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WHITE PAPER

SOLID HYDROGEN CARRIERS

Advanced metal hydride technology for
hydrogen storage, purification and compression
applications

June 2024

Metal hydrides are solid hydrogen carriers that can be used in multiple applications such as high-purity hydrogen storage or thermochemical hydrogen purification and compression. Fraunhofer IFAM's recent technological advances prove that metal hydride composites offer various advantages over conventional metal hydrides, for example, full charge-discharge cycle times of a few minutes.
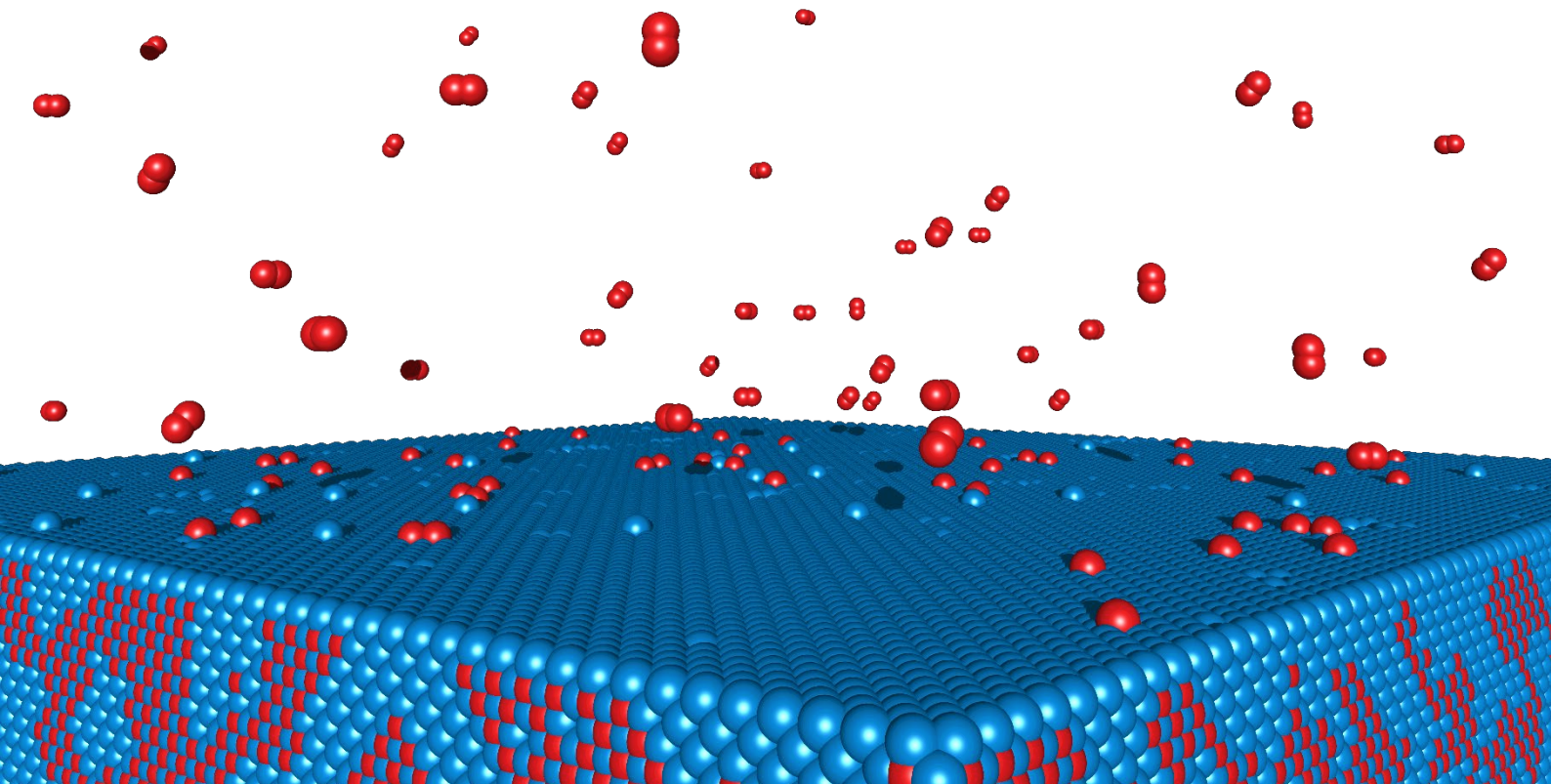
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INTRODUCTION

The new hydrogen economy requires a variety of storage, distribution and dispensing technologies. **Solid hydrogen carriers (SHC)** and in particular metal hydrides (MH) are a commercially viable alternative to compressed gas or liquid hydrogen storage solutions. SHC allow to safely store hydrogen with high purity (7.0), at low pressures (1 to 40 bar), in a very compact manner (up to 150 kg H_2/m³ compared to 39 kg H_2/m³ for hydrogen at 700 bar) and without boil-off or blow-off losses (Figure 1) [GUP16]. MH bind hydrogen in a chemical way, i.e. in the event of an unintended leak of the storage vessel, the gas will not be released into the surroundings all at once but at a small rate. This ensures a high level of intrinsic technical safety.
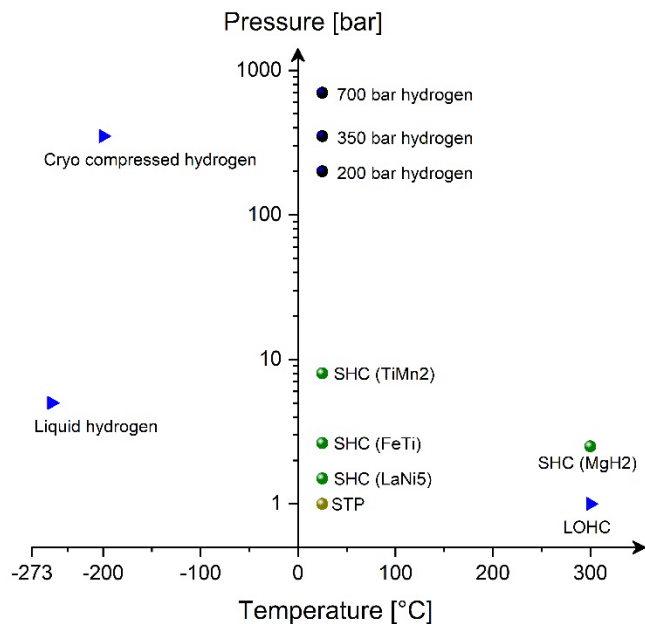
Figure 1: Hydrogen energy carriers in comparison (SHC: solid hydrogen carriers; LOHC: liquid organic hydrogen carriers; STP: standard temperature and pressure).

For some years, multiple industries have used MH for high-purity hydrogen storage applications to run fuel cell-powered **submarines, railed vehicles, stationary power devices** and **portable electronics**, among other things (Figure 2). Furthermore, MH are used for vibration-free thermochemical **hydrogen compressors**, thermochemical **heat pumps**, and systems for **hydrogen purification**. MH can also serve as reversible **hydrogen gettering materials**, thus, selectively removing hydrogen from gas mixtures.

In application-oriented research projects, Fraunhofer IFAM has explored ways to improve metal hydride technology comprising

- the development of hydrogen absorbing metal alloys with optimised working gas pressure and temperature range for storage and compression applications,
- the fast activatability of MH-forming metal alloys, i.e., a fast initial hydrogen uptake, by optimised microstructure and/or the use of catalytic species,
- the increase of the durability and reliability of MH composites,
- the optimization and analysis of heat and mass transfer of MH systems,
- the development and testing of MH vessels,
- the development of MH storage devices with high volumetric and gravimetric storage capacity, and
- the cost reduction of MH materials production and recycling.

Figure 2: Metal hydrides for hydrogen storage applications to run wheel loaders, submarines, forklift trucks, railed vehicles, stationary power devices and portable electronics.

Fraunhofer IFAM's mission is to develop MH systems towards commercialization. Compared to conventional MH technology that often employs highly porous MH materials in form of granules or powders, Fraunhofer IFAM uses advanced MH composites that consist of the MH-forming metal alloy and secondary auxiliary materials, such as graphite and/or polymers. These secondary materials ensure that MH composites retain their shape and allow them to increase reaction kinetics over the whole lifetime. Miniaturized sensors can be employed to determine the state-of-charge of MH composites and to detect specific signs of degradation.

METAL HYDRIDES AS SOLID HYDROGEN CARRIERS

Gaseous hydrogen (H_2) reacts at ambient or elevated temperatures with many metals or intermetallic alloys (Me) forming solid metal hydride compounds (MeH_x). The formation of a MH releases a chemical reaction enthalpy of several tens of kilojoules per mole of hydrogen (ΔH_R), depending on the specific metal or alloy involved in the reaction (cf. Equation 1 and Figure 3). In addition, the MH formation goes along with a slight volume expansion of the material.
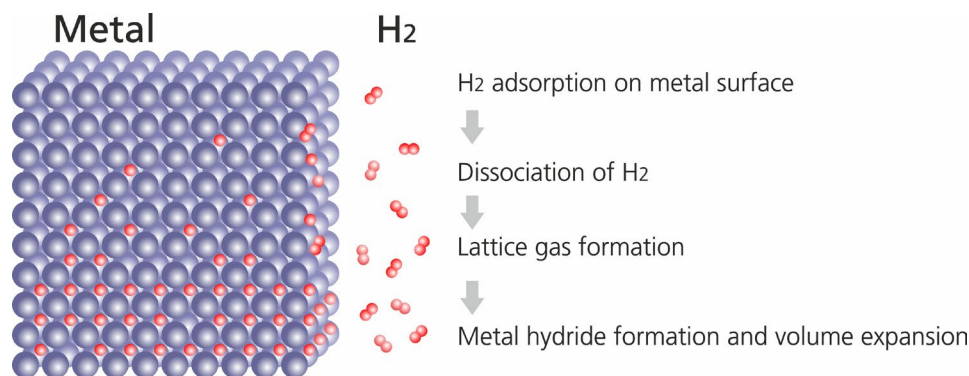
$$Me_{(s)} + \frac{x}{2}H_{2\,(g)} \;\rightleftharpoons\; MeH_{x\,(s)} + \Delta H_R \qquad\qquad (1)$$

Figure 3: Metal–hydrogen interaction with steps towards the formation of a metal hydride (schematic). The hydride formation is exothermal and goes along with a volume expansion.

Conversely, the dehydrogenation of MH materials, that is, the release of high-purity hydrogen from the MH, is an endothermic process that consumes heat. This is important in the context of fuel cells (FC), because waste heat from FC systems can be used to release hydrogen from MH storage devices, thereby, reducing the effort of FC cooling.

MH formation and decomposition are closely related to the hydrogen gas pressure and the temperature in the reaction zone (Figure 3). After adsorption of hydrogen on the surface of the metal, hydrogen dissociates and diffuses into the metal lattice forming a lattice gas. After saturation, the MH phase nucleates and grows. The thermodynamics of hydride formation can be described by pressure-concentration-isotherms (PCT) and the derived van´t Hoff plot (Figure 4). A PCT curve shows a characteristic plateau for hydrogen absorption and desorption. Here, the solid solution (lattice gas) and the MH phase coexist. The plateau pressure for absorption and desorption are temperature dependent. The PCT curve characteristics are very important for all

MH applications. For example, in the plateau region hydrogen uptake and release go along with small pressure changes at a given temperature. On the other hand, the plateau gas pressure increases exponentially with increasing temperature. This relation can be used for hydrogen compression applications as follows: The MH is formed at a low temperature and at low pressure. Then the valves of the storage compartment are closed and the temperature is slightly increased, thus, the pressure is rising and hydrogen can be released from the again open compartment at high pressure. For example, according to the PCT in Figure 4, the MH forms at 25 °C (298 K) and at 15 bar. At 100 °C (373 K), hydrogen is released at 78 bar. In this example, a 25 % temperature increase triggers a 520 % pressure increase!
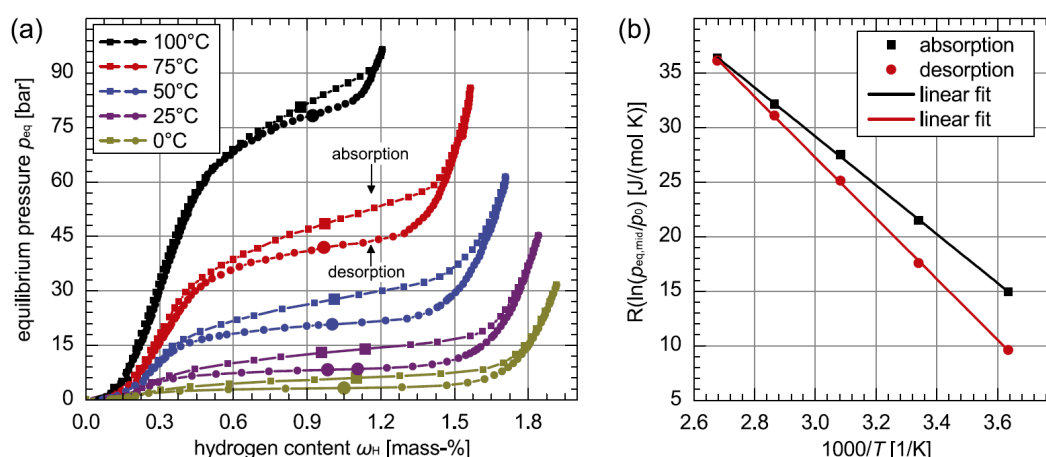

Figure 4: Pressure and temperature dependence of hydride formation and decomposition (here: Ti-Mn alloy [HER13]): A – Pressure-concentration-isotherms (PCT); B – corresponding van´t Hoff plots for hydrogen absorption and desorption.

The PCT curves and the derived van´t Hoff plots are unique fingerprints for every metal alloy composition and the respective MH. Metallurgy allows the production of metal alloys with tailored temperature and pressure characteristics. Thus, MH materials for various applications with specific properties can be prepared. The following table lists a small selection of technically important MH materials with indicated medium working temperature and pressure for hydrogen release:

Material	Temperature [°C]	Pressure [bar]
$FeTiH_2 - FeTi$	25	4
$TiMn_2H_3 - TiMn_2$	25	8
$LaNi_5H_6 - LaNi_5$	25	2
$MgH_2 - Mg$	300	2
$Mg_2NiH_4 - Mg_2Ni$	300	4

Commercial MH storage devices are available with a wide range of hydrogen storage capacities – from a few normal liters (portable cartridges) to several hundred normal cubic meters (stationary storage). Most MH storage devices have modular designs. They consist of one or more pressure containers (modules) holding the MH material that traditionally comes in form of lumps, granules, or powders. Inside each module, some free space is mandatory to counteract the volume expansion of the MH-forming material, thus, preventing additional mechanical stress on the container walls. Nevertheless, powder-based approaches have various drawbacks in view of the usable space, the effective heat and mass flows and, thereby, on the storage dynamics.

Fast hydrogen uptake and release cycles can be guaranteed if the heat of the chemical reaction is quickly transported inside and away from the reaction zone. The heat transfer characteristics

inside the reaction bed can be significantly improved by MH composites that consist of the MH material and secondary materials with a high intrinsic thermal conductivity like carbon, aluminium, or copper. The heat transfer away from the reaction bed requires suitable heat exchangers. The long-term stability of the hydrogen uptake and release characteristics of MH devices can be obtained by the preservation of the structural integrity of the reaction bed that can deteriorate by multiple causes, for example, MH particle migration or crack formation in the reaction zone lowering the effective thermal conductivity.

METAL HYDRIDE COMPOSITES

Fraunhofer IFAM has developed advanced MH composite materials (Figure 5) that are tested in storage modules and complete MH storage devices. These modern concepts provide more durable, more stable, and thus safer and less expensive MH storage and compression solutions than are available today. Special R&D focus is on the relation between the MH-forming metal alloys, the secondary auxiliary materials such as carbon or aluminium, and the internal structure that unites all these materials in <u>one</u> composite material with tailored properties that are relevant for a specific application:

Figure 5: Metal hydride composites.

- Hydrogen storage capacity (volumetric and gravimetric),
- working temperature and gas pressure of the MH device,
- fast hydrogen absorption and desorption kinetics by tailored thermal conductivity, and
- high mechanical stability of the MH composites throughout cycling and therewith lowest material degradation.

The first step on the route towards MH composites with tailored properties is to employ metallurgical processes to produce the hydride-forming metal alloys in form of fine particles with specific physical and chemical properties [KAL09, KAL10]. These processes include atomization of a metallic melt, melt spinning, electrolytic extraction, mechanical alloying, grinding and decrepitation. Thereafter, the master alloy particles are homogeneously blended with the secondary auxiliary materials, for example graphite, aluminium flakes or polymers, before being compacted by uniaxial pressing into composites of a defined geometrical shape (Figure 6 and Figure 7) [POH10, POH13, POH15].
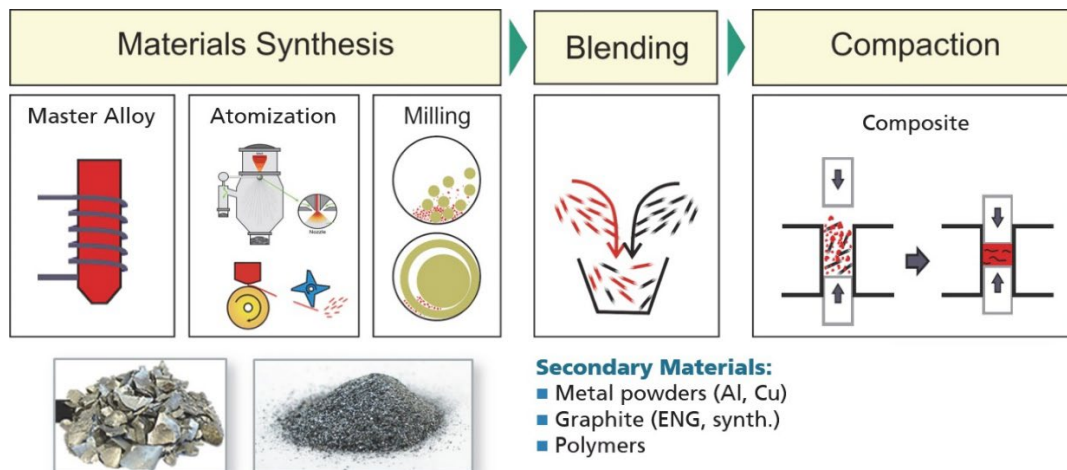
Figure 6: Schematic of MH composite production combining a MH-forming metal alloy and secondary auxiliary materials with highest thermal conductivity and other functional properties.
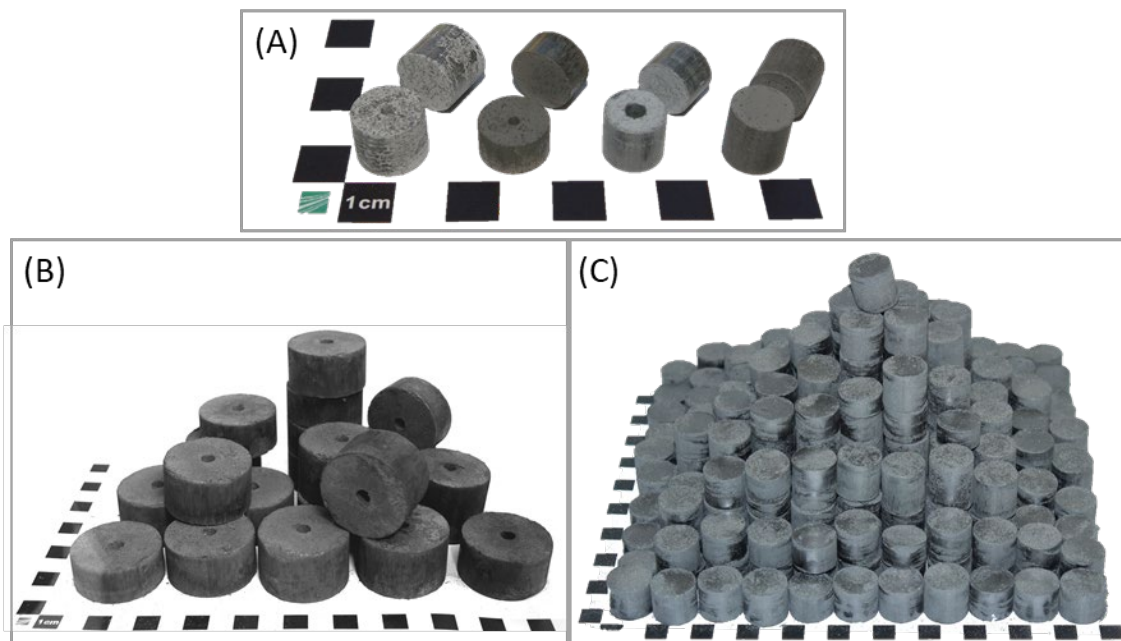

Figure 7: Arrangement of metal hydride composites made of different materials and with different parameters. Subfigure A (from left to right): Mg-, $TiMn_2$-, $LiNH_2$- and $NaAlH_4$-based composites. Subfigure B: $TiMn_2$-based composites processed in Ar atmosphere. Subfigure C: $TiMn_2$-based composites manufactured at ambient air.

The secondary auxiliary materials can serve three main purposes:

1. They enhance the structural integrity and raise process efficiency when the material mixture is being compacted.
2. They improve the hydrogen uptake dynamics by increasing the effective thermal conductivity (typical target values are between 5 and 30 W/(m·K).
3. They provide the reaction zone with much greater mechanical stability to withstand the volume changes that occur during hydrogen uptake and release.

Research has shown graphite to be especially suitable as a secondary auxiliary material as it provides the highest return with the least effort. For example, heat conductivities of several tens of W/(m·K) can be achieved using a few mass-% of expanded natural graphite (ENG) as secondary auxiliary material. Interestingly, the internal structure of MH-ENG composites is anisotropic due to the compaction process (Figure 8) which can be beneficial for the technical design of MH storage containers, particularly, for the heat exchanger layout.
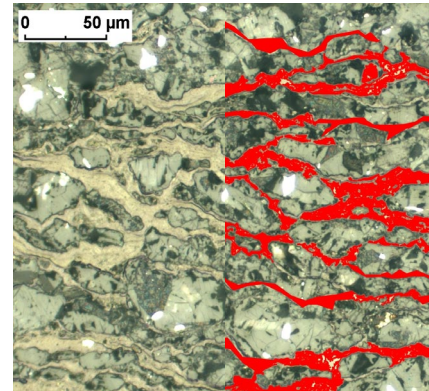

Figure 8: Microscopic cross-section view of a MgH₂-ENG composite. MgH₂ is colored grey to white and the horizontally aligned graphite is indicated in brown color (red in false color).

METAL HYDRIDE DEVICES

MH composites with cylindrical geometry and an anisotropic internal structure are a very good choice for rapidly responding MH storage devices. For convenience in the production process, the tablet-shaped composites are stacked on top of each other inside a cylindrical pressure vessel. Small radial gaps are filled as soon as the storage material begins to expand during initial hydrogen uptake. Heat is transferred mainly towards the heat exchange boundary, i.e., the outer surface of the container (Figure 9) from where a heat transfer fluid (gas or liquid) transfers the reaction heat further.

DESIGN

The design of a MH device is not only influenced by the type of application for which the device will be used but also by the type of heat sinks and heat sources to which the device can be coupled. For example, the exhaust heat of a FC can be elegantly used the trigger the endothermic hydrogen release from the MH device if the heat flow and temperature levels are adjusted properly.
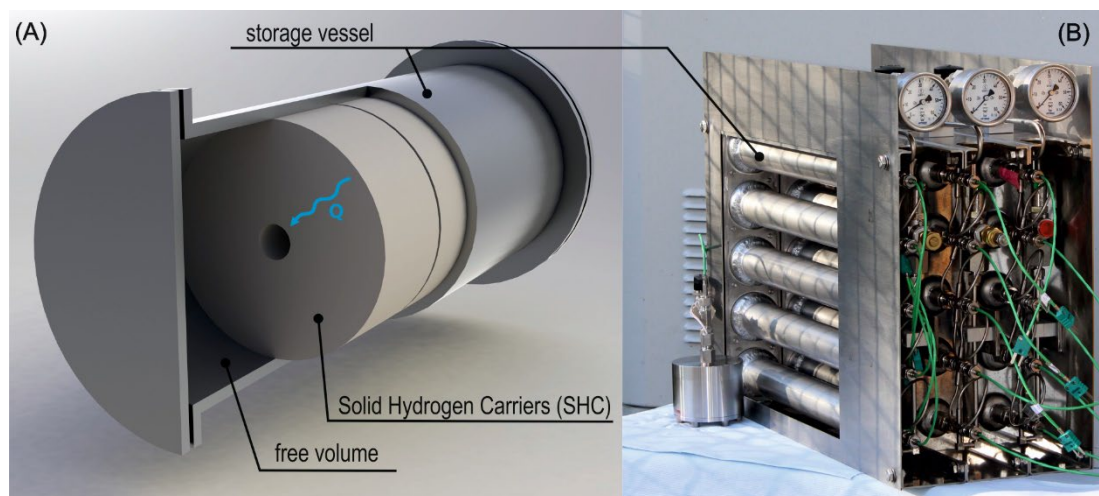

Figure 9: A: Schematic drawing of a MH-based SHC storage module (left), including heat transfer (Q) during hydrogen desorption. B: A 15-module storage device equipped with temperature, pressure, and filling level sensor.

Typical methods for identifying and monitoring MH composite characteristics either focus on values related to heat and mass flow (volumetric, gravimetric, or calorimetric analyses) or on single-point measurements, for example, by inserting thermocouples into the hydride bed to measure the temperature locally (Figure 9). For example, Figure 10-A illustrates the hydrogen absorption and desorption characteristics of a Ti-Mn–ENG composite. From this it follows that proper thermal management allows to charge and discharge storage devices within a few minutes. Figure 10-B shows the same composite after 20 hydrogen uptake and release cycles. The composite has been removed from the storage device after cycling for further analysis and obviously exhibits a good mechanical stability.
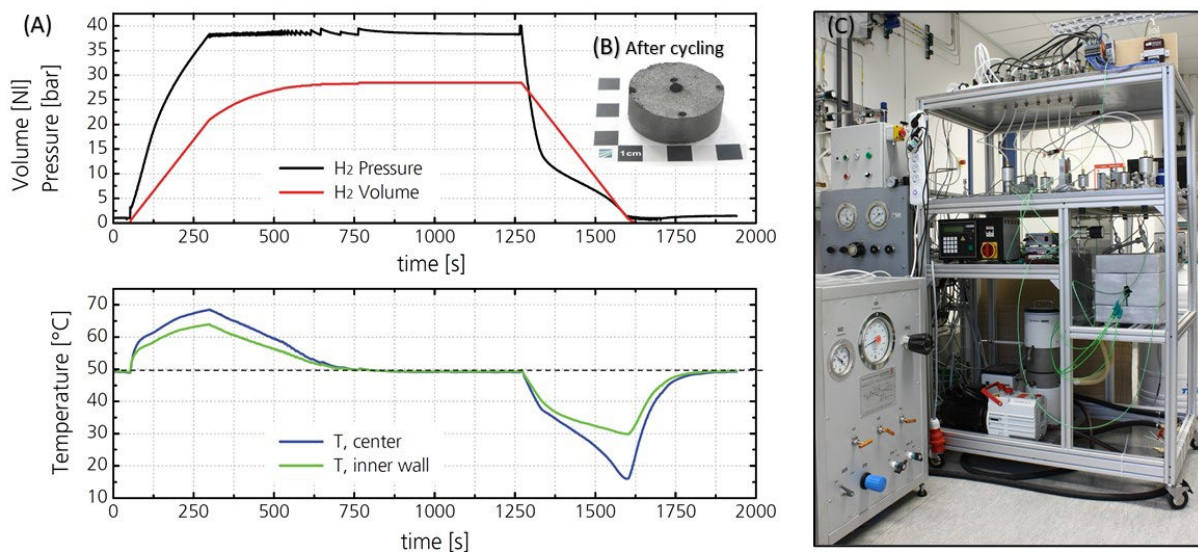

Figure 10-A: Absorption and desorption characteristics of a Ti-Mn–ENG composite following 20 hydrogen uptake and release cycles. Inset B shows the tested composite after cycling. The predrilled holes were used to insert thermocouples. Figure 8-C shows the metal hydride device test rig at Fraunhofer IFAM (in-house development).

VOLUME EXPANSION

The hydride formation goes along with a material-specific volume expansion between 10 and 30 vol.-%. Consequently, MH increase their volume during hydrogen uptake, too, although the degree of expansion depends not only on the kind of materials used but also on the internal structure of the composite. For example, pores inside the composite can partly or even fully accommodate the volume change. Furthermore, an anisotropic internal structure can lead to directional dependence of the expansion. Nevertheless, the hydrogen uptake generates stress on the composite material from which mechanical forces may act on the pressure vessel walls. For system safety, the forces need to be monitored and must be considered in the design of the pressure vessel. Fraunhofer IFAM has successfully developed and applied several ways to quantify stresses inside MH composites and the resulting forces acting on walls of MH storage devices [HEU15a, HEU17, HEU18].

STATE-OF-CHARGE

Due to the PCT characteristics, particularly the flat plateau region, gas pressure measurements are unreliable to determine the filling level (state-of-charge) of MH materials in dynamic applications. Fraunhofer IFAM invented a dynamic filling level sensor for MH devices that is based on the measurement of internal stresses in MH composites that evolve during hydrogen uptake and release [HEU15b]. This sensor can also provide information on degradation effects of the hydrogen storage material, for example due to gas impurities, which is beneficial to predict the lifetime of the hydrogen storage material.

Figure 11: State-of-charge sensor for MH storage devices.

Current R&D at Fraunhofer IFAM focuses on designing and evaluating of miniaturized sensors. Prototypes with diameters of less than 1.6 cm (0.63 inch) have already been produced and successfully tested in the laboratory (Figure 11).
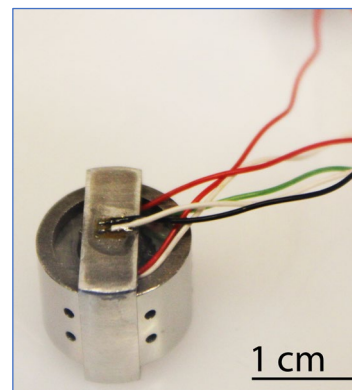
R&D SERVICES

Fraunhofer IFAM provides interdisciplinary expertise and all-inclusive know-how on metal hydride technology. The spectrum of our R&D services comprises paper studies (technical design studies, literature and patent search, freedom-to-operate analyses, value-added chain analyses including and life cycle cost analyses) as well as technical projects (preparation and testing of MH materials, design and testing of MH storage devices, system integration of MH storage devices into FCs systems and testing thereof).

Please contact us for more details.

350 BAR HYDROGEN LABORATORY AT FRAUNHOFER IFAM

Since 2008, Fraunhofer IFAM invests into a 350 bar Hydrogen laboratory for the development of sorption materials. Last installations were done in 2022. The following equipment is reserved for development of metal hydrides and R&D services:

Equipment	Characteristics
Membrane Compressor (Diekers)	**350 bar** max. output pressure, Hydrogen purity 6.0
Piston compressor (HDT)	**200 bar** max. output pressure, Hydrogen purity 5.0
PCT Pro (Setaram)	**Sieverts apparatus (PCT)** for determination of pressure composition isotherms. (200 bar 400°C)
GasPro HA (KEP, Setaram)	**Sieverts apparatus (PCT)** for determination of pressure composition isotherms, molecular vacuum pump installed (200 bar, 400°C)

ISOSORP® Gas HP-Flow II (Rubotherm)	Thermogravimetric suspension balance for determination of **kinetics and cycle stability** (200 bar, 400°C)
Rubotherm Series IsoSORP SA (Waters GmbH)	Thermogravimetric suspension balance for determination of **kinetics and cycle stability,** several gas inlets for gas mixtures etc, molecular vacuum pump installed (350 bar, 400°C)
novoclav (büchiglasuster)	Stirred batch **reactor for hydrogenation** of metals, inner volume 600 ml (450°C, 200 bar)

Further equipment is used for alloy synthesis:

Equipment	Function
2 x Glovebox Ar (M. Braun)	Sample preparation in inert atmosphere
Arc melting devices: MAM-1 (Edmund Bühler), AM 500 (Edmund Bühler)	Melting of up to 500 g (Fe-based) with cooled Cu crucible and suction casting option
Induction melting devices	Several induction melting devices with different crucibles are used for melting of reactive alloys

Please contact us for more details.

Figure 12: Impressions of the 350 bar Hydrogen laboratory at Fraunhofer IFAM in Dresden.

CONCLUSION

Solid hydrogen carriers like metal hydrides offer advantages compared to state-of-the-art high pressure or liquid hydrogen storage technology. Because hydrogen is chemically bound to a host metal, the volumetric storage density can go up to 150 kg H_2/m³ at low operation pressures in the order of 1 to 40 bar. Metal hydrides can be used for hydrogen storage, hydrogen purification and thermochemical hydrogen compression.

Advanced metal hydride composites that are manufactured using a simple production process have distinct advantages over conventional powder or granular materials, for example, in view of operation dynamics and system storage density. Modern metal hydride devices allow hydrogen uptake and release cycles in the order of a few minutes only. The safe operation of metal hydride devices can be improved with thermomechanical sensors that determine the state-of-charge as well as degradation effects.

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