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Engineering Solutions in Scale-Up and Tank Design for Metal Hydrides

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Abstract. A holistic approach is required for the development of materials and systems for hydrogen storage, embracing all the different steps involved in a successful advance of the technology.

The several engineering solutions presented in this work try to address the technical challenges in synthesis and application of solid-state hydrogen storage materials, mainly metal hydride based compounds.

Moving from the synthesis of samples in lab-scale to the production of industrial sized batches a novel process development is required, including safety approaches (for hazardous powders), and methods to prevent the contamination of sensitive chemicals. The reduction of overall costs has to be addressed as well, considering new sources for raw materials and more cost-efficient catalysts.

The properties of the material itself influence the performances of the hydride in a pilot storage tank, but the characteristics of the system itself are crucial to investigate the reaction limiting steps and overcome hindrances. For this, critical experiments using test tanks are needed, learning how to avoid issues as material segregation or temperature gradients, and optimizing the design in the aspects of geometry, hull material, and test station facilities.

The following step is a useful integration of the hydrogen storage system into real applications, with other components like fuel cells or hydrogen generators: these challenging scenarios provide insights to design new experiments and allow stimulating demonstrations.

Introduction

The hydrogen economy is often considered as a viable way to address many of the issues related to future energy strategies. Whether it is alternative or complementary to other routes to deal with energy harvesting and distribution in a sustainable way, one can identify its characteristics steps to form a closed cycle where only energy and non-polluting elements are exchanged with the environment [1]. Namely, these steps are hydrogen *generation/production*, *storage*, and *use*.

The work presented hereafter focuses on solving engineering challenges that develop in the second step of the hydrogen cycle; more specifically, in the field of hydrogen storage using metal and complex hydrides in solid state.

To evaluate the practical feasibility of these materials, after assessing their properties in the laboratories, it is necessary to research and develop their full life cycle. The analogy with the aforementioned cycle is quite strong: the *synthesis* of these hydrides is a fundamental step; it is followed by the capacity to exploit a proper vessel to *store* and accumulate the material in a way that is efficiently enhancing its properties and, finally, profitably *use* this hydride system in an application. All the three steps are linked to each other; with a number of iterations and experiences, the interconnections between the processes would be enough to provide parameters and feedbacks and optimize the life cycle of the materials.

Synthesis Scale-Up

The first challenge encountered in the engineering development of metal hydride technologies is related to the capability to produce quantities of materials, which go beyond the usual amounts required in laboratory testing. The iterative production of small batches is not feasible considering a large scale employment of hydrides, whether they apply in vehicular or stationary applications.

Among the possible ways to synthesize materials for solid-state hydrogen storage, a versatile and well-known procedure is the ball milling technique. High-energy ball milling is a non-equilibrium process that modify the microstructural features of powders by repeated application of mechanical energy while the powder is trapped between the colliding spheres and between spheres and vial wall [2]. It has been proven that several beneficial effects can be achieved using this technique: in addition to obtaining a homogeneous and intimate mixture of different powders, the process introduces defects in the crystals and reduces the sizes of the particles and of the crystallites, thus increasing the reactivity of the milled powders towards hydrogen.

Increasing the size and the number of the batches of milled powders implies the use of mills and accessories, which are closer to the industrial environment rather than to the laboratory set-up.

Process development. Thus, the process has to be re-developed to meet the new needs and still guarantee the properties obtained in the laboratory scale production.

One immediate difference is the requirement of additives, which can help the process itself without altering the properties of the material. For example, most of the times, the presence of a lubricant is a stringent requirement to mill kilograms of powders in vessels, which have several liters of volume: independently from the exact nature of the process, there would be a higher surface and several dead corners where the products might adhere and accumulate.

In the field of hydrides, another crucial aspect is the contamination prevention, as most of the powders are prone to react with moisture and oxygen, even violently. The protection of the atmosphere inside the milling vial became more challenging with the altered size and the possibility to perform the whole process under inert gas atmosphere in a glove box is impractical. Therefore, to maintain an unreactive atmosphere during milling, loading and unloading of powders is a procedure to develop and protocol for the different processed materials.

In a general outlook, the method requires new safety concepts, too. A completely oxygen-free atmosphere is the first step for a safe process, but it is sometimes difficult to achieve and so acceptable levels have to be determined for the milling, and subsequently for the handling of products and cleaning of the machines [3].

Material cost reduction. Of course, the cost is an important factor influencing the possibility of producing bigger quantities of hydrides. If the scale-up of the process does not necessarily consume more energy, and can even result in a more efficient yield of product, the cost of raw resources is obviously strongly dependent on the quantity of the batch.

There are different strategies to try to reduce the costs of starting materials, considering that the produced hydrides are seldom meant for a broad market and their principal application is research and development. As the catalyst mixed with hydrides is often a relevant expense, the use of cheaper and smaller amounts of additives has been investigated several times. If the properties of the resultant material are comparable, a sensible cost reduction can be achieved without compromising the quality of the production.

Also the use of hydrides synthesized from waste is an interesting route for cost reduction. Sometimes the main component is available as production and/or treatment by-products: this can be the case of aluminum alloys used for the synthesis of NaAlH_4 [4], or the production of hydrogen storage grade MgH_2 from a specific Mg alloy wastes [5,6]. Some of these samples display good kinetics and reversibility, especially when processed in large batches that allow an even distribution of impurities; of course, a slightly reduced H_2 capacity is unavoidable, but is an acceptable compromise when considering the inexpensive source of material.

As a further example, in Fig. 1 the results of different batches of a reactive hydride compounds (RHC, specifically $2\text{LiH}+\text{MgB}_2$) milled in a Simoloyer CM08 are displayed. The effect of different catalysts used to replace the expensive TiCl_3 is shown; it is not evident from the first absorption, where there is a small difference just in the reaction time, however, in the tenth cycle it is possible to notice how the reaction, without catalyst or with TiO_2 , is compromised. The use of a less pure source ($3\text{TiCl}_3\cdot\text{AlCl}_3$ instead of TiCl_3) is a good compromise for this system.

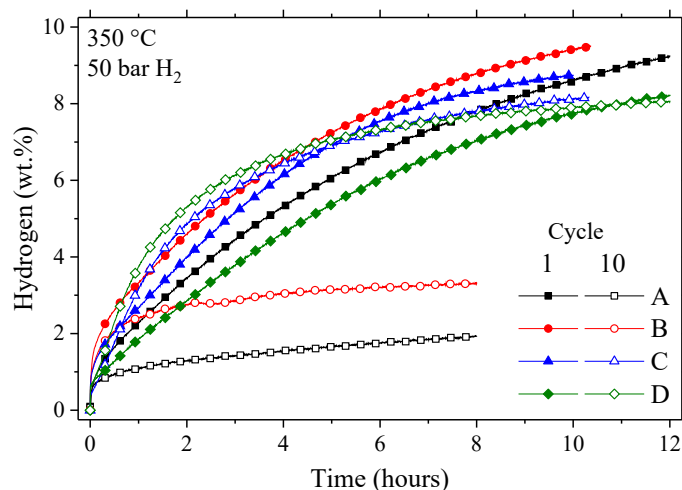


Figure 1. Hydrogen absorption for the 1st and the 10th cycle of Li-RHC batches with different additives: A. no catalyst; B. TiO_2 ; C. $3\text{TiCl}_3\cdot\text{AlCl}_3$; D. $3\text{TiCl}_3\cdot\text{AlCl}_3$ and graphite.

Several batches were prepared and characterized, with and without the addition of graphite. The results are highly reproducible, which is a positive outcome considering that the size of the batches was of 500 g.

Tank Systems Development

Whether the purpose of the tank is just the analysis of the material characteristics out of the laboratory scale, as in many research projects, or the more complex assessment of a whole storage system, it is important to conceive and design the vessel appropriately. So, in the outlook of a complete cycle, this means according both to the known properties of the storage material and to the requirements of the intended use.

Among the different possible limiting steps in the hydrogen absorption/desorption reaction, namely hydrogen transport, intrinsic kinetics, and heat transfer, researchers usually observe a shift from the second to the third while increasing the size of the investigated sample [7]. Therefore, dealing properly with heat transfer is crucial for the development of storage tanks for metal hydrides.

Managing the reaction-limiting step. Several strategies have been adopted for achieving an improved thermal management [8] (e.g. improving the inside of the vessel with metallic fins or a circulating fluid, or increasing the thermal conductivity of the material with additives or by compaction). In fact, most of the hydrides present a low value of thermal conductivity, which ranges from 0,1 to $1,0 \text{ Wm}^{-1}\text{K}^{-1}$ and this can be improved by almost two orders of magnitude creating pellets, where the density is conveniently increased without hindering the hydrogen transport [9,10]. Moreover, these compacted solids can be enriched with the addition of a conductivity-enhancing element as graphite [11,12], which has already been listed as a useful additive for lubrication during milling.

Critical experiments on test tanks. Many challenges can arise with a deeper study of storage tanks for metal hydrides.

The study of temperature gradients in tanks is a useful tool to analyze the behavior of the specific solution adopted and to provide reliable data for numerical simulation. A high number of

thermocouples distributed inside a research vessel and on its surface is always recommendable, but inserting many elements through the wall of a pressure vessel can compromise the tightness of the design. A possible alternative involves the use of a calibrated infrared camera to record and study the gradients on prepared surfaces of the vessel; however, the experiment has to be designed accordingly and the temperature gradients can only be measured on the surface.

As mentioned in the previous paragraph, a powerful tool to design and develop storage tanks is the use of computer simulations, which can help gaining a deeper understanding of the limiting step and providing a solution to optimize the tank system. The finite element method, for example, allows studying the distribution of temperature inside and outside the tank, taking into account the material properties and the interaction with the surrounding environment.

Another phenomenon, which cannot be detected in the laboratory scale, but often occurs in larger scale vessels, is material segregation. Complex hydrides contain compounds that undergo a phase change at a temperature lower than the operative one: if the design is not optimized liquids can pass through filters intended for powders; additionally, in the case of RHC, the components can undergo long range segregation and not react with each other anymore. Several solutions can be implemented to solve this issue, including the use of carbon scaffolds [13], polymer matrices, or combining the material in pellets [9,10].

Indeed, this development process requires steps to improve the knowledge and understanding of the behavior of a material in the system. In Fig.2 three different generations of tanks developed for Li-RHC are shown. The shapes and the hull material are optimized for the function: after the first set of experiments, where material segregation was observed, a second design was realized with a bigger diameter and an increased number of thermal sensors. Moreover, the second example was built in a special steel to be able to examine the internal reactions with neutron radiation. The third vessel, the first containing pellets to avoid liquid segregation, is realized using a special heat and creep resistant steel to make the coupling with a solid oxide fuel cell (SOFC) possible.

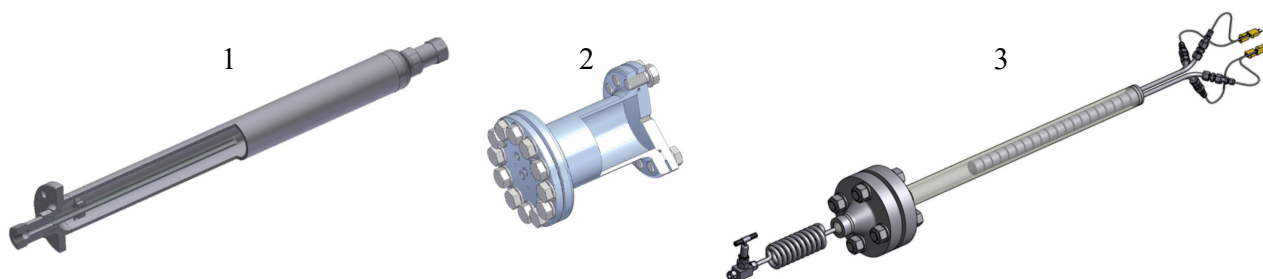


Figure 2. Three different generations of storage tanks for Li-RHC samples (the scale varies in the different sketches).

Hull material selection is sometimes hard because not all the steels or special alloys can meet multiple requirements at the same time; the susceptibility to hydrogen embrittlement in particular conditions is not often considered in standards and directives.

The advances in the design of tanks requires a parallel development of testing facilities. Sievert type apparatuses are obviously not appropriate and loading stations with flowmeters are required. The flexibility of the heating/cooling system is also important, but challenging: for example, depending on the desired rate of reaction the required heat exchange, both in absorption and desorption, can increase from few to hundreds kW [14].

System Integration

The last step to close the life cycle of a metal hydride is to integrate entirely the storage system in an experiment, a simulated application or a real one. These last two usually generate a set of requirements that are rarely found in basic experiments. Successfully coupling a storage system to a fuel cell and operating it in several scenarios is, therefore, a worthwhile challenge.

Experiments in real applications. A possible example is the use of a modular hydride tank designed to be coupled with a proton-exchange membrane fuel cell (PEMFC) in a vehicular

application; in the specific case, it is an urban concept prototype lightweight vehicle [15]. From the perspective of the storage system, it is fundamental to know the PEMFC real requests in terms of hydrogen flow, total and instantaneous. The versatility of a modular approach allows studying different set-ups in term of H₂ quantity, sorption, and release, before reaching the final version [15].

The first experiments on such a system, regular absorption and desorption cycles with static settings, validated the design and generated interesting data in terms of H₂ flow, pressure and temperatures, which could be critically analyzed to design a new set of experiments and move closer to the real application. Dynamic tests, with variation in the H₂ flow simulating a driving cycle, were designed and performed, repeated in different scenarios, and adjusted to complete the off-board characterization of the system [16]. Inserting the hydride tank in the chassis with the PEMFC was the last rewarding step; it gave the possibility of following the behavior of the tank and of the material according to the performances of the fuel cell and of the vehicle in general. The profitable use of the warm exhaust of the PEMFC enhanced the results expected from the laboratory. Finally, the vehicle could take part to exhibition and competitions and therefore be a valid demonstration of hydrogen technologies.

System integration with solid oxide fuel cell (SOFC). A more challenging scenario is provided when considering SOFC, due to the high temperature at stake. The materials in the fuel cell are under stress for temperature and thermic differences; however, these can be considered ideal conditions for some reactive hydride composites. The distance from the thermodynamic equilibrium temperature exerts a driving force for fast reaction kinetics. In the study proposed in Fig.3, the use of a hydride tank represents an effective way to exploit part of the thermal energy of the cell, increasing the system efficiency [17]. An integrated system with SOFC reversible to solid oxide electrolyzer cell (SOEC) would be optimal for RHC ($\sim 48\text{-}50 \text{ kJ (mol H}_2\text{)}^{-1}$). In fact, the hydride can be used to store hydrogen and to release heat during the electrolyzer operation, and to feed the fuel cell with hydrogen when electrical energy is required.

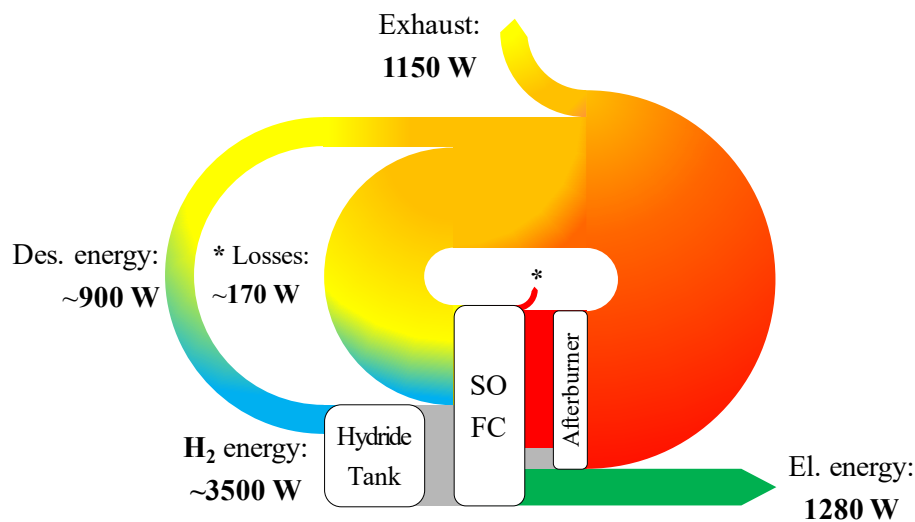


Figure 3. Sankey diagram of heat flows in an integrated system with hydride tank and SOFC [17].

As it can be seen, recovering heat is important for the overall efficiency of the system, thus the scale considered in this example does not allow reaching the highest values: a 100 % fuel consumption, without the need of the afterburner and an improved use of the thermal energy is possible only in systems around 20 kW. The thermal losses do not increase proportionally; therefore, they represent a much smaller fraction in bigger systems.

Summary

A complete approach, which ranges from the development of materials to the development of systems for hydrogen storage and their integration with fuel cells, was presented in this short article. For each of the different steps necessary to improve the science and technology of hydrides, some meaningful examples were described and examined. A more complete overview of the single aspects can be found in literature, but joint efforts and collective studies are valuable for the advancement of the field.

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