



Review

Tuning kinetics and thermodynamics of hydrogen storage in light metal element based systems – A review of recent progress

H. Wang^{a, b}, H.J. Lin^{a, b}, W.T. Cai^{a, b}, L.Z. Ouyang^{a, b}, M. Zhu^{a, b, *}^a School of Materials Sciences and Engineering, South China University of Technology, Guangzhou, 510640, PR China^b Key Laboratory of Advanced Energy Storage Materials of Guangdong Province, South China University of Technology, Guangzhou, 510640, PR China

ARTICLE INFO

Article history:

Received 11 August 2015

Received in revised form

9 October 2015

Accepted 12 October 2015

Available online 22 October 2015

Keywords:

Hydrogen storage materials

Mg based alloys

Complex hydrides

Nanostructured materials

ABSTRACT

High capacity hydrogen storage is a key issue for future hydrogen energy. The hydrides, constituted of light elements such as Li, B, C, N, Na, Mg, Al, Si, etc., are excellent candidates for high gravimetric and volumetric density of hydrogen storage. However, these light-weight hydrides generally suffer from poor reversibility under moderate temperature and pressure conditions due to over high thermodynamic stability and/or sluggish kinetics. This review summarizes recent advances in the effort of overcoming thermodynamic and kinetic challenges for Mg based hydrides and complex hydrides. With respect to kinetic enhancement, great achievements have been achieved through several successful approaches such as nanoscaling, catalyzing, and compositing. In particular, a simple and massive fabrication method was developed to *in-situ* form multi-valence nano-catalyst in Mg based hydrides by conventional melting and hydrogenation treatment. Also, the reversibility of complex hydrides can be greatly improved through nanoscaling and doping catalysts. Comparatively, the thermodynamic destabilization effect is limited by applying the strategies of nanoscaling, ionic substituting for complex hydrides, alloying for Mg based hydrides, and altering the reaction route. For the approach of nanoscaling, both theoretical calculation and experimental results prove that thermodynamic destabilization can only be achieved by reducing the size of hydrides down to several nanometers, which is extremely difficult to realize and maintain, and thus, nano-confinement has been adopted. On the other hand, although the reversibility of most of Mg based alloys is generally poor, fully reversible hydriding has been achieved in some Mg based solid solution alloys with reduced reaction enthalpy. On the whole, based on the current status of the research progress, the existing Mg based and complex hydrides could not fully satisfy the application requirements of hydrogen energy storage, and the sustainable research effort are still making to solve their intrinsic thermodynamic and kinetic challenges.

© 2015 Elsevier B.V. All rights reserved.

Contents

1. Introduction	281
1.1. Hydrogen energy and current state of hydrogen storage materials	281
1.2. Advantages and challenges for Mg based hydrides and complex hydrides	281
2. Mg based hydrides	282
2.1. Overview	282
2.2. Novel Mg based hydrides	282
2.3. Nanoscaling	282
2.4. Composite and nanocomposite	284
2.5. Catalysis	285
2.6. Destabilizing by altering reaction path	288
3. Complex hydrides	288

* Corresponding author. School of Materials Sciences and Engineering, South China University of Technology, Guangzhou, 510640, PR China.

E-mail address: memzhu@scut.edu.cn (M. Zhu).

3.1. Overview	288
3.2. Nanoscaling	288
3.3. Catalysis	291
3.4. Cation/anion substitution and exchange	293
3.5. Reactive hydride composites	294
3.6. Ammine metal borohydrides	297
4. Summary	298
References	298

1. Introduction

1.1. Hydrogen energy and current state of hydrogen storage materials

Hydrogen has gravimetric energy density of 142 MJ/kg and its burning by-product is only water. In addition, it can be easily transformed to different energy forms such as heat and electricity. Therefore, hydrogen is the ideal media to store and transfer energy harvested from renewable energy sources such as solar energy, geographic thermal energy, wind energy, etc. [1], which is of great significance to solve the current global energy and environment challenge.

On-board and distributed power suppliers are the two most important application fields for hydrogen energy in the clean energy system. To meet those application purposes, the hydrogen storage method should satisfy the following basic requirements. (1) It can provide hydrogen energy comparable to current fuel, which means high volumetric and gravimetric density of hydrogen storage; (2) It can be uptake/released under moderate temperature and hydrogen pressure with enough high rate; (3) It should be environment benign and cost economically. For the gas state storage of hydrogen, 70 MPa pressure is required to reach a hydrogen density of ~5 wt.% by using carbon fiber reinforced Al alloy container. At temperature lower than 20.35 K, hydrogen liquefies with density less than 40 kg/m³ if counting the container. Hydrogen can also be reversibly stored in solid materials with high volumetric and gravimetric density, which has great advantages as fuel supplier.

Mg₂Ni is the first hydrogen storage material found in 1960s, which can reversibly react with H₂ to form Mg₂NiH₄ of 3.6 wt.% hydrogen capacity [2]. Almost at the same time, hydrogen storage in LaNi₅ alloy was discovered [3]. Those discoveries aroused prosperous research activities and the development of other hydrogen storage alloys, such as TiFe, ZrCr₂ and V based solid solution alloy [4,5]. The electrochemical performance of RENi₅ (RE = Rare earth metals) based metal hydrides promoted the invention of Ni-MH battery in 1980s, which has been widely used as power supplier for various electronic devices and hybrid electric vehicles [6]. In recent years, RE–Mg–Ni based AB₃ type alloys [7], have been developed to meet the demands of pursuing higher energy density Ni-MH battery.

However, traditional metal hydrides could not satisfy the requirements of high density hydrogen storage for large-scale hydrogen energy applications [8]. Therefore, numerous hydrogen

storage materials, including light metal hydrides, complex hydrides, chemical hydrides, carbon nanotube, and metal organic frameworks (MOFs), have been extensively investigated for reversible hydrogen storage in recent years [9–11]. Hydrogen exists in the form of its molecules or atoms, falling into two classes of physisorption and chemisorption materials. Table 1 lists the hydrogen storage properties of representative materials.

The hydrogen storage density of physisorption materials depends on the specific surface area. For example, specific surface area up to 2560 m²/g was achieved in activated carbon, leading to a hydrogen storage density of 4.5 wt.% at 77 K [12]. However, high capacity hydrogen storage in porous materials only achieves at very low temperature for physisorption until now, because of the weak interaction between hydrogen molecular and absorbents. The binding energy is normally less than 10 kJ/mol, and the hydrogen storage capacity is usually less than 1 wt.% at ambient temperature. New techniques are aiming to increase the surface area and modify the surface interaction of physisorption materials.

With respect to chemisorption materials, the bonding of H in hydride is too strong in light element based hydrides to release under moderate temperature and hydrogen pressure conditions. Particularly for complex hydrides and chemical hydrides, the reversibility, i.e., the recovery of original hydrides by rehydrogenation is generally poor. Actually, the reversibility has yet not been realized for most of chemical hydrides, such as ammonia boron and sodium boron hydride.

1.2. Advantages and challenges for Mg based hydrides and complex hydrides

In general, light elements, namely Li, B, C, N, Na, Mg, Al and Si, should be the main components of high capacity hydrogen storage materials because their hydrides have high gravimetric and volumetric density. Therefore, Mg based hydrides and complex hydrides with the hydrogen density exceeding the target for on-board application set by DOE [13], being 7.6 wt.% for MgH₂ and 18.4 wt.% for LiBH₄, respectively, are of particular interesting in recent years [14]. In addition, Li, Na, Mg and Al are abundant in the earth that makes massive utilization of their hydrides possible.

However, Mg based hydrides and complex hydrides have unfavorable thermodynamic characteristics, which are aroused from the strong bonding nature of H with light elements. In addition, the rehydrogenation of complex hydrides is also very difficult owing to the complicated reaction steps. The thermodynamic stability could

Table 1
Hydrogen storage properties of different types of materials.

Materials	Capacity (wt.%)	Temperature (°C)	Hydrogenation pressure (bar)
MgH ₂	7.6	300–350	2–15
LiBH ₄	13.9	180–600	100–150
NH ₃ BH ₃	19.6	130	–
Carbon nanotube	2.7	25	500
MOFs	16.4	–196	70

Download English Version:

<https://daneshyari.com/en/article/1607426>

Download Persian Version:

<https://daneshyari.com/article/1607426>

[Daneshyari.com](https://daneshyari.com)