

Computational Investigation of Hydrogen Storage in Magnesium based Alloys

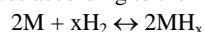
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Introduction

Hydrogen is an appealing energy carrier, in particular for mobile applications such as cars and boats. There are, however, many challenges to overcome before hydrogen becomes practical and storage is the greatest technical issue. A suitable hydrogen storage must among other things be able to contain at least 6 weight percent of hydrogen and be able to desorb hydrogen gas at atmospheric pressure when heated to ca. 100°C, the operating temperature of the fuel cell.

Many metals are known to react reversibly with hydrogen gas to form metal hydrides according to the following equation:



These metals thereby act as hydrogen “sponges” and can store a great amount of hydrogen per unit volume. However, one must keep in mind that many metals are heavy and can thus be impractical for hydrogen storage in vehicles.

Magnesium as Hydrogen Storage

Magnesium (Mg) is a light, inexpensive metal that can absorb hydrogen to form a hydride MgH_2 , where the weight percent of hydrogen is 7.6. Experiments show, however, that hydrogen binds too strongly in the Mg, having a binding energy of 0.39 eV/atom, and the hydride must therefore be heated to more than 247°C to release the hydrogen [1,2]. The dissociation of hydrogen molecules at the surface of Mg and the diffusion of hydrogen through the hydride are also so slow that loading and unloading of hydrogen takes excessively long time. Experiments have shown that the dissociation process can be enabled by adding a catalyst, e.g. palladium (Pd), on the surface of the Mg crystal. Measurements also indicate that binding energy can be reduced and diffusivity increased by adding small amounts of transition metals (TM), e.g. Ti, to the magnesium. The task remains, however, to find a Mg-TM alloy that remains stable during hydrogenation and dehydrogenation.

Theoretical calculations

We have carried out theoretical calculations based on density functional theory to study how binding energy and diffusivity of hydrogen change in magnesium hydride when transition metals are added. The calculations make use of a plane wave basis set, ultrasoft pseudopotentials, the PW91 gradient dependent functional and the VASP code [3,4].

Results

According to our calculations the binding energy of hydrogen in pure magnesium hydride is 0.38 eV/atom and the corresponding hydrogen release temperature is 246°C. Both values are in very good agreement with experimental values. Release temperature calculations make use of classical mechanics for determination of all vibrational modes in the

crystal. Each vibrational mode is then treated quantum statistically.

A cubic crystal structure with the unit cell of Mg_7TiH_x has been synthesized under high pressure [5]. Our calculations have shown that $x=18$ and that the hydrogen ions sit near boundaries between tetrahedral and octahedral holes in the lattice. The structure of the hydride is shown in figure 1. The calculations give a binding energy of 0.25 eV/atom and a 55°C release temperature. A large increase in diffusivity of hydrogen is also predicted from the calculations. The problem is, however, that the alloy decomposes during dehydrogenation.

We have performed systematic calculations in order to find a transition metal that is likely to form a stable Mg-TM alloy. The structure of Mg_7TiH_x was used to model other Mg-TM hydrides. The calculations were performed for 10 lightest transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) and an optimal hydrogen load was determined for each of the Mg-TM hydrides. Trends in weight percentage, binding energy and diffusivity were investigated with respect to different transition metals. The calculations show that formation of all Mg-TM hydrides is theoretically favorable and that binding energy is reduced and diffusivity increased as compared to with pure magnesium hydride. Scandium (Sc) and Zinc (Zn) are most likely to form a stable Mg-TM alloy. This is in accordance with experiments on Mg-Sc systems, carried out in Philips Research laboratories. Not much is known about Mg-Zn systems.

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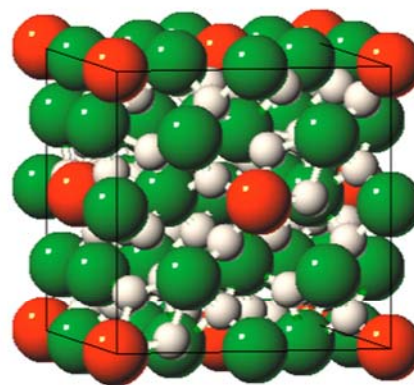


Figure 1: Structure of Mg_7TiH_{18} . The hydrogen ions sit near boundaries between tetrahedral and octahedral holes.

References

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