



Recent advances in metal hydrides for clean energy applications

Ewa C.E. Rönnbro and Eric H. Majzoub, Guest Editors

Metal hydrides are a fascinating class of materials that can be utilized for a surprising variety of clean energy applications, including smart solar collectors, smart windows, sensors, thermal energy storage, and batteries, in addition to their traditional application for hydrogen storage. Over the past decade, research on metal hydrides for hydrogen storage increased due to global governmental incentives and an increased focus on hydrogen storage research for polymer electrolyte membrane fuel cell operation. Tremendous progress has been made in so-called complex metal hydrides for hydrogen storage applications with the discovery of many new hydrides containing covalently bound complex anions. Many of these materials have applications beyond hydrogen storage and are being investigated for lithium-ion battery separator and anode materials. In this issue of *MRS Bulletin*, we present the state of the art of key evolving metal-hydride-based clean energy technologies with an outlook toward future needs.

Introduction

Hydrogen storage will be a cornerstone technology for energy utilization in the 21st century as components of a hydrogen economy come together. **Figure 1** represents the clean, nonpolluting cycle of the “hydrogen economy”¹ utilizing hydrogen as an energy carrier to eventually replace fossil fuels and enable an environmentally friendly world with a sustainable infrastructure, including hydrogen production, storage, and delivery. By using renewable resources such as sunlight to split water, hydrogen may be produced cleanly, and can efficiently be stored in metals and other complex host frameworks for use in fuel cells, which could power many motive and non-motive applications, including forklifts, wheelchairs, lawn mowers, bicycles, portable power, laptops, stationary and grid applications.^{2,3} The product from operating a fuel cell is water, and implementing a hydrogen-based economy is therefore the cleanest long-term solution to generate power.

Metal hydrides are a fascinating and important class of materials that can be used for various energy applications and devices, including batteries, hydrogen storage, thermal energy storage, heating/cooling devices, thin films for smart solar collectors, smart windows, and sensors.⁴⁻⁸

Several interesting physical phenomena have been observed with the introduction of hydrogen into a metal or metal alloy (e.g., electric, magnetic, optical, and mechanical transitions).

Phase transitions occur reversibly from normal conductance to superconductivity, from metals to semiconductors or insulators, or from ferromagnetic to paramagnetic under certain pressures and temperatures. Some of these phenomena are described in this issue.

The last *MRS Bulletin* theme issue devoted to hydrogen storage in 2002⁹ came at a time of resurgent interest brought about by Bogdanovic's seminal paper¹⁰ illustrating reversible hydrogen storage in sodium alanate, NaAlH_4 when doped with transition metals. A few alanate compounds had been previously studied, but without transition metal dopants, they were effectively irreversible. This discovery more than doubled the weight percent of hydrogen stored in solid compounds from about 1.6% for LaNi_5H_6 to 5.5% for NaAlH_4 . The research that followed this discovery, largely funded through the US Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) and Basic Energy Sciences (BES), led to the discovery and study of a great many new compounds and even compound classes for hydrogen storage. During these years, research focus shifted to hydrogen-rich complex metal hydrides, and in this issue, Graetz and Hauback review progress on alane and alanates, and Wang et al. review borohydrides and amides. It is impossible to cover all progress and phenomena, but we have selected specific areas to showcase the breadth of potential clean energy applications.

Ewa C.E. Rönnbro, Pacific Northwest National Laboratory, Energy and Environment Directory; Ewa.Ronnbro@pnnl.gov
Eric H. Majzoub, University of Missouri–St. Louis, Department of Physics and Astronomy; majzoub@umsl.edu
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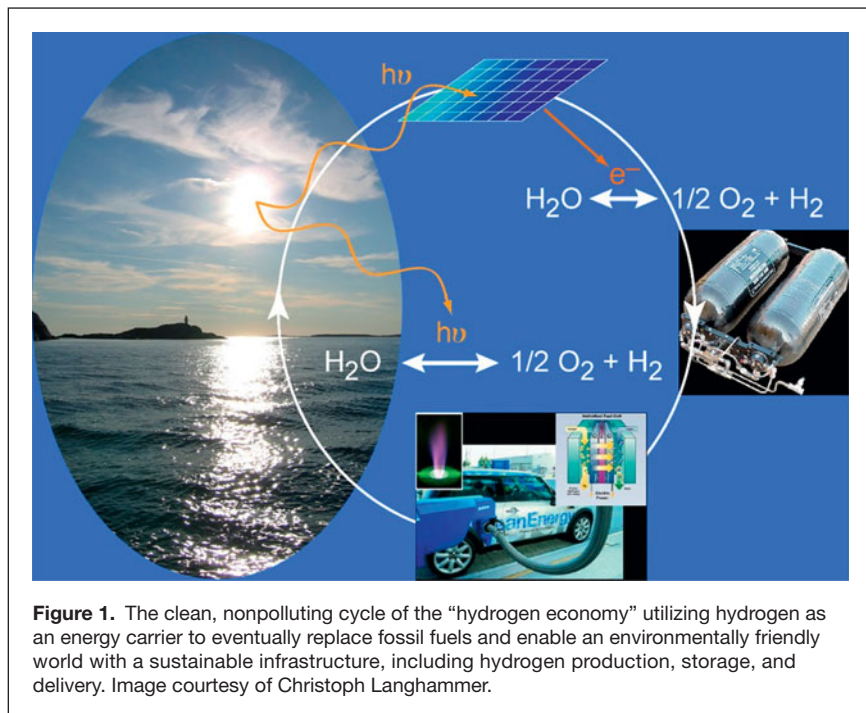


Figure 1. The clean, nonpolluting cycle of the “hydrogen economy” utilizing hydrogen as an energy carrier to eventually replace fossil fuels and enable an environmentally friendly world with a sustainable infrastructure, including hydrogen production, storage, and delivery. Image courtesy of Christoph Langhammer.

Metal hydride basics

Metal hydrides are comprised of metal atoms and hydrogen forming chemical bonds. Many metals react with hydrogen at elevated temperatures and various pressures to form binary metal hydrides such as LiH, MgH₂, VH₂, and TiH₂. Intermetallic compound hydrides include alloys of various compositions, such as the well-known “battery-type alloy” LaNi₅, which will be further discussed later. Most of these are metallic and have fairly good thermal conductivity.

A metal hydride is prepared by heating under hydrogen pressure. When a metal absorbs hydrogen gas to form a metal hydride, the hydrogen molecule dissociates on the metal surface, then diffuses into the bulk and exothermically forms a chemical energy-rich metal-hydrogen bond, with the hydrogen atoms located in tetrahedral and/or octahedral sites in the metal matrix. First, a solid solution with a smaller amount of hydrogen is formed (α phase). Thereafter, when the hydrogen content increases, a hydride phase (β phase) nucleates and grows. The metal lattice typically expands 10–20% upon hydrogenation. It is common to describe the thermodynamics of the hydride formation by pressure-composition isotherms, as illustrated in **Figure 2**. The plateau represents the coexistence of the α and β phases. The two-phase region has a plateau pressure (P_{eq}) related to the changes in enthalpy (ΔH) and entropy (ΔS), according to the van't Hoff equation: $\ln(P_{eq}/P_{eq0}) = (\Delta H/R)(1/T) - \Delta S/R$, where R is the gas constant. The plateau pressure, and thus the operation temperature, can be tuned by alloying

with different metals. The ability to tune the plateau pressure allows hydrogen storage materials to be engineered for specific applications. The metal hydrides are typically reversible and are known to show cycle lives of thousands to ten thousands of cycles in different applications.

Materials discovery methodology

Materials have historically been discovered using systematic screening efforts, by trial and error, and/or intuition. With the recent increase in demand for new energy-related materials, it has become a challenge for the experimentalist to efficiently screen through and characterize composition space to identify new materials for specific applications. It became necessary to identify new methodologies for materials design. Over the past two decades, first-principles codes have advanced, providing computational tools to be used in conjunction with experimental investigations to resolve complex materials discovery problems. This is evidenced by the proliferation of

open-source and proprietary first-principles codes, including ABINIT,^{11,12} Quantum-Espresso,¹³ and VASP,^{14–17} which contain an array of built-in capabilities for determining optical and elastic properties, finite temperature thermodynamics, atomic diffusion barriers, and magnetic resonance chemical shifts. Extensive information can be found on these packages on the Internet.

Majzoub and Rönnebro¹⁸ developed a materials discovery methodology based on theory guiding experiments by identifying potential low-energy crystal structures to be synthesized, combined with chemical intuition and focused experimental synthesis techniques. Attention was focused on complex metal hydrides that can be used for a variety of applications, including onboard vehicular H₂ storage, stationary storage, portable power, or thermal energy storage. The complex metal hydrides are ionic solids composed of alkali and/or alkaline

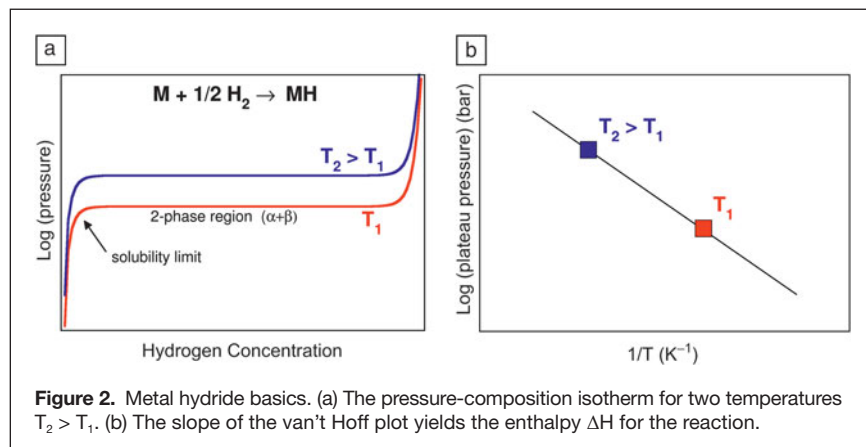


Figure 2. Metal hydride basics. (a) The pressure-composition isotherm for two temperatures $T_2 > T_1$. (b) The slope of the van't Hoff plot yields the enthalpy ΔH for the reaction.

earth cations and complex anion groups centered on Al, B, or N, such as alanates $[\text{AlH}_4]^-$, $[\text{AlH}_6]^{3-}$; borohydrides $[\text{BH}_4]^-$; imides; and amides $[\text{NH}_2]^-$, $[\text{NH}]^{2-}$, where the hydrogen participates in a covalent bond. These mixtures of cations and anions can produce quite complicated crystal structures, for example $\text{Li}_4(\text{BH}_4)(\text{NH}_2)_3$.¹⁹ Bi-alkali or mixed-cation materials are also observed, such as $\text{NaK}(\text{BH}_4)_2$.²⁰ The discovery methodology is summarized in **Figure 3** and is generally applicable to any compound space, including battery materials.

Computational methods

Theoretical condensed matter methods, such as density functional theory, successfully explain many material properties, including lattice parameters, elastic constants, and cohesive energies.²¹ Reviews of these established methods may be found in the literature. In the mid- to late-2000s, many international R & D programs focused attention on hydrides for transportation, where volumetric and gravimetric densities are as important as the kinetics of hydrogen sorption. Theoretical methods were developed and refined to search the new “space” of compounds that were proposed, based on light elements bonding covalently with hydrogen to form anionic complexes. These include alanates, borohydrides, and the amides and imides discussed previously.

Searching for new hydride compounds

Because the complex metal hydrides are essentially salts, the cations and anions may be combined in many ways, subject only to thermodynamic stability. Hypothetical compounds may be examined using standard first-principles techniques to determine whether they will spontaneously phase separate or decompose. An example of phase separation is found in the mixed cation compound of NaBH_4 and KBH_4 prepared by high-energy mechanical milling. Mechanical alloying results

in a new phase, identified via x-ray diffraction to consist of $\text{NaK}(\text{BH}_4)_2$ with symmetry R-3. The compound is unstable with respect to phase separation, resulting in a return to the starting materials NaBH_4 and KBH_4 over about 36 hours.²⁰ Other compounds such as $\text{Ti}(\text{BH}_4)_3$ spontaneously decompose at room temperature.²²

Two principal methods for computational discovery of new materials include structure searching within existing crystal structure databases, or using crystal structure prediction methods. The database search method may be quite successful for simple binary (one cation, one anion) materials, where an extensive database (e.g., Inorganic Crystal Structure Database)²³ provides many prototype structures. Crystal structure prediction techniques for ionic compounds were developed specifically for hydrides and have been successfully applied to hydrogen storage compounds. The prototype electrostatic ground state method,²⁴ has been used to predict stable hydrides ($\text{LiK}(\text{BH}_4)_2$), to confirm the structure of newly synthesized hydrides ($\text{NaPH}_2\text{B}_2\text{H}_6$), and to study polymorphs of many compounds, such as $\text{Ca}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$.^{25,26} The method has also been successfully extended to nanoparticle systems. Subsequent calculations may determine thermodynamic stability and possibly identify useful reactions.

Another experimental methodology used to screen for new metal hydrides is a combinatorial thin-film method called “hydrogenography,” which was invented by Griessen’s group to screen for optical transitions in thin films.²⁷ The article by Yoshimura et al. in this issue highlights this interesting optical phenomenon and metal hydride applications for smart windows and sensors.

Searching for favorable hydride reactions

The calculation of the total free energy of a crystal structure as a function of temperature via the phonon density of states, permits a study of polymorphic phase transitions, thermodynamic stability and phase diagrams, and enthalpies of phase transitions. Using modern computational resources, one is now able to perform finite temperature calculations on a large database of compounds. Once this information is compiled, it may be easily used to search for reactions that occur between compounds as a function of temperature and hydrogen pressure, using the Gibbs free energy in the grand canonical ensemble and linear programming (GCLP method). The article by Michel and Ozoliņš in this issue describes advances in these computational methods in detail.

Creating nanostructured materials to engineer performance

The thermodynamic stability of many complex hydrides results in large enthalpies for

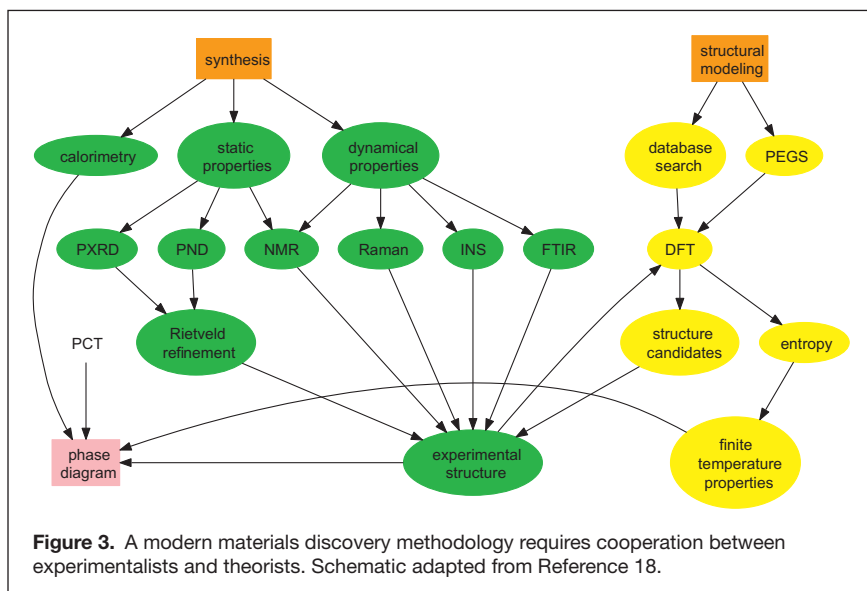


Figure 3. A modern materials discovery methodology requires cooperation between experimentalists and theorists. Schematic adapted from Reference 18.

hydrogen sorption (e.g., LiBH_4 with 18 wt% hydrogen, but an enthalpy of about 74 kJ/mol H_2). To be practically useful for onboard vehicle storage and operation at near-fuel cell temperatures of $\sim 80^\circ\text{C}$, these enthalpies must be reduced. On the other hand, for thermal energy storage applications, enthalpies must be high. One novel approach to tuning the thermodynamics and kinetics of these systems has been the utilization of large surface areas and short diffusion paths of confined nanoparticles. An early strategy was to ball-mill the materials to reduce particle size.²⁸ Although mechanical milling of complex hydrides produces particle sizes in the submicron range, it produces only short-term gains because the solid-state reactions involving mass transport quickly grow the particle sizes as the dehydriding or rehydriding reaction proceeds. Incorporation of hydrides into host frameworks possessing high surface area and large pore volume is another approach to reducing particle size. These frameworks may be prepared using templating or self-assembly, or a combination of the two. The article by de Jongh et al. in this issue discusses these nanostructured “frameworks” as well as the hydride/framework surface interaction and how these affect the changes in the kinetics and thermodynamics of the sorption reactions.

Nanostructured carbons were some of the first materials studied for their impact on the hydriding reactions of MgH_2 and LiBH_4 .²⁹ Gross et al. used carbon aerogels produced from calcination of resorcinol-formaldehyde (RF-aerogels, RFA), with pore sizes in the 13–25 nm range. In the case of LiBH_4 , the RFA are wetted and quickly wicked into monolithic pieces above the melting temperature of LiBH_4 . LiBH_4 @RFA is shown to have a reduced desorption temperature and, remarkably, the hydriding reaction is made reversible, ostensibly by a reduction in the kinetic barriers.

More recent work involves block-polymer templated carbons with carefully controlled pore morphology and much smaller pore sizes. Majzoub's group has prepared nanoporous carbons (NPCs) with cylindrical pores 2–4 nm in diameter packed in a hexagonal morphology following the work of Meng et al.³⁰ In contrast to the RFA carbons, the pore size is small enough that x-ray diffraction and calorimetry (DSC) indicates amorphous LiBH_4 . However, the incorporated material still indicates intact $[\text{BH}_4]^-$ anions through visible bending and stretching modes observed by Fourier transform infrared spectroscopy. Most importantly, in the LiBH_4 @NPC materials, the synthesis of diborane (B_2H_6) may be controlled through the pore size of the carbon, which suggests the reaction pathway may be controlled to some extent.³¹ Despite these efforts to reduce enthalpy, the enthalpy for the dehydriding reaction is measured to be roughly 72 kJ/mol H_2 , unchanged from the bulk, which is too high for onboard vehicle fuel cell applications.

Several research groups have studied the effects of incorporation of NaAlH_4 in nanoporous carbon fibers³² and high-surface area activated carbons (HSA) (see the article by de Jongh et al.). High-pressure differential scanning calorimetry (DSC) in the work of de Jongh's group has shown definitive evidence of the

exothermic wetting of NaAlH_4 @HSA, and clear indication of hydride/carbon surface interaction. Additionally, temperature programmed desorption indicates that the dehydriding reaction is single-step, skipping the intermediate Na_3AlH_6 phase.³³ This observation is consistent with theoretical calculations for the decomposition of nanoparticulate NaAlH_4 .^{34,35}

Metal organic framework templates

Most well-ordered templates for systematically controlled experiments on pore size effects are metal-organic frameworks (MOFs). These are coordination polymers, or engineered crystals composed of metal-oxide centers connected through organic linkers.³⁶ There are many types of MOFs being explored for a variety of applications. This is an active area of research, and reviews may be easily found elsewhere. For a complex metal hydride to be confined in a MOF, the structure must be stable in a hydrogen atmosphere and also in the presence of the metal hydride. The first MOF to be utilized in this manner was the Cu-based benzene-tricarboxylate (Cu-BTC, also known as HKUST-1 for its discovery at Hong Kong University of Science and Technology). Cu-BTC has an interior pore diameter of about 15 Å. The pores of the Cu-BTC MOF can be infiltrated with NaAlH_4 in THF solution via a simple infiltration and mild heating to subsequently remove the THF.³⁷ The infiltrated small clusters of NaAlH_4 show dramatically lower desorption temperature more suitable for applications in a moderate temperature range.

Experiments on NaAlH_4 melt infiltrated into MOF-74 are remarkable.³⁸ MOF-74 is a much more robust framework and can withstand the 180°C temperature necessary for melt-infiltration of the NaAlH_4 . The pore structure of MOF-74 includes cylindrical columns, similar to those of NPC, described previously, but with greater monodispersity in pore size due to the exceptional order of the MOF. NaAlH_4 @MOF-74 is reversible, with or without doping, and also shows no signs of Bragg peaks in x-ray diffraction analysis, indicating amorphous NaAlH_4 within the pores.

Advanced metal hydride batteries for various applications

The best-known use of metal hydrides is in the commercial nickel metal hydride (NiMH) battery. The NiMH battery was commercialized in 1991 for small consumer applications. Since then, larger scale batteries for hybrid electric vehicles have been developed.³⁹

The metal hydride battery offers several advantages compared to other batteries; it does not have the safety issues of Li-ion batteries because the electrolyte is a water-based alkaline solution, and there are no issues regarding dendrite growth on the negative electrode. It is environmentally friendly, without the poisonous Cd found in the Ni-Cd batteries, and is lead-free. Currently, a Li-ion battery has about twice the gravimetric and volumetric density of rare-earth-based NiMH. If the hydrogen storage capacity of the metal hydride battery can be doubled or tripled, it will have a significant advantage

over Li-ion batteries. This is a research area where materials development is needed. NiMH batteries are known to perform reliably, and the calendar life is longer than that of Li-ion batteries with significantly less capacity drop. NiMH batteries can reversibly provide high power density in shorter intervals for peak shaving on the grid or for high-power applications, as discussed in the article by Ye et al. in this issue.

The commercially available NiMH cylindrical battery entered the market in 1991 with an energy density of 54 Wh/kg. With technology improvements, it now achieves about 100 Wh/kg for smaller consumer cells. Since the 1990s, a variety of different sizes have been produced, from 30 mAh buttons to 250 Ah prismatic cells for buses. Power increased from 200 to 2000 W/kg with charging efficiencies of 85%. Operation temperatures range from -30°C to 70°C while still providing $>90\%$ capacity at 70°C . Almost all NiMH batteries have anodes made of lanthanum nickel (LaNi_5)-type alloys, often tuned to compositions such as $\text{La}_{5.7}\text{Ce}_{8.0}\text{Pr}_{0.8}\text{Nd}_{2.3}\text{Ni}_{59.2}\text{Co}_{12.2}\text{Mn}_{6.8}\text{Al}_{5.0}$ for better corrosion protection to prolong cycle life.⁴⁰ The cathode is based on nickel hydroxide with a capacity of ~ 300 mAh/g to allow the chemical reaction to occur. The voltage is 1.1–1.2 V, and the electrolyte is 6 M KOH. The cycle life of metal hydride batteries of up to ten thousands of cycles has been reported, depending on depth of discharge, and capacities of 320 mAh/g limited by hydrogen content in the alloy of about 1.5 wt% hydrogen.

There are metal hydrides with theoretically much higher capacities of up to ~ 2000 mAh/g; however, the Ni-based cathode limits capacity to about 300–350 mAh/g. There are new battery concepts developed that use metal hydrides to increase capacities, including (1) advanced NiMH battery, (2) metal hydride air battery, (3) metal hydrides for Li-ion batteries, and (4) magnesium battery using $\text{Mg}(\text{BH}_4)_2$ as the electrolyte.

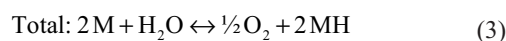
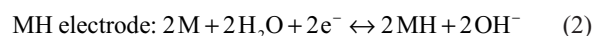
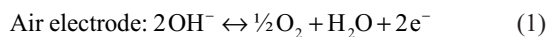
Advanced NiMH battery

Improvements in NiMH are continuing, and in the article in this issue by Ye et al., recent advances are highlighted to enable high rate performance for electric vehicles. They point out that a large surface area and particle size management is crucial for performance improvements, and more research is needed in this area to optimize the battery alloy. If the detailed electrochemical surface reaction on the metal hydride electrode in NiMH batteries was better understood, improved cycle life and depth of charge/discharge issues could be addressed, and NiMH batteries would become good candidates for large scale breakthroughs of batteries for grid storage and vehicle applications.

Metal hydride air battery

A solution to allow for higher capacity metal hydrides is to use an air cathode. To enable capacities >400 Wh/kg (>200 Wh/kg effective when including the weight of the electrolyte and battery compartment), the $\text{Ni}(\text{OH})_2$ cathode can be replaced by a lightweight air cathode to enable even higher capacity metal

hydride anode materials, forming a metal hydride air battery (MHAB). It also utilizes a reversible electrochemical hydriding process in a nonflammable aqueous alkaline electrolyte of 6 M KOH, similar to NiMH batteries. The reversible reactions are described in the reactions (1–3) below, and unlike Li- and Pb-based batteries, minimal side reactions occur, which allow for full charge/discharge and hence longer cycle life.



Issues with cathode degradation can be avoided with a third charging electrode, as shown in **Figure 4**. The MHAB concept has been demonstrated with rare-earth based metal hydrides with ~ 300 Wh/kg capacities.⁴¹ The key challenge to increase performance and specific energy density relative to state-of-the-art MHAB is to establish an ultrahigh-capacity metal hydride anode material that does not corrode in the water-based electrolyte.

Metal hydrides for Li-ion batteries

Metal hydrides can also be used as a negative electrode for Li-ion batteries, as shown by Tarascon's group in 2008.⁴² They measured a reversible capacity of 1480 mAh/g or 2090 mAh/cm³ when using a MgH_2 electrode in a Li-ion battery, and found that the design of nano-sized materials had a significant positive effect on performance.

The magnesium battery

Magnesium batteries have come into focus as an alternative to Li-based batteries because of the high volumetric capacity of almost 4000 mAh/cm³, abundance, and low cost. A key challenge in developing a rechargeable Mg battery is to identify a halide-free electrolyte. Mohtadi et al. recently proposed a new class of electrolytes based on magnesium borohydride,

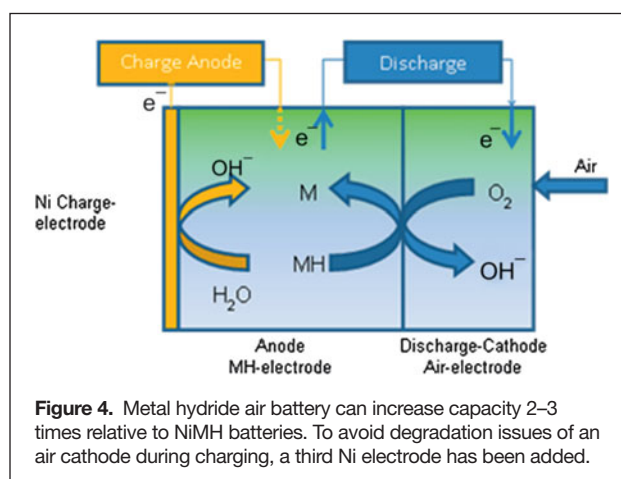


Figure 4. Metal hydride air battery can increase capacity 2–3 times relative to NiMH batteries. To avoid degradation issues of an air cathode during charging, a third Ni electrode has been added.

$\text{Mg}(\text{BH}_4)_2$ in THF or dimethyl ether solvents.⁴³ This is the first time that a Mg battery has been shown to be electrochemically reversible, and this finding opens up a new class of borohydride-based electrolytes.

Thermal energy storage

Thermal energy storage (TES) is an enabling technology for renewable energy and grid applications, but it can also be used for waste heat recovery and to improve building and transportation efficiencies. There is currently no commercially available TES system, but with the need to increase energy efficiencies, TES is an application that is coming more into focus. Metal hydrides (MH) can store up to 3000 kJ/kg and 1000 kWh/m³ in the temperature range of 100–1200°C, depending on the choice of the material composition, thus exceeding the gravimetric and volumetric energy density of all commercially available materials. State-of-the-art TES uses molten salts and stores 153 kJ/kg and about 100 kWh/m³ at 565°C. Low-temperature MH systems up to 200°C have been demonstrated using very expensive rare-earth metals based on LaNi_5 type alloys and mischmetals (i.e., alloy of rare-earth elements). Medium temperature systems operating in the range of 250–500°C and 20–40 bar H_2 pressures have recently been demonstrated based on MgH_2 ,^{44,45} but this particular hydride most likely will not yield the high efficiency target when operated above 600°C, which is the requirement for concentrating solar power (CSP), and hydrogen pressures are impractically high. New, tuned high-temperature metal hydrides with high energy densities need to be developed. Rönnebro's group has recently shown a low-cost high-temperature metal hydride to operate at 650°C and 1 bar H_2 pressure. This is a higher temperature and lower pressure than almost all other metal hydrides, which is desirable for higher efficiencies and practical applications.

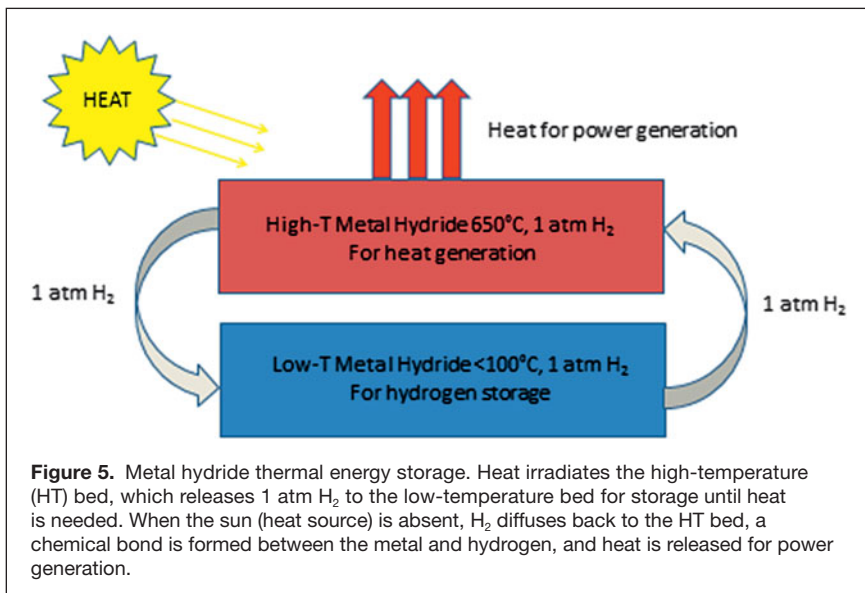
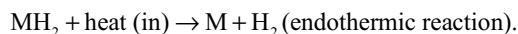
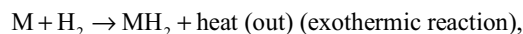


Figure 5. Metal hydride thermal energy storage. Heat irradiates the high-temperature (HT) bed, which releases 1 atm H_2 to the low-temperature bed for storage until heat is needed. When the sun (heat source) is absent, H_2 diffuses back to the HT bed, a chemical bond is formed between the metal and hydrogen, and heat is released for power generation.

Metal hydride TES basics

The reversible metal hydride technology stores renewable energy or waste heat in a dual-bed metal hydride system for heating (Figure 5). This concept is based on a thermal cycle driven by gas-solid chemical reactions accompanied by heats of formation, which provides maximum efficiency. The material is a metal or an alloy reversibly absorbing hydrogen to form a metal hydride. Thermal energy is stored in the chemical bond between the metal and the hydrogen. The heat of reaction absorbed in liberating the hydrogen is the same as the heat of reaction obtained when forming the hydride. No hydrogen is consumed hence, theoretically, very little heat is lost. By changing composition, the metal hydride can be engineered to operate at specific temperatures and pressures with formation enthalpies of 30–140 kJ/mol H_2 . When the metal hydride material is exposed to heat, hydrogen is released. When absorbing hydrogen, heat is released. The overall concept is illustrated in Figure 5. The general reaction, where M is the metal (or alloy) and H is hydrogen is:



By tuning the metal hydride composition, optimized performance can be obtained that meets the requirements for the specific heating/cooling device.

Conclusion

Metal hydrides are an important class of materials that can be utilized in various clean energy applications to enable renewable energy and grid technologies and to improve energy efficiencies in buildings and in transportation sectors. Metal hydrides are unique since they can participate in the whole “energy cycle” from collecting renewable energy (solar, wind, water) to storing energy for power generation. By tuning the composition of the metal hydride, operation temperature and pressure are established to satisfy the needs of a specific application. Many metal hydride based technologies are emerging to fill in the gaps in the energy cycle and with increased governmental and industrial investments, a more rapid advancement is anticipated toward an economy that includes renewable energies.

Acknowledgments

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