

Editorial

State-of-the-Art and Progress in Metal-Hydrogen Systems

Terry D. Humphries ^{1,*}, Craig E. Buckley ¹, Mark Paskevicius ¹ and Torben R. Jensen ²

¹ Physics and Astronomy, Curtin University, GPO Box U1987, Perth, WA 6845, Australia; c.buckley@curtin.edu.au (C.E.B.); mark.paskevicius@gmail.com (M.P.)

² Interdisciplinary Nanoscience Center and Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark; trj@chem.au.dk

* Correspondence: terry_humphries81@hotmail.com

1. Introduction

Hydrogen is heralded as a future global energy carrier [1–9]. The development of hydrogen as a clean energy solution is gaining unprecedented global attention, as many countries are now recognising its potential in various applications and including hydrogen in its energy portfolio. This includes stationary, portable, and transport use today, including hydrogen fuel cell vehicles, trains, and ferries. However, hydrogen storage remains a critical challenge in expanding infrastructure for hydrogen-based transportation and industrial utilisation.

Metal hydrides have received much interest over the past several decades, which is evident from a previous related Special Issue published in *Inorganics*: “Functional Materials Based on Metal Hydrides” [10]. Reversible solid-state hydrogen storage at ambient conditions with moderate energy exchanges with the surroundings is the ultimate challenge to realise a hydrogen-based society. Varieties of novel hydrogen-rich materials have been investigated in the past decades, which has provided many novel compositions, fascinating structures, and functionalities [8,11–14]. Today, metal hydrides are explored for a range of applications, including hydrogen exports, remote area power systems, solid-state batteries, thermochemical energy storage, and hydrogen diffusion [15–23]. Indeed, the International Energy Agency (IEA) is involved in the development of hydrogen and hydrogen storage materials, where Task 40 “Energy Storage and conversion based on hydrogen” has recently released a number of review articles on the research being conducted in this area [24–30].

The aim of this Special Issue of *Inorganics*, entitled “State-of-the-Art and Progress in Metal-Hydrogen Systems”, is to inspire continued research within this important class of materials, in particular for energy-related applications. This Special Issue also serves as a collection of contributions presented at the International Symposium on Metal-Hydrogen Systems, held in Perth, Western Australia, 30 October–3 November 2022 [31]. This meeting, MH2022, is the 17th meeting in a distinguished series of conferences dating back to 1968. This conference was due to be held in 2020; however, COVID forced it to be postponed to 2022. The conference Chair was Prof. Craig Buckley, and the Vice-Chair was Assoc. Prof. Mark Paskevicius, both from Curtin University, Australia. MH2022 had a total of 159 participants from 22 countries. Five plenary talks were presented by Prof. Ping Chen (Dalian Institute of Chemical Physics, Chinese Academy of Sciences), Prof. Petra E de Jongh (Utrecht University, The Netherlands), Prof. Evan Gray (Griffith University, Australia), Dr Patrick Hartley (CSIRO, Australia), and Dr Michael Hirscher (Max Planck Institute for Intelligent Systems, Germany). There were 40 invited and 87 contributed talks and 30 posters on the topic of the fundamentals and applications of metal–hydrogen systems. The contributions covered a wide range of materials topics, including complex hydrides, metal hydrides, and chemical, organic, and nanoporous materials.

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Steering Committee for their help in planning and successfully organizing the symposium. We gratefully acknowledge the sponsors and supporting partners of MH2022: Curtin University, The Australian Renewable Energy Agency (ARENA), Toyota, and the exhibitors Anton Paar, Hidden Analytical, Hidden Isochema, John Morris Group, and Suzuki Shokan. Furthermore, the Guest Editors would like to thank all the reviewers who spent their valuable time thoroughly reviewing and improving the articles published in this Special Edition.

2. An Overview of Published Articles

As expressed above, the field of metal hydrides is diverse, and this is exemplified by the varied topics covered in the 14 articles published in this Special Edition. This section provides a brief overview of the included manuscripts, of which they are divided into discreet, albeit cross-cutting, subsections that include: Hydrogen Release and Uptake, Electrolytes, Physical Properties, and Metallic Alloys.

2.1. Hydrogen Release and Uptake

Varieties of novel hydrogen containing compounds with fascinating compositions and structures are continually discovered [1,13,32–37], well-illustrated by the $\text{Na}[\text{BH}_3(\text{CH}_3\text{NH})\text{BH}_2(\text{CH}_3\text{NH})\text{BH}_3]$ material presented by Zhang et al. (in contribution 1). This compound releases 4.6 wt.% of pure hydrogen below 150 °C contrary to the parent counterpart $\text{Na}[\text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3]$. This work illustrates a new route to suppress the release of unwanted gaseous by-products by the introduction of organic methyl groups bonded to nitrogen.

Lithium and sodium borohydride, LiBH_4 and NaBH_4 , are known to possess high gravimetric and volumetric hydrogen densities of 18.5 and 10.6 wt.% and 121 and 113 $\text{kg}\cdot\text{m}^{-3}$, respectively [37–43]. However, their high thermal stabilities hamper utilisation as hydrogen storage materials for practical applications. Interestingly, F. Peru et al. investigated the composite $0.71\text{LiBH}_4\text{--}0.29\text{NaBH}_4$ with a eutectic melting point of 219 °C, which allows convenient melt infiltration into a nanoporous carbon material (CMK-3) with a pore size of ~5 nm (contribution 2) [44]. This material reveals an uptake of ~3.5 wt.% H_2 after five hydrogenation/dehydrogenation cycles facilitated by carbon–hydride surface interactions and possibly enhanced heat transfer.

Magnesium hydride, MgH_2 , has attracted much attention during the last few decades owing to a high hydrogen content of 7.6 wt.% and possesses good reversibility [23,24,45–48]. However, hydrogen release and uptake occur at temperatures higher than 300 °C and with slow kinetics. The third and fourth paper contributed to this collection reveals new strategies for improving both kinetic and thermodynamic properties of magnesium hydride. Huang et al. (contribution 3) demonstrated that the operating temperature for pristine MgH_2 can be decreased from 322 to 214 °C through the employment of Ti_3CN . Furthermore, the hydrogen-release kinetics of MgH_2 are also improved, as observed by a decrease in activation energy from 121 to 80 $\text{kJ}\cdot\text{mol}^{-1}$ for the release of hydrogen. Another strategy, developed by Qin et al. (contribution 4), is to use hydrogen-containing additives such as lithium borohydride in magnesium hydride. A new composite of $\text{MgH}_2\text{--LiBH}_4$ (5 wt%) released ~7.1 wt.% H_2 within 40 min at 300 °C, where a reference sample of MgH_2 only released <0.7 wt.% H_2 . Importantly, the kinetics of hydrogen release are improved by a factor of ten ($\times 10$) compared to that of the pure MgH_2 material. This effect is suggested to be due to the creation of ion transfer channels, which can inhibit the agglomeration of MgH_2 particles.

TiFe is a well-established hydrogen storage material due to its low cost, elemental abundance, and near-ambient temperature and mild pressure for hydrogen absorption [15,49]. This makes it perfect for stationary applications [50]. The main hindrance is the difficulty to activate the material for the absorption of hydrogen in the first cycle, where high pressures of ~50 bar and high temperatures of ~400 °C are often required. Contribution five by Sartori, Amati, and Gregoratti et al. studied the influence of adding 4 wt.% Zr to the

material and found that the kinetics of the first hydrogenation are greatly improved. The authors employed scanning photoemission microscopy to investigate the composition and chemical state of the various phases present in this alloy and how they change upon hydrogenation/dehydrogenation and found the presence of different oxide phases that were not seen by conventional SEM investigation.

2.2. Electrolytes

Recently, a variety of new complex hydride-based electrolytes were discovered [51–56]. They deviate from classical ionic compounds by offering high cationic conductivity at moderate temperatures, also with divalent cations. The high cationic conductivity is often assigned to weak interactions, such as dihydrogen bonds, providing structural flexibility [26,57]. A new example is magnesium borohydride, templated by isopropylamine, $\text{Mg}(\text{BH}_4)_2 \cdot (\text{CH}_3)_2\text{CHNH}_2$, which also has hydrophobic domains, presented by Kristensen et al. (contribution 6). Aluminium oxide nanoparticles and heat treatment produce a highly conductive composite, $\sigma(\text{Mg}^{2+}) = 2.86 \times 10^{-7}$ and $2.85 \times 10^{-5} \text{ S cm}^{-1}$ at -10 and 40 °C, respectively, with a low activation energy, $E_a = 0.65$ eV. Nanoparticles stabilise the partially eutectic molten state and prevent recrystallisation even at low temperatures and provide a high mechanical stability of the composite.

Electrochemical reactions taking place in a solid-state battery cell can be considered multi-phase reactions taking place at interfaces, involving cationic diffusion in the solid state [26,58]. Hydrogen storage systems based on complex hydrides, such as metal borohydrides or metal alanates, reveal similarities. In both cases, multiple solid phases nucleate and grow or are consumed as hydrogen is released or stored or electrochemical reactions take place in a battery. These reactions are limited by the kinetics of atoms or ion diffusion at grain boundaries in the solid state and also by solid state transformations. Thus, Vajo and co-workers (contribution 7) proposed to explore these challenges by investigating combined electrolytes and hydrogen storage systems. This includes the use of eutectic molten composites. An increase in reaction rates was observed in several cases, but the kinetics may become more complex. A reduction in reaction temperature may be observed, but the results also suggest that electrolytes improve intraparticle transport phenomena.

2.3. Metallic Hydrides for Hydrogen Purification and Compression

If the world is to move towards a hydrogen economy, hydrogen must be produced in high purity to avoid any poisoning of catalysts during consumption, e.g., in a fuel cell [59]. Palladium has been determined to be extremely effective towards the application of hydrogen-purification/separation membranes. In contribution 8, Endo et al. discusses the preparation of high-purity palladium (Pd) films using the electroplating method, which is considered a simple and cost-effective technique. However, electroplating can result in stress accumulation in the film, making it challenging to obtain a dense single Pd film. This study successfully addressed this issue by optimising the electroplating process, resulting in a high-purity Pd film with unique surface characteristics. Notably, the plated film exhibited superior mechanical properties compared to rolled Pd films, including twice the displacement and four times the breaking point strength. As such, this research demonstrates the practical feasibility of using electroplating to produce Pd-based membranes for hydrogen purification applications.

For practical applications of hydrogen gas, convenient compression using low amounts of energy is crucial. Metallic hydrides have proven useful for the development of metal hydride–hydrogen compressors [15,30,60]. This is successfully demonstrated by X. Zhang et al. (contribution 9) where the rare earth series AB_5 and Ti/Zr-based AB_2 hydrogen storage materials are investigated. A four-stage compressor is developed with output pressures of 8.90, 25.04, 42.97, and 84.73 MPa operating at 363 K. The first pressure stage was achieved by a CaCu_5 -type hexagonal structure, the others by TiCr_2 and ZrFe_2 type alloys.

There are many aspects to overcome to enable metal hydrides to be the ideal hydrogen storage medium, but several researchers are utilising a variety of methods to overcome

these problems. Large volume expansions within these powders are observed upon cycling of hydrogen, and this can lead to the occurrence of stress on the walls of the container and the possibility of catastrophic failure [15,30,49]. Zheng et al. (contribution 10) used silicone oil as a glidant to promote stress-free conditions for V-based BCC metal hydrides and have reported that the addition of 5 wt.% silicone oil slightly reduced the initial hydrogen storage capacity of $V_{40}Ti_{26}Cr_{26}Fe_8$ (particle size $\sim 325 \mu\text{m}$) but improved the absorption reversibility, regardless of the oil viscosity. The maximum strain on the surface of the hydrogen storage container decreased by $\geq 22.5\%$ after adding 5 wt.% silicone oil.

During absorption and desorption of hydrogen, metal hydrides interact with hydrogen via multiple bonding interactions, including covalent, ionic, and van der Waals forces [61]. This inherently produces heat during absorption and absorbs heat during desorption [22,27]. This heat must be dissipated if a steady reaction rate is to occur and avoid physical degradation, including agglomeration or side reactions that are more favourable at high temperatures. Liu et al. (contribution 11) submitted a review on improving heat transfer and stability for hydrogen storage and compression applications. Currently, several researchers have adopted the method of forming composites of alloy powders with high thermal conductivity materials, such as exfoliated natural graphite (ENG), but there are many options, including liquid-based methods, polymers, and metal foams. This article highlights the state of the art in this field of research.

2.4. Physical Properties

Fundamental research into the physical properties of metal hydrides is required if technological progress is to continue in the future [1,10,14,25,27]. Jacob, Babai, and Bereznitsky et al. (contribution 12) have concentrated on determining the elastic moduli of $Zr(Mo_xFe_{1-x})_2$, $x = 0, 0.5, 1$, as well as hydrogen absorption in $ZrMo_2$, in an attempt to shed light on the unusual trend in hydride stabilities in this system. In general, the stabilities of these hydrides exhibit a unique trend, with stability increasing from $x = 0$ to 0.5, but destabilisation is observed for the end member $ZrMo_2$ hydride. They found that the bulk modulus (B) significantly increases from 148.2 GPa in $ZrFe_2$ to 200.4 GPa in $ZrMo_2$, which is in contrast to the moderate variation in the shear modulus (G). The increase in B suggests a bulk stiffening in $ZrMo_2$.

Pan et al. (contribution 13) provided a study detailing how protons move within yttrium-doped barium zirconate, which is known to be one of the fastest solid-state proton conductors. This study used density functional theory with the Perdew–Burke–Ernzerhof functional to calculate the total electronic energy for each proton pair in an effort to catalogue and understand their motion, especially when the protons are in close proximity to one another. Overall, it was determined that protons are in close proximity to each other and the dopant in the lowest-energy configuration, significantly affecting the backbone structure. This knowledge is important for developing superior materials for proton-conduction applications.

The search for highly tuneable hydrogen storage materials is an ongoing field, especially as the addition of functional groups can produce novel materials with interesting properties such as superconductivity, photoluminescence, etc. Alkali organometallic complexes are known to have favourable thermodynamics and hydrogen capacities, but not many transition metal–organic complexes have been reported. The contribution by Wang, Pei, Yu, and Cui et al. (contribution 14) have demonstrated the formation of yttrium phenoxide and lanthanum phenoxide via metathesis of sodium phenoxide with YCl_3 and $LaCl_3$, respectively. Their properties were elucidated using theoretical calculations, quasi in situ NMR, and UV-vis spectroscopies. Although the hydrogenation of these rare-earth phenoxides was not successful, further research on these materials may lead to progress.

3. Conclusions

The necessity for reliable methods to store renewable energy is driving the development of hydrogen production, utilisation, distribution, and storage. The most-efficient

method of storing hydrogen is by using metal hydrides, whereas, simultaneously, many of these metal hydrides are finding applications in a variety of functions, including solid-state batteries, thermal energy storage, compression, etc.

The presentations, posters, and manuscripts that have arisen from MH2022 in Australia are a testament to the world-class research being undertaken in this area. The Editors of this Special Edition “State-of-the-Art and Progress in Metal-Hydrogen Systems” welcome you to read the contributed articles in the issue.

Conflicts of Interest: The authors declare no conflict of interest.

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