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Metal hydride hydrogen storage and compression systems for energy storage: modeling, synthesis, and properties

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***Abstract*—Metal-based hydrides and intermetallic substances offer a practical alternative for storing energy from renewable sources. Given the appropriate adjustment of pressure and temperature constraints, they can absorb and reversibly release hydrogen. They are anticipated to significantly impact the shift towards clean energy and the use of hydrogen as an effective energy carrier. The paper summarizes Energy Storage (ES) methods that use hydrogen and Metal Hydrides (MH). It highlights the findings of the research and development efforts in this field. The emphasis is on carefully choosing MH materials, namely AB5- and AB2-type intermetallic substances, for Hydrogen Storage (HS) and compression activities. This selection is made by analyzing the Pressure-Composition-Temperature (PCT) characteristics of the components in systems containing H2 gas. The article also discusses the characteristics of integrated ES systems that use MH hydrogen storage and compression and the MH-based elements produced at IPCP and HySA Technologies.**

Keywords— Energy Storage, Metal Hydrides, Hydrogen Storage, Hydrogen Compression

I. Introduction to Energy Storage and Metal Hydrides

Renewable Energy Storage (RES) is a significant obstacle that humanity faces and is crucial to the shift towards a carbon-neutral future [1]. Attaining such a lofty objective can only be accomplished by creating materials that adhere to rigorous sustainability and efficiency standards projected for the next decades. Hydrides and other well-recognized chemical families, including oxides, sulfates, and carbide particles, are gaining attention as a potential category of Energy Storage (ES) materials[2]. The diverse nature of hydrogen's structure, characterized by its ability to form multiple bonds with other substances, including metallic, ionized, and covalent bonds, offers a wide range of compounds with distinct properties. This presents exciting opportunities for creating and advancing novel substances and composites with valuable and practical characteristics [3].

The disparity between energy generation and use necessitates highly effective ES solutions, primarily when relying on renewable energy as the primary source. RES exhibit temporal fluctuations in power output due to their non-uniform nature [4]. The most viable approach to handling variations in electric power supply and using excess energy is hydrogen as a highly efficient energy carrier. Hydrogen is generated via water electrolysis when there is an excess of electricity. During low solar radiation, when there is inadequate power output, hydrogen gets oxidized in a Fuel Cell (FC) to generate electricity as needed [5].

Hydrogen-based ES is advantageous for energy-intensive systems with a capacity of 12 kWh and a wide variety of power units, mainly when there is a need to restrict the system's physical space [6]. When the working life approaches five years, the expense of owning backup electrical systems (12 kW/130 kWh) using hydrogen ES becomes more economical compared to other ES technologies. The primary obstacle impeding the development of hydrogen ES systems is the secure and effective storage and distribution of hydrogen.

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Hydrogen Storage (HS) in Metal Hydrides (MH) is a potential method for storing hydrogen via reversible reactions with metals, alloys, and intermetallic substances [7]. This method shows potential for small-to-medium-scale uses, ranging from 0.01 to 30 Nm3 of hydrogen (H2). In addition to storing hydrogen compactly at low pressures, MH systems use the heat generated during fuel cell operations to discharge hydrogen, enhancing the system's general effectiveness. Incorporating MH in the "electrolyzer fuel cell" electrical system enables effective heat administration, offering end-users both heating and cooling capabilities and providing electric power. The surplus heat can be utilized to power an MH hydrogen compressor, which enables the storage of H2 in the compressed gas. The use of MH for thermally powered hydrogen compressing is promising because of its several benefits, such as the lack of moving components, a straightforward design and functioning, and the delivery of highly pure hydrogen. This study presents the findings on creating combined ES systems that use MH hydrogen storage and compression and their corresponding MH-based elements.

The following sections are organized in the specified sequence: Section 2 describes the materials used in the study. Section 3 examines the suggested Metal hydride hydrogen storage and compression devices for energy storage. Section 4 presents the study's conclusion and conclusions.

II. Materials

Based on the examination of the published information and the findings of the first tests, it was determined that a two-stage compression process is appropriate for compressing hydrogen to 140 atm within an operating temperature range of 25 °C to 140 °C. It recommends utilizing LaNi5 as the MH materials for the first phase and La0.5Ce0.5Ni5 for the second phase [8]. These metals, which only form a single hydride stage, are readily triggered and exhibit high rates of irreversible hydrogen absorption and adsorption. They have a small hysteresis, good cycle equilibrium, and can tolerate contaminants in hydrogen generated by electrolysis. The cycle efficiency of two-stage H2 contraction, using these AB5-type metals, is restricted by the movement of hydrogen from phase 1 to phase 2 at a pressure of around 35 atm, resulting in a productivity of about 85 H2/kg [9]. Nevertheless, this disadvantage was reduced by increasing the quantity of the MH materials in stage 1 of a hydrogen compressor by 10%–35% in weight compared to phase 2.

Many aspects determine the selection requirements for MH materials used in HS and compressing applications. The reversibility of hydride creation and breakdown processes is essential within the particular range of operating temperatures and hydrogen pressures required for the application. The substance must possess a substantial capacity for reversible HS under the specified working conditions. The features of these networks, which include H2 gas and hydride-forming substances, are defined by their pressure, structure, and temperature features. The reversed capacity is linked to the length of the stagnation on the Pressure Compression Technique (PCT) [10]. The path of the procedure, whether it is hydrogenation/H2 acceptance or dehydrogenation/H2 discharge, relies on the relationship between the real H2 pressure and the plateau pressure at the current temperature. The plateau gradient and hysteresis, characteristic of the PCT behavior in most practical systems, play a crucial role in Hydrogen Compression (HC) operations. This is because they considerably reduce the compression proportion and process efficiencies within the specified temperature range.

Additional significant characteristics of MH composites for HS and HC involve rapid hydrogen absorption and desorption dynamics, resilience to impurity-induced poisoning in the H2 supply, effortless activation, cyclic security, affordability, and manufacturing simplicity [11]. Most frequently utilized "low-temperature" intermetallic hydrides typically have an HS density ranging from 1.2 to 1.8 wt%. However, using solid solution metals based on the system achieves a higher H storage capacity of approximately 2.4 wt%. These materials and certain AB2-type intermetals can be employed in hybrid HS systems that are imposed with H2 gas at high forces and below-freezing temperatures. HS substances based on magnesium have better HS concentrations. Their use is limited to circumstances where a high-temperature heat origin is accessible due to the need for high working heat.

Although the hydride components have a much higher HS concentration than liquid hydrogen, the overall HS concentration at the structure stage will be lower. This is because the concentrations of the substances are restricted and there are variations in the concentrations of the underlying materials. The system's capacity to store hydrogen in large volumes will have comparable values for different substances, although still relatively high. When it comes to fixed ES systems, the primary factors for selecting components will be how they perform under specific conditions (such as pressure and temperature vary), ease of stimulation, the speed at which they can absorb and release hydrogen, and their cycle security [12]. The HS concentrations will be of secondary importance in this regard.

The most often used hydride elements for hydrogen preservation, battery system availability, and hydrogen compressing uses are intermetallics of AB5 and AB2 types [13]. The primary factor for this is the adjustability of hydrogen absorption characteristics in these materials by minor modifications in their constitution. This provides a chance to synchronize those substances' pressure/temperature operational capabilities with the circumstances of the use in question.

III. Method

This section discusses the hydrogen storage and compression systems for energy storage.

A. Hydrogen storage

When exposed to H2 gas at a temperature of 25°C and the pressure at which it absorbs hydrogen reaches its maximum on the pressure-composition isotherm, every component can utilize approximately 80% of its maximum capacity at a temperature of 55°C and a hydrogen pressure of 4 atm [14]. This capacity is sufficient to provide hydrogen to a low-temperature fuel cell system, employing the heat distributed throughout the process to heat the MH bed. Most of the MH materials can release H2 at pressures higher than ambient and temperatures below freezing, activating the electrical system throughout the wintertime.

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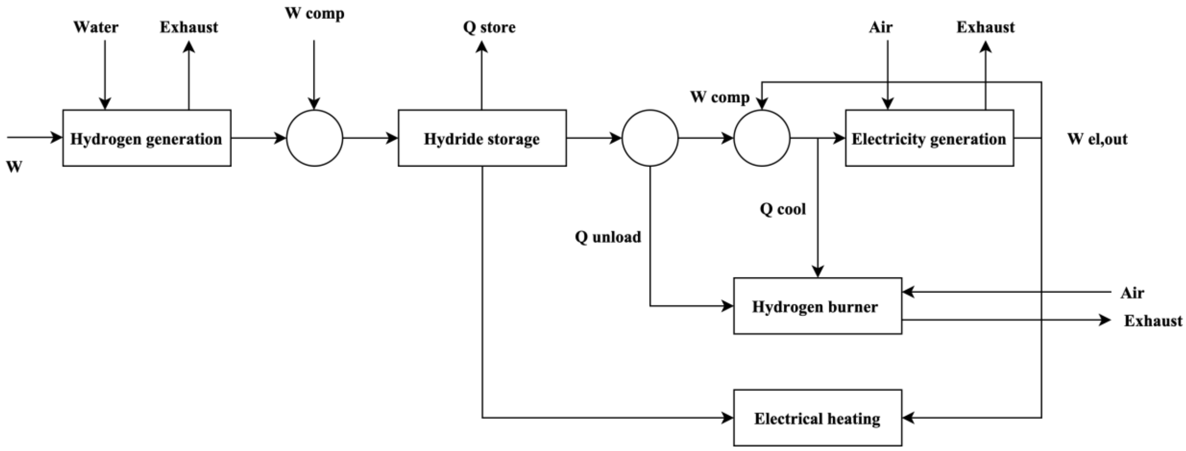

Fig. 1. Process of HS system

Figure 1 depicts the proposed process architecture of the HS system. The primary energy and mass transfers are provided. Once the hydrogen gas has been generated and dried, it is next compressed to the necessary storage pressure. The compressed air is introduced into the storage vessel, which reacts with the metals to generate an MH. Since hydride production is exothermic, it is necessary to extract heat (Qstore). To recover the hydrogen later, the hydride must undergo endothermic breakdown, which requires the application of heat (Qunload). The hydrogen gas that has been released is subjected to cooling, compression, and reconversion into energy (Wel, out). This article explores two potential methods for supplying the necessary heat for hydrogen discharge. One possible option (case 1) involves combusting a certain quantity of the hydrogen emitted in a burner. Case 2 is an electrical heating system that utilizes the power generated by the repowering procedure. The first option requires an extra combustion system, resulting in a more complicated configuration—the second option was achieved with far less technical work.

It is essential to mention that the HS capabilities of MH materials are the highest possible values based on theory. The quantities of H2 sent from the MH to the stack are contingent upon the pace at which hydrogen is supplied, which in turn is influenced by the power of the stacks. The rapid rate of endothermic H2 adsorption causes the MH bed to cool, reducing the speed of H2 release. The usable capacity of H2 in the MH will decrease when H2 is released at a specific rate relative to the electrical power of the stacks. This drop was reduced by enhancing heat transfer among the MH and the heated fluid and implementing other technical measures.

The system utilizes standard composite pistons, which consist of a stainless-steel liner injury with either carbon or glass fibers. These cylinders are heated or chilled from their surroundings through natural air conduction or by the passage of a heating/cooling fluid. In the latter scenario, the cylinders are enclosed in a stainless steel jacket that facilitates warming or cooling. This system has a low mass, simple design, and affordable cost. However, it is characterized by a suboptimal thermal transfer between the MH and the heating/cooling liquid, leading to somewhat sluggish hydrogen charging and releasing processes.

The MH containers use several tanks with an inside diameter of around 40 mm, fitted with internal copper vents and externally heated or cooled. A tiny quantity of enlarged organic graphite was included in the MH powder. This addition enhanced the MH's safe filling densities and optimized heat transport inside the MH bed. Despite being more time-consuming and costly, this technique effectively increased the rate of H2 delivery to the fuel cell stack. The cooling system of the stack is directly connected to the heating system of the MH tank. The weight of the tanks increases significantly due to the improvements in heat transmission, although this is not a problem for stationary uses and even certain specific mobility applications. For instance, the mass was deliberately augmented by enclosing the MH canisters in leads in the MH tank, which was created for storing hydrogen on a fuel cell-powered forklift. This was done to offer the required counterbalance mass for the secure operation of the forklift.

B. Hydrogen compression

Hydrogen compression is essential when a hydrogen ES system saves hydrogen in compressed gas canisters or MHs with a normal H2 absorbing pressure at an acceptable temperature for H2 charging that surpasses the H2 pressure produced by the electrolyzer [15]. As stated in the beginning, using MH for H2 compressing has many advantages, such as enhancing the system's performance by harnessing waste heat generated during electrolyzer operations. The chilling temperature is -25 C, and the heating temperature is 140 C. The MH H2 compressors assessment was constructed using the computed isotherms.

These values vary according to the specific design characteristics of the MH compressors and the circumstances under which they are operated. Nevertheless, for a well-engineered compressor, the variations are relatively low. The Russian company created an instance of a Two-Stage Compressor (TSC) 2-3.0/140, according to oversight [16]. The compressor operates at a low temperature of -10 °C and a high temperature of 140°C, with a flow rate of 10 Nm3/h. The first phase of the compressor, which uses LaNi5 as the working material, operates at a low pressure of 3.2 atm and a high pressure of approximately 30 atm. It achieves a cycle efficiency of around 70 NL/kg. The second phase, which uses La0.5Ce0.5Ni5, operates at a low pressure of approximately 30 atm and a high pressure of 140 atm, achieving a cycle efficiency of about 120 NL/kg. The compressor has a cycle

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time of 35 minutes and includes three hydrogen compression groups.

C. System integration

Both methods (storage and compression) use gas cylinder packages as their primary HS units, with MH HS units as supplementary HS spaces. The gas cylinder packing is pressurized with an MH compressor throughout the system's functioning [17]. The MH units are recharged via the electrolyzer's outputs or, if the outgoing pressure is insufficient, via the compressor's discharged line via a reduction device. Once assessed, fewer MH units are relocated to other locations, including H2 fuel cell stacks for consumption. The larger MH tanks are continuously connected to a hydrogen supply line for the fuel cell arrays. These reservoirs are intermediate storage units that link the electrolyzer's result and the MH compressor's intake.

It uses an H2 cylinder packaging with a gas-providing system connecting three gas pipelines. These pipelines convey hydrogen to fuel cell testing places (at a pressure of 12 atm), other hypothetical features that require medium-pressure hydrogen (at 85 atm), and hydrogen distribution for refueling fuel cell automobile designs (at a pressure range of 35 to 220 atm), such as forklifts.

Although several integrated energy systems, such as electrolyzers, MHs, and fuel cells, have been created, the predominant method for HS has been via MHs. To their understanding, one advancement in incorporating MH compressors in a hydrogen-based energy system was carried out with the help of the Europe-funded program. The compressor in Cyprus can compress hydrogen gas from 5 to 250 atmospheres with a maximum output of 2.4 Nm3/h. This closely matches the performance of the MH compressor used in the hydrogen manufacturing, distribution, and storage systems (Figure 2).

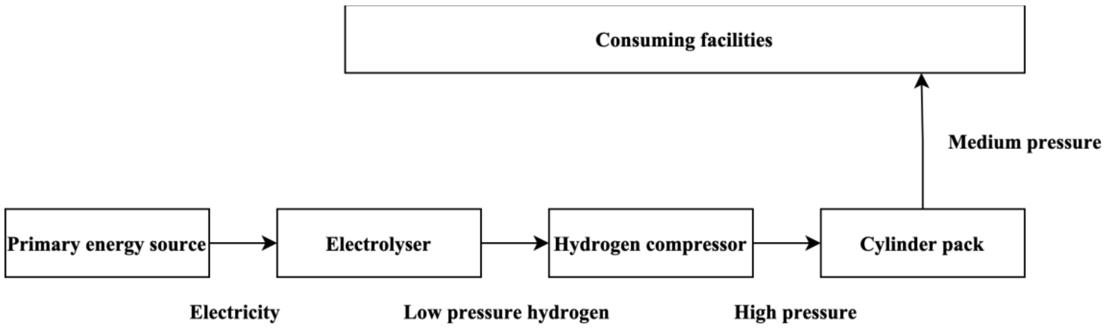

Fig. 2. Hydrogen production, storage, and compression process

The compressor offers a distinct advantage due to its ability to operate within a small temperature range (15 to 80 C). This enables the use of cost-effective and uncomplicated heat sources, such as solar panels, to power the compression of H2. Nevertheless, this gain has been obtained by increasing the number of steps (up to six), which is known to affect thermodynamic effectiveness and dependability negatively. In contrast, the MH compressors used in the ES systems analyzed in this research utilize two-stage and three-stage configurations. The issue of obtaining heat at a relatively high-temperature perspective (120-150°C), essential for these advancements, was resolved using suitable thermal management technologies. However, this matter requires more investigation in future research.

D. Mesoscale modeling methods for MH microstructures

Metal-to-hydride stage changes are the methods by which hydrogen is stored in metals via reactions [18]. Accurately modeling these phenomena in dynamic, non-equilibrium systems is difficult due to the intricate interplay between surface/interfacial reactions, dispersion, structural transformations, and substantial volume expansion. Each process operates at the atomic level and is highly impacted by the tiny structures of the original metal and the formed hydride. These factors play a crucial role in determining the kinetic and thermodynamic properties of the process. Hence, it is essential to effectively combine various modeling methods that include diverse spatial and temporal dimensions to thoroughly investigate the interdependent development of significant chemical and material phenomena. A mesoscale modeling system serves as a cohesive foundation for incorporating atomistic techniques, which generally provide greater precision for chemical reactions at the nanoscale. Continuum techniques offer far more adaptability and expandability and depict substances at the microstructural scale. The modeling framework has broad applicability to the creation of MHs and is now being expanded to include a numerical method of surface processes.

E. Synthesis and processing method

This section summarizes the manufacturing techniques used to manufacture hydride-forming compositions and MHs that exhibit enhanced hydrogen sorption characteristics [19]. The process of melting and casting remains the preferred approach for manufacturing alloys that can generate hydrides. This approach readily expanded, but the resultant microstructures are often coarse, leading to sluggish hydrogen sorption dynamics. Pouring eutectic compositions can create tiny nanocrystalline structures in their original cast condition. Mechanochemical techniques are now the most widely used synthesis technique for producing hydride-forming materials and their hydrides. Enhancing mechanical power systems is a simple method to create nanostructuring and metastability. However, a concern arises over the grinding medium's possible contamination of the end product. Recently, there has been a growing interest in using nanostructuring techniques derived from traditional metallurgy, such as extreme plastic distortion and forged. These methods have attracted interest

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due to their ability to integrate the benefits of melting/casting with mechanochemical approaches. The gas component condensing approach exemplifies the bottom-up production technique for nanotechnology hydride-forming materials.

F. Effect of oxygen on the properties of metal-H systems

Metals always include oxygen as a constituent. The quantity of the substance is contingent upon the precursor components' oxygen content and the time-temperature conditions during their creation, including the gaseous atmosphere and the melting container [20]. Oxygen impacts many aspects of the interactions between metal and hydrogen. These include the breakdown of H2 and its ability to penetrate the outer layer of the metal, the movement of hydrogen into the interior of the material, the choice of hydrogen's location within the metal structure, and, especially, the metal's capacity to store hydrogen and its effect on the thermodynamics of the metal-hydrogen interactions. The crucial factors of HS in substances, including oxygen, are the impact of oxygen on surface and bulk characteristics, as briefly outlined below [21].

(a) Macroscopic behavior - When placed inside the metal sublattice, oxygen atoms occupy the most significant hexagonal interstitial positions.

(b) Macroscopic behavior - Interstitial oxygen hurts the strength and disintegration heat of oxyhydrides that include oxygen instead of hydrides that do not contain oxygen. It lowers the number of hydrogen atoms that occupy interstitial locations around octahedra loaded with oxygen.

(c) Macroscopic behavior - At elevated temperatures, dissolved oxygen in the metal alters the process of hydriding and dehydriding, leading to oxygen displacement across the different phases and its subsequent separation to produce stable hydrogen oxides that do not disintegrate. The chemical makeup of the hydrides in the Ti H2 system is controlled by adjusting time and temperature variables during the oxidation procedure of TiH2.

(d) Surface behavior - The phenomenon of surface oxide in the kinetics of hydrogen absorption in alloys has been extensively investigated for a considerable period. A recent study used electron microscopes and resistance experiments to examine the impact of surface oxides on the hydriding process of thin Ti films. At a temperature of 350 °C, thin layers of titanium coated with its natural oxide exhibit a satisfactory rate of hydriding. The hydride forms in a layered manner, starting at the contact between the backside of the film and the backing material. At a temperature of 300 °C, the study of the effect of stress on hydriding shows that the step that limits the pace of reaction is the diffusion of hydrogen over the oxide layer instead of the breaking of H2 molecules at the surface—understanding the diffusion process and determining diffusion rates necessary in enhancing the performance of substances for future applications.

IV. Conclusion and Findings

The efficiency of MH hydrogen storage and compression techniques has been shown in small- to medium-sized ES systems. This paper has defined the methodology for selecting MH elements of AB5 and AB2 types for HS and compression devices using MH technology. This technique relies on analyzing the PCT characteristics of substances. It considers the usable H2 capacity for HS or the cycle efficiency for H2 compression, which depends on the temperatures and pressures of H2 absorption and adsorption.

Two medium-sized ES devices, developed under the direction of hydrogen storage devices, have been shown. The systems can use several primary sources of electricity, such as the grid, solar panels, and wind turbines, to produce hydrogen via water electroplating. The low-pressure hydrogen generated is compressed using an MH hydrogen compressor and then stored in gas cylinder packages at 140-220 atm pressure, serving as the primary HS source. Hydrogen is gathered and kept at a pressure lower than 120 atm in metallic hydride HS tanks. Both HS tanks provide hydrogen to fuel cell stacking with a maximum electrical output of 35 kW. The high-pressure cylinder packages deliver hydrogen for fuel cell and other purposes.

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