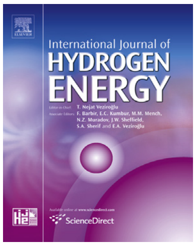
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Fluorographene nanosheets enhanced hydrogen absorption and desorption performances of magnesium hydride

Liuting Zhang, Lixin Chen*, Xuezhang Xiao*, Xiulin Fan, Jie Shao, Shouquan Li, Hongwei Ge, Qidong Wang

State Key Laboratory of Silicon Materials, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 8 May 2014
Received in revised form
13 June 2014
Accepted 16 June 2014
Available online xxx

Keywords:
Hydrogen storage
Fluorographene
MgH_2-FG composite
Reversibility
Kinetics

ABSTRACT

Fluorographene (FG), which inherits the properties of graphene and fluorographite (FGi), was successfully fabricated through a simple sonochemical exfoliation route in N-methyl-2-pyrrolidone (NMP) and then MgH_2-FG composite was prepared by ball milling. The dehydrogenation and rehydrogenation performances of MgH_2-FG composite were investigated systematically comparing with as-received MgH_2 and MgH_2-G composite. It is found that the as-prepared FG exhibited a significant catalytic effect on the dehydrogenation and rehydrogenation properties of MgH_2. The MgH_2-FG composite can uptake 6.0 wt% H_2 in 5 min and release 5.9 wt% H_2 within 50 min at 300 °C, while the as-received MgH_2 uptakes only 2.0 wt% H_2 in 60 min and hardly releases hydrogen at the same condition. The hydrogen storage cycling kinetics in the first 10 cycles remains almost the same, indicating the excellent reversibility of the MgH_2-FG composite. SEM analysis shows that the particle size of MgH_2-FG composite was ~200 nm, much smaller than that of as-received MgH_2 (~20 μm). TEM observations show that MgH_2 particles were embedded in FG layers during ball milling. The dehydrogenation apparent activation energy for the MgH_2 is reduced from 186.3 kJ mol^{-1} (as-received MgH_2) to 156.2 kJ mol^{-1} (MgH_2-FG composite). The catalytic mechanism has been proposed that F atoms in FG serve as charge-transfer sites and accelerate the rate of hydrogen incorporation and dissociation, consequently enhance the dehydrogenation and rehydrogenation properties of MgH_2-FG composite. Furthermore, the FG can inhibit the sintering and agglomeration of MgH_2 particle, thus it improves the cycling dehydrogenation and rehydrogenation of MgH_2-FG composite.

Introduction

Due to the environment and energy crises, a new clean energy carrier for mobile and stationary applications should be our top priority. Hydrogen, which could attain nearly zero emission of pollutants from power generators, is regarded as one of the most promising environmentally clean energy carriers. However, reversible storage of hydrogen with high capacity hinders hydrogen energy for practical applications. Current

---

* *Corresponding authors*. Tel./fax: +86 571 8795 1152.
E-mail addresses: lxchen@zju.edu.cn (L. Chen), xzxiao@zju.edu.cn (X. Xiao).

http://dx.doi.org/10.1016/j.ijhydene.2014.06.090

Please cite this article in press as: Zhang L, et al., Fluorographene nanosheets enhanced hydrogen absorption and desorption performances of magnesium hydride, International Journal of Hydrogen Energy (2014), http://dx.doi.org/10.1016/j.ijhydene.2014.06.090

research efforts mainly focus on materials composed of light elements and with high hydrogen content [1]. Magnesium hydride, which has high volumetric and gravimetric hydrogen storage capacity (110 g H_2/L and 7.6 wt% H_2 for MgH_2) [2], is hopeful to be used as hydrogen storage material in future. Nevertheless, various modification approaches have still been tried to alleviate the unfavorable thermodynamic and kinetic barriers of MgH_2 [3,4], *e.g.* catalytic activation for enhancing reaction kinetics [5], synthesizing nano-structured materials [6,7], mixing MgH_2 with metal hydrides [8,9], borohydrides [10] and other additives [11–13]. Recently, there have been emerging approaches that alter not only the MgH_2 kinetics but also the system thermodynamics by synthesizing Mg-based alloys [14–16], thin films [17] or interlayers [18]. Wang et al. opened a new way to tune the thermodynamic and kinetic performances of Mg-base hydrogen storage alloys in the presence of In [14]. Zhou et al. also demonstrated that the formation of magnesium solid solution alloys with alloying elements such as In, Al, Ga, and Zn was an effective approach to destabilize MgH_2 [15]. In addition, Kalisvaart et al. opened the possibility of creating ultrathin alloy interlayers (Mg–AlTi multilayers) that provide further thermodynamic improvements in metal hydrides [18]. However, the alloys were shown to have lower hydrogen storage capacity than that of pure MgH_2.

Carbon has many allotropes, including graphite, activated carbon, carbon nanotubes, nanowires, amorphous carbon, carbon black, and recently widely investigated graphene, *etc.* Magnesium–carbon composites obtained by mechanical milling Mg or MgH_2 with different carbon allotropes are promising materials for hydrogen storage. Earlier, Imamura and co-workers [19,20] investigated the performance of composites synthesized by milling magnesium with graphite in various organic liquids (benzene, cyclohexene, cyclohexane or tetrahydrofuran), they found that mechanical milling resulted in generation of large amount of dangling carbon bonds in graphite, leading to the formation of C–H bonds and new hydrogen-storing sites, which play a vital role in the hydrogen uptake and release step. Since then, many other carbon allotropes have been extensively studied to improve the hydrogen storage performance of MgH_2, catalyzed by single-walled carbon nanotubes [21–23], multi-walled carbon nanotubes [24,25], activated carbon [26], amorphous carbon [27,28], carbon black [29], carbon nanofibers [30] and graphene [31] etc. All the carbon additives showed beneficial effects on improving the dehydrogenation and rehydrogenation of MgH_2. In the research of Huang and co-workers [25], graphite shows better catalytic behavior for hydrogen desorption in contrast to carbon black and multi-walled carbon nanotubes. According to their study, many charge-transfer sites formed between cleavage-decomposed graphite and finely separated magnesium, which facilitates catalytic activation of hydrogen molecules and consequently improves dehydrogenation and rehydrogenation properties of magnesium-graphite composites. Recently, Liu and co-workers [31] found that highly crumpled graphene nanosheets can provide edge sites and hydrogen diffusion channels, prevent the nanograins from sintering and agglomerating, thus, leading to an excellent catalytic effect on dehydrogenation and rehydrogenation of MgH_2.

In our early studies, we found that fluorographite (FGi) can greatly destabilize borohydrides ($LiBH_4$ [32] and $NaBH_4$ [33]) by forming nano-micro dots on the surface of FGi and with the help of the exothermal reaction between FGi and borohydrides. And recently, Gong et al. [34] developed a novel and feasible method to prepare fluorographene (FG) by FGi through a simple sonochemical exfoliation process in NMP. It is well known that carbon materials have beneficial effects on dehydrogenation and rehydrogenation of MgH_2. So far as we know, the use of FG on the dehydrogenation and rehydrogenation performance of MgH_2 has never been investigated before. Here, we prepared FG through sonochemical exfoliation of FGi in NMP, and then added newly prepared FG into MgH_2 by ball milling to obtain magnesium–carbon composite. The dehydrogenation and rehydrogenation performances of magnesium–carbon composite were systematically investigated and the catalytic mechanism was also proposed.

Experimental

Synthesis of graphene

Graphene (G) was obtained through reducing the graphene oxide (GO), which was synthesized by a chemical oxidation of graphite powder (Sinopharm chemical Reagent Co. Ltd ≥99.85%) with a modified Hummers method [35], at 900 °C in a quartz tube under Ar-H_2 (9:1 v/v) flow for 40 min.

Synthesis of FG

FG was prepared through the method developed by Gong and co-workers [34]. Briefly, 15 mg FGi was added to 500 ml NMP solution in a round-bottomed flask to form FGi dispersions and the mixed solution was refluxed at 60 °C for 2 h. After the solution was cooled down to room temperature, ultrasonication was carried out for 32 h. Then the obtained dispersions were vacuum-filtered through a microporous membrane (0.45 μm) and rinsed by deionized water several time. Finally, FG was obtained through freeze drying for 48 h.

Preparation of magnesium–carbon composites

Materials handling and sample preparation were performed in an argon-filled glove box, where the water and oxygen concentrations were kept below 1 ppm. The composites were synthesized from commercially available MgH_2 (Alfa Aesar, 98%) and as-synthesized G or as-prepared FG, referred as MgH_2-G or MgH_2-FG, respectively. Typically, the MgH_2 powder was mixed with 10 wt% as-synthesized G or as-prepared FG, then the mixtures were ball milled for 5 h under 0.1 MPa Ar pressure at a speed of 450 r/min. The ball-to-powder ratio was 40:1. For comparison, the as-received MgH_2 was also ball milled at the same condition to find out the effect of ball milling, referred as BM-MgH_2.

Characterization

The synthesized materials were characterized by X-ray diffraction analysis (XRD, PANalytical, Netherlands, Cu K_α