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Hydrogen storage characteristics of magnesium impregnated on the porous channels of activated charcoal scaffold

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ABSTRACT

Ball milled (30 h) MgH_2 is impregnated on the pores/grooves of activated charcoal scaffold using a programmed heat treatment at 550 °C under 5 bar pure hydrogen ambient. The result obtained by this approach is better and more consistent than the materials prepared by metal infiltration at 650 °C or vacuum heated samples under 550 °C. The activation energy value (88 kJ/mol) obtained in the case of impregnated catalyst free material is far better than the activation energy value of the unconfined material (149 kJ/mol). The impregnated material can absorb hydrogen almost closer to its actual capacity at ~1 bar under 170 °C. The low temperature desorption characteristics and ab/desorption behaviors are extensively analyzed and described.

Introduction

Hydrogen storage is a critical technical bottleneck to realization of the green hydrogen economy (USDOE H_2 storage target: 0.055 kg H_2/kg storage system for 2017, and 0.075 kg H_2/kg storage system for longer term. System weight is the total weight of reactants + media + system components). Magnesium hydride (MgH_2), with its impressive gravimetric hydrogen density (7.6 wt%), looks promising for this role but its high dissociation enthalpy (75 kJ/mol) ensures that hydrogen desorption under normal conditions can be achieved only above 300 °C. This value is much higher than the targeted maximum hydrogen delivery temperature, 85 °C [1,2]. Since this difficulty is a thermodynamic limitation of the system, the traditional catalyzing approaches do not seem to put any dramatic developments in its performances. Researchers have shown that doping of transition metals in the surface/bulk lattice of magnesium or alloying with Mg can significantly alter the thermodynamics of the system [3–6]. In this line, studies were also extended to other Mg bearing hydrides (e.g., Mg_2NiH_4, $(x\%Mg + y\%LaNi_5/FeTi)H_n$, etc) but still

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MgH_2 remains the better material than any of its alloyed counterparts or composites [7–12]. Nanostructuring by mechanical milling is another commonly used strategy [13–15] to improve the sorption performance of MgH_2 but the performance of the ball milled MgH_2 downgrades during recycling runs mainly due to the aggregation and/or the uncontrolled growth of particles.

The theoretical calculations performed by Cheung et al. [16] revealed that the stability of MgH_2 drops sharply when the size was reduced down to ~1 nm. The study further concluded that no thermodynamic changes can occur for any sizes above 2 nm. However, Paskevicius et al. [17] have later observed that MgH_2 with particle sizes of ~7 nm is less stable than the bulk material. The observed variation in thermodynamics was, albeit little, still an observable quantity. Propelled by these understanding, many research efforts have thereafter been made to engineer performance improved-long cycle sustainable MgH_2 which apparently identified that confinement of MgH_2 on the nanopores of scaffolds is the best option. In order to nanoconfine/impregnate hydrogen storage materials, the methods such as solution mediated wet impregnation, impregnation through vaporization and melt infiltration were often tried by researchers. Among them melt infiltration is a commonly employed strategy for various systems [18–21]. However, when porous carbon was used as a scaffold for MgH_2 system, this method presents only a limited success. This is because, the molten Mg hardly gets passed inside the pores due to wetting effects [18] and apparently the actually confined Mg amounts to only 10–15%. Researchers have shown that Ni or Cu metals deposited porous carbon scaffolds can offer better pore filling, but it makes the scaffold heavier and it affects the overall capacity.

Generally scaffolds with sizes less than 10 nm are widely sought in the literature. However, scaffolds with such smaller sizes are not cost effective and also the confinement cannot be achieved by simple activation treatments. Given with these facts, we devised a simplest confinement strategy with a very cost effective scaffold, activated charcoal. Our interest in this scaffold is because, it possesses a highly channeled-nanosize grooved network with a flexible pore size from a small to medium range (in a typical case, the pore size is ~5–50 nm and the channel groove size is ~30–100 nm) where previously size reduced Mg/MgH_2 in solid state can be easily embedded. Although a thermodynamic tuning may not be expected in this method, the other relevant aspects such as thermal energy transfer, diffusion of hydrogen, interfacial effects and catalytic activity of carbon, etc, can make it attractive for applications [22–24]. After various material processing trials, we have observed that a strategy which offer better impregnation (when activated charcoal is employed as scaffold) is "vacuum heating of a previously size reduced MgH_2 (30 h ball milled) at 200 °C → programmed heating till 450 °C under H_2 ambient → rapid heating till 550 °C under 5 bar H_2 ambient → cooling down to 200 °C under ~30 bar hydrogen. The TPD and kinetic profiles of the catalyst free materials processed through the present approach is as competitive as the materials catalyzed by good catalysts like Nb_2O_5. The achieved consistent low temperature desorption with a high margin reduction in the activation energy barrier makes it promising for applications.

Experimental

All the required chemicals have been purchased from Sigma Aldrich chem. Ltd. Ball milling experiments were performed by using Spex 8000 shaker mill. Activated charcoal (AC100) was employed as the scaffold material. The pore size and volume analysis curve is presented in the supporting information (Fig. S1). This analysis revealed that the specific pore size available in this material is in the range of ~2–40 nm with a cumulative pore volume of ~0.7 cm^3/g. Hence, considering that all the pores can be occupied by MgH_2, only ~1 g can be impregnated in the pores of every 1 g scaffold which brings down the overall capacity to just half the theoretical capacity of MgH_2. However, since the chosen scaffold possesses a highly channeled nanostructure with an average groove size range of ~30–70 nm (see Fig. 1, more micrographs are given in the supporting information Fig. S2) more MgH_2 can be confined. Additionally, among the total surface area of 756 m^2/g, about 276 m^2/g is the external surface area. Hence, after considering the fact that an outer surface coverage with at least a layer of ~10–20 nm thick MgH_2 does always occur, the overall picture suggests that at least ~0.55 g charcoal can be employed for impregnating every 1 g MgH_2 (this choice was checked by employing $0.55 \pm x$ g activated charcoal in the experiments but the results confirmed 0.55 g is the best). Two sets of samples were prepared for impregnation works. In one set, MgH_2 was initially ball milled for 30 h (1:60 ball to powder ratio) without any catalyst and the milled powder was then mixed with suitable amount of activated charcoal for 30 min. In the other set MgH_2 was milled along with 2 wt% Nb_2O_5 catalyst for 30 h and then suitable amount of charcoal was mixed with the milled powder for 30 min. 2 wt% catalyst concentration was chosen based upon an optimization run (see supporting information Fig. S3). From the comparative TPD analysis of 1, 2, 3 and 5 wt% Nb_2O_5 catalyzed MgH_2 shown in Fig. S3, it is clear that 2 wt% is the best catalyst concentration under our experimental conditions. All the material processing has been performed under highly air/moisture restricted Ar atmosphere.

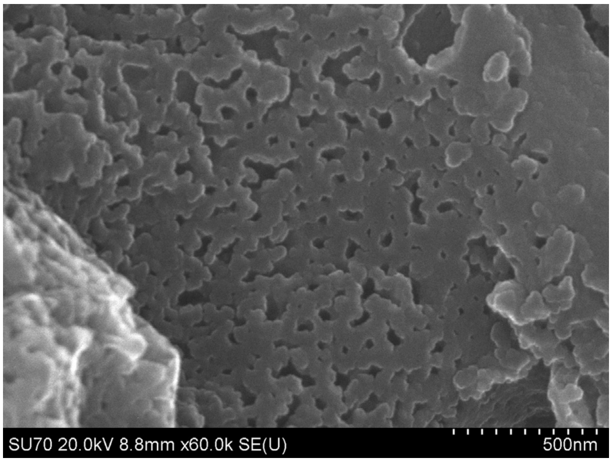

Fig. 1 – Scanning electron micrograph picture of activated charcoal scaffold used in the present study.