

MgH₂-AEROGEL COMPOSITE FOR SOLID-STATE HYDROGEN STORAGE

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1. Introduction

Hydrogen, with the highest energy-to-mass ratio among chemicals, is considered as a non-polluting synthetic fuel which could replace oil-based fuels for transport applications. Technologies to make compact, light weight and hydrogen capable (target of 5.5%wt for 2015 from Energy Department) solid-state hydrogen storage systems are desired to realize the development of hydrogen based power train [1].

In the present study, we investigate the MgH₂-aerogel system for hydrogen storage and release at ambient pressure. Furthermore, the proposed hydride embedded sol-gel synthesis (Hydride Sol-Gel Process) could be easily extended to industry applications.

2. Experimental

2.1 Hydride Sol-Gel Process

In a typical ball mill experiment, a mixture of 7g MgH₂ (Alfa Aesar) with 2mol%Ni and together with stainless steel balls, with a weight ratio of the sample to ball is 1:10, were put into a steel vial. All the samples were handled in a glove box filled with argon to minimize the oxidation on the samples. The mixture was then milled using a ball mill apparatus (Spex SamplePrep 8000 Series Mixer/Mill) for 2 hours. After that, in the synthesis of MgH₂-aerogels [2], first a portion of tetramethylorthosilicate (TMOS) (88.5 ml, Sigma), distilled water(43.2ml) and methanol(145.8ml, Alfa Aesar) were mixed into a beaker, which was then stirred for 2h for hydrolysis. Then, 4g of milled powder of MgH₂ was added into 6g of the sol, and was kept stirred for a few seconds. 0.5ml 2M NH₃ (in methanol) was involved to introduce gelation. The wet MgH₂/Ni gels were put into anhydrous ethanol immediately after gelation. The gels were washed using ethanol several times to remove all the residue water, and were aged for a week. The wet MgH₂/Ni gels were then dried with supercritical CO₂.

2.2 Sample Characterizations

MgH₂/Ni-aerogels were crushed into powder for further tests. The morphology of the composite particle was examined by Scanning Electron Microscopy (SEM) (JEOL 6400F). The structural properties of the samples were examined by X-ray diffraction measurement (Rigaku D-max/B) using Cu K α radiation. Desorption and thermal behavior of milled hydride

powder and hydride embedded aerogels were studied by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA, TA instruments). All the samples were tested using DSC with a heating rate of 5^oC/min under argon protection at ambient pressure. All the samples were also tested using TGA with a heating rate of 15^oC/min under argon protection at ambient pressure.

3. Results and Discussion

Figure 1 is the SEM image that demonstrates morphology of ball milled MgH₂/Ni powder and MgH₂/Ni-aerogel, respectively. It can be seen that there is no apparent change in the particle sizes for MgH₂. In the MgH₂/aerogel sample, the particles were surrounded by some amorphous shells, the silica aerogel structures, implying that MgH₂ was embedded in the silica matrix.

Figure 2 shows the X-ray diffraction profiles for the milled powder of MgH₂ with 2mol%Ni and the MgH₂/Ni-aerogel. It can be seen that peaks for β -MgH₂, γ -MgH₂ and Ni in the milled powder can be easily specified. Comparing those two profiles, one can tell that the main profile for the MgH₂/Ni-aerogel is exactly the same as that of the purely milled MgH₂/Ni powder. It also demonstrates that no apparent oxidation of MgH₂ occurred during the hydride embedded sol-gel synthesis. It is worthwhile to point out that all the peaks are quite broad, implying that MgH₂ particles' grain size in both ball milled MgH₂/Ni powder and MgH₂/Ni-aerogel are distributed in a very small and similar size range. Figure 3 shows the DSC profiles for milled hydride powder and its corresponding aerogel composite, and TiO₂-aerogel composite which has the same amount of TiO₂ powder added during sol-gel synthesis as the amount of hydride

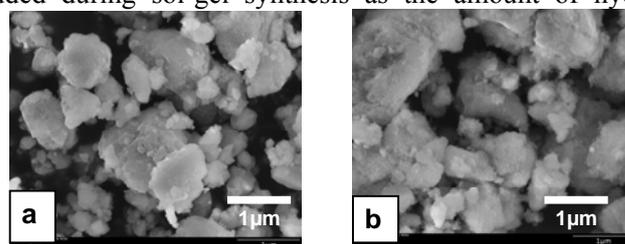


Figure 1. SEM micrograph of the morphology of ball milled MgH₂/Ni powder(a) and MgH₂/Ni-aerogel(b).

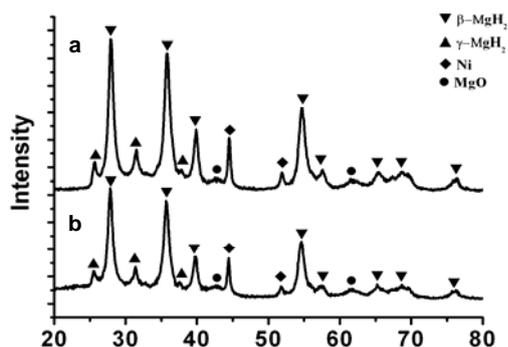


Figure 2. XRD patterns of MgH₂/Ni powder(a) and MgH₂/Ni-aerogel(b)

powder added for MgH₂-aerogel composite. It can be seen that the milled hydride powder has two hydrogen releasing peaks: One is peaked at 289°C, and the other is at 363°C. We attribute the two release temperature ranges to the bimodal distribution of the MgH₂ particles resulting from ball milling. While, the MgH₂-aerogel composite has only one releasing peak(226°C) with a temperature shift of 20 °C compared to the pure milled powder, which could be attributed to its lower thermal conductivity rather than the pure power. We speculate that the disappearance of the second hump in the composite sample is due to the uniformity of the composite porous structure.

To investigate the thermal stability of aerogel scaffold, we synthesized a second kind of aerogel composite. We embedded an inactive and thermal stable oxide, a TiO₂ powder in silica aerogel using the same synthesis procedure as described above. From the results shown in Fig. 3(c), it can be seen that the oxide embedded aerogel exhibited stable thermal properties during the heating process.

For the investigation on the hydrogen storage capacity of

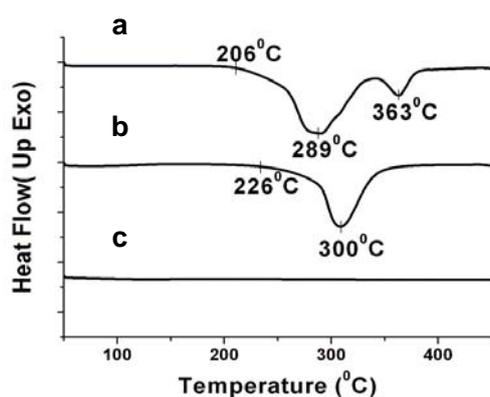


Figure 3. DSC profiles for MgH₂/Ni milled powder(a) and MgH₂/Ni-aerogel(b), and TiO₂-aerogel (c).

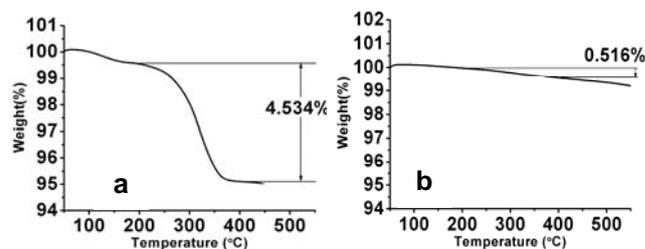


Figure 4. TGA profiles for the hydrogen desorption of MgH₂/Ni-aerogel(a) and TiO₂-aerogel(b)

MgH₂/Ni-aerogel, the composite was measured using TGA shown in Fig. 4. TGA analysis was conducted with TiO₂-aerogel as a baseline. It can be seen that the MgH₂/Ni aerogel composite has a total of 4.5wt% weight loss, while the TiO₂-aerogel sample has a 0.5wt% weight loss until 350°C. Since the TiO₂-aerogel has very stable thermal behavior as shown in Fig. 3(c), its weight loss during heating is from some chain side groups such as -OH and -OCH₃ [3]. As the MgH₂-aerogel and the TiO₂-aerogel materials were synthesized under the same condition with the same amount (weight) of solids (MgH₂ and TiO₂), we conclude that the net weight loss or hydrogen desorption until 345°C is 4wt%.

4. Conclusions

In conclusion, we established a simple hydride embedded sol-gel synthesis (Hydride Sol-Gel Process) for MgH₂/Ni-aerogel composite. The MgH₂ particles remained intact in the composite. An onset hydrogen desorption temperature of 226°C temperature was observed, and up to 4wt% H₂ capacity was obtained for a releasing temperature below 345°C at ambient pressure. Furthermore, when the pore size of the aerogel composite is tuned to below several nanometers, it is anticipated that hydrogen physisorption could contribute significantly and thus both chemisorption and physisorption are combined and realized in one material [4].

Acknowledgements

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