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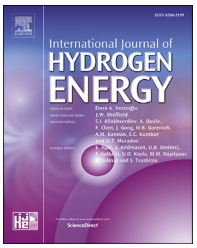

Preparation of Li-Mg-N-H hydrogen storage materials for an auxiliary power unit

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ABSTRACT

Solid hydrogen storage materials as H_2 supply for PEM fuel cells have been attempted over the past decades because of their high efficiencies in H_2 storage. However, most investigations were focused on the stage of tank design for the storage materials. The Li-Mg-N-H hydrogen storage system was for the first time integrated into a HT-PEM fuel cell stack for a prototype auxiliary power unit, the maximum working temperature being 200 °C. With a designed output of 1 kW, a few kilograms of storage materials are needed. By using commercially available raw materials, an up-scaled preparation of the storage material was performed using laboratory facilities. Preparation conditions were established with the aid of FTIR, TG-DSC and x-ray diffraction to ensure the desired quality of materials. Prior to power the fuel cell stack, the storage materials need to go through an exothermic metathesis, and severe temperature overshooting is expected, which may cause deterioration in material performance and safety issue. Operation conditions were tested and the temperature overshooting could be effectively prevented under adequate conditions.

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Introduction

Using PEM fuel cells to convert the chemical energy of H_2 into electric energy is an attractive proposal for high efficiency energy conversion [1]. However, the coupling of fuel cell stacks with solid-state H_2 tank for mobile application proves to be a challenge. Under European Investigation Framework Program 7, a prototype auxiliary power unit comprising of a tank coupled with PEM fuel cell stack system was built based on promising solid-state storage materials. H_2 storage tanks filled with solid state materials of traditional materials such as metal alloys, sodium alanate or magnesium hydride haven been reported [2,3]. As an innovation of the project, two types of hydrogen storage materials were combined into a single tank, one of which was the Li-Mg-N-H as a component with high H_2 capacity, while the other component was a metal alloy with fast kinetics. Better kinetics both in H_2 desorption and absorption were predicted by modeling and proved in the experiment [4,5].

Lithium nitride was found to react with hydrogen to form $LiNH_2$ and LiH [6,7]. This reaction involves an amount of 11.2 wt% H_2. Later on, improvements have been made on the hydrogen sorption performance by substituting $LiNH_2$ for $Mg(NH_2)_2$, reported independently by a few groups [8–10]. Attempts at coupling of PEMFC and H_2 storage medium were seen in the literature using $NaAlH_4$ as storage

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material [11–14]. But to our best knowledge, reports on the H_2 storage tank with Li-Mg-N-H system are so far unknown, possibly due to the fact that Li-Mg-N-H is a relatively new hydrogen storage system that appeared around the new millennium [8–10]. With mild hydrogen sorption temperatures and reversible H capacity of 5.5 wt%, this storage system has gained much attention. Starting from the amide-hydride pair of $Mg(NH_2)_2$/LiH, the H_2 sorption reactions are as follows:

$$Mg(NH_2)_2 + 2LiH \rightarrow Li_2Mg(NH)_2 + 2H_2 \quad 5.6\ wt\ \% \tag{1}$$

In order to build a prototype with 1 kW working with H_2 stored in the solid materials, a few kilograms of materials were required. Although $Mg(NH_2)_2$/LiH has been intensively studied in the literature [15–22], the starting component $Mg(NH_2)_2$ is commercially unavailable and was previously synthesized in small quantities and investigations were conducted mostly in the laboratory tests, i.e., on a scale of a few grams of sample.

Fortunately, the mixture of MgH_2/$LiNH_2$ at 1:2 M ratio, whose components are commercial products, is regarded as an equivalent storage system to $Mg(NH_2)_2$-2LiH [10,23]. Though the mixture of MgH_2/$LiNH_2$ can be readily converted to $Mg(NH_2)_2$-2LiH through an exothermic metathesis conversion in Eq. (2), undesired side reactions may occur if the metathesis is not fully completed, which affects both the H sorption performance and the reversibility of the storage system [24].

$$MgH_2 + 2LiNH_2 \rightarrow Mg(NH_2)_2 + 2LiH \tag{2}$$

Zhang et al. reported a modified MgH_2/$LiNH_2$ system with a combined additive consisting of $ZrCoH_3$-$LiBH_4$. Hydrogen sorption kinetics was found to be enhanced by this co-dopant, compared to $LiBH_4$ alone [25]. The authors demonstrated a capacity of 5 wt% and stable cycling performances with the composition, which was confirmed in our previous work [26]. Therefore, we decided to adopt the composition $2LiNH_2$-$1.1MgH_2$-$0.1LiBH_4$-3 wt% $ZrCoH_3$ proposed by Zhang et al. for the materials preparation.

In this paper, we will report a method for the quality control over the ball milling during the preparation process to ensure a full metathesis conversion. Since the metathesis reaction is exothermic, temperature overshooting in a pressurized tank renders a severe hazard, especially with large amounts of materials inside. Furthermore, inert products due to the reactions between the additive $LiBH_4$ and Li-Mg-N-H imides will be yielded at elevated temperature, which impairs the reversibility and lowers the capacity [27]. Hence, an operation process needs to be developed to avoid temperature overheating.

Experimental

Sample preparation

$LiNH_2$ (95%, Sigma-Aldrich), MgH_2 and $LiBH_4$ (95%, Alfa Aesar) were stored in the glovebox and used as received without pretreatment. $ZrCoH_3$ was prepared from ZrCo ingot (SAES Getters S.p.A., Italy) by exposing to 1 MPa H_2 at ambient temperature and milled before use.

To prepare about 3 kg storage materials, 4 milling vials of 500 ml of stainless steel were installed on a Retsch PM-400 planetary ball mill, each with about 100 g mixture with the composition of $2LiNH_2$-$1.1MgH_2$-$0.1LiBH_4$-3 wt% $ZrCoH_3$. About 400 g storage powder was prepared in a single batch. The ball-to-powder ratio was fixed to 3. Ball milling was conducted at 200 rpm for various periods.

Methods

Fourier Transform Infrared Spectroscopy (FTIR) measurements were performed on a Perkin Elmer Spectrum GX FT-IR system to identify the N-H vibrations in $Mg(NH_2)_2$ and $LiNH_2$ [28]. The powdery samples were mixed with KBr with agate mortar and pestle, and pressed into pellets followed by data acquisition at a resolution of 4 cm^{-1}.

Phase identification was performed by X-ray diffractometry (XRD) on a Philips X'PERT diffractometer (Cu Kα radiation). In order to protect samples against air, a sample holder consisting of a Kapton foil hood and a silicon single crystal base was used. Powdery samples were spread evenly onto the silicon crystal and then sealed with the Kapton foil hood inside the glovebox. The measurement was conducted in the 2θ range between 10° and 80° at a step length of 0.02°.

Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG) measurements were performed on a TG-DSC combined system Sensys Evo, Setaram, housed inside a glovebox under Ar atmosphere. Approximately 5–8 mg sample was loaded into the crucible of alumina. Measurement was carried out under He flow of 20 ml/min at preset heating rates.

For the quantification of H desorption, a home-made Sieverts' system was used to measure the H_2 amount evolved from the materials upon temperature elevation.

Results and discussion

Previous investigations on the $LiNH_2$- MgH_2 system reveal that adequate ball milling is crucial for the hydrogen sorption performances. Insufficient milling leads to side-reactions in the subsequent hydrogen uptake/release process, resulting in low hydrogen capacities, whereas inert substances form by overdone milling [24,29,30]. In order for the material to desorb hydrogen according to reaction (1), the mixture has to undergo the metathesis conversion reaction (2) so that the mixture becomes the amide-hydride pair of $Mg(NH_2)_2$/LiH.

Shown in Fig. 1 are TG curves for samples prepared under milling periods ranging from 2 h till 106 h. The major weight loss shifted to lower temperatures as the milling time increased from 2 h to 106 h, which suggests that sufficient mixing of the constituent components is necessary for better hydrogen desorption. One conspicuous feature of the TG measurements is that some weight loss occurred at temperatures below 100 °C for the samples ball milled for 40 h or less, in contrast to those subjected to longer milling times. This phenomenon may be attributed to the unevenness of the mechanical effects among the balls and vial walls. For the short milling process, the H gas that did not evolve during the milling step was then desorbed upon heating. For the samples with longer milling times, we noticed upon opening the

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