



Viewpoint Paper

Recent progress in hydrogen-rich materials from the perspective of bonding flexibility of hydrogen

Shigeyuki Takagi^{a,*}, Shin-ichi Orimo^{a,b}^a Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan^b WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

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ABSTRACT

The bonding flexibility of hydrogen is a source of various interesting functionalities in hydrides. Here, we illustrate the benefits of this flexibility through several selected examples of recent progress in the development of hydrogen storage materials. From the viewpoint of electronegativity, we discuss the diverse cohesion and materials science underlying the bonding flexibility of hydrogen in hydrides.

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1. Introduction

Hydrogen, although having only one electron, exhibits an exceptionally rich chemistry, forming various chemical bonds in materials. For an intuitive understanding, Fig. 1 illustrates such a bonding flexibility of hydrogen with a tetrahedral diagram (hereafter, “hydrogen diagram”). The spheres occupying each vertex of the diagram represent four ideal chemical-bonding states in which hydrogen occurs: (i) interstitial hydrogen (H^0 , ~ 0.53 Å in radius [1]) dissolved in the metal lattices, (ii) proton (H^+ , ~ 0 Å in radius [2]) normally found in acids, (iii) hydride ion (H^- , 1.4 – 2.1 Å in radius [1,3]), as in the perovskite hydrides, and (iv) covalently bonded hydrogen (H^{cov} , ~ 0.37 Å in radius [4]), as in the complex hydrides.

In actual materials, hydrogen occurs in intermediate states away from the vertices. A good example is the perovskite hydride $LiNiH_3$, which possesses a metallic electronic structure in which substantial hybridization occurs between the Ni *spd* and H *1s* states [5,6], even though the ideal perovskite structure is normally observed in ionic hydrides. In this case, hydrogen would occur at the edge between H^- and H^{cov} in the hydrogen diagram. In addition, several materials that contain multiple hydrogen atoms with obviously different chemical-bonding states exist [7–12]. For instance, the complex transition-metal hydride $Na_2Mg_2FeH_8$ contains two H^- ions in addition to a transition-metal hydride complex, $[FeH_6]^{4-}$, whose cohesion is dominated by covalent

interactions (H^{cov}) [10]. In this case, the two types of hydrogen would appear separately in the diagram. As such, the hydrogen diagram covers all such flexible chemical-bonding states.

The bonding flexibility of hydrogen leads to various functionalities in hydrides, including hydrogen storage [7,10,13–17], fast ionic conductivity [18–23], superconductivity [24–28], magnetism [29,30], and metal–insulator transition [8,31]. The monovalency of the H^- ion provides tunability of the charge state when incorporated into materials or substituted for elements with different valence charge states. This tunability enables the inclusion of a wider variety of cations, thereby enabling tuning of material properties, such as hydrogen dissociation temperature [10,11] and the occurrence of spin ordering [29]. The high solubility of monoelectronic H^0 in metals allows the fine tuning of the electron count, leading to a drastic change in the optical properties of host materials [8,31]. In particular, the recent discovery of a 190-K superconducting phase in hydrogen sulfide under compression [30] has led to a renewed interest in hydrogen-rich materials [27,28]. In these materials, a large amount of hydrogen would have already undergone a form of chemical precompression, leading to metallization at a pressure much lower than that predicted for pure hydrogen [24].

Besides the technological importance of hydrides, there is also a considerable scientific interest in unraveling their diverse cohesion. A key to the flexibility of hydrogen would be the specific electronegativity, which is of average magnitude among all the elements, leading to a drastic change in the chemical-bonding states depending on which elements hydrogen interacts with and on the presence of even small perturbations. In turn, the specific

* Corresponding author.

E-mail address: shigeyuki.takagi@imr.tohoku.ac.jp (S. Takagi).

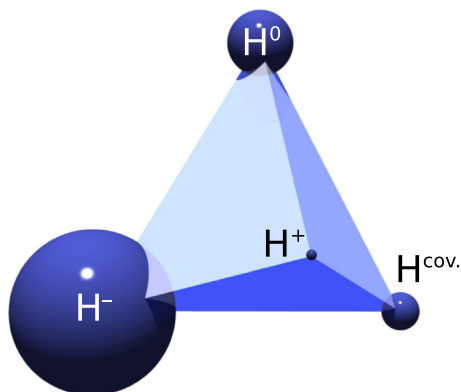


Fig. 1. Hydrogen diagram. This diagram illustrates the bonding flexibility of hydrogen with a tetrahedron; the spheres located at each vertex represent a proton (H^+), a hydride ion (H^-), covalently bonded hydrogen ($H^{\text{cov.}}$) and neutral hydrogen (H^0).

electronegativity of hydrogen causes difficulty in quantitatively understanding the chemical bonding related to hydrogen and thereby often provokes controversy [32–35].

In this Viewpoint, recent progress in the development of hydrogen storage materials is taken as an example to explain the benefits of the bonding flexibility of hydrogen. We then discuss the diverse cohesion in hydrides and the materials science underlying this flexibility from the viewpoint of electronegativity.

2. Recent progress in solid-state hydrogen storage

Solid-state hydrogen storage is divided into several classes according to the storage medium used. A prototypical medium is metallic hydrides, such as $TiFeH_2$, in which hydrogen interstitially dissolves into the metal lattices, primarily as H^0 . Some of these materials exhibit very promising properties, such as fast reaction kinetics, reversible hydrogen uptake/release under modest temperature and pressure conditions, and high volumetric hydrogen capacity; however, their gravimetric hydrogen capacities are insufficient for automotive applications [36] (e.g., the US Department of Energy's system target for 2017 is 5.5 mass% [37], which is much higher than the 1.9 mass% of $TiFeH_2$ alone).

Among the methods spanning many approaches, one involving the use of complex transition-metal hydrides has a clear advantage in volume and weight efficiencies and has thus attracted attention for many years. The major disadvantage of this method is the high hydrogen dissociation temperature that arises from the high thermodynamic stability of the complex transition-metal hydrides, which makes reversible room-temperature applications challenging. For example, dimagnesium iron(II) hydride (Mg_2FeH_6), which is composed of only abundant elements, reversibly stores 150 kg H_2/m^3 and 5.5 mass% of hydrogen; however, its operating temperature reported is approximately 773 K [38].

The complex transition-metal hydrides used as the storage medium in this method refer to the insulating hydrides that contain homoleptic transition-metal hydride complexes such as $[FeH_6]^{4-}$ [7,13,39]. The ligand-field effects play a key role in the formation of the hydride complexes [10,12,40–43], as discussed in detail below.

Fig. 2 shows a schematic for the formation of the electronic structure of a prototypical complex transition-metal hydride, Mg_2FeH_6 , from energy levels of the constituent elements (note that this material consists of two magnesium atoms and an FeH_6 structural unit, in which the iron atom is octahedrally coordinated by

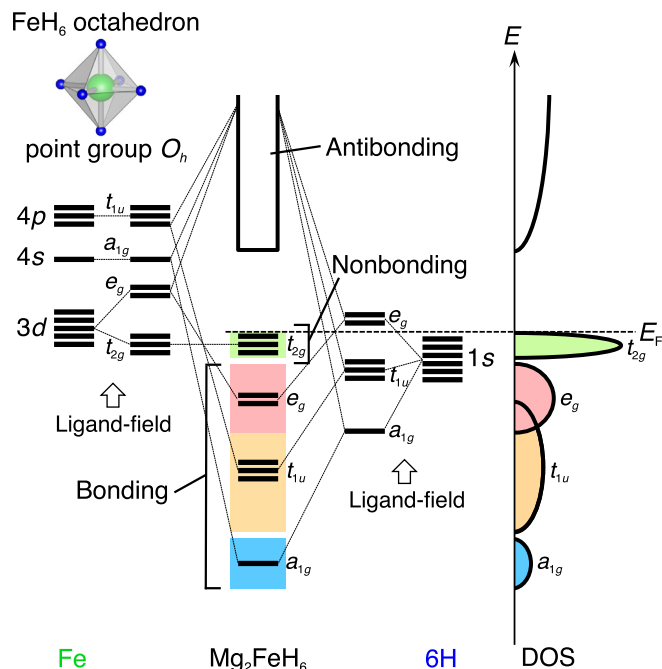


Fig. 2. Schematic of the formation of the electronic structure of Mg_2FeH_6 from the energy levels of the Fe 3d, Fe 4s, Fe 4p, and H 1s orbitals in the octahedral ligand field with O_h point group symmetry.

six hydrogen atoms). In the octahedral H ligand field with O_h point-group symmetry, the Fe 3d, 4s, and 4p orbitals hybridize with H 1s orbitals (sp^3d^2 hybridization), forming six bonding states (nondegenerate a_{1g} , threefold degenerate t_{1u} , and twofold degenerate e_g symmetry states), three nonbonding states (threefold degenerate t_{2g} symmetry states) and the corresponding antibonding states (a_{1g}^* , t_{1u}^* , and e_g^* symmetry states). All of the bonding and nonbonding states are fully occupied by the eighteen electrons, and the Fermi level falls in the gap between nonbonding and antibonding states. The electropositive Mg orbitals occur further above the antibonding states and thus donate a total of four electrons to the FeH_6 unit. As such, the cohesion of the FeH_6 unit is dominated by the Fe-H covalent interactions stabilized by the charge transfer from electropositive Mg, leading to high thermodynamic stability in this material. On the basis of hydrogen diagram in Fig. 1, the six hydrogen atoms forming the hydride complexes can primarily be understood as $H^{\text{cov.}}$.

From the electronic structure viewpoint, one expects that the thermodynamic stability of Mg_2FeH_6 can be tuned through modifying the covalent interactions in the hydride complexes by altering the charge transferability of counterions, i.e., by cation selection. In this context, Miwa et al. theoretically examined the correlation between the cation electronegativity and the thermodynamic stability in a series of $(M, M')_2[FeH_6]^{4-}$ complex transition-metal hydrides in which two Mg atoms in Mg_2FeH_6 are substituted by the various elements with different electronegativities [17], similar to the approach Nakamori et al. used to investigate a series of $M(BH_4)_x^-$ borohydrides [14].

The black open circles in Fig. 3 show the standard heats of formation of complex transition-metal hydrides $(M, M')_2FeH_6$ as a function of the cation electronegativity on the Allred-Rochow scale [44]. As expected from the bonding scheme, a linear correlation between them is clearly observed; i.e., the thermodynamic stability of Mg_2FeH_6 can be tuned by substitution of Mg with elements having different electronegativities.

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