

Metal Hydrides and Related Materials. Energy Carriers for Novel Hydrogen and Electrochemical Storage

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1. INTRODUCTION

The seventh edition of the International Renewable and Sustainable Energy Conference (IRSEC) was held in Agadir (Sofitel Royal Bay, November 27–30, Morocco) under the Program Chair of Prof. Ahmed Ennaoui (IRESEN). IRSEC, as one of the biggest conferences in north Africa, aims at creating an international forum to facilitate discussions and exchanges in all aspects of renewable and sustainable energy. This Viewpoint will summarize the scientific presentations and stimulated discussions during the Special Session (November 28–29) on Metal Hydrides' Energy covering topics of metal hydrides and energy related issues for innovative processes and technologies, with a focus on magnesium-based hydrides, intermetallic hydrides, complex and melt hydrides, porous materials, and thin films.

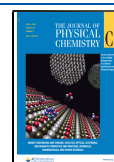
Materials such as metal hydrides are distinctive owing to the presence of the lightest element of the periodic table (H), being bonded to a metal. The chemical bond due to the metal–hydrogen interaction type and equilibrium conditions could be translated into a multitude of properties and applications, such as solid-state hydrogen and heat storage, thermal and electrochemical batteries, chemical compression, hydrogen sensors and photochromic devices. For the sake of optimization of properties and functionalities of metal hydrides, this meeting, gathering experts and international scientists, aimed at presenting the recent advances in the field of materials for energy storage and conversion. The addressed topics moved from fundamental aspects to technological challenges for safer hydrogen storage, high-capacity electrodes and Li/Mg solid-state battery electrolytes, with high ionic conductivities. The discussions covered advanced characterization studies, such as operando/in situ X-ray scattering, electrochemical data analysis, thermodynamics, reactions kinetics, and ionic/electronic properties determination, combined with theoretical calculations. The recent implication of borohydrides in all-solid-state batteries is one of the questions discussed here, in addition to the central application with respect to hydrogen storage technologies.

2. MEETING AND DISCUSSIONS

2.1. Solid-State Hydrogen and Heat Storage for Energy Conversion. Renewable energies, such as photovoltaic and wind power, are characterized by intermittent production, so their storage is necessary for an efficient management. Among several solutions proposed, the use of hydrogen as an energy carrier is under investigation. Compared

to batteries, hydrogen allows storing larger amounts of energy in small volumes, over a long time, i.e., no self-discharge issues, with low environmental impact.¹ Hydrogen can be absorbed in the form of a metal hydride under mild conditions, i.e., close to room temperatures and atmospheric pressure. This solution ensures a safe storage and reduces the volume required for storing even large quantities of hydrogen. Solid-state hydrogen storage based on hydrides has been investigated in recent years, with the goal to improve hydrogen gravimetric and volumetric density and to match thermodynamic requirements necessary for dehydrogenation reactions with an equilibrium close to ambient conditions. Accordingly, Marcello Baricco (Department of Chemistry and NIS, University of Turin, Italy) presented a talk on “Metal Hydrides as Hydrogen Carriers”, showing the advances in the field of application of metal hydrides, as well as an outline of the recent results obtained on melt hydrides as energy carriers. Using state-of-the-art characterization techniques, he reported the results obtained in his research group on hydrogen sorption and assessments of thermodynamic properties for metal hydrides and intermetallic compounds (e.g., MgH₂, La(Ni,Al)₅H₇).^{2,3} On the basis of hydrogen sorption properties, he showed applications of solid-state hydrogen tanks coupled with PEM fuel cells.⁴ A novel category of materials was presented, dealing with disordered solid solutions with a high configurational entropy $S_{\text{conf}} > 1.5R$, where R is the gas constant, which are commonly defined High-Entropy Alloys (HEA). Lattice distortion in bcc HEA allows hydrogen to accommodate not only in tetrahedral interstitial sites but also even in the octahedral ones, increasing the hydrogen gravimetric density. An in-house developed method,⁵ based on maps related to atomic radius, electronegativity, and electronic concentration, has been used to identify HEAs to be used as hydrogen carriers. As an example under study, hydrogen sorption properties of the TiV_{0.6}Cr_{0.3}Zr_{0.3}NbMo alloy, which consists of a solid solution with cubic centered body structure plus a fraction of intermetallic compounds, was discussed. Hydrogen storage at large scale remains a challenge and the HyCARE project,⁶ supported by the European Fuel Cells and Hydrogen Joint

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Undertaking,⁷ was also presented. The project involves the production of about 5 tons of a metal alloy, which will fill special containers for large-scale stationary hydrogen storage. The thermal management of the plant will take place through an innovative approach, making use of phase change materials (PCM), significantly increasing the efficiency of the process. The amount of stored hydrogen will be around 50 kg, which will represent the highest quantity ever stored in Europe with this technique. Additional details on the concept and the research behind are also given below by Erika M. Dematteis.

Takayuki Ichikawa (Graduate School of Engineering, Hiroshima University, Japan) delivered a talk on “Metal Hydrides for H₂ storage, heat storage, chemical compression, and anode of Li-ion batteries”. In several decades, metal hydrides were studied for hydrogen storage with high volumetric density of hydrogen. Recently, several functional applications of metal hydride have been developed, such as those listed in the title of the presentation.

Metal hydrides are candidate materials for heat storage. Hydrogen absorption/desorption reactions can be written according to following equation, including the heat of reaction:



Here, ΔH_{ab} is the enthalpy change for hydrogen absorption. Reaction 1 indicates that the hydrogen absorption/desorption reaction can be used as a reversible thermochemical heat storage system. The thermochemical heat storage system has a higher heat storage capacity if compared to sensible heat and latent heat systems.⁸ Titanium hydride (TiH₂) is considered to be suitable for practical applications, due to the high ΔH_{ab} of about 144 kJ/mol H₂. In order to use TiH₂ as a thermochemical heat storage medium, the hydrogenating reaction of Ti must be controlled under a wide temperature range. So, the hydrogen absorption reaction should be fast even at low temperatures. However, a high temperature of 400 °C is required to realize the hydrogen absorption reaction of pristine Ti.

In previous works about kinetic improvement of hydrogen sorption reactions in magnesium,⁹ magnesium hydride (MgH₂) is the one of the most studied metal hydride materials for solid-state hydrogen storage, owing to its high gravimetric capacity and low cost. The hydrogen absorption reaction kinetics is improved by metal or metal oxide additives. Among them, it has been revealed by Barkhordarian et al.¹⁰ that Nb₂O₅ has superior properties. Following this report, Ichikawa's group reported that Mg catalyzed by Nb₂O₅ can absorb hydrogen even at room temperature.¹¹ In these studies on MgH₂, several kinds of solid additives were investigated to improve the hydrogen absorption reaction of Ti. However, remarkable additive effects were not found. In addition, the reproducibility of the results is rather poor for all samples, which suggests that the reactivity changed during experiments. Therefore, Ichikawa has studied the hydrogen absorption reaction of Ti to improve the kinetics. The experimental details of this work were presented by Keita Shinzato (Ph.D. student in Ichikawa's group). He reported a study aimed to improve the hydrogen absorption kinetics of Ti by the ball-milling method with suitable additives.¹² In particular, the degradation of reactivity for hydrogen on dehydrogenated TiH₂ was investigated. From the obtained results, it is clarified that the pristine Ti itself should have an active surface to absorb hydrogen. However, the reactivity was lost after 1 day, even keeping the sample in a glovebox filled with purified argon, i.e., with few ppm of water

and oxygen. It is considered, from the above results, that Ti can easily oxidize, so that the reactivity for hydrogen is lost by the presence of a surface oxide layer. However, when Ti was ball-milled with acetone, the hydrogen can be easily absorbed, even at room temperature. Thus, it is found that acetone modified the surface of Ti. In addition, the hydrogen absorption properties of Ti were more improved by ball-milling with graphite. Although Ti milled with acetone was also deactivated after 7 days, the reactivity with hydrogen of the Ti milled with graphite was kept rather high for more than 7 days.

With respect to the chemical compression using metal hydrides, the van't Hoff equation (2) leads to important thermodynamic properties on the hydrogen absorption/desorption reaction of the material:

$$\ln P_{eq}/P_0 = \Delta H/R \cdot 1/T + \Delta S/R \quad (2)$$

where P_{eq} is the equilibrium pressure at a fixed temperature (T), P_0 is standard pressure, ΔH is the formation enthalpy of the metal hydride, R is the gas constant, and ΔS is the entropy of hydrogen gas at standard conditions. If a metal hydride is selected, ΔH is determined, indicating the variable value is only temperature. Therefore, eq 2 suggests that P_{eq} depends on reaction temperature, so that hydrogen can be compressed by increasing the temperature. In the presentation, it has been shown that the hydrogen can be compressed from 5 to 82 MPa by heating a Ti–Cr–Mn alloy from room temperature (RT) up to 250 °C. In order to realize a metal hydride-based compressor, the sorption properties as well as cyclic durability were studied at high temperatures and pressures. It is revealed from the investigation that a high-vanadium-containing V–Ti–Cr alloy is stable after 10 cycles, but a low-vanadium-containing V–Ti–Cr alloy is continuously degraded over a number of cycles up to 100 cycles.^{13,14}

Finally, Ichikawa discussed the question of interaction of lithium with metal hydrides for application as anode material for lithium-ion batteries. Metal hydride can react with lithium according to the following reaction:



The equilibrium voltage can be deduced from the free energy (FE) written by

$$2FE = \Delta H_{ab}^0 - T(\Delta S_{ab}^0 + \Delta S^0(H_2)) - 2\Delta H^0(LiH) + 2TS(LiH) - 2TS(Li) \quad (4)$$

Because $\Delta S^0(H_2)$, $\Delta H^0(LiH)$, $S(LiH)$, and $S(Li)$ are known, information on hydrogen absorption enthalpy and entropy changes can be obtained from equilibrium voltage measurements. TiH₂, MgH₂, and VH₂ were investigated as anode materials. As a result, quite a good relationship between thermodynamics of hydrogen absorption and reaction voltage (V vs Li⁺/Li) has been obtained for these three hydrides.^{15–17}

In the current context of sustainable, clean and safe energy, the development of novel solid-state hydrogen storage materials, with high-hydrogen density, capacities and good reversibility, is stringently required, as stated by Claudia Zlotea (CNRS-ICMPE, Thiais, France) in her presentation on “Multi-Principal-Element Alloys based on refractory elements for hydrogen storage”. She presented recent progress in hydrogen absorption in novel Multi-Principal-Element Alloys (MPEAs) based on refractory elements. These materials belong to a new metallurgical paradigm, based on the alloying of four or more elements with equal concentrations (Figure 1a).¹⁸ Most of

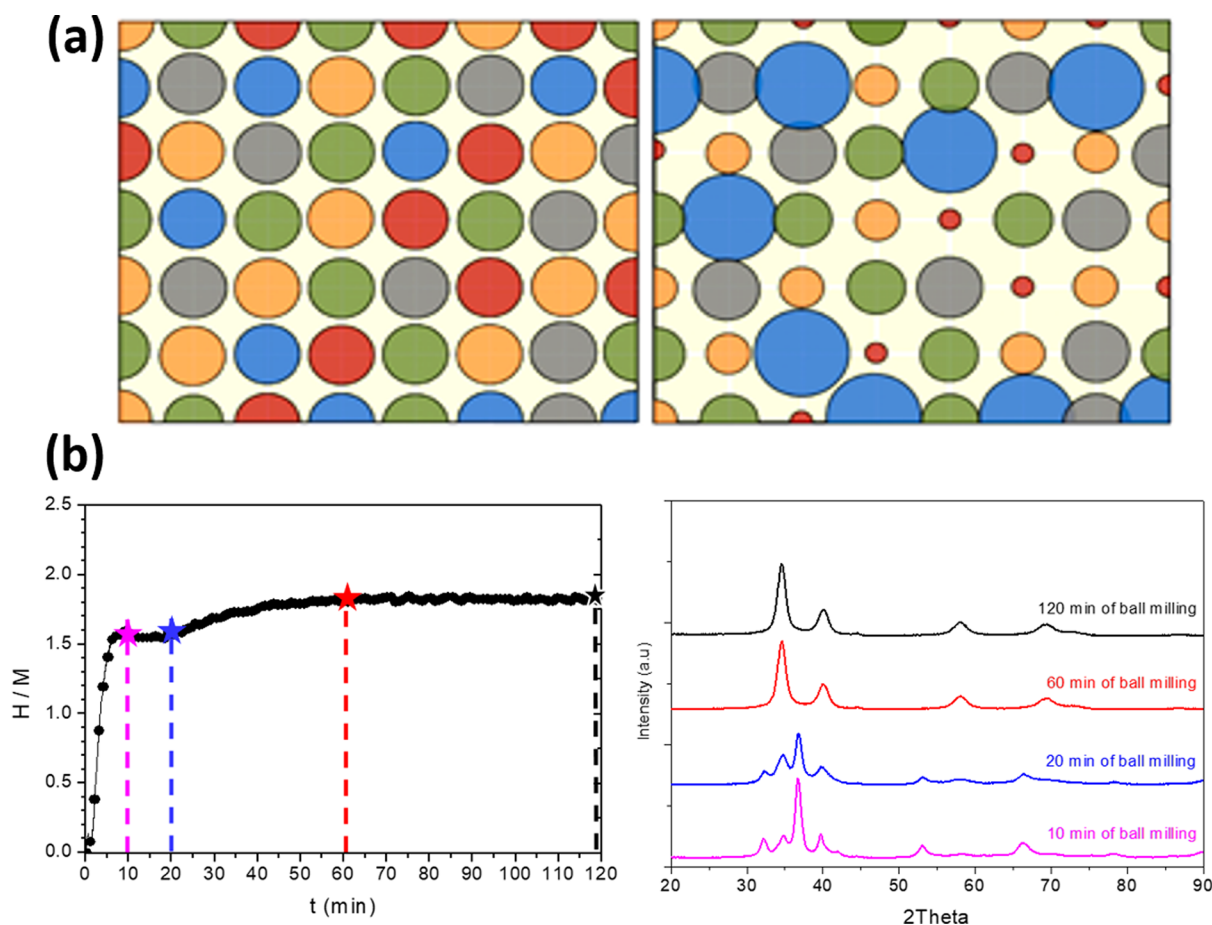


Figure 1. (a) Idealistic illustration of the concept of MPEAs (left); atomic size mismatch among different component elements in MPEAs (right). Adapted with permission from ref 19. Copyright 2016 Elsevier. (b) Hydrogen uptake profile during reactive ball milling of TiVZrNb under H₂ atmosphere (left) and the XRD patterns after 10, 20, 60, and 120 min of milling process (right) (corresponding to the stars in the left figure). Adapted with permission from ref 22. Copyright 2019 MDPI.

reports concerning these alloys describe their structure, microstructure, and mechanical properties,¹⁹ whereas functional properties, such as hydrogen sorption, are scarcely investigated.²⁰ Among all multiprincipal-element effects, the development of large lattice strain distortions due to the atomic size mismatch among different component elements is particularly interesting for hydrogen storage (Figure 1b). This parameter is defined as $\delta = \sqrt{\sum_i c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}$, where c_i and r_i are the atomic fraction and the atomic radius, respectively, of element i and $\bar{r} = \sum_i c_i \cdot r_i$. The creation of large interstitial sites might be beneficial for the insertion of large amount of hydrogen.

One of the most promising MPEA with improved hydrogen storage performances is the bcc TiVZrNbHf alloy.²¹ The hydrogenation of this alloy is a single-step reaction, with a storage capacity as high as 2.5 H/M (2.7 wt %), which is larger than that for conventional transition metal hydrides (H/M = 2.0) and unexpectedly comparable to that of rare-earth metal hydrides (H/M > 2.3). On the basis of these results, the quaternary TiVZrNb alloy, as well as quinary TiVZrNbTa and TiZrNbHfTa alloys, have been synthesized by classical melting methods or by mechano-synthesis under an inert atmosphere.^{22,23} To directly produce hydrides, researchers in Zlotea's group have employed the reactive ball milling under hydrogen gas, starting from the pure metal powders (Figure

1b). The TiVZrNb and TiVZrNbTa alloys are single-phase bcc and undergo a one-step reaction with hydrogen, forming a dihydride phase (H/M = 2). On the contrary, the TiZrNbHfTa MPEA behaves as a conventional bcc metals, with two distinct phase transitions at different pressures, forming the monohydride and then the dihydride phases. She suggested that the lattice distortion, δ , might play an important role: larger δ would favor a single-step reaction, whereas small δ values would favor a two-step transformation, as encountered for conventional bcc alloys. The hydrogen absorption/desorption in TiVZrNb and TiVZrNbTa alloys is completely reversible, and the capacities vary between 2 and 3 wt %. Despite a fading of the capacity for the first cycle, the reversible capacity of these materials stabilized around 2 wt % (for at least 10 cycles), without disproportionation or irreversible segregation during hydrogenation. In summary, Zlotea said this new research topic is only at the beginning but holds the promise of interesting fundamental findings for hydrogen storage. However, large research efforts are required to rationalize the reaction with hydrogen due to countless numbers of elemental combinations, playing with chemical composition, elemental concentration, valence electron concentration, lattice distortion, etc.

Erika M. Dematteis (CNRS-ICMPE, Thiais, France) gave a presentation on "Hydrogen storage properties of Mn and Cu substituted TiFe intermetallic compounds" toward the

development of these materials for large scale stationary application in the frame of the HyCARE project.⁶ The project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement no. 826352, in the frame of the Horizon 2020 research and innovation program. As an introduction, she highlighted the fact that the increase of air pollution and global temperatures demonstrates how essential it is to look for alternatives to fossil fuels. The efficient storage of renewable energy would enable the transition toward CO₂-free energy. In this scenario, hydrogen can be produced from renewable sources and, as an efficient energy carrier, it can be stored for a long period. Metal hydrides are safe materials for solid-state hydrogen storage under mild conditions and with high volumetric densities. TiFe is a low-cost and efficient intermetallic compound for hydrogen storage. It crystallizes in the CsCl-type cubic structure. Upon hydrogen absorption, the consecutive formation of monohydride, β -TiFeH, and dihydride, γ -TiFeH₂, occurs, with a total volume expansion of 18% and a maximum gravimetric capacity of 1.86 wt % H₂.²⁴ However, TiFe exhibits some drawbacks and particular features as hydrogen storage material. First, it is difficult to activate toward hydrogen absorption. Second, pressure–composition isotherms are characterized by two subsequent plateau pressures. All these properties are at the origin of controversial results concerning the crystal structure of TiFe hydrides/deuterides.²⁴ Elemental substitutions in the TiFe intermetallic compound can significantly change activation processes and hydrogen storage properties. The activation process is also significantly influenced by the presence of secondary or oxide phases. Interestingly, it has been shown that the compound TiFe_{0.90} requires almost no activation process for the first hydrogenation.²⁵ Partial substitution of Fe by Mn is also reported to reduce the need of alloy activation and, moreover, promotes lower equilibrium pressures at room temperature.²⁶ Thus, substituted Ti(Fe_{1-x}Mn_x)_{0.9} alloys combine easy activation and low plateau pressures, being good candidates for hydrogen storage applications. The influence of stoichiometry and Mn/Cu-to-Fe substitution in TiFe-type alloys on structural properties during reversible hydrogen loading have been investigated, evidencing a very tailorable system as a function of compositions. The Mn and Cu substitution in TiFe intermetallic compounds enables remarkable understanding on hydrogen storage, basic structural knowledge and support to the industrial application of these alloys for the development of an integrated hydrogen tank. The goal is the development of an optimized composition as a function of the thermodynamic window (i.e., temperature and pressure boundaries) defined by the HyCARE project,⁶ which aims at storing 50 kg of hydrogen by developing a storage tank with use of a solid-state TiFe-based material in large scale. The tank will be based on an innovative concept, linking hydrogen and heat storage in phase change materials to improve energy efficiency and to reduce the footprint of the whole system. It will be connected to a 20 kW Proton Exchange Membrane (PEM) electrolyzer as hydrogen provider and to a 10 kW PEM fuel cell as a hydrogen user. In 2021, the tank will be installed in the site of ENGIE Lab CRIGEN, a research and operational expertise center dedicated to gas, new energy sources and emerging technologies.

Metal–organic frameworks (MOFs) are crystalline materials and have high and regular porosity. They boast of topological and chemical tuneability.²⁷ They are therefore promising

materials for supporting (sub)nano-objects within their pores,^{28–31} for instance, for applications in hydrogen–metal interactions and heterogeneous catalysis. Accordingly, Petra Ágota Szilágyi (Queen Mary University of London) presented the recent progress in this field and research works carried out at the School of Materials Science and Engineering in the presentation entitled “Metal–Organic Frameworks: Templates, Supports, and Surface Functionalization of Pd Nanoclusters”. They were able to demonstrate that both nanoclusters and single atoms of Pd may be immobilized and stabilized on functionalized MOFs in a combined experimental–theoretical approach (Figure 2).^{32,33} Their newest research, revealed that

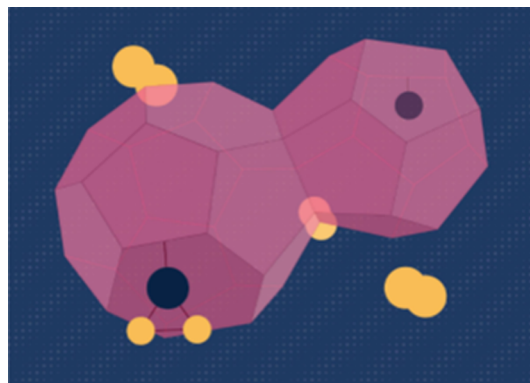


Figure 2. Illustration of the immobilization of single “naked” atoms of Pd on NH₂-MIL-101(Cr) and the interaction of the single atoms with H₂ molecules. Reprinted with permission from ref 33. Copyright 2017 The Royal Society of Chemistry.

the adequate matching of linker functionality and guest materials, mostly based in transition metals, may allow for the controlled formation of nanoclusters,³⁴ based on a powerful combination of experimental and modeling approach. She emphasized that, in this size regime, the properties of materials display a higher size than chemistry dependence; therefore this approach seems to unlock the opportunity of the synthesis and eventual design of nanocomposites with unprecedented properties.

Wojciech Grochala (Center of New Technologies, University of Warsaw, Poland) attracted the attention on the importance of “Waste materials from thermal decomposition of hydrogen storage materials—the case of BN synthesis from (NH₄)₃Mg(BH₄)₅ precursor”. One typical requirement underlying the use of chemical hydrogen storage materials in the solid state is related to reversibility of hydrogen desorption, which should either be fast enough to permit charging of the vessel at the hydrogen filling station or at least be so easy that the chemical transformations of material recovered from the replaceable “cartridge” are possible at chemical factory.³⁵ However, in many cases reversibility of H₂ desorption is bleak, as evidenced by a large number of protonic-hydridic materials. In such a case, the thermally decomposed chemical hydride constitutes a waste. In his presentation, he showed that a “waste”, albeit useless for hydrogen reloading, may actually consists of technologically useful material. For instance, the case of (NH₄)₃Mg(BH₄)₅ was described which, upon pyrolysis, yields amorphous BN as shown in Figure 3 (mostly quasi-hexagonal but also some quasi-cubic).³⁶ BN is a very important ultrahard and refractory material that finds numerous uses. This synthetic pathway provides indeed for the formation of a-

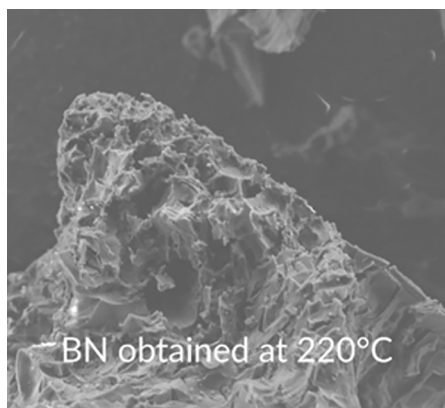


Figure 3. SEM image of amorphous BN obtained from pyrolysis of $(\text{NH}_4)_3\text{Mg}(\text{BH}_4)_5$ precursor. Reprinted with permission from ref 36. Copyright 2020 The Royal Society of Chemistry.

BN already at 220 °C, thus at temperature at least 1000 °C lower than the current commercial protocols.

2.2. Metal Hydrides for Electrochemical Energy Storage. Michael Heere (IAM-ESS, Karlsruhe Institute of Technology, Germany) presented a talk on “Dynamics and structural evolution in a solid-state Mg-ion conductor” based on magnesium tetrahydroborate, colloquially referred to as magnesium borohydride, and its dynamics with a comprehensive overview given in ref 37. The development of the field of [complex] metal hydrides has been enormous in the last 10 years, and Mohtadi and Orimo stated that the present research on complex metal hydrides is experiencing a “renaissance as energy materials”.³⁸ For the success of future complex metal hydride-based research, the development of highly conductive electrolytes and electrodes is one of the main requirements for a successor of the Li-ion battery.³⁹ A first Mg-ion conductor based on complex metal hydrides was reported in 2012. Mohtadi et al.⁴⁰ demonstrated the possibility to employ magnesium borohydride, $\text{Mg}(\text{BH}_4)_2$, dissolved in 1,2-dimethoxyethane (DME) in a rechargeable magnesium battery. Recently, new compounds synthesized from $\text{Mg}(\text{BH}_4)_2$ and organic complexes, such as ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$, a b b r e v i a t i o n “ e n ”) a n d d i g y l m e ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{OCH}_3$),^{41,42} were reported to have exceptionally high magnesium-ion conductivity. The reported values were conductivities of $\sigma = 6 \times 10^{-5} \text{ S cm}^{-1}$ at 70 °C in the solid state for $\text{Mg}(\text{en})_{1.0}(\text{BH}_4)_2$ and of $\sigma = 2 \times 10^{-5} \text{ S cm}^{-1}$ at 77 °C for $\text{Mg}(\text{BH}_4)_2$ -diglyme_{0.5}. Nevertheless, the mechanochemical synthesis tends to form X-ray amorphous $\text{Mg}(\text{BH}_4)_2$ and it was postulated by all authors that the latter is beneficial for the conductivity in Mg-ion conductors. In the ongoing studies, Heere is employing total scattering to elaborate the local structure, electrochemical impedance spectroscopy for ionic conductivities measurements and quasi-elastic neutron scattering (QENS) studies were employed to investigate the dynamics of porous and amorphous $\text{Mg}(\text{BH}_4)_2$. QENS of $\text{Mg}(\text{BH}_4)_2$ shows that the low-energy excitation spectrum strongly depends on the local (crystal or X-ray amorphous) structure, as can be seen by the comparison of as-received γ - $\text{Mg}(\text{BH}_4)_2$ and ball milled, amorphous compound. While as-received γ - $\text{Mg}(\text{BH}_4)_2$ shows almost no quasi-elastic scattering up to 37 °C, the amorphous sample clearly shows a different low-energy excitation spectrum with a higher rotational mobility of the $[\text{BH}_4]$

tetrahedra. A high rotational mobility is proposed to be a fundamental necessity for high Mg-ion conductivity. This is supported by an almost 2 orders of magnitude higher conductivity in the ball milled sample compared to as-received γ - $\text{Mg}(\text{BH}_4)_2$ at 80 °C. Recently, Le Ruyet et al.⁴³ reported the same correlation of an amorphous phase found in a Mg–B–N–H system by NMR with a high conductivity of $3 \times 10^{-6} \text{ S cm}^{-1}$ at 373 K for a solid-state Mg conductor based on $\text{Mg}(\text{BH}_4)(\text{NH}_2)$. In general, the work on Mg–B–N–H systems and exploration for instance of dihydrogen bonds seems to increase.⁴⁴ Heere evidenced particularly the neutrons source as a unique probe for nondestructive structural and dynamical studies of energy materials, especially for future investigation by fast measurements,⁴⁵ and for the development of highly conductive solid-state Mg electrolyte. He stated that neutrons are one of the main requirements for successful post-Li battery research. With these very suitable conductivities in mind, $\text{Mg}(\text{BH}_4)_2$ is very promising as a precursor with organic ligands in solid-state Mg electrolytes, while the structure of $\text{Mg}(\text{en})_{1.0}(\text{BH}_4)_2$ has not yet been reported. For general information on borohydrides, he referred to refs 46 and 47.

The University of Glasgow (UK) was represented by Siobhan C. Stevenson (The Gregory research group), who provided a presentation on “Mixed borohydride-halides as potential solid-state electrolytes”. She investigated the complex lithium–sodium borohydride-halides as a new class of Li^+ conductor with the potential for application as solid-state electrolytes in Li-ion batteries. The structure, stability and ionic conductivity of these new materials were studied as a function of both metal and non-metal composition and compared with the behavior of the known phases of LiBH_4 (Figure 4). This study considered the viability of solid

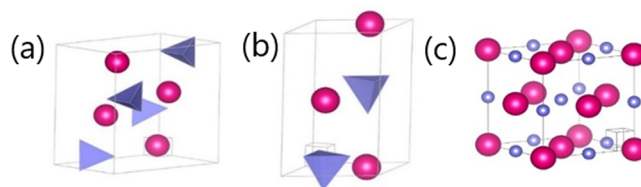


Figure 4. Crystal structures of the polymorphs of LiBH_4 : (a) “low temperature” LT phase (orthorhombic $Pnma$); (b) “high temperature” HT phase (hexagonal $P6_3mc$); (c) “high pressure” HP phase (cubic $Fm\bar{3}m$).

solutions of the form $\text{Li}_y\text{Na}_{1-y}(\text{BH}_4)_{1-z}\text{X}_z$, where X = halide and where X, y, and z could be varied independently. The extent of the metal solubility (y) was explored for fixed values of X and z. Similarly, the limits of borohydride solubility ($1 - z$) were determined for fixed y (e.g., $y = 0.5$) and X = I. Within the experimentally defined solubility ranges, certain judicious substitutions were discovered to stabilize cubic rock salt borohydride phases, a structure that is otherwise only observed for LiBH_4 at high pressure.⁴⁸ The NaCl-type unit cells expand (linearly) with increasing z for X = I. No solid solution was found for either $z = 0$ or $z = 1$. Solid solution members with fixed metal content, $y = 1$ are isostructural to HT- LiBH_4 itself and all exhibit superionic Li-ion conductivity.^{49,50} She demonstrated that high conductivity is also prevalent in the mixed-ion HP phases.

Jean-Pierre Bonnet (LRCS, Amiens, France/Hiroshima University, Japan), in close collaboration with Takayuki Ichikawa (mentioned above), delivered a talk on recent

research works entitled “CaH₂–LiBH₄ as negative electrode for solid-state lithium-ion batteries: an unexpected electrochemical behavior”. The work was carried out during his sabbatical leave at the Graduate School of Engineering (Hiroshima University). Metal hydrides were introduced by Bonnet’s group in France more than 10 years ago as prospective lithium-ion batteries negative electrode materials. Binary, ternary, and complex metal hydrides can be employed, working as conversion materials, giving metal(s) and LiH during reduction.^{51,52} Owing to a very low working potential of about 0.5 V vs Li⁺/Li⁰, very small polarization (<0.2 V) and a large reversible capacity of 1480 mAh·g⁻¹, MgH₂ constitutes herein one of the most investigated metal hydrides for electrochemical applications. However, metal hydrides suffer the unwelcome drawbacks of constrained electrochemical reversibility and slow kinetics in the usual liquid electrolytes. In 2015, Ichikawa et al.¹⁵ made a major breakthrough with the use of a solid-state electrolyte (LiBH₄) with MgH₂ anode, obtaining a high reversible capacity of 1650 mAh·g⁻¹ with an extremely low polarization of 0.05 V and durable cyclability. The purpose of Bonnet’s work is to study the electrochemical behavior of an anode composite CaH₂/LiBH₄/acetylene black vs Li, using LiBH₄ as electrolyte. An unexpected large plateau (>1500 mAh·g⁻¹) at about 0.18 V is observed and tentative explanations were given, with the help of study on composites involving Ca(BH₄)₂, CaB₆, and SrH₂ in place of CaH₂. It seems here that both CaH₂ and LiBH₄ (with theoretical capacities of 1274 and 4992 mAh·g⁻¹, respectively) are involved in the conversion reaction.

In the same context, Abdel El Kharbachi (Helmholtz Institute Ulm, Germany) talked about the “Optimization of metal hydride anodes and LiBH₄-based electrolytes for all solid-state lithium-ion batteries”. The work was carried out during his research stay in the Hauback group (IFE, Norway). The first part deals with the mechanistic properties of the MgH₂ anode as a function of milling conditions, particle size, cyclability, and electrolyte type (liquid or solid).^{53,54} The effect of an electrochemically “active” oxide such as CoO on the cycling performance of the MgH₂ anode was shown in a solid-state battery, using a LiBH₄ solid electrolyte at 120 °C (Figure 5). The addition of CoO seems to improve the cyclability, thanks to the reduced diffusion pathways and less polarized electrodes.⁵⁵ The findings pointed to a means of guided formation of MgH₂–CoO nanocomposites, acting as a conversion-type electrode for all-solid-state Li-ion batteries. The second part of his talk focused on optimizing the ionic

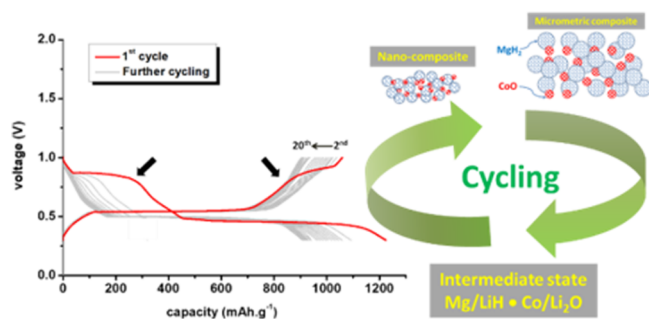


Figure 5. Electrochemical cycling of the cell 75MgH₂-25CoO/LiBH₄/LiBH₄/Li disc and illustration of the different phase transformations leading to a nanocomposite electrode. Adapted with permission from ref 55. Copyright 2018 The Royal Society of Chemistry.

conductivity of LiBH₄-based electrolytes with addition of an amorphous halide–sulfide system. LiBH₄ is a good Li-ion conductor only above its solid-state phase transition temperature ($T_{tr} \sim 110$ °C). The high- T phase can be stabilized by partly substituting BH₄⁻ with halides, e.g., Li(BH₄)_{0.75}I_{0.25}, thus suppressing the phase transition and preserving high ionic conductivity on cooling to RT. El Kharbachi presented further their approach of investigation of the properties of the Li(BH₄)_{1-y}X_y (X = Cl, Br, I) phases when embedded in a 0.75Li₂S·0.25P₂S₅ amorphous matrix for application in all-solid-state lithium batteries.⁵⁶ It has been found that the LiBH₄-based system improves the ductility and conductivity of the composite electrolyte, which is a priori important for the engineering of the cells. Although structural details need to be studied further, the electrochemical performance and cycling stability were shown to be suitable for application in secondary lithium batteries.

2.3. Metal Hydride Thin Films for Optical Hydrogen Sensors.

Lars J. Bannenberg (Faculty of Applied Sciences, Delft University of Technology) presented recent progress on “Metal hydride-based optical hydrogen sensors beyond palladium”. As hydrogen is playing a key role in the transition to a sustainable economy and hydrogen–air mixtures are highly explosive, hydrogen detection in a fast, reliable, and accurate manner is crucial to ensure its safe handling. Thin film metal hydride-based optical hydrogen sensors provide an attractive option to sense hydrogen in a variety of conditions and have an attractive safety benefit over other methods of detection. In fact, they do not require the presence of electrical leads near the sensing area. These sensors rely on a change of the optical properties arising from a change in the hydrogenation of the metal hydride sensing layer in response to a different partial hydrogen pressure in the environment of the sensor.⁵⁷ The metal hydride most considered so far as a sensing layer is palladium: it can readily dissociate hydrogen at room temperature and has a suitable optical contrast. However, apart from hysteresis, palladium-based thin films suffer from a limited operating range and are only able to monitor hydrogen at relatively high partial pressures. To circumvent the undesirable hysteresis arising from the first-order metal-to-metal hydride transition, one can, e.g., alloy palladium with gold, which can, for high-enough Au concentrations, eliminate the first-order transition. However, unlike, e.g., nanoparticles, these continuous thin films of Pd_{1-y}Au_y still feature a hysteresis resulting from the clamping of the Pd_{1-y}Au_y thin film to the substrate. Together with the markedly different hydrogen solubility of nanoparticles and thin films, it indicates that different ways of nanostructuring can have a profound impact on the response of a metal hydride to hydrogen.⁵⁸ Another approach to design effective hydrogen sensors is to separate the hydrogen dissociation and sensing functionality. Both palladium-capped tantalum and hafnium thin films offer a stable and hysteresis-free optical response to hydrogen over an exceptionally large pressures of at least six orders (Figure 6a). Remarkably, in situ neutron reflectometry shows that the hydrogen content in both cases proves to be linear with the optical signal (Figure 6b). In a wider perspective, the results on tantalum and hafnium illustrate that palladium-capped transition metals provide ample opportunities to design optical hydrogen sensors with desirable properties.^{59,60}

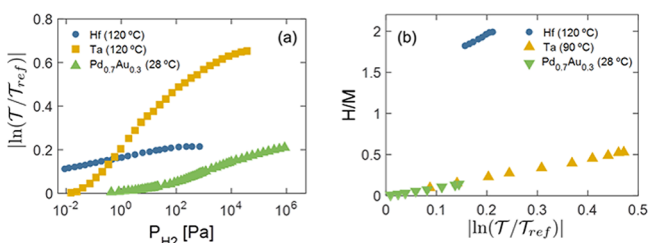


Figure 6. (a) Comparison of the sensing range and optical contrast for a Pd-capped 40 nm hafnium thin film (120 °C), a Pd-capped 40 nm tantalum thin film with a 4 nm Ti adhesion layer (120 °C) and a 40 nm Pd_{0.7}Au_{0.3} thin film with a 4 nm Ti adhesion layer (28 °C). The white-light transmission T was measured relative to that of the dehydrogenated reference state T_{ref} . (b) Hydrogen-to-metal ratio H/M as a function of the optical contrast as determined using *in situ* neutron reflectometry. Adapted with permission from ref 60. Copyright 2019 Elsevier.

3. SUMMARY AND OUTLOOK

As important as the production of CO₂-free energy is, so is the motivation to develop efficient storage of renewable energies for mobile and stationary applications. There is no doubt that metal hydrides continue to attract the overall materials science community, and it is not only restrained to a specialized hydrogen field. This is mainly the case when it is the matter of coupled technologies with other systems such as fuel cells, heat management, and batteries.

Hydrogen is considered an energy carrier and its chemical energy can be converted into electricity through a chemical reaction with oxygen from a fuel cell. Therefore, coupling energy storage systems with renewable energy sources through an electrolyzer, which can transform electric energy into hydrogen chemical energy, is considered a high sustainable process of production and exploitation of renewable energies. Integrated systems are constituted by a metal hydride tank and a PEM fuel cell, in which the waste heat generated in the fuel cell is used to supply the necessary heat required for desorption of hydrogen from the tank. The field of application of the integrated power system is in combination with renewable sources: the hydrogen can be produced by electrolysis of water using the energy from a renewable source (e.g., photovoltaic); it is then stored and converted into electric energy by the proposed integrated power system, that allows energy storage in the form of hydrogen and its reuse when the renewable source is not available, for example, at night if solar power is exploited. The developed power system could replace batteries and could be applied in the case of a production plant not connected to the power grid, such as in remote areas. As an example, an integrated power system, showing a total energy production of 4.8 kW h, over more than 6 h of working activity, is reported in ref 4. In the SSH2S (Fuel Cell Coupled Solid-State Hydrogen Storage Tank) project, a solid-state hydrogen storage tank based on complex hydrides has been developed and it was fully integrated with a High-Temperature Proton Exchange Membrane (HT-PEM) fuel cell stack. The hydrogen storage tank was designed to feed a 1 kW HT-PEM stack for 2 h to be used for an Auxiliary Power Unit (APU).⁶¹

With respect to batteries, hydrides can be utilized as anodes with high capacity (e.g., 2 Ah·g⁻¹ for MgH₂). A lot of effort has been expended to improve the cyclability, and significant results have been reached in a solid-state battery with LiBH₄

solid electrolyte. Demonstration of high-energy density fuel cells with suitable cathodes will be the challenge of upcoming research studies.^{62,63} As mentioned for the beneficial contribution of electrodes, solid-state electrolytes based on borohydrides are a typical example that the battery community is now taking seriously along with the popular garnet-type solid electrolytes.^{64,65} It has been demonstrated that the ionic conductivity is a prerequisite for application in batteries, but unfortunately it is not win; in fact, other important issues need to be tackled, such as chemical compatibility, interfaces, heterogeneity, and mechanical properties, so important for the cell engineering and design, in addition to the structural and volumetric changes during cycling. At first, borohydrides meet some of these criteria regarding conductivity and ductility, (thermo)chemistry, and low-density materials. Future research might be directed to the understanding and assessment of interfaces and physical and mechanical properties of the selected solid-electrolyte and electrodes. The specificity of the application may become a determining aspect in the selection of the suitable configuration. Substantial research efforts are being conducted to study new approaches toward the utilization of borohydrides and *closo*-type complex hydrides in composites.^{66,67} Thanks to their ductility and ionic conductivity, borohydrides can be also employed as additives for binder-free solid-state batteries. Since the demonstration of LiBH₄ thin film growth,⁶⁸ this could be considered for mitigating the formation of dendrite and oxidation layers on the surface of lithium metal. Another direction is focused on the development of Mg²⁺ conducting solid electrolytes for application in Mg batteries, which offer higher volumetric capacity compared to lithium at low cost. At present, the technology can be only possible at high- T owing to the low ionic conductivity and Mg²⁺-ion mobility.⁶⁹ In addition, metal hydrides can be utilized as optical hydrogen sensors for the detection of hydrogen at low pressure levels according to changes in the optical properties, which is a step forward regarding the increase of the safety for advanced hydrogen-based systems.

Lastly, compared to the traditional conferences for hydrogen community (MH, E-MRS, Gordon, etc.) there no doubt that IRSEC is a particular place to meet scientists and experts in the African context undergoing full energy boom. The eighth edition of IRSEC will continue the tradition of drawing the best scientists in the field of sustainable energy, which will be held in Tangier (Morocco), November 25–28, 2020. We thank the local organizers and students, the participants, and the speakers of this Special Session for their excellent contributions.

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