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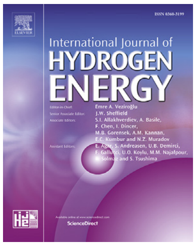

Remarkable hydrogen storage properties and mechanisms of the shell–core MgH_2@carbon aerogel microspheres

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ARTICLE INFO

Article history:
Received 15 September 2017
Received in revised form
18 December 2017
Accepted 2 January 2018
Available online xxx

Keywords:
Magnesium hydride
Carbon aerogel microspheres
Hydrogen storage materials
Reversible de/hydrogenation

ABSTRACT

Carbon aerogel (CA) microspheres with highly crumpled graphene–like sheets surface and network internal structure have been successfully prepared by an inverse emulsion polymerization routine, subsequently ball milled with Mg powder to fabricate Mg@CA. The Mg change into MgH_2 phases, decorating on the surface of the CA forming MgH_2@CA microspheres composite after the hydrogenation process at 400 °C. The MgH_2@CA microspheres composite displays MgH_2–CA shell–core structure and shows enhanced hydrogenation and dehydrogenation rates. It can quickly uptake 6.2 wt% H_2 within 5 min at 275 °C and release 4.9 wt% H_2 within 100 min at 350 °C, and the apparent activation energy for the dehydrogenation is decreased to 114.8 kJ mol^{-1}. The enhanced sorption kinetics of the composite is attributed to the effects of the in situ formed MgH_2 NPs during the hydrogenation process and the presence of CA. The nanosized MgH_2 could reduce the hydrogen diffusion distance, and the CA provides the sites for nucleation and prevents the grains from agglomerating. This novel method of in situ producing MgH_2 NPs on zero–dimensional architecture can offer a new horizon for obtaining high performance materials in the hydrogen energy storage field.

Introduction

Hydrogen, with the advantages of high energy storage, no carbon emission and plentiful in the water which occupies about 70% of earth, is recognized as the most promising substitute for fossil fuel. A variety of materials have been studied in search for a suitable hydrogen storage system to satisfy storage density, beneficial thermodynamics, kinetics as well as low cost [1,2]. Solid state hydrogen storage using metal hydrides is also considered to be more efficient and safer than pressurized or cryogenic hydrogen storage [3]. Magnesium (Mg) exhibits great potential application in the hydrogen storage field because of its nontoxic, low cost, abundant, high theoretical H_2 storage capacity of 7.6 wt% and excellent reversibility [4,5]. However, Mg–based hydrides are strongly

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https://doi.org/10.1016/j.ijhydene.2018.01.004

hindered by the thermodynamically stable and poor kinetics, which the decomposition enthalpy and entropy are as high as 75 kJ mol^{-1} H_2 and 135 J K^{-1} mol^{-1} H_2 [6], respectively. Due to the thermodynamically stable of the Mg–H bond, the release of hydrogen demands an operating temperature above 300 °C [7]. Meanwhile, the sluggish hydrogenation and dehydrogenation kinetics also limit the commercialization process [8]. Over the past decades, tremendous attempts have been undertaken to overcome these thermodynamic and sorption kinetic drawbacks, such as reducing the particle size to nanoscale [9–11], alloying with mental elements [12–16], introducing various catalysts [17–23] and building complex hydrides system [24,25]. Despite the obvious enhancement in the kinetics, high desorption temperature is still required for the reactions to occur. To reduce the desorption temperature, theoretical chemists suggested that several nanometers (<10 nm) size particle of MgH_2 may work [26–29]. Inspired by this prediction, experimentalists have developed novel technologies to synthesize MgH_2 nanoparticles, such as the sonoelectrochemistry [30], chemical reduction in solution [9,31], and the vapor–transport approach [32]. However, those approaches still face some problems including the oxidation and inhomogeneous size distribution of Mg particles owing to the high surface energy of Mg–based hydrides. To stabilize nanosized Mg or MgH_2, porous carbon has been employed and achieved some significant results [33–35].

To date, various carbon materials have been introduced to energy and fuel cells filed [36,37], and mechanical milling is the most common and effective way to disperse carbon materials additives into the Mg/MgH_2 system. Since the early works of MgH_2 catalyzed by graphite in Imamura's team [38], many carbon materials (multi–walled carbon nanotubes [39], single walled carbon nanotubes [40], activated carbon [41]) have been proved in succession that they can promote the de/hydrogenation kinetics as well as lower the de/hydrogenation temperature of MgH_2. Liu et al. [42,43] have investigated the performance of lamellae graphene nanosheets (GNS) with MgH_2 composite which obtained by the method of ball milling. They suggested that the smaller GNS with defective region generates favourable catalytic effects, which could provide more edge sites and hydrogen diffusion channels, prevent the nanograins from sintering and agglomerating, promote of the de/hydrogenation kinetics of MgH_2 at the same time. Although the thermodynamically stability could be solved to some extent by mixing MgH_2 with porous hosts, these strategies are plagued by an irregular spatial distributions, which caused by particle growing at higher temperature and the kinetic properties deteriorate [44]. To prevent particle growth, interparticle contact has to be avoided. For achieving this goal, one feasible strategy is to anchor nanoparticles on the porous support materials with high surface area. The porous structure of the support will control over the particle size as much as possible [45,46].

Recently, carbon aerogel has attracted considerable attention for its various technical applications such as catalyst supports, deionization devices, or battery and supercapacitor due to its high porosity, adjustable pore and particle size [47–49]. And it is accepted that carbon materials play a positive role on de/hydrogenation of MgH_2. Carbon aerogel has been provided tremendous promising applications in energy storage attention because of its large surface area and superior electronic [50,51]. Zhao–Karger et al. [52] formed MgH_2 nanoparticles successfully with a size of <3 nm by direct hydrogenation of Bu_2Mg inside the pores of a carbon scaffold. The activation energy for the dehydrogenation was lowered by 52 kJ mol^{-1} compared to the bulk material, and a significantly reduced reaction enthalpy of 63.8 kJ mol^{-1} was found for the nanoconfined system. Similarly, Au et al. [53] prepared of MgH_2 nanoparticles supported on high surface area carbon aerogels with the pore sizes varying from 6 to 20 nm. The release hydrogen temperature is 140 °C lower than bulk MgH_2. Fast cycling is possible (80% of the capacity absorbed within 15 min at 18 bar and 300 °C), without a change in the hydrogen sorption properties, showing that the growth of the nanoparticles is effectively prevented by the carbon support. Therefore, carbon aerogel microspheres derived from inverse emulsion polymerization routine, with highly crumpled graphene–like sheets surface and network structure, could possess more beneficial effects on the hydrogen sorption properties of MgH_2.

In this work, CA microspheres have been successfully prepared via inverse emulsion polymerization routine, and subsequently ball milled with Mg powder to fabricate Mg@CA composite. After hydrogenation process, the MgH_2–CA shell–core structure of the composite displays high surface area of CA microspheres with the role of mechanical support and the high loading of MgH_2 NPs with uniform dispersion could realize easily. In addition, because of CA microspheres' network structure and large amount of void space, it may either provide additional hydrogen diffusion channels or act as an inhibitor for preventing the agglomeration of hydrides, which could enhance the de/hydrogenation performances. The mechanism for improving the hydrogenation and dehydrogenation of MgH_2 is also clarified in this work. This novel method of in situ producing MgH_2 phase gives a new horizon for designing high performance hydrogen storage material.

Experimental

Preparation of CA microspheres and MgH_2@CA microspheres composite

All chemical agents were analytical grade, obtained from commercial sources and directly and without further purification. Carbon aerogel (CA) microspheres were synthesized by an inverse emulsion referred to the literature [54]. Firstly, formaldehyde and resorcinol dissolved in distilled water, with Na_2CO_3 as a catalyst, stirring for 30 min, and the homogeneous solution was obtained. Subsequently, the solution was poured into hexamethylene containing surfactant SPAN80 to form inverse emulsion, and the emulsions were stirred at 40 °C for 40 h, dislodged the hexamethylene by suction filtration and washed by distilled water. Then the residuum was dried at room temperature accompanying CO_2 supercritical fluid. Finally, carbon aerogels were obtained by pyrolysis under Ar flow at 1050 °C, which were activated in CO_2 atmosphere subsequently, then the carbon aerogel microspheres were obtained.

Please cite this article in press as: Peng D, et al., Remarkable hydrogen storage properties and mechanisms of the shell–core MgH_2@carbon aerogel microspheres, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.01.004