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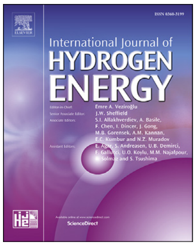

An extensive study of the Mg–Fe–H material obtained by reactive ball milling of MgH_2 and Fe in a molar ratio 3:1

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ABSTRACT

A mixture of MgH_2 and Mg_2FeH_6 was synthesized by reactive ball milling of magnesium hydride and iron in hydrogen atmosphere. The material is highly nanocrystalline, with typical dimensions of the order of 10 nm; after hydrogen cycling at ~400 °C, well defined XRD peaks of Mg_2FeH_6 can be observed. Volumetric measurements of hydrogenation/dehydrogenation provide clear evidence of the presence of both hydrides even at lower temperatures. The relative content of magnesium-iron hydride increases on increasing H_2 cycling temperature, passing from ~44% at 335 °C to ~54% at 390 °C. Already at 250 °C the composite releases ~3wt% H_2 in ~1000 s, while above 340 °C, more than 4wt% H_2 can be discharged in less than 100s, following the Johnson-Mehl-Avrami-Kolmogorov equation, with an exponent $n = 1$, compatible with a reaction controlled transformation. Finally, also the electrochemical performances in a lithium cell have been investigated: the material is able to undergo a conversion reaction and gives on the first discharge more than 1400 $mAhg^{-1}$. The overpotentials decrease after materials activation by H_2 sorption treatments. Moreover, for the first time, the partial reversibility of the conversion reaction for materials containing magnesium iron hydride is here reported.

Introduction

Mg_2FeH_6 has the highest known volumetric density of hydrogen (150 kg m^{-3}) and for this reason has been largely investigated. It has been synthesized for the first time by Didisheim et al. [1] in 1984 by means of the direct hydrogenation of Mg and Fe powders at 20–120 bar, during several days (2–10) at high temperatures (450–520 °C). X-ray diffraction [1] and, more recently, neutron diffraction [2,3] measurements prove that Mg_2FeH_6 is a complex hydride, in which hydrogen is located at the vertex of octahedra centered around Fe; the $[FeH_6]^{4-}$ ions are bound to Mg^{2+} ions [4],

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forming a crystalline solid with cubic symmetry (space group Fm-3m). The synthesis of pure magnesium iron hydride is extremely difficult due to the immiscibility of Mg and Fe, which causes the absence of a Mg–Fe alloy with the proper stoichiometry, ready for H_2 sorption. Huot et al. reported that Mg_2FeH_6 can be synthesized also by high energy ball milling of Fe with either Mg or MgH_2 in various atmospheres (inert gas or hydrogen) [5–8]. In general all these methods provide samples in which only part of the sample is transformed to the mixed hydride [1,5–8]: usually one obtains between 50 and 80% of Mg_2FeH_6, and in one case, on proper conditions, a 88% conversion was reported [6]. Also some attempts to obtain Mg_2FeH_6 by hot extrusion at different temperatures have been reported [9].

Very recently, Xiao et al. reported the synthesis of Mg_2FeH_6@MgH_2 core–shell nanostructure by means of a multi step procedure: reactive ball milling has been followed by heat treatments and then by reactive ball milling assisted by diethyl ether [10]. These nanostructures consisted of a Mg_2FeH_6 core with a particle size of 40–60 nm and a MgH_2 shell with a thickness of ~5 nm. Favorable sorption properties were observed [10]. Indeed, their dehydrogenation starts already at 220 °C and they are able to release ~5.0 wt% H_2 within 50 min at 280 °C [10].

Mg_2FeH_6 has been synthesized starting from extremely different proportions of the initial compounds of Mg and Fe: proportions from 2:1 up to 40:1 were investigated by Bogdanovic et al. [11], while Puszkiel et al. studied compositions ranging from 2:1 up to 15:1 [12]. Donaie et al. performed electron energy-loss spectroscopy and diffraction measurements on a specimen with an initial stoichiometry of 4:1 [13], and also Xiao et al. [10] performed the synthesis of Mg_2FeH_6@MgH_2 core–shell nanostructures starting from a proportion 2.8:1. However, a systematic investigation of the evolution of the Mg_2FeH_6 content in these synthesized samples has never been reported.

Magnesium iron hydride has been investigated not only for its high volumetric hydrogen density, but also as a thermochemical storage system. Indeed, during dehydrogenation the material absorbs heat and releases hydrogen, which can be stored; on the contrary during hydrogenation, the stored heat is released [14] and can be used to generate electricity. This process can be useful to compensate for fluctuations in the production from renewable energy sources, such as solar power plants [15]. Quite recently it has been shown that Mg–Fe–H system can be used at temperatures up to 550 °C [15,16].

Moreover, the electrochemical reaction of lithium ion with Mg_2FeH_6 has been recently investigated [17]. Mg_2FeH_6 undergoes a conversion reaction in lithium batteries, with an average potential plateau of 0.25 V, corresponding to a discharge capacity of 1577 $mAhg^{-1}$, i.e. 6.6 Li [17].

In this work we present a systematic investigation of the structural, morphological and functional properties of an Mg–Fe–H material obtained by reactive ball milling of MgH_2 and Fe in molar ratio 3:1. We adopted a multi-technique approach by combining X-ray diffraction from a synchrotron radiation source (XRD), transmission electron microscopy (TEM), thermal analysis (TGA-DTA), H_2 adsorption/desorption measurements and galvanostatic cycling in lithium cells. Our goal is to illustrate the close relation between the structural and morphological properties obtained during the material synthesis and the corresponding functional properties.

Materials and methods

Crystalline MgH_2 (hydrogen-storage grade) was purchased from Sigma Aldrich. Fe consisted of a metallic powder from the Alfa-Aesar company; XRD diffraction indicates that no iron oxides were present in this powder, at least within the experimental limits of this technique (>2–3%) [18].

Samples were prepared by reactive ball milling in a high pressure vial by Evico Magnetics, with a hydrogen atmosphere of ~50 bar and stainless steel balls with a diameter of 6 mm. A mass ratio of 10:1 between balls and sample was used. Each batch consisted of ~3 g of material. The milling procedure performed by means of a Fritsch Pulverisette P6 mill lasted 40 h for each sample, divided in cycles of 30 min milling and 5 min rest. A rotation speed of 350 rpm in reverse mode was used for both samples. During ball milling the temperature of the vial never exceed 31 °C.

According to the above described procedure, we prepared two Mg–Fe–H samples: Sample A containing MgH_2:Fe = 3:1 M ratio (1.74 g MgH_2 and 1.26 g Fe) and Sample B, a benchmark material, constituted by magnesium hydride catalyzed by means of limited amount of Fe, i.e. with molar ratio MgH_2:Fe = 40:1 (2.85 g MgH_2 and 0.15 g Fe).

XRD measurements were performed in sealed quartz capillaries (1.0 mm in diameter) at the MCX beamline in the ELETTRA Italian Synchrotron Facility using an X-ray energy of 10 keV corresponding to a wavelength of 1.24 Å.

Simultaneous TGA-DTA measurements were conducted by means of a Setaram Setsys Evolution 1200 TGA system [19]. The furnace was continuously flooded with high purity argon (40 ml/min). For each experiment, a sample mass of ~10 mg was used. The temperature rate was 3 °C/min.

Hydrogen absorption/desorption measurements were performed in a homemade Sieverts apparatus described in Refs. [20,21]. Each measurement was performed using a mass of 0.3–0.5 g of material. The temperature was kept constant within ±3 °C.

Samples morphology was investigated by transmission electron microscopy using a FEI Tecnai 200 kV cryo-TEM instrument. In order to prevent possible damages due to the interaction of samples with the electron beam, experiments were carried out at 80 keV in cryo-condition by cooling the sample holder with liquid nitrogen.

Electrochemical tests were carried out on sample A in the as milled state and after H_2 desorption/adsorption cycles at 400 °C. Electrodes were prepared by adding to the hydrides PVdF Kynar 2801 and Super P, in order to get an active material/SuperP/polymer weight ratio of 5/3/2. The final mixture was pressed on 10 mm diameter Cu disks with a mild pressure, in order to obtain electrodes with around 1–2 mg/cm^2 active material. Assembled electrochemical cells were Swagelok fittings type cells, where the electrode was faced to a lithium metal foil through a Whatmann borosilicate fiber separator swollen with a 1 M electrolyte solution of $LiPF_6$ in ethylene carbonate – dimethyl carbonate (EC:DMC) 1:1 mixture (LP30, Merk Selectipur). Galvanostatic cycling tests