Perspective

The Coupling of Synthesis and Electrochemistry to Enable the Reversible Storage of Hydrogen as Metal Hydrides

Published as part of Precision Chemistry special issue "Precision Chemistry for the Hydrogen Cycle".

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Cite This: *Precis. Chem.* 2024, 2, 563−569

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ABSTRACT: Given its high gravimetric energy density and status as a clean fuel when derived from renewables, hydrogen (H_2) is considered a premier candidate for energy storage; however, its low volumetric density limits its broader application. Chemical storage through the reversible incorporation of H_2 into chemical bonds offers a promising solution to its low volumetric density, circumventing subpar energy densities and substantial infrastructure investments associated with physical storage methods. Metal hydrides are promising candidates for chemical storage because of their high gravimetric capacity and tunability through nanostructuring and alloying. Moreover, metal hydride/H_2 interconversion may be interfaced with electrochemistry, which offers potential solutions to some of the challenges associated with traditional thermochemical platforms. In this Perspective, we describe anticipated challenges associated with electrochemically mediated metal hydride/H_2 interconversion, including thermodynamic efficiencies of metal hydride formation, sluggish kinetics, and electrode passivation. Additionally, we propose potential solutions to these problems through the design of molecular mediators that may control factors such as metal hydride solubility, particle morphology, and hydride affinity. Realization of an electrochemically mediated metal hydride/H_2 interconversion platform introduces new tools to address challenges associated with hydrogen storage platforms and contributes toward the development of room-temperature hydrogen storage platforms.

KEYWORDS: *Hydrogen storage, metal hydrides, hydrogen hydride interconversion, hydrogen reduction reaction, electrocatalysts*
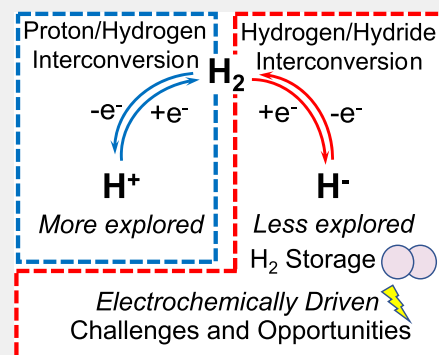
■ INTRODUCTION: THE BROAD NEED FOR HYDROGEN STORAGE

Fossil fuels are attractive stores of energy because the chemical potential is compactly stored in chemical bonds. Unfortunately, using fossil fuels releases carbon into the atmosphere, leading to unevenly distributed societal costs.[1] Therefore, a conundrum is presented: modern life requires energy for food production, medicines, and fuels, creating the imperative to advance our understanding of energy conversion processes while obviating the usage of fossil fuels. Generation of energy from renewables such as solar, thermal, wind, and hydroelectric sources has the potential to lift the dependency on fossil fuels, but the intermittency of these sources must be addressed through storage. Chemical bonds are an attractive means to store energy due to their high energy density, stability, and ease of utilization, particularly for applications where energy density is critical.[2] Taking a cue from nature, solar hydrogen is expected to play a major role in the transition away from legacy fuels, as molecular hydrogen (H_2) has among the highest energy densities of chemical fuels on a gravimetric basis.[3,4] Considerable effort has been expended to understand the interconversion of the proton (H^+) and H_2, affording the

technologies known as hydrogen evolution (HER) and hydrogen oxidation reactions (HOR) when performed electrochemically.

Despite the high gravimetric density of H_2, molecular hydrogen is a gas of extremely low volumetric density; accordingly, storage of H_2 presents a major technological hurdle to the adoption of hydrogen as a fuel source.[2,3] Current efforts to store H_2 can be broadly divided into either physical or chemical methods (Figure 1). Physical methods include compression,[5,6] cryogenic cooling, and absorption onto tailored materials,[7] while chemical methods reversibly incorporate H_2 into chemical bonds. Physical methods are attractive due to their high cyclability and simplicity in operation, but suffer from low gravimetric densities and high infrastructure costs. Chemical storage methods can exhibit
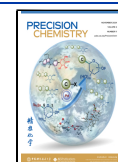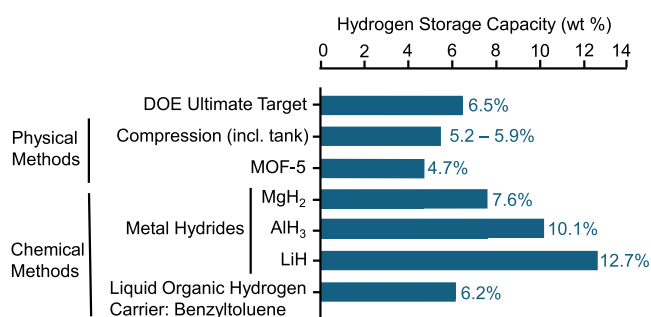
Figure 1. DOE ultimate target for hydrogen storage capacity along with the storage capacity (wt %) of select physical and chemical methods.

superior gravimetric densities but typically exhibit poor reversibility. Both routes may have high energetic costs associated with storage and/or retrieval of the H_2, limiting the net energy that may be extracted through subsequent oxidation of H_2. Numerous recent scholarly works summarize efforts to store H_2 and a broad discussion of these methods is beyond the scope of this perspective.[3,8,9]

In this Perspective, we focus on several unique avenues that chemists may contribute to the field of hydrogen storage. Chemical bonds are the currency of the chemist, and accordingly, molecular design strategies may play a valuable role in the incorporation of hydrogen into addressable and cyclable chemical bonds with properties well suited for storage applications. While incorporation of hydrogen into covalent bonds of organic molecules is a cornerstone of organic chemistry, liquid organic carriers (LOCs) typically do not have gravimetric densities that meet Department of Energy (DOE) hydrogen storage targets.[10] Prior analysis has identified metal hydrides, particularly those composed of light elements such as Li, Mg, Al, and Ti, as promising candidates with gravimetric densities superior to those of physical methods. However, the interconversion of H_2 and hydride (H^-), in stark contrast to that of H^+/H_2, is comparatively less explored and represents a frontier in fundamental chemistry and renewable energy technologies. It is of potential interest to interface stored H_2 equivalents directly with electrochemical systems to yield an electrochemically mediated hydrogen storage system, obviating the operational complexity of traditional thermochemical platforms. While the viability and utility of such a platform is unclarified, such a target would spur new lines of fundamental inquiry and introduce new tools to address intrinsic challenges associated with hydrogen storage. Here, we identify the potential advantages, challenges, and advancements required to electrochemically mediate the interconversion of H_2 and H^-.

■ PHYSICAL AND CHEMICAL PROPERTIES OF METAL HYDRIDES: BACKGROUND

In contrast to their covalent organic analogues, the hydrogen atoms of metal hydrides are reduced by two electrons, resulting in considerable ionic character. The H_2/H^- standard redox potential is -2.3 V versus SHE,[11] the negative reduction potential reflects the energetic costs of the accumulation of negative charge in a compact ionic radius (1.29 Å).[12] Ionic hydrides react readily with water or weakly acidic bonds to form H_2,[13] a consequence of the high pK_a value of H_2 (35).[14] In aprotic solvents, ionic hydrides are generally regarded as either insoluble or display trace solubility due to their high

lattice energies,[14] relegating reactivity to the surface of the insoluble metal hydride.

For reasons that will be elaborated below, we will now primarily focus our discussion of ionic hydrides to magnesium hydride as a case study. Magnesium hydride (MgH_2, Figure 2A) is an attractive candidate for hydrogen storage applications
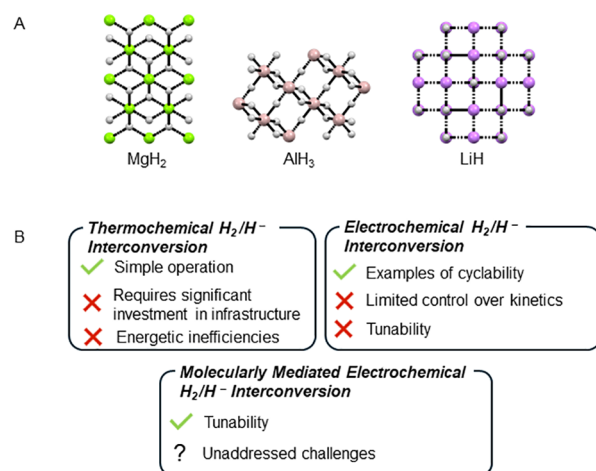

Figure 2. (A) Solid state structures of select metal hydrides with hydrogen weight percentages over 7%.[24−26] (B) Advantages and disadvantages of thermochemical, electrochemical, and molecularly mediated electrochemical H_2/H^- interconversion.

due to its large hydrogen gravimetric capacity of 7.6%, a value that exceeds mandates set forth by the DOE technical targets for onboard hydrogen storage.[15] Few hydrogen carriers match the theoretical gravimetric capacity of MgH_2, although notable exceptions include AlH_3 (10.1%), LiH (12.7%), NH_3 (17.8%), and $NH_3 \cdot BH_3$ (19.6%) (Figure 2A). However, the afore-mentioned examples suffer from major technological hurdles not detailed here, which have precluded their incorporation into workable hydrogen storage devices.[8]

When considering a material for hydrogen storage applications, the thermodynamics of the reaction of H_2 with the hydrogen carrier is of foremost importance. The enthalpy and entropy of the reaction of magnesium metal with H_2 are -17.8 kcal/mol and -32.3 cal/mol·K respectively.[16,17] These values reveal a deeper consideration for any hydride storage system: the free energy change of a reaction of a metal with H_2 to form a metal hydride should be close to thermoneutral to avoid energy losses during storage or retrieval of hydrogen. For this reason, metals that have very exothermic reactions with H_2, such as Li, present an enormous challenge for efficient H_2 storage under thermodynamic efficiency considerations. A common strategy to achieve more favorable thermodynamics in magnesium based systems is to alloy Mg with other elements that form less stable hydrides; however, this strategy comes at the cost of gravimetric density.[9,18] Another strategy to decrease the thermodynamic penalty of H_2 storage is to decrease the particle size through "nanostructuring" of both the Mg and MgH_2 particles resulting in high surface areas, greater numbers of grain boundaries, and larger surface energies.[19,20] For a comprehensive review on nanostructured metal hydrides, refer to the work of Stavila and co-workers.[21] Nanostructuring Mg and MgH_2 is an attractive strategy to alleviate excessive thermodynamic penalties, but retaining nanostructuring during cycling remains a major challenge.
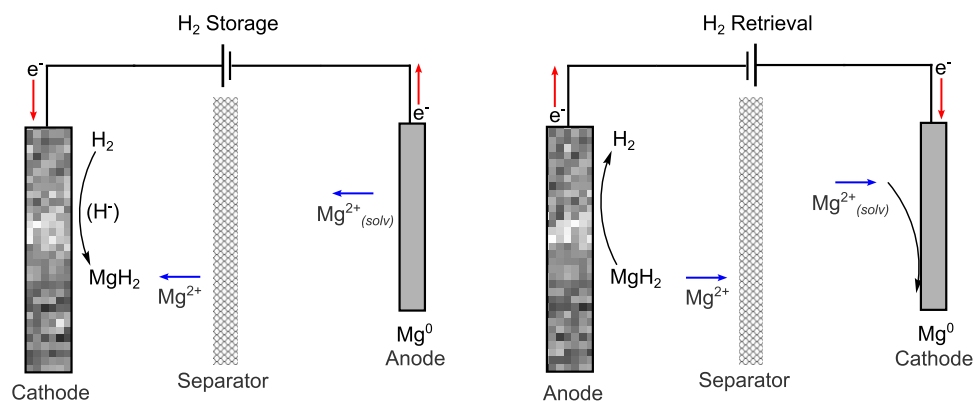
Figure 3. Schematic of an electrochemically mediated hydrogen storage system. The left image depicts H_2 storage, while the right panel depicts H_2 release/retrieval. The system depicted here is a magnesium-hydride-based system, but alternative metal hydrides may also be viable.

Numerous studies have leveraged chemical synthesis to prepare magnesium-based nanomaterials as hydrogen storage materials. Reduction of Mg based salts with strong chemical reductants may yield magnesium metal nanoparticles that exhibit superior properties for the storage and release of H_2 (*vide supra*). Recent work has focused on the reduction of particle sizes and confinement strategies to cap particle size.[21]

Besides thermodynamic considerations, calculations indicate that the dissociation of H_2 on a magnesium surface has a high activation barrier of 21.9 kcal/mol.[22] This high barrier is attributed to magnesium's lack of accessible orbitals of suitable symmetry to cleave H_2 under benign conditions. Pioneering work by Bogdanović et al. demonstrated the catalytic preparation of MgH_2 from H_2 and magnesium mediated by magnesium anthracenide and a Ti/Cr catalyst at room temperature and pressures, highlighting the role of molecular catalysis in hydrogen storage.[23]

POTENTIAL SOLUTIONS: MOLECULAR ELECTROCATALYTIC H_2 REDUCTION, CHALLENGES, AND DESIGN CRITERIA

Based on the physical and chemical properties of ionic hydrides, the following broad challenges can be expected for both thermochemical metal hydride and electrochemically mediated H_2 storage (Figure 2B):

(a) Poor thermodynamic efficiency dictated by the charge-balancing metal cation

(b) Sluggish kinetics for hydrogen uptake and release

(c) Control of particle morphologies

(d) Potential solvent and/or cell component degradation

(e) Low solubility of ionic hydrides

While the thermodynamic efficiency of hydrogen storage and retrieval is fundamentally pinned to the metal of the metal hydride, integration of molecular design with electrochemical H_2/H^- interconversion offers advantages over traditional thermochemical methods, particularly if high temperatures are required, to address the remaining challenges detailed above.

There is precedent for the electrochemical interconversion of H_2 and H^- for non-Mg based systems. Perhaps the most successful systems for the electrochemical storage of H_2, as defined by cyclability, are based on $LaNi_5$ which can be cycled over 1,000 times.[27] However, $LaNi_5$ has a gravimetric energy density of ~1.5%, placing this class of materials well below most current methods of hydrogen storage. In contrast,

aluminum-hydride-based systems have shown enormous promise with respect to gravimetric, volumetric, and overall thermodynamic considerations but suffer from high overpotentials.[28] Studies have observed the effect of additives in these systems, illustrating the role of electrocatalysis in addressing sluggish reaction kinetics.[29,30] Despite the promise shown by aluminum-hydride-mediated electrochemical hydrogen storage, additional work is required to improve the overall reaction kinetics.

A Mg-based electrocatalytic system for the interconversion of H_2 and H^- is depicted in Figure 3. Such a system is conceptually similar to metal-air batteries, which feature a high surface electrode for the reduction of an electron accepting gas (O_2). During discharge, metal-air batteries typically form metal peroxide, superoxide, or oxides with the concomitant release of energy. Upon charging, the discharge product is oxidized back to O_2 and the metal cation is replated onto the counter electrode in its reduced form. In an electrochemical hydrogen storage system, H_2 is reduced to a metal hydride at the cathode for storage, and, when required, the metal hydride is oxidized back to H_2. However, a key difference between a metal-air battery and an electrochemical H_2 storage system is that the primary function of the H_2 storage system is not to derive energy through the interconversion of H_2 and H^- but to compactly store and release H_2 at minimal energetic cost instead. Anticipated challenges and design principles to circumvent these challenges of an electrochemical H_2 storage system are as follows:

(I) M^0/M^{x+} *and molecular electrocatalysts couples must be near that of the H_2/H^- couple.* The H_2/H^- standard redox potential is −2.3 V versus SHE.[11] To minimize energetic losses during hydrogen storage or retrieval, the charge-balancing metal M^0/M^{x+} couple should be close to the H_2/H^- standard redox potential. Magnesium charge balances two hydrides, is a relatively light metal, and has a standard reduction potential of −2.37 V,[31] making it an attractive metal hydride for H_2 storage. Hydrogen produced through metal hydride mediated electrochemical storage is likely to be used in conjunction with fuel cells. The standard potential of the reaction (eq 1)

$$2H_2 + O_2 \rightarrow 2H_2O \tag{1}$$

is 1.229 V vs SHE.[31] However, under practical conditions, the operating voltage of a typical fuel cell is lower, and any H_2/H^- interconversion reaction that is not thermoneutral or has a kinetic barrier will be at the expense of the net fuel cell power output. Therefore, minimizing the exothermicity of the
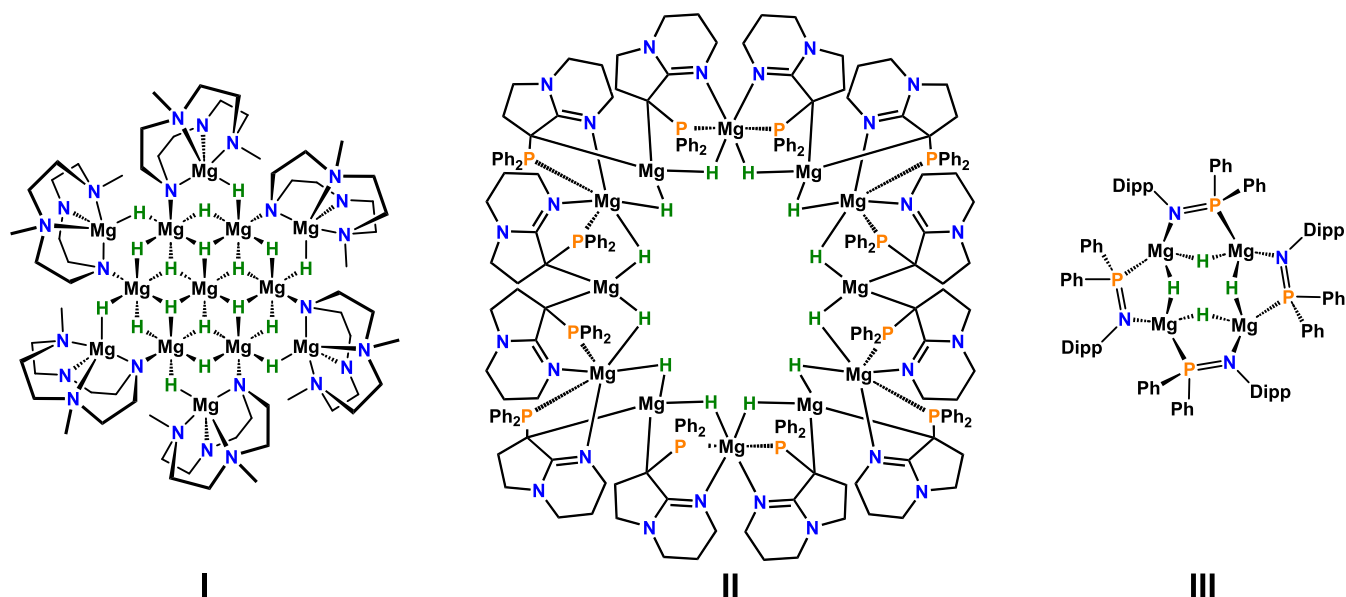
Figure 4. Line drawings of selected molecular magnesium hydride clusters that have been structurally characterized by single-crystal X-ray diffraction studies. Molecular metal hydride clusters have been demonstrated to release H_2 at temperatures below that of bulk MgH_2.

hydrogen storage or retrieval reactions is germane to energetically efficient hydrogen storage. Based on this criterion, Mg and Al are suitable targets while Li is not.

Electrochemically mediated hydrogen storage introduces a knob to allow for careful modulation of reaction rates: molecular electrocatalysts and synthetic design. As demonstrated by Bogdanović, it is possible to decouple metal hydride formation from the direct reaction of H_2 with the bulk metal through the use of a mediator. Magnesium anthracene reacts directly with H_2 to afford MgH_2, but without a titanium cocatalyst, hydrogenation of anthracene also occurs.[32] These results indicate that molecular mediators have considerable potential as catalysts for the formation of MgH_2, but if molecular mediators are to be utilized, the mediator must induce homolytic rather than heterolytic cleavage of H_2 as the latter introduces a proton that now must be accounted for.

Incorporation of molecular mediators to leverage tailorable kinetic profiles for the reduction and oxidation of H_2 also necessitates that that reduction potential of the mediator be near that of the H_2/H^- couple. Many electron transfer reagents have been introduced with reduction potentials near -2.3 V versus SHE,[33−36] and through careful molecular design, these electron transfer reagents may potentially function as a mediator ([Med]) for the interconversion of H_2 and H^- (eq 2).

$$H_2 + 2[Med]^- \leftrightarrow 2H^- + 2[Med] \tag{2}$$
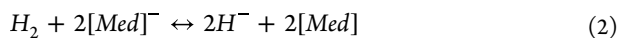
Structure−function studies may elucidate critical requirements for the stabilization of intermediates during the required reduction and oxidation reactions of a hydrogen storage system.

While the use of molecular mediators may offer the possibility to mitigate kinetic challenges associated with hydrogen storage, notable recent work examined the metal surface catalyzed reduction of H_2 to H^- directly on a polarized electrode surface.[37] Tuning of the electrode potential enabled the transfer of a hydride to a range of molecular hydride acceptors in solution. These results indicate it is possible to not only decouple metal hydride formation from the direct

reaction of metal and H_2, but solution mediators may need to not also directly react with H_2 and can instead address important considerations detailed below.

(II) *Reversible plating of the metal must occur on the cathode.* A prerequisite of a cyclable electrochemical hydrogen storage system is the ability to interconvert H_2/H^- and the supporting metal M^0/M^{x+}. Historically, the controlled electrochemical cycling of many metals, including magnesium, has been a major challenge, but recent advancements in electrolyte design, cathode and anode engineering, and solid electrolyte interphase forming additives have greatly enhanced the viability of a magnesium-based hydrogen storage system.[38] A potential challenge to the implementation of a metal hydride-mediated electrochemical hydrogen storage system is the intrinsic reaction of hydrogen with magnesium electrodes. Fortunately, the background rate of reaction of bulk magnesium metal with hydrogen at room temperature is negligible.[39] Research on alternative metals, such as aluminum, have also shown great potential to yield rechargeable systems.[40]

(III) *Control of size and morphology of metal and metal hydrides.* Controlling the size of both the metal and the metal hydride is of critical importance to maximize surface area and minimize energetic losses through the formation of thermodynamically stable bulk ionic hydride structures. Within the domain of magnesium-based hydrogen storage materials, numerous strategies have been developed to either confine Mg/MgH_2,[41] form composites,[42−44] form metastable MgH_2 phases,[45] or develop new solution processes[46] to modulate the size of the materials.[21]

Chemists have leveraged synthetic design to access molecular magnesium hydride or soluble magnesium hydride clusters.[47] With careful selection of a supporting ligand, reaction conditions, and solvent, a variety of structurally characterized and organic solvent soluble magnesium hydride complexes have been prepared. Notable examples of molecular magnesium hydride clusters include the tridecanuclear cluster $[Mg_{13}(Me_3TACD)_6(\mu_2-H)_{12}(\mu_3-H)_6]A_2$ **I** ($A = [AlR_4]^-$, TACD = 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane) **II**,[48]

dodecameric cluster $[(PN5)_{12}Mg_{12}H_{12}]$ (PN5 = phosphino enamide),[49] and tetrameric cluster $[(Ph_2PNDipp)MgH]_4$ (Dipp = 2,6-diisopropylphenyl) **III** (Figure 4).[50] Generally, the ancillary ligands required to support magnesium hydride clusters are anionic, sterically bulky, and rely on heteroatoms to coordinate to the magnesium centers. Many of the aforementioned complexes are kinetically protected against MgH_2 precipitation,[47] although it would be desirable to identify solubilized MgH_2 clusters in equilibrium with solid MgH_2, thereby enabling the solubilizing ligand (L) to act in catalytic fashion and shuttle MgH_2 to and from the electrode surface (eq 3).

$$MgH_{2(s)} + L \leftrightarrow MgH_2@L \tag{3}$$

Several molecular magnesium hydride clusters have been demonstrated to release hydrogen at temperatures considerably lower than that of bulk MgH_2, highlighting the promise of molecular magnesium hydride clusters as hydrogen storage materials.[51,52]

An additional consideration for the inclusion of a ligand to solubilize MgH_2 is the relative stability of the ligands under electrochemical operating conditions. The heteroatoms present in the supporting ligands of **I−III** and similar complexes may degrade to form magnesium pnictide phases, and although most molecular magnesium hydride complexes are formed under fiercely reducing conditions, it remains to be seen how solubilizing ligands survive hundreds or thousands of cycles of hydrogen storage and release. The unknown long-term stability of MgH_2 solubilizing ligands mirrors a closely related challenge in the lithium-ion battery community: electrolyte reductive stability and lessons learned in this field may be applicable here.[53]

(IV) *Metal hydrides display poor electrical conductivity and electrode passivation must be prevented.* While oxide-free magnesium metal is electrically conductive,[54] MgH_2, as with most ionic hydrides, does not display appreciable electrical conductivity.[55] Therefore, the deposition of MgH_2 on an electrode surface during hydrogen storage processes would be detrimental to system performance. Similar concerns are encountered with electrochemical storage systems involving poorly conductive discharge products such as in metal-air batteries.[56] The passivation of electrodes in metal-air batteries is caused by local concentrations of discharge products exceeding their solubility limit. The conceptual similarities between metal-air batteries and an electrochemical metal hydride-mediated hydrogen storage system imply that similar mitigation strategies, such as modification of charge/discharge protocols or inclusion of electrolyte additives, electrode overlayers, or electrocatalysts to the cell,[57] may be leveraged to store hydrogen. In particular, suitable solution stabilizing ligands and electrocatalysts may be designed to spatially control the deposition and dissolution processes of metal hydrides. Electrocatalysts with tunable redox potentials and modalities of H_2/H^- activation along with ligands supporting magnesium hydride clusters detailed in design criteria (III) are envisioned to modulate solubility of MgH_2 and thus provide an avenue to address the passivation of electrodes.

(V) *The metal and metal hydrides must be electrochemically accessible.* While direct deposition of MgH_2 on an electrode may be potentially undesirable due to surface passivation, shuttling and deposition of MgH_2 away from the electrode surface may reduce the round-trip cycling efficiency. Strategies would need to be developed to shuttle MgH_2 back to the

electrode through solubilization (Figure 5), or an electro-catalyst must be capable of mediating the direct oxidation of
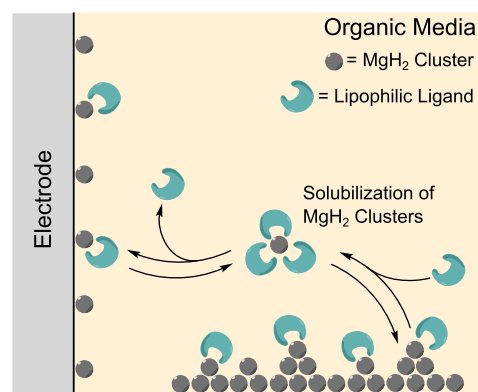

Figure 5. Ligands of I−III depicted in Figure 4 may serve as potential metal hydride shuttles in an electrochemically mediated hydrogen storage system, thereby bypassing the poor conductivity of metal hydrides.

MgH_2. While oxidation of transition metal hydrides has been thoroughly investigated,[58] oxidation of ionic metal hydrides has been, by comparison, less thoroughly explored and greater fundamental insight is required. The oxidation of C−H bonds by organic mediators is of critical importance for synthetic chemistry and potential mediators may be identified within this literature.[59] Similarly, recent advances in H^- conductive materials such as oxyhydrides may be leveraged to overcome poor electronic conductivity.[60]

■ FUTURE PERSPECTIVES AND CONCLUSIONS

Hydrogen is expected to play a pivotal role in a future built on renewable energy sources, and accordingly, strategies to reversibly store hydrogen in a compact manner are of critical importance. There are many intrinsic challenges associated with the storage of hydrogen that have limited its adoption as a fuel, and many lines of inquiry have sought to address these challenges. In this perspective, we describe anticipated challenges associated with electrochemically mediated metal hydride/H_2 interconversion processes and potential solutions to said challenges. Several examples of electrochemically mediated metal hydride/H_2 interconversion exist, but major challenges associated with the realization of such a technology include thermodynamic efficiencies of metal hydride formation, sluggish kinetics, and electrode passivation. To mitigate these challenges, we propose potential solutions to these problems through molecular design of molecular mediators that may control factors such as metal hydride solubility, particle morphology, and hydride affinity. The coupled use of molecular design and electrochemistry would introduce new avenues of hypothesis-driven inquiry of hydride/H_2 interconversion processes and potentially obviate barriers currently faced with the implementation of hydrogen storage technology. Overall, electrochemically mediated metal hydride/H_2 interconversion is still in its infancy, and significant advancements are necessary to resolve the current problems. Fortunately, advancements in battery technologies, synthetic molecular design, and heterogeneous electrochemistry are anticipated to bridge the gap between conceptual demonstration and workable devices. While the discussion here is primarily limited to Mg, other metal systems are expected to

benefit from similar design criteria. The melding of synthetic molecular design, possessing capabilities to ameliorate kinetic challenges, with the operational simplicity and control of electrochemistry is ripe for exploration and offers the potential to address many challenges that currently limit metal hydride hydrogen storage technologies.

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https://pubs.acs.org/10.1021/prechem.4c00030

Author Contributions

The manuscript was written through the contributions of all authors. All authors assisted during the manuscript preparation. All authors have given approval for the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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