

Editorial

Beyond Hydrogen Storage—Metal Hydrides as Multifunctional Materials for Energy Storage and Conversion

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Following the E-MRS (European Materials Research Society) fall meeting 2019, Symposium L, this Special Issue of *Inorganics*, entitled “Beyond Hydrogen Storage—Metal Hydrides as Multifunctional Materials for Energy Storage and Conversion”, is dedicated to the wide range of emerging energy-related inorganic hydrogen-containing materials. We have collected six publications with more than 130 journal pages, which clearly document the flourishing future metal hydride-based materials due to their excellent physical and chemical properties. The guest editors hope that you will enjoy and learn from the breadth of science presented in this open-access Special Issue where fundamental scientific concepts are explored beyond the classical hydrogen storage applications of metal hydrides.

The urgent need for energy storage materials for a sustainable and carbon-free society is the main stimulant for the new dawn in the development of batteries, hydrogen storage materials, and thermal energy storage. For example, all-solid-state batteries based on hydroborate electrolytes, including alternative cations such as Na^+ and Mg^{2+} , are considered safer and cheaper (due to the higher abundance of the metals), with potentially higher energy densities when compared to state-of-the-art Li-ion batteries [1–3]. Hydrogen fuel cell systems also serve as perfect solutions to address the intermittent energy supply from renewable sources by providing an uninterrupted sustainable supply of electricity for stationary applications as well as to provide an energy source for benign zero-emission vehicles, with clean water as the only by-product [4,5]. Renewable energy sources combined with efficient ways of energy storage will be a key enabler to future technologies. Active materials for energy storage require a certain structural and chemical flexibility to reversibly store hydrogen (for hydrogen storage) or cations, e.g., lithium (for batteries). Other combinations of materials ensure that certain physical and chemical property criteria are met to act as solid-state electrolytes, separators, or even membranes.

Robert C. Bowman Jr.’s contribution to this Special Issue actually made it to space—SPACE—the final frontier! Between June 2009 and October 2013, the Planck Mission of the European Space Agency (ESA) deployed a metal hydride compressor with gas-gap heat switches. The concept, development, testing, and space flight operation for the Planck Sorption Cryocoolers are eloquently described [6]. Six individual sorbent beds filled with $\text{LaNi}_{4.78}\text{Sn}_{0.22}\text{H}_x$ were employed for absorption and desorption of hydrogen. Thus, a liquid hydrogen phase was continuously generated in each Planck Sorption Cryocooler by coupling a Joule–Thomson expander to hydrogen gas initially pressurized to ~ 30 bar and subsequently discharged at a pressure of ~ 0.3 bar. The pressures were varied by alternately heating

and cooling this hydride including temperature modulation with an integrated Gas-Gap Heat Switch (GGHS). The novel GGHS used the low-pressure hydride $ZrNiH_x$ to vary thermal conductance between the bed containing the $LaNi_{4.78}Sn_{0.22}H_x$ sorbent and the rest of the compressor system. The Planck Mission was turned off after more than four successful years of space flight operation in 2013, with the Planck Sorption Cryocoolers providing sufficient cooling for excellent operation during this mission.

Eli Grigorova et al. describe the “Investigation of hydrogen storage characteristics of MgH_2 based materials with addition of Ni and activated carbon” [7]. The subjects of this investigation are the hydrogen absorption and desorption characteristics of the two composites. Firstly, 80 wt % MgH_2 –15 wt % Ni–5 wt % activated carbon (synthesized from Polyolefin Wax (POW), a waste product of polyethylene production at low pressure) and 90 wt % MgH_2 –5 wt % Ni–5 wt % POW, were prepared by ball milling under argon atmosphere. The structure, composition, and surface properties of the two samples before and after hydrogenation are characterized by X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). The maximum hydrogen absorption capacity of the composites at a temperature of 573 K and after 60 min of hydrogenation is 5.3 wt % for the material with higher Ni content and 5.5 wt % for the lower Ni content. The results from TEM characterization, e.g., the polycrystalline SAED (Selected Area Electron Diffraction), show the presence of graphite, Mg, and monoclinic Mg_2NiH_4 . The presence of both additives, i.e., nickel and activated carbon derived from POW, has a positive impact on hydrogenation kinetics and the capacity achieved.

Efi Hadjixenophontos et al. give an excellent overview of novel complex metal hydrides, summarizing the activities of the Marie Skłodowska-Curie Actions (MSCA) Innovative Training Network (ITN) ECOSTORE [8]. Borohydride- and nitride-based materials were the main focus of the ECOSTORE project as they are not only of interest within hydrogen storage materials research, due to their high hydrogen storage capacities of up to 18 wt %, but they are also promising materials for electrochemical energy storage such as solid-state ionic conductors and conversion materials for anodes. The review by Hadjixenophontos and co-workers discusses both aspects of metal borohydrides in detail, covering fundamental aspects of thermodynamics and crystal chemistry as well as application relevant topics including tailoring the kinetics of the reactive complex hydride system $LiBH_4/MgH_2$ with cost-effective additives to enable practical applications. For battery applications, the role of large, stable anions as solid conductors and the effect of anion mixing to enhance ionic conduction is highlighted for Na^+ ion batteries. As indicated by the authors, Mg^{2+} ion conductors are gaining more and more attention as well. In particular, solid-state Mg-ion conductor materials were immensely accelerated by Roedern et al. through a new compound, $Mg(en)(BH_4)_2$ (*en*-ethylenediamine) with a Mg-ion conductivity of $\sigma = 6 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at $T = 343 \text{ K}$ [9]. The synthesis process was based on ball milling and thermal treatment, and it was reported that an amorphous phase, possibly amorphous $Mg(BH_4)_2$, is beneficial for overall conductivity. Elaborating the influence of amorphous $Mg(BH_4)_2$ on the conduction process has recently been published [10]. In addition, Jensen et al. demonstrated a conductivity of $\sigma = 3.3 \times 10^{-4} \text{ S cm}^{-1}$ at $T = 353 \text{ K}$ for $Mg(BH_4)_2 \cdot NH_3$ [11]. The conclusions of this work in connection with an earlier study [12] suggest a novel ion conduction mechanism in these materials [11]. In general, the work on Mg^{2+} conductors and especially $M-B-N-H$ systems ($M = Li, Mg$) has a positive impact on material properties thus increasing their potential as new battery materials [13–16].

Thermochemical energy storage is an emerging research field to accommodate future requirements for green energy sources, e.g., concentrating solar thermal power plants, with higher operating efficiencies, and, most importantly, cost competitiveness [17,18]. A variety of materials has been studied for this purpose, including metal carbonates, hydroxides, and hydrides [5,17,19]. The paper by Claudio Corgnale specifically deals with Lithium Hydride (LiH), which has great potential due to its high reaction enthalpy of $190 \text{ kJ}\cdot\text{mol H}_2^{-1}$ [20]. However, related technical issues have encouraged researchers to find solutions to overcome the high stability of LiH by adding Si, Ge, Sn, or Al. Corgnale describes three different scenarios of the thermochemical energy storage system coupled with a low-temperature metal hydride and evaluates them utilizing a techno-economic

model. The techno-economic model is expanded into a sensitivity analysis, which concludes that the raw cost of lithium is the main contributor to the overall cost of the energy storage system. Thus, further research into the metal hydride selection is required to make the overall system cost more competitive [21–23]. Corngale unequivocally presents an important approach to evaluating materials/systems for thermochemical energy storage, an approach that is relevant to any future analysis of such systems.

Improved kinetic activity, increased storage capacity, scale-up, and long-term cycling stability are several important aspects related to the practical use of metal hydrides as emphasized in the article by Daniele M. Gattia et al. [24]. This study describes the use of economically viable materials, ball-milled MgH_2 with the addition of Fe as a catalyst, plus the use of Expanded Natural Graphite to improve thermal conductivity within the compressed cylindrical pellets. These pellets underwent 45 sorption cycles of 1.2 bar H_2 desorption and 8 bar H_2 absorption at 310 °C in a Sievert's apparatus. Each pellet was characterized at different time periods, namely, directly after compaction/before cycling, after the 20th cycle, and after the final 45th cycle using XRD, Rietveld analysis, and Scanning Electron Microscopy. The results show that although there is a slight decrease in kinetics after the initial cycle, the kinetic activity and hydrogen capacities for both desorption and absorption remain relatively stable for the duration of the 45 cycles. This is also correlated with the changes of crystallite size of the main component, MgH_2 , indicating very few sintering effects during the course of the experiment. The microstructural changes during cycling also show that the morphology remains intact in both the radial and axial directions. Gattia et al. showcase the effectiveness of inexpensive energy storage materials in pellet form over long cycling periods thereby demonstrating the highly practical nature of these systems for potential use in the future.

Jakob B. Grinderslev et al. describe in their paper, "Synthesis, Crystal Structures and Thermal Properties of Ammine Barium Borohydrides", candidates for solid-state NH_3 and H_2 storage as well as fast cationic conductors [25]. The authors focus on the synthesis method of two ammine barium borohydrides, $\text{Ba}(\text{BH}_4)_2 \cdot x\text{NH}_3$ ($x = 1, 2$), and investigate those by time-resolved temperature-varied in situ synchrotron radiation powder X-ray diffraction, thermal analysis, infrared spectroscopy, and photographic analysis. They report the compound $\text{Ba}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ to crystallize in an orthorhombic unit cell with space group symmetry $Pnc2$, thus being isostructural to $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ [26], forming octahedral $[\text{Ba}(\text{NH}_3)_2(\text{BH}_4)_4]$ complexes connected in a two-dimensional layered structure, interconnected by dihydrogen bonds, $\text{N}-\text{H}^{\delta+} \cdots ^{\delta-}\text{H}-\text{B}$. A new structure type is observed for $\text{Ba}(\text{BH}_4)_2 \cdot \text{NH}_3$, which crystallizes in an orthorhombic unit cell with space group symmetry $P2_12_12_1$, forming a three-dimensional framework structure of $[\text{Ba}(\text{NH}_3)(\text{BH}_4)_6]$ complexes. The crystal structure is built from distorted hexagonal chains, where NH_3 groups form dihydrogen bonds to the nearby BH_4^- -groups within the chain. $\text{Ba}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ is unstable at room temperature and releases NH_3 in two subsequent endothermic reactions with maxima at 49 and 117 °C, eventually reforming $\text{Ba}(\text{BH}_4)_2$. Finally, the authors demonstrate that the thermal stability and composition of the gas release for the ammine alkaline earth metal borohydrides can be correlated to the charge density of the metal cation.

To conclude, the Special Issue: "Beyond Hydrogen Storage—Metal Hydrides as Multifunctional Materials for Energy Storage and Conversion" is a collection of six research articles dedicated to the wide range of emerging energy-related inorganic hydrogen-containing materials. A recent quote from Mohtadi and Orimo states that the present research on complex metal hydrides is experiencing a "renaissance as energy materials", motivating future research on metal hydrides [27]. This statement is certainly evident, from not only the articles published in this Special Issue, but also from the enthusiasm and knowledge displayed by the participants and presenters at the European Materials Research Society (E-MRS) symposium itself.

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