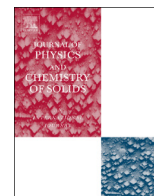




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A review of catalyst-enhanced magnesium hydride as a hydrogen storage material



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ABSTRACT

Magnesium hydride remains an attractive hydrogen storage material due to the high hydrogen capacity and low cost of production. A high activation energy and poor kinetics at practical temperatures for the pure material have driven research into different additives to improve the sorption properties. This review details the development of catalytic additives and their effect on the activation energy, kinetics and thermodynamic properties of magnesium hydride.

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1. Introduction

Hydrogen energy has been the topic of much research in the past few decades due to the possibility of a largely pollution-free energy which can be sourced from a variety of renewable sources such as solar, wind and wave power. Hydrogen is abundant, produces water when combusted and has a substantially greater energy density than gasoline (141.2 MJ/kg cf. 47.3 MJ/kg [1]). The consequences of reduced reliance on fossil fuels provides governments world-wide with the two-fold motivation of lower cost of fuel imports and a partial solution to environmental issues through reduced carbon dioxide emissions from the combustion of hydrocarbons. Advances in technologies such as fuel cell design and manufacture as well as increasing energy provision from renewable resources leads to growing commercialisation as evidenced by several leading automobile manufacturers now testing prototype hydrogen cars, for example, General Motors' HydroGen4 and the Toyota FCV Concept—both fuel cell vehicles.

While techniques for production of hydrogen will continue to improve, there is already an established technology for producing hydrogen from water as well as other sources. At the other end of the energy vector, hydrogen can be used in fuel cells for electricity generation or used to fuel a combustion engine. The unresolved issue in the use of hydrogen – particularly in the area of mobile applications – is safe and efficient storage of the hydrogen [2,3]. Current hydrogen vehicle prototypes often use compressed gas

with the inherent problems of poor volumetric energy density (4.4 MJ/l at 700 bar), high cost of containment and safety issues. Liquefied gas systems increase the energy density to 8.4 MJ/l at the cost of reduced efficiencies in the provision and maintenance of cryogenic cooling (20 K).

Solid state storage offers several advantages including high energy density, lower costs of containment and greater safety. For example, a tank with an intermetallic hydride at a pressure of 2 bar can store the same amount of hydrogen as the same volume of gas at 1800 bar [3]. Unfortunately, such metal hydrides capable of this storage are extremely heavy, out-weighting the other advantages. Solid state storage in light-weight materials has consequently been an area of active research. Although many different types of materials have been investigated and still are being investigated, there remain significant problems with each of the areas of possible hydrogen storage materials. Carbon-based storage and other techniques employing physisorption (van der Waals attraction) offer light-weight, inexpensive storage but typically require low temperatures to achieve sufficient hydrogen capacity. Metal hydrides, including the intermetallics typically have fast kinetics and can be tailored to appropriate temperature and pressure ranges to support fuel cells and low cost containment, but still have low gravimetric energy densities (1–3 wt%) and are often expensive due to the rare metal constituents. Complex hydrides and chemical hydrides, including the borohydrides, alanates and amides are often not reversible or require high temperatures for release of the hydrogen.

Magnesium is a material which offers some promise as a hydrogen storage material. It is a light-weight metal, found in abundance in the earth's crust (predominantly as carbonates) and

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sea water (as a chloride) and is relatively cheap to extract. The metal reacts with hydrogen reversibly to form magnesium hydride (MgH_2) which has a moderately high storage capacity of 7.6 wt% (cf. LiH at 12.6 wt%).

As for other potential hydrogen storage materials, there are drawbacks which prevent the immediate application of MgH_2 to hydrogen-based energy systems. In its pure form, MgH_2 requires quite high temperatures to release the hydrogen (ca. 350 °C). Repeated application of the heat necessary for this temperature is expensive as well as reducing the viability for mobile applications. As the magnesium reacts with hydrogen at the solid–gas interface first, the subsequent hydriding requires the diffusion of hydrogen through the magnesium hydride layer which is known to be slow [4]. The poor kinetics limit the rate at which hydrogen can be stored. Additionally, because the reaction is exothermic (storing the hydrogen) or endothermic (releasing the hydrogen), heat transport in the material is an important factor and MgH_2 has very low thermal conductivity of about 0.4 W/m K [5].

The purpose of this paper is to review the progress in the development of catalytic additives to enhance the practical hydrogen storage properties of MgH_2 . Because of the large scope of activity in the area, the review is limited to composite materials in which Mg is the predominant material and any other materials present serve primarily as additives, catalysts or support systems for heat management, gas flow or particle size management. In particular, the additives reviewed are metal-based additives, such as elemental metals, alloys, metal oxides and halides. Reviews are available for other types of hydrogen storage materials involving MgH_2 , such as the complex hydrides [6–8]. Extremely high pressure (GPa) modification of materials is another burgeoning area of research in hydrogen storage materials and a recent review is given by Song [9]. Different mechanochemical synthesis methods for hydrogen storage materials are reviewed by Huot et al. [10], use of nano-materials, including carbon scaffolding is reviewed in Niemann et al. [11], Zlotea et al. [12] and Cheng et al. [13] and the use of carbon additives such as nanotubes, expanded graphites or graphene in Lototskyy et al. [14] and Tjong [15].

1.1. Magnesium hydride

Magnesium hydride can be synthesised directly from the pure metal in the presence of hydrogen gas. Thermodynamically, the reaction should proceed at quite low pressure (< 1 bar) and low temperatures (at least below 50 °C), however, in practice the kinetics are slow [16,17] requiring higher pressures and temperatures to provide pressure drive and thermal energy to improve the kinetics. Without any additives, activation (breaking through the oxide or hydroxide surface layer) also requires energy necessitating higher temperatures—at or above 350 °C under hydrogen pressures to 70 atm [18]. For absorption, the reaction is limited by combined steps of physisorption and dissociation of the molecular hydrogen, diffusion through any existing hydride layer and nucleation of the hydride. For desorption, the process consists of nucleation of the metal phase, diffusion of the atomic hydrogen through the metal and hydride and recombination to molecular hydrogen at the surface. The rate-limiting process for desorption is diffusion of the hydrogen through the hydride material [17].

As pressure of hydrogen is first applied to Mg, a solid solution of hydrogen in magnesium forms, followed by nucleation and growth of the hydride phase. At 300 °C, the equilibrium pressure of the plateau region (hydride phase growth) is 0.87 bar. After the hydride reaction has reached completion, forming the MgH_2 , the maximum hydrogen uptake of 7.6 wt% is achieved and no further uptake is observed for higher pressures. Measuring pressure composition temperature (PCT) isotherms at different temperatures

allows use of the van t'Hoff equation to calculate enthalpy and entropy for the reaction. The relatively high enthalpy of ca. –75 kJ/mol [19,20,21] confirms the strong Mg–H bonds necessitating high temperatures for release of the hydrogen. The entropy values determined are 130–136 J/mol/K.

Clearly, bulk MgH_2 is not a suitable hydrogen storage material due to the high temperatures required for desorption and the slow kinetics. Because of this, a considerable amount of research has been done on ways to improve the hydrogen sorption properties. Combination with small amounts of other materials acting as catalysts or reaction path modifiers has shown improvement in absorption and desorption kinetics.

2. Additives

Transition metals are known to promote the dissociation and re-combination of hydrogen and where this is a limiting rate for the absorption or desorption reaction, kinetics could be improved by the addition of small amounts (typically 1–5 mol%) of such materials. Liang et al. [22] ball-milled 5 mol% Ti, V, Mn, Fe, and Ni with MgH_2 for 20 h to investigate the kinetics and the thermodynamics of the mixtures. Desorption times were observed to decrease markedly with V the most effective additive, but the enthalpy and entropy were unchanged. In this article, non-transition metals (Ca and Al) as well as non-metals (C) were also investigated and were found to have no effect on the kinetics despite reduced grain size due to the milling process.

A range of metals, including Pd, Fe, V, Zr, Ti and Mn as well as combinations of those metals were used as a catalysts by Zaluska et al. [23]. Nano-crystalline magnesium of varying grain size was produced by ball-milling Mg under Ar with different concentrations of additive for times ranging from 15 min to 20 h. The most effective combinations were V and Zr and a mixture of Mn and Zr.

Magnesium with 10 wt% of Co, Ni or Fe was ball-milled for varying times from 0 to 10 h under hydrogen (and under Ar for the Co mixtures) by Bobet [24]. It was found that crystallite size decreased with increasing milling time and that milling under Ar produced smaller crystallite sizes than the same materials under hydrogen. MgH_2 was successfully produced for the longer milling times.

Also using reactive ball-milling, Wang et al. [25] milled Mg with 10 wt% TiO_2 up to 6 h, sampling at intervals. Hydrogen content reached 2.5 wt% after 10 min at 160 °C and 20 bar hydrogen pressure. Desorption was close to complete after 10 min at 350 °C and 1 bar of hydrogen. It was suggested that not only did the TiO_2 enhance absorption through facilitating dissociation at the surface of the Mg, but that embedded TiO_2 particles also provided a diffusion pathway for H atoms, enhancing the diffusion rate.

Oelerich et al. [26] investigated metal oxides as additives for the MgH_2 system, using 5 mol% of additives Sc_2O_3 , TiO_2 , V_2O_5 , Cr_2O_3 , Mn_2O_3 , Fe_3O_4 , CuO, Al_2O_3 and SiO_2 . The magnesium hydride was milled for 20 h prior to additives and each additive was milled with the MgH_2 for a further 100 h. They found that all the oxides enhanced sorption kinetics, that Cr_2O_3 was most effective for absorption (about 4.5 wt% hydrogen in 2 min) while V_2O_5 and Fe_3O_4 were the most effective for desorption with all samples desorbed in 5 min at 300 °C. Importantly, they note that little as 0.2 mol% of the additive was effective.

In a subsequent paper, the same authors compared the use of 5 mol% V, VN, VC and V_2O_5 additives by reactive ball-milling with MgH_2 and found all the compounds significantly improved absorption, achieving maximum hydrogenation in ca. 2 min [27]. Interestingly, elemental vanadium had little or no effect. It was

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