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# Carbon nanotubes enhanced hydrogen ab/desorption in Magnesium-based nanocomposites

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**Abstract**—This work investigates the effect of carbon nanotubes (CNTs) on hydrogen ad/desorption when formed nanocomposites with magnesium. It is found that CNTs significantly enhanced both the hydrogen storage capacity and kinetics, owing to the atomic interaction of C-Mg, residual of tubular structure of CNTs and dispersive effect of carbon in ball milling process. By first principles calculations, C-Mg interaction forms a channel for hydrogen atoms to transport into Mg structure. Tubular CNTs allow hydrogen to easily move within Mg matrix. Additives of carbon improve the ball milling effect to produce much finer Mg grains that enable the fast hydrogenation and increase the fraction of Mg hydrides, e.g. increase the capacity.

**Keywords**—CNTs; Magnesium-based nanocomposite; hydrogen adsorption; hydrogenation capacity and kinetics

## I. INTRODUCTION

With the increasing importance of the hydrogen economy, there is a great need for research to develop practical hydrogen storage systems. The main challenges in the field of hydrogen storage are to devise new materials or composites to achieve high volumetric/gravimetric capacity and fast kinetics. Mg has attracted tremendous efforts in the last few decades for hydrogen storage materials due to its high capacity, low cost and abundance [1-6]. However, its application for on-board hydrogen storage system is hindered by high reaction temperatures and sluggish kinetics. Although nanostructuring and catalytically enhancing Mg has achieved a big improvement of hydrogen storage, there still exists a gap to practical application that needs to be covered. CNTs have unique tubular structures that exhibit unusual properties [7]. CNTs as potential hydrogen storage materials are of much interest [8-10]. It is reported that ball milled carbon has been demonstrated to be able to adsorb large amount of hydrogen [11, 12]. The hydrogen adsorption properties were significantly improved when Mg was milled with graphite [13, 14]. It is expected that the tubular structures can facilitate the hydrogen transportation inside, thus CNTs are able to be more effective than graphite.

Density Functional Theory (DFT) calculations have shown considerable predictive power for the analysis of catalytic mechanisms [15]. Much insight can be gained for the process of designing alloy catalysts from first principle simulations [16].

In this paper, we report the recent advances in experimental work of CNTs effects on the hydrogen ad/desorption kinetics and capacity of Mg. The results are explained with intrinsic mechanisms of atomic Mg-C interactions from the first principles calculations. The possibility that tubular structures of CNTs remained after 10 hour of ball milling has also been discussed by comparing the difference between additives of CNTs and other forms of carbon structures.

## II. EXPERIMENTAL

### A. Experimental

All experiments and handling were conducted in a glove box in Argon atmosphere. MgH<sub>2</sub> based samples were prepared using the composition of MgH<sub>2</sub>-Carbon in five forms such as purified single-wall CNTs (ps), graphite (g), active carbons (ac), carbon black (cb) and fullerene (c60), and mechanically milled by using a Spex 8000 ball mill for 10 hours. MgH<sub>2</sub> was prepared by heating Mg powders (purchased from Lancaster) to 400 °C in a custom-made hydrogen storage rig. 90 wt% of the Mg powders was hydrided according to the volumetric calculations. A hardened steel crucible and six steel balls of 12 mm in diameter were used for milling. The ball to powder weight ratio was 12.5:1. The hydrogen storage capability of these samples was evaluated by a custom-made automatic Sieverts apparatus, which measures the pressure and temperature simultaneously, so that the pressure can be monitored as a function of time at different temperatures. Under an initial pressure of 2 MPa, absorption rate was measured by monitoring the pressure drop as a function of time. The desorption kinetics was measured at 573K in vacuum (10<sup>-5</sup> atmospheric pressure). Firstly, the H in as-prepared

sample was completely desorbed at 350 °C. Then, the absorption/desorption was performed at different testing temperatures and data was collected. Little capacity and kinetics change was observed with absorption/desorption cycling in the present experiments.

### B. First principles calculations by DFT model

In order to clarify experimental results and understand the Carbon enhanced hydrogenation performance of Magnesium-based materials, *ab initio* density functional theory (DFT) was used to investigate Mg-C atomic interactions and how these interactions affect the hydrogen diffusion. The DFT calculations were performed using the plane-wave basis VASP code implementing the generalized gradient approximation (GGA) of the Perdew, Burke, and Ernzerh of exchange correlation functional. An all-electron description, the projector augmented wave method (PAW), was used to describe the electron-ion interaction [17].

## III. RESULTS AND DISCUSSION

### A. Hydrogen adsorption

Different levels (0, 1, 5, 10 wt%) of purified single-wall CNTs were added into Mg and milled for 10 hours. The samples were then used to measure the hydrogen absorption property at 300°C. The time-dependent hydrogen absorption dynamic curves were plotted in Figure 1. It is shown that all

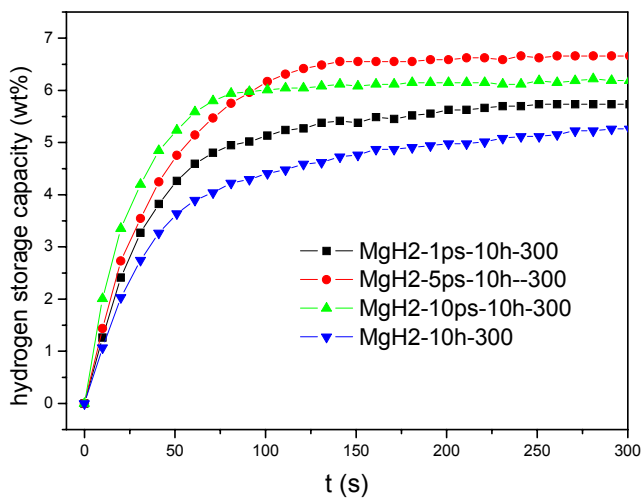


Figure 1. Hydrogen adsorption of Mg-CNTs samples with different addition levels at 300°C

levels of CNTs additives increased the hydrogen storage capacity among which the sample with 5 wt% CNTs shows the highest. About 1.8 wt% higher hydrogen can be absorbed within 300 seconds compared with the sample of no CNTs additives. In addition, the hydrogenation kinetics was also markedly improved with CNTs additives. It should also be noted that the hydrogenation rate increased monotonously with CNTs additives while the capacity of the sample with 10 wt% CNTs was less than that with 5 wt% CNTs. This implies

that the CNTs may facilitate hydrogen diffusion in Mg to form Mg hydrides. More CNTs additives will provide more sites for hydrogen diffusion enhancement, consequently, increase the hydrogenation rate under the present experimental conditions. The mechanism will be discussed in more detail in the following sections.

Figure 2 shows the H<sub>2</sub> capacity on Mg basis only. Compared with Figure 1, it is clear that the difference of hydrogen capacity between the two samples of 5 and 10 wt% CNTs is caused by a decrease of the percentages of Mg in the Mg-CNTs systems in the 10 wt% CNTs sample. This suggests that only Mg serves as the hydrogen absorbent under the present study, and that there is an optimum CNTs addition level to achieve the highest capacity, e.g. 5wt% in the range investigated.

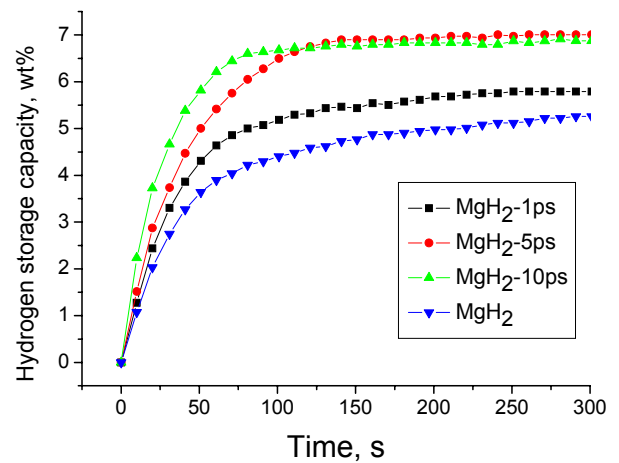


Figure 2. Reproduced from Figure 1 by excluding the CNTs additives from the Mg-CNTs systems

### B. Energetic barrier for hydrogen diffusion

*Ab initio* DFT calculations confirmed the strong interactions between Mg and C atoms. The interactions will restructure the electronic distribution around Mg and C atomic nucleus. The calculations show that the carbon atoms close to Mg surface

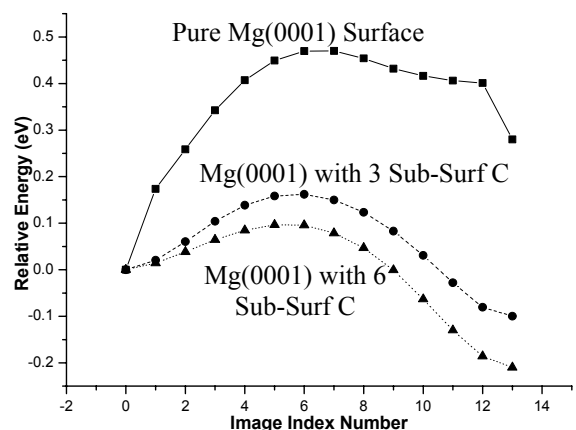


Figure 3. Energy profile of three Mg surface structures

can automatically transport into the sublayer without any energy barrier to form 3- or 6-subsurface carbon atomic configuration according to the vacancies of Mg structure. As an example of 6-subsurface carbon atomic structure,  $Mg^{2+}$  becomes  $Mg^{2.74+}$  due to the Mg-C strong interactions which enable the electronic redistribution. This will form an electronic channel in the centre of the carbon atoms. This channel facilitates the hydrogen atoms diffusing into Mg structures and decreases the energy barrier for hydrogen diffusion. A detailed discussion can be found in Ref. [18] and the energy barrier variations with incorporated C atoms are shown in Figure 2. Compared with pure Mg(0001) surface, the diffusion barrier of hydrogen was significantly decreased in C-incorporated Mg surface, from 0.48eV for pure Mg atomic structure to 0.15eV and 0.1eV for incorporated 3- and 6-subsurface carbon atoms, respectively. It is known that the diffusion coefficient increased exponentially with the diffusion energy barrier, so this decrease of the energy barrier by introducing carbon atoms into Mg greatly enhanced the hydrogen diffusion in Mg-CNTs systems.

### C. Mechanisms of CNTs enhancement on hydrogen adsorption

Now the hydrogenation behaviors of Mg-C systems at different temperatures are investigated. Mg milled with different forms of carbons enhanced the hydrogen storage properties both at high and low temperatures as shown in Fig.3.

Among all the forms of carbon additives, CNTs are most effective at both temperatures of 300 and 150°C. Hydrogen storage between adding CNTs and other additives was not much different at 300°C, but the difference was remarkable at 150°C. One reason is because the Mg-C interactions can provide enough hydrogen dissociation and diffusion sites and the hydrogenation is thus controlled by hydrides formation at a high temperature. The  $MgH_2$ -CNTs composite has the best hydrogenation kinetics although the differences are not significant. At lower temperature of 150°C, however, the hydrogen diffusion becomes a predominant factor, so CNTs play an important role as a tubular structure for easier hydrogen transportation inside. Besides the effect of Mg-C interactions revealed by the DFT calculations, this phenomena indicates that after 10 hour ball milling some of the CNTs can keep their tubular structures to some extent, which can provide channels for hydrogen transportation at low temperatures. Therefore, CNTs improved the hydrogen storage properties much more significantly than other forms of carbons.

In addition, carbon can improve the ball milling efficiency because it can assist high dispersion of Mg ( $MgH_2$ ). This will be able to produce smaller Mg particles in which much finer grains will be obtained [19]. As the hydrides formed by Mg combining with hydrogen atoms, the occupation of hydrogen atoms at the vacancies within the Mg structures greatly hinders further hydrogen atomic diffusion, resulting in the stopping of hydriding if the thickness of the hydrides exceeds a critical value. Therefore, the finer grains milled Mg with carbons also improve the kinetics and increase the fraction of hydrides formation, e. g. an increase of the capacity.

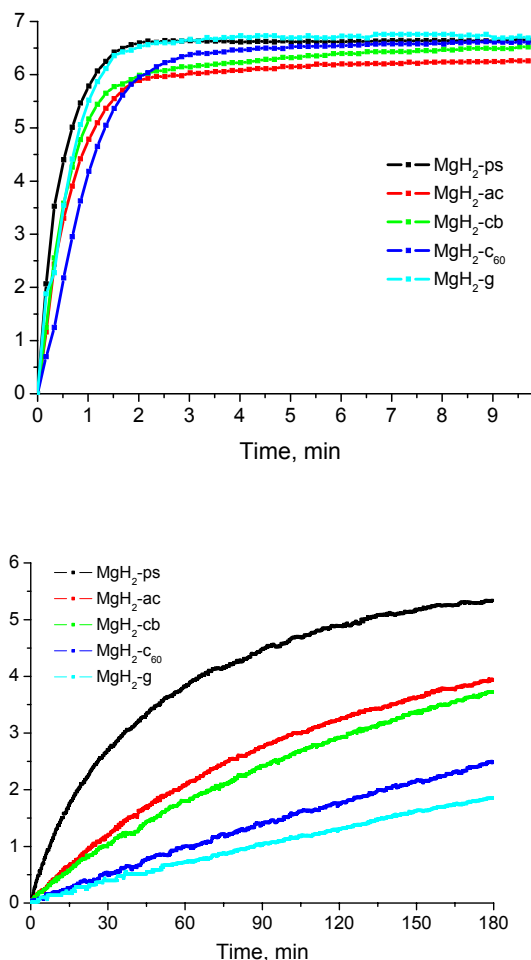


Figure 4. Hydrogen adsorption for 10 hour milled  $MgH_2$ -C samples at (a) 300°C and (b) 150°C

### D. Desorption

The desorption kinetic curves of  $MgH_2$ -carbon systems at 350°C are shown in Figure 5. It is found that the carbon additives are also effective in catalytic enhancement of hydrogen desorption of Mg among which CNTs improved the kinetics more significantly than any other forms of carbon additives, e.g. desorbing 100% hydrogen in 3-4 minutes. This implies that the Mg-C interactions that enhance the hydrogen diffusion into Mg during hydriding may also facilitate the transportation of hydrogen atoms from the broken Mg-H bonding towards the Mg surface. The tubular structures remained after ball milling are also functional for enhancing diffusion of the hydrogen atoms during desorption. It should be noted that the order of the effectiveness of other carbons for absorption and desorption is different. The reason is unclear.

The desorption data can be analyzed by using the Johnson – Mehl – Avrami theory [20],

$$\alpha = 1 - \exp[-(kt)^n] \quad (1)$$

Where  $\alpha$  is the time-dependent phase fraction of  $\text{MgH}_2$ ,  $k$  is the rate constant that depends on pressure and temperature, and  $n$  is the reaction order that is related to the transformation mechanism. A linear interpolation of the plots from data of the desorption kinetics curves in Figure 5,  $\ln(-\ln(1-\alpha))$  vs  $\ln(t)$ , yields the value of  $n$ . For the present study, the values of  $n$  are around 1.5 for the  $\text{MgH}_2$ -C systems, indicating that the phase transformation of  $\text{MgH}_2$  to Mg has a zero nucleation rate and desorption of the  $\text{MgH}_2$  is controlled by hydrogen diffusion. Thus, any methods that can enhance the hydrogen diffusion in Mg will improve both the desorption kinetics of Mg-based hydrogen storage materials [21].

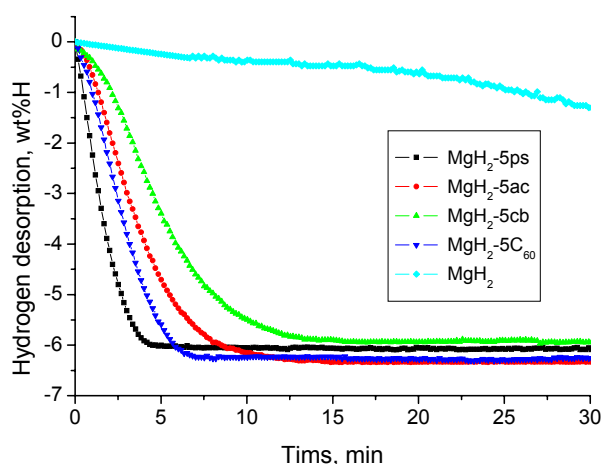


Figure 5. Hydrogen desorption for 10 hour milled  $\text{MgH}_2$ -C samples at  $350^\circ\text{C}$

#### CONCLUSIONS

Milling Mg with additives of carbon improves both the capacity and kinetics for hydrogen storage due to the Mg-C interactions and fine grains resulting from ball milling.

CNTs are most effective on enhancement of hydrogen storage properties, especially at low temperatures. This is attributed to their unique tubular structures that facilitate hydrogen atomic transportation inside. This indicates that for hydrogen absorption, the hydriding process is controlled by hydride formation rate at a high temperature while is a diffusion-limited growth reaction at a low temperature.

CNTs also play the most important role for hydrogen desorption kinetics among the investigated carbon forms due to the enhancement of hydrogen diffusion by their specific tubular structures.

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