Hydriding and Dehydriding Reactions In Mg-Based Hydrogen Storage Materials: Thermodynamics and Kinetics

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Abstract

The high hydrogen storage capacity, environmental friendliness, and high Clarke number properties of magnesium-based materials make them one of the most attractive hydrogen storage choices. The restricted thermodynamics and kinetic properties, however, provide significant difficulties for their engineering applications. Here, we examine recent advancements in their thermodynamics and kinetics, focusing on the models and the effects of different model parameters. Following that, the effects of alloying, composites, and nano-crystallization on thermodynamics and dynamics are thoroughly covered. In particular, the correlations between different modification tactics and the hydrogen capacity, dehydrogenation enthalpy and temperature, and hydriding/dehydriding rates are outlined. Additionally, the classical kinetic theories and microscopic hydrogen transferring behaviour are explored in relation to the mechanism of hydrogen storage processes of Mg-based materials. An assessment of the remaining challenge issues and future prospects concludes this review.

Keywords: *Magnesium-based hydrogen storage materials; Hydriding/dehydriding reactions; Thermodynamics; Kinetic models; Analysis method*

INTRODUCTION

Reducing carbon dioxide emissions is one of many sectors' key concerns as a result of the global environmental and energy crises.

Numerous plans have been put out to reduce CO2 emissions. Although natural resources like solar electricity, wind, geothermal, and tidal energy are the top contenders for renewable energies, they have intermittent, capacity-unstable, and unpredictable characteristics because of their reliance on the environment and time zones. As a result, large-scale energy storage and conversion devices are required for the actual applications because the current power grid systems cannot handle the direct usage of such unstable energy sources. Due to their high energy density, lack of CO_2 emissions, and variety of renewable energy sources, there is a growing consensus that hydrogen (H_2) energies can provide a more effective energy solution to combat global warming.

It is essential to develop the supply chains for H_2 production, purification, storage, and consumption in order to support the widespread application of H_2 energy. The process for transporting and using hydrogen is among them the most difficult. There are currently three main methods for storing hydrogen:

(1) liquid hydrogen in cryogenic tanks

(2) high-pressure gas cylinders

(3) solid-state hydrogen storage.

Among these, solid-state H_2 storage has drawn a lot of attention due to its potential to operate at relatively ambient pressure and moderate

temperatures while also achieving higher energy densities and better operability. T. Graham produced the first material-based H_2 storage finding in 1869 in Pd [1], where the distance between hydrogen atoms is greatly reduced when the hydrogen atoms are in close proximity. Due to the limited geological Pd reserves, considerable effort has since been put into developing extensive hydrogen storage materials. The creation of non-noble metal materials like LaNi5 and FeTi during the 1970s was a major innovation [2,3]. These materials not only make solid-state H_2 storage less expensive, but they also show that H_2 may be reversibly absorbed and desorbed in reasonably benign reaction circumstances [4].

The successful discovery of intermetallic H_2 storage materials has spurred interest in light metal hydrides, which aim to increase hydrogen storage density [5]. Magnesium (Mg)-based compounds, which boast the benefits of good capacity up to 7.6%, satisfying the US Department of Energy (DOE) objective, great reusability, environmental friendliness, and high Clarke number characteristics, are one of its prospective play areas [6,7]. Due to the remaining difficulties, Mg-based H_2 storage systems (such as those used in FCVs) have not yet been widely commercialised on a large scale. The slow dehydrogenation reaction rate and high operating temperature are the bottlenecks. These problems are intimately related to the thermodynamics and kinetics of hydrogenation reactions. To be more precise, the creation of robust chemical bonds between Mg and hydrogen atoms during the H_2 storage cycle results in great thermodynamic stability and a substantial reaction enthalpy change.

For instance, the enthalpy change (ΔH) of magnesium metal, which is around 75 kJ/mol, results in high working temperature and low equilibrium pressure, which finally prevents further practical usage. Additionally, the Mg/MgH_2 surface's lack of active sites results in high energy barriers for diffusion and dissociation processes, which lowers hydrogenation/dehydrogenation rates. To improve the thermodynamic and kinetic properties of Mg-based H_2 storage materials, various investigations have been conducted. In this review, we concentrate on the thermodynamic and kinetic fundamentals of hydriding and dehydriding reactions, and discuss the advanced methodologies employed for improving the properties of Mg-based hydrogen storage materials. In particular, the significance of nano size effect, alloying and composite structure on improving the thermodynamic properties is elucidated. The influence of catalytic, surface treatment, and nano-sizing on kinetic performances are also discussed. Subsequently, the remaining challenges in developing novel Mg-based hydrogen storage materials are summarized. It is expected that our endeavor in this review can inspire more new ideas to expedite the development in related fields and beyond.

Mg-based materials hold exceptional benefits as a solution for the unavoidable problem of H_2 storage, such as good capacity, fulfilling the DOE final aim, etc., but are constrained by slow thermodynamics and kinetics (High dehydrogenation temperature and low H_2 release rate). The thermodynamics of a reaction is significantly influenced by factors like temperature, enthalpy, and entropy, among others. The Gibbs free energies can be calculated to produce the P-C-T curve.

It also reviews current developments in the kinetic behaviours of materials for storing hydrogen based on magnesium. Four kinetic steps (physisorption, chemisorption, penetration and diffusion, nuclear, and growth) as well as the factors that affect their rates are specifically covered in detail. arious geometrical contraction models, e.g., Jander model, G-B model, V-C model, etc., were discussed based on the hypothesis that hydrogen diffusion is the rate-determining step [8]. In addition, a classical JMAK model was discussed to analyses the nucleation and growth of β phase. On the basis of these models, the activation energy, release rate, penetration process of H_2, nucleation and growth of β phase as well as the phase interface migration, etc. could be accurately predicted. To improve the kinetics of Mg-based H_2 storage materials, various strategies were adopted to lowering the energy barrier or create new diffusion path, including ball milling, catalyst addition, core-shell structure, using external field, etc. These approaches improve the hydrogen absorption/desorption behavior and are helpful for further development of Mg-based hydrogen storage materials. In summary, great efforts have been devoted to study the thermodynamics and kinetics of H_2 storage materials so far.

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