarily focused on optimizing heat transfer, primarily through the adaptation of the topology-optimized tree structure developed by Lange et al. [10].

The branching configuration of the heat exchanger structure creates a large surface area that is in contact with the metal hydride. The use of such structures also highlights the advantage of AM: geometries that were previously inconceivable with conventional manufacturing methods become feasible through the utilization of AM. The heat exchanger structure employed by Lange et al. was adapted and integrated to the final HMHS design.

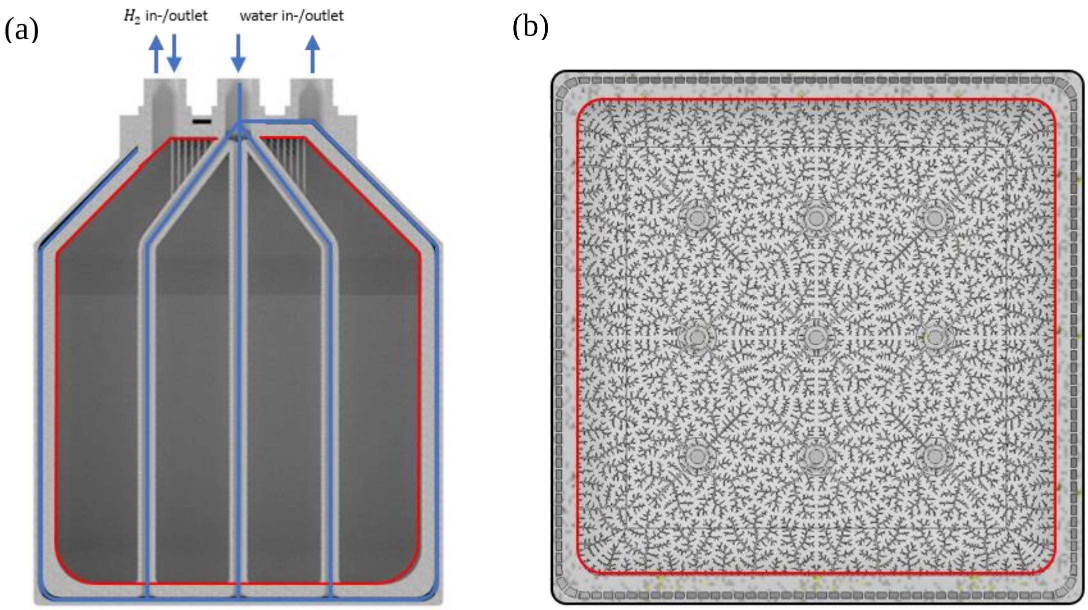

Figure 5: CAD representation of the metal hydride tank; (a) side view with the cooling circuit as well as the volume space into which the heat exchanger structure is inserted; (b) sectional view with the integrated heat exchanger structure as well as the reinforcing struts in the cooling jacket.

Views of the CAD design are depicted in Figure 5. The CAD file of the metal hydride tank is provided as supplementary material [14]. In (a), the functionality of the heat exchanger is shown. The blue contour represents the water-cooling circuit, which flows through the cooling structure inside the tank and the cooling jacket via the water in- and outlet. The metal hydride as well as the hydrogen is filled into the tank through the hydrogen in- and outlet. The red contour represents the volume space in which the selected heat exchanger structure is integrated. The structure, however is not integrated in the whole tank as that would hinder the loading of the metal hydride. Instead, the last 30 mm at the top of the tank are free of tree-like heat exchanger structures.

Additionally, the developed design is well-suited to prevent damages due to expansion and contraction of the metal hydride. Metal hydride undergoes volumetric expansion and contraction while charging and discharging with hydrogen. In the process larger particles disintegrate into multiple smaller ones. Depending on the design of a HMHS smaller disintegrated particles can fall to the bottom of the tank and accumulate there. During charging, expansion of the accumulated hydride can lead to a deformation of the tank in the respective region and possibly damage the tank. Considering the newly developed tank is mounted such that the gravitational acceleration is orthogonal to the fluid flows at the inlets and outlets, disintegrated powder particles will not accumulate at the bottom of the tank but will accumulate in the multiple tree-like structures. Thus, the design prevents large deformations of the tank structures due to expansion and contraction of metal hydride.

In addition to the integration of optimized heat exchanger structures, AM also offers the advantage that the tank consists entirely of a single component. This eliminates the need for welds connecting the lower and upper parts. Furthermore, the connecting struts between the cooling jacket and the tank, as shown in Figure 5 (b) between the red and the black contour, cannot be produced using conventional manufacturing methods.

The final design of the tank was validated via an FEA simulation based on the expected maximum pressure of 50.05 bar. The simulation showed that, with a wall thickness of 7 mm, the maximum stresses in the material were not reached and the tank, therefore, withstands the loads.

To show the inner design of the tank, a demonstrator was manufactured from polylactic acid (PLA) in the material extrusion of polymers (MEX/P)-process. The demonstrator can be seen in Figure 6, a CAD file is provided by Röver et al. as supplementary material [14]. It is noted, that the designs were optimized for manufacturing by PBF-LB/M and are expected to also be producible in this process. The height of the demonstrator was reduced in comparison to the functional model and the model was adapted to show the interior of the tank. On the right side of the picture, an excerpt part of the heat exchange structure is shown.

The aim of the design optimization of a metal hydride tank for hydrogen in this paper was to focus on heat exchange. The design freedom due to AM was utilized to integrate topology optimized structures into the tank. The final design allows for faster loading time via better heat dissipation. In subsequent work, the developed design should be manufactured in stainless steel 316 L by the PBF-LB/M process and assessed experimentally. Future works may also improve the design by the development of a topology optimization simulation combining mechanical topology optimization and heat transfer topology optimization. This way, a design could be developed for that the two key objectives of prevention of bursting of the tank and fast charging of the tank could be achieved even more efficiently.

Figure 6: PLA demonstrator of the designed metal hydride tank showing the interior of the tank and an excerpt of the heat exchange structure.

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Keywords: EFCF2023, low temp. Fuel Cells, low temp. Electrolysers, H_2, low temp. hydrogen storage tank, metal hydride tank, additive manufacturing, heat exchanger