

Metals in Hydrogen Technology

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1. Introduction and Scope

The world transition to a sustainable and reliable carbon-free economy is the greatest challenge of the 21st century. The growing environmental awareness on climate change and health diseases caused by the massive use of fossil fuel supplies calls for immediate and radical changes. In view of a long-term energy provision solution, the only available alternative to the production of energy from fossil fuels is to harvest energy from renewable energy sources, such as sunlight, wind, tide, and biomasses. However, due to their intermittent nature and uneven availability on Earth, a complete exploitation of renewable energy sources is difficult. Therefore, energy storage media are needed. Hydrogen is widely considered as a key element for a potential energy solution. The possibility to produce hydrogen utilizing renewable energy sources and to store it presents multiple advantages. On the one hand, energy will be harvested and stored nearly without the production of harmful pollutants, and on the other hand, the security of energy supply will be guaranteed. In addition, the implementation of hydrogen as an “energy carrier” is expected to result in the effective and synergic utilization of renewable energy sources. In order to achieve these aims, hydrogen storage technology is a key technology towards the use of H₂ as an energy carrier. The shift from conventional fuels to hydrogen triggers great challenges that must be addressed quickly. However, in recent decades enormous progress has been made in developing hydrogen storage materials and hydrogen infrastructures, and more has to be made to efficiently support such an epochal transition. In this regard, the study of the interaction of metals, metal alloys, and metal-based compounds with hydrogen is extremely important.

2. Contribution to The Special Issue

Researchers from around the world were asked to contribute to this Special Issue and to underline the role of metal-based systems in hydrogen technology. As the result of their efforts, nine original research works were published.

2.1. Hydrogen Absorption in Metals with Subsurface Transport

To shed light on the transport mechanism of the hydrogen on the surface and through the lattice of metal and metal alloys is of crucial importance to design new solid-state hydrogen storage devices. Due to the difficulty of monitoring these processes in the microscopic scale, the use of simulation tools is mandatory.

Based on previously published data, Tanabe et al. [1] developed a numerical model that describes the hydrogen absorption kinetics in metal-based systems. This model takes into account the kinetics of surface dissociative adsorption, subsurface transport, and bulk diffusion. This model represents a flexible tool to perform numerical simulations of the kinetic properties of different hydrogen storage systems possessing different dimensions and structures under variable operating conditions. It must be mentioned that this model also considers the relationship between the temperature changes in metals and the temperature-dependent kinetic parameters.

2.2. Hydrogen Storage in Complex-Metal-Hydride-Based Systems

In recent decades, complex metal hydrides such as borohydrides, alanates, and amides have been intensively investigated as potential material for hydrogen storage applications [2–5].

In this Special Issue Pistidda et al. [6] reported on a cost-effective and easily scalable process for producing NaBH_4 and LiBH_4 using waste metal alloys and the metaborates of the respective borohydrides. In this work, the synthesis process was carried out through a commonly applied industrial method (ball milling BM). NaBH_4 and LiBH_4 , under a hydrogen atmosphere, were successfully synthesized with a high yield of conversions (i.e., >99%). In the case of NaBH_4 , starting from $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ the synthesis could be carried out also in the absence of an external source of hydrogen (i.e., >99%).

For borohydrides such as LiBH_4 , the reversibility of the dehydrogenation process obtained under thermal input is a key issue to be addressed in order to consider this material suitable for hydrogen storage applications. Wu et al. [7] reported on the hydrogen desorption properties and reversibility of LiBH_4 doped with AlH_3 . As the main result of their investigation, they observed that compared to pristine LiBH_4 , the addition of AlH_3 led to sensible improvements of the desorption properties, however, upon rehydrogenation the full reversibility of the material could not be achieved.

Although under moderate temperature and hydrogen pressure conditions the reversibility of single borohydrides is poor, their use in combination with selected reaction partners might lead to obtaining a hydrogen storage system possessing high hydrogen storage capacities and excellent reversibility. This approach is the so-called reactive hydride composite (RHC) [8–10]. Among the possible RHC systems containing borohydrides, in the last decade, $2\text{LiBH}_4 + \text{MgH}_2/2\text{LiH} + \text{MgB}_2$ has been one of the most investigated due to its high hydrogen storage capacity and expected low operating conditions. In their contribution, Capurso et al. [11] report on the improvement of the hydrogen storage properties of $2\text{LiBH}_4 + \text{MgH}_2/2\text{LiH} + \text{MgB}_2$ via the tuning of both the synthesis parameter as well as type and quantity of used additives. For the preparation of this system, an optimal set of additive content and of milling parameters (i.e., milling time, milling velocity, and degree of filling of the milling vials) were determined.

Alanates have been the first class of complex metal hydrides for which the reversibility of the thermally activated decomposition process was proven to be possible under moderate temperature and hydrogen pressure conditions. This finding led to the renewed interest of the scientific community in complex metal hydrides as potential hydrogen storage media. Milanese et al. [3], in their work, report on the preparative methods; the crystal structure; the physico-chemical and hydrogen absorption-desorption properties of the alanates of Li, Na, K, Ca, Mg, Y, Eu, and Sr. In addition, they describe some of the most interesting multication alanates. For the most promising alanate-based RHC systems, a brief description of their hydrogen sorption properties is also given.

In their work, Puzsziel et al. [12] report new insights into the hydrogenation process of the system Mg-Fe-H under equilibrium conditions (i.e., temperature and hydrogen pressure). In particular, the mechanism of formation of the complex metal hydride Mg_2FeH_6 from a stoichiometric mixture of Mg and Fe equal to 2:1 was studied using a series of advanced investigation techniques (i.e., volumetric analyses, X-ray diffraction (XRD), and X-ray absorption near edge structure (XANES), and the combination of scanning transmission electron microscopy (STEM) with energy-dispersive X-ray spectroscopy (EDS) and high-resolution transmission electron microscopy (HR-TEM).

2.3. Development of a Characterization Method for Metal-Based Hydrogen Storage Materials

The search for new metal-based materials possessing high hydrogen density is extremely important for the development of future hydrogen storage devices. In this Special Issue, Babikhina et al. [13] report on the development of a technique to measure the hydrogen concentrations of metal-based materials using a hydrogen analyzer. For this work, several specimens with variable amounts of hydrogen density were used. The reliability of the developed technique was evaluated using stoichiometric zirconium hydride.

2.4. Development of a Hydrogen Compression Unit Based on Metal Hydrides

The development of a reliable hydrogen refueling infrastructure is a key step toward the wide spread use of hydrogen in automotive applications. Nowadays, the hydrogen compressors used in the refueling stations are mostly of the mechanical type. However, their reliability is poor and their application in a large-scale fuel-cell market is unfeasible. In their contribution, Corgnale et al. [14] describe an alternative technology to compress hydrogen in an efficient and scalable manner. In particular, they report on a two-stage hybrid system based on electrochemical and metal hydride compression technologies. For the high-pressure stage (i.e., 100–875 bar using metal hydrides), a techno-economic analysis is presented and discussed. In addition, they developed a model of the metal hydride system integrating a lumped parameter mass and energy balance model with an economic model. A novel metal hydride heat exchanger configuration is also presented. For operating this system, several potential metal hydrides were considered. For the complete system, efficiency and costs were assessed based on the data reported in the literature of currently available materials at industrial levels.

3. Conclusions

The Special Issue “Metals in Hydrogen Technology” is a collection of nine research articles dealing with the use of metal-based systems in hydrogen storage technology. The reported information provides a solid scientific base, which without a shadow of doubt will help many scientists develop new hydrogen storage systems.

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