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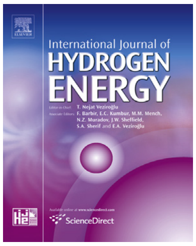

Kinetic enhancement of $LiBH_4$–MgH_2 composite by pre-milled MWCNTs observed by *in situ* X-ray diffraction measurements

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ABSTRACT

$LiBH_4$–MgH_2 composite is one of the most promising solid-state hydrogen storage materials because it exhibits good reversibility as well as lower total reaction enthalpy. Nevertheless, its utilization for onboard hydrogen storage is hindered by poor reaction kinetics. In order to improve the kinetics, pre-milled multi-walled carbon nanotubes (MWCNTs) were added to $LiBH_4$–MgH_2 composite. Thereafter, we measured *in situ* X-ray diffraction patterns of $LiBH_4$–MgH_2 and $LiBH_4$–MgH_2-MWCNTs composites at various temperatures to study the decomposition process. The pre-milled MWCNTs played an effective role in reducing the MgH_2 and $LiBH_4$ dehydrogenation temperatures. In addition, MgH_2 grain growth was inhibited by the formation of Mg in both the samples, and the inhibition started at a temperature lower by ~50 °C in the composite with MWCNTs compared with the $LiBH_4$–MgH_2 composite.

Introduction

$LiBH_4$–MgH_2 composite is a promising material for solid-state hydrogen storage owing to its properties such as good reversibility, lower total reaction enthalpy, and high hydrogen capacity (11.4 wt%) [1]. It decomposes in two steps: first MgH_2 releases hydrogen gas to form Mg particles, and then $LiBH_4$ decomposes into LiH, MgB_2, and hydrogen gas at temperatures above 450 °C under hydrogen backpressures [2]. In the dehydrogenation process, the new MgB_2 phase is the key phase for both enthalpy reduction and better reversibility. However, thermodynamic effects cannot be easily observed because of the sluggish kinetics of each constituent in the composite and between $LiBH_4$ and MgH_2, such as the incubation period before the formation of MgB_2 [3].

Carbon materials are well-known catalysts in improving kinetics because carbon is a good charge reservoir with rooms available for facilitating chemical reactions [4]. Furthermore they are preferable when compared with other catalysts such as metal or oxide nanoparticles because of their light weight, diverse structures (1 ~ 3-dimensional structures), and easily tunable functionalities. Among carbon materials, carbon nanotubes exhibit high thermal and electric conductivities arising from the abundant delocalized π-electrons. Especially,

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single-walled carbon nanotubes (SWCNTs) significantly improve the $LiBH_4$–MgH_2 composite dehydrogenation process because the interaction between the host composite and SWCNTs leads to better diffusion of hydrogen [5]. In the $LiBH_4$–MgH_2 composite, the nanoconfined $LiBH_4$ into the activated carbon (AC) releases H_2 at lower temperatures, and the Mg particles also come in close contact with melted $LiBH_4$ in the presence of AC, thus resulting in the formation of MgB_2 [4].

The catalytic effects of CNTs on individual materials such as $LiBH_4$ or MgH_2 have been extensively investigated. Wu et al. [6] reported that CNTs exhibit excellent catalytic effects on MgH_2 dehydrogenation reactions compared with other carbon materials such as graphite, AC, carbon black, and fullerene. They observed that the high surface area of catalysts or grain/particle size reduction in composite materials may be minor factors in improving de/rehydrogenation properties. Therefore, novel CNTs structures may facilitate hydrogen diffusion and interaction between CNTs and MgH_2, thus resulting in improving kinetics and consequently releasing more hydrogen.

$LiBH_4$ composite with carbon additives also exhibits significantly reduced dehydrogenation temperatures [7]. In the system, the thermodynamic effect was suggested by forming a new phase, Li_2C_2 [8], as well as the mentioned kinetic improvements. However, the formation of new phases is a controversial issue because those phases cannot be clearly observed. Agresti et al. [9] reported that MWCNTs prepared via high energy ball-milling significantly reduce the dehydrogenation temperatures of $LiBH_4$ because the MWCNTs act as heterogeneous nucleation centers for the formation of the dehydrogenation product, LiH. However, the prepared MWCNTs have minimal effect on the thermodynamic properties.

The pre-milling effects of MWCNTs on dehydrogenation processes of the composite system have not yet been reported. Therefore, we studied the effects of pre-milled MWCNTs on dehydrogenation of $LiBH_4$–MgH_2 composite by measuring *in situ* X-ray diffraction patterns under He 1 bar at various temperatures. Further, we analyzed the microscopic phenomena originating from the close contact between pre-milled MWCNTs and MgH_2 and $LiBH_4$ particles in the composite using differential scanning calorimetry (DSC), thermogravimetry mass spectroscopy (TG-MS), and Raman spectroscopy.

Experimental details

Sample preparation

The initial microcrystalline powders, $LiBH_4$ (Alpha Aesar, 95%) and MgH_2 (Sigma Aldrich, hydrogen-storage grade) were obtained commercially. The MWCNTs were JC 420 (JEIO, Korea); the O. D. = 20–40 nm and the length = 5–20 um.

All samples were then prepared by high-energy ball milling in a SPEX 8000M Mixer/Mill with a ball-to-powder (BPR) ratio of 20:1 for 2 h. Before a use, the MWCNTs were pre-milled with a BPR of 10:1 for 1.5 h to ensure faster kinetics by increasing the specific surface area [9]. Finally, the $LiBH_4$–MgH_2-premilled MWCNTs (**LMW**) mixture was ball-milled under an argon atmosphere at the above mentioned milling condition. The molar ratio between $LiBH_4$ and MgH_2 was 2:1 to match the stoichiometry of the dehydrogenation reaction, and the weight ratio of MWCNTs to $LiBH_4$ was 1 [9]. A $LiBH_4$–MgH_2 (2:1 M ratio) composite without MWCNTs (**LM**) was also prepared using the same ball-milling condition to that of LMW. All the samples were handled in a continuously purified helium or argon-filled glove box and sealed containers at room temperature.

Characterization

In situ X-ray powder diffraction measurements were performed to obtain structural and phase information as a function of temperature using 5 A and 10 C beamlines at the Pohang Accelerator Laboratory (PAL, Korea). X-rays of 16 keV ($\lambda = 0.765$ Å) were selected using a Si double crystal monochromator. Because insertion devices were used to obtain very bright and high-energy X-rays, the *in situ* structural and phase variations of samples can be studied over a high-Q range. The scattered X-rays were recorded on a MAR345 image plate located at 290–310 mm apart from the sample. Therefore, a signal can be obtained at Q up to ~4.8 A^{-1} for ~60 s (measuring time, one pattern) by the image plate at off-center.

The powder samples were packed into thin single-crystal sapphire tubes (O.D. = 1.5 mm, thickness = 0.15 mm, CRYTUR, Czech) having high thermal and chemical (resistant to liquid $LiBH_4$) stability. The tubes were connected to a lab-made gas supply system to pressurize H_2 atmosphere inside the tube as follows. The sapphire tube was inserted into the Swagelok male gland, and the gap between the tube and the gland was filled with a high-temperature-resistant epoxy. This gland was joined to a VCR T-fitting, one port of which is connected to the gas supply system through a 1/16″ tube.

The sample tubes were heated by hot nitrogen gas from a gas heater at a ramp rate of 5 °C/min. A thermocouple was placed at a site immediately beyond the hottest end of the heating elements to measure the feedback temperature for PID control of heating power. Sample temperature was estimated by placing a thermocouple at the sample position without the sample tubes before the experiments. An inaccuracy of approximately 20 °C exists because we could not measure temperatures at the exact sample position during the *in situ* XRD measurements. The patterns analysis (grain size, weight fraction) was performed using the FullProf [10] based on the Rietveld method. All the diffraction patterns are presented as a wavevector transfer, $Q = 4\pi/\lambda \sin\theta$, to compare patterns obtained at different wavelengths.

The thermal behavior of the samples was investigated using high-pressure differential scanning calorimetry (DSC204 HP, NETZSCH) at a ramp rate of 5 °C/min, and the initial H_2 pressure of 3 bar. Thermogravimetry (TG 209 F1, NETZSCH) experiments with a mass spectrometer (Transpector CPM, INFICON) were conducted at a heating rate of 5 °C/min. The relative weight loss and the released gas species were determined during desorption. Argon was used as the carrier gas at a flow rate of 70 ml/min.

The BET surface areas of the as-received and ball-milled MWCNTs were determined from N_2 adsorption experiments at 77 K using a BELSORP-miniII. The samples were degassed for 2 h at 150 °C to remove any moisture or adsorbed contaminants on the surface. Scanning electron microscopy (SEM) micrographs of MWCNTs were acquired with a JEOL

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