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Hydrogen sorption kinetics, hydrogen permeability, and thermal properties of compacted $2\text{LiBH}_4$-$\text{MgH}_2$ doped with activated carbon nanofibers

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To improve the packing efficiency in tank scale, hydrides have been compacted into pellet form; however, poor hydrogen permeability through the pellets results in sluggish kinetics.

In this work, the hydrogen sorption properties of compacted $2\text{LiBH}_4$-$\text{MgH}_2$ doped with 30 wt. % activated carbon nanofibers (ACNF) are investigated. After doping with ACNF, onset dehydrogenation temperature of compacted $2\text{LiBH}_4$-$\text{MgH}_2$ decreases from 350 to 300 °C and hydrogen released content enhances from 55 to 87 % of the theoretical capacity. Furthermore, the sample containing ACNF releases hydrogen following a two-step mechanism with reversible hydrogen storage capacities up to 4.5 wt. % $\text{H}_2$ and 41.8 g$\text{H}_2$/L, whereas the sample without ACNF shows a single-step decomposition mainly from $\text{MgH}_2$ with only 1.8 wt. % $\text{H}_2$ and 15.4 g$\text{H}_2$/L. Significant kinetic improvement observed in the
doped system appears due to the enhancement of both hydrogen permeability and heat transfer through the pellet.

**Keywords:** Metal hydrides, carbon, hydrogen storage, dehydrogenation, reversibility.

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1. **Introduction**

Lithium borohydride (LiBH$_4$) has attracted considerable attention due to its high theoretical volumetric and gravimetric capacities of 121 kgH$_2$/m$^3$ and 18.5 wt. % H$_2$, respectively [1-3]. However, high dehydrogenation temperature ($T$>400 °C), sluggish kinetics, severe hydrogenation conditions ($T$= 600 °C and $p$(H$_2$) = 350 bar), and poor reversibility hinder its practical use [4]. Among several approaches, the reactive hydride composites (RHCs) of LiBH$_4$ with other hydrides, such as LiBH$_4$-AlH$_3$ [5], Mg$_2$FeH$_6$-LiBH$_4$ [6], LiNH$_2$-MgH$_2$-LiBH$_4$ [7], and especially LiBH$_4$-MgH$_2$ [8-10] have been widely proposed. During dehydrogenation of 2LiBH$_4$-MgH$_2$, the formation of MgB$_2$ leads to the reduction of dehydrogenation enthalpy by 25 kJ/mol H$_2$ with theoretical storage capacity of 11.4 wt. % H$_2$ [11]. However, its long incubation period of MgB$_2$ formation (~15 h) resulted in slow kinetics, for example, up to 25 h to complete desorption [8]. By doping 2LiBH$_4$-MgH$_2$ with catalysts and additives of transition metal compounds, e.g., MoS$_2$, CoNiB, halides (NbF$_5$, TiF$_3$, CeF$_3$, LaF$_3$, FeF$_3$, TiCl$_3$, CeCl$_3$, VCl$_3$, and CuCl$_2$), CeH$_2$, SiO$_2$, and titanium isopropoxide (Tiso) [8, 12-16], substantial kinetic improvement was observed. For example, onset dehydrogenation temperature of 2LiBH$_4$-MgH$_2$ decreased from 350 to ~200 °C after doping with 20 wt. % MoS$_2$ [13] and incubation period disappeared by doing with NbF$_5$ and Tiso [8, 14]. Besides transition metal-based compounds, carbon materials have been widely used to develop de/rehydrogenation performance of hydrides. Introduction of carbon
fragments in hydride phase not only leads to fast hydrogen diffusion and thermal conductivity, benefiting hydrogen ab/desorption kinetics, but also prevents particle agglomeration during cycling [17-19]. Incubation period of $2\text{LiBH}_4\cdot\text{MgH}_2$ was significantly reduced by doping with 10 wt. % graphitic carbon nitride (C$_3$N$_4$); however, capacity loss up to 1.5 wt. % H$_2$ during cycling was observed due to irreversible reaction of C$_3$N$_4$ and MgH$_2$ [20].

An approach pursued to enhance material packing efficiency, thermal conductivity, and morphological stability during cycling is the compaction of the hydrogen storage material in form of pellets [21-22]. However, high compaction pressure could degrade hydrogen permeability through the compacted hydride, resulting in poor kinetics [21]. Compacted MgH$_2$ doped with 10 wt. % expanded natural graphite (ENG) showed good thermal conductivity and hydrogen permeability in the radial direction of the pellet [23]. Compacted LiBH$_4$ nanoconfined in activated carbon nanofibers (ACNF) impregnated with TiO$_2$ revealed superior hydrogen permeability in the axial direction, whereas compacted LiBH$_4$ showed no sign of hydrogen permeability [24]. Woven fibrous structure of ACNF appeared both to benefit hydrogen permeability and reinforce the pellet structure, yielding to good mechanical stability during cycling [24-25]. Although kinetic improvement can be achieved significantly by material confinement, hydrogen capacity is significantly lowered due to the weight of carbon host. Recently, dehydrogenation kinetics of $2\text{LiBH}_4\cdot\text{MgH}_2$ in loose powder form was enhanced by doping with 1-30 wt. % ACNF [26]. Due to good hydrogen diffusion and heat transport within ACNF, reduction of dehydrogenation temperature and fast hydrogen sorption kinetics were obtained with increased ACNF content.

In the present work, a thorough study of the hydrogen sorption properties as well as the materials features, such as hydrogen permeability and thermal properties of compacted $2\text{LiBH}_4\cdot\text{MgH}_2$ doped with 30 wt. % ACNF is reported. The choice of investigating this
Specific system is due to its excellent performance in the loose powder form [26]. Compacted samples of 2LiBH₄-MgH₂ with and without ACNF, owning the pellet densities of ~0.8-1.0 g/cm³ are prepared. De/rehydrogenation kinetics and reaction mechanisms of compacted samples are investigated. Mechanical stability upon cycling, hydrogen permeability, and thermal conductivity are also characterized.

2. Experimental details

Activated carbon nanofibers (ACNF) were prepared by activation of polyacrylonitrile (PAN)-based electrospun nanofibers [27-28]. PAN (M₇ = 150,000 g/mol, Sigma-Aldrich) was dissolved in N,N-dimethylformamide (DMF, Carlo Erba Reagent) and stirred at room temperature overnight to obtain a 10 %w/v solution. Electrospinning conditions including solution flow rate, applied voltage, tip-to-collector distance, and temperature were 1.5 mL/h, 10 kV, 15 cm, and 35 °C, respectively. The obtained PAN nanofibers were stabilized in air at 280 °C for 3 h and subsequently carbonized in N₂ at 1000 °C for 1 h to obtain carbon nanofibers (CNFs). CNFs were activated by soaking in concentrated KOH solution (30% w/v) for 2 h at 80 °C, drying at room temperature for 24 h, and heating at 800 °C under N₂ atmosphere for 15 min to obtain activated carbon nanofibers (ACNFs). Neutralization of ACNFs was done by immersing in 0.5 M HCl solution at room temperature for 30 min and washing with deionized water until neutral pH was reached. The obtained ACNFs were dried at 120 °C for 24 h and treated at 500 °C under vacuum for 3 h. The powder samples of LiBH₄ (≥90 %, hydrogen storage grade, Sigma-Aldrich) and powder Mg (≥99 %, Sigma-Aldrich) were milled under 2:1 molar ratio (LiBH₄:MgH₂) in a stainless-steel vial by using a SPEC Sample Prep 8000D DUAL Mixer/Mill. Ball-to-powder weight ratio (BPR) and milling time were 10-20:1 and 5-10 h, respectively. The mixture was hydrogenated at 350 °C under 80 bar H₂ for 12 h to obtain 2LiBH₄-MgH₂ composite. ACNFs (30 wt. %) were doped
into $2\text{LiBH}_4\text{-MgH}_2$ by ball milling technique with BPR and milling time of 10:1 and 30 min, respectively, to obtain $2\text{LiBH}_4\text{-MgH}_2\text{-30 %ACNFs}$. Loose powder samples (58-60 mg) of $2\text{LiBH}_4\text{-MgH}_2$ and $2\text{LiBH}_4\text{-MgH}_2\text{-30 %ACNFs}$ were pressed into the pellets by using a uniaxial laboratory hydraulic press with compaction pressure of 600 MPa on 12- to 13-mm diameter die sets to obtain compacted samples, denoted as 2Li-MH and 2Li-MH-ACNF, respectively.

Dehydrogenation profiles of compacted samples were investigated by simultaneous differential scanning calorimetry (DSC)-thermogravimetry (TG) using a Netzsch STA 449 F3 Jupiter. Compacted samples (10-20 mg) were heated from room temperature to 500 °C (5 °C/min) under N$_2$ flow of 50 mL/min. Relative contents of hydrogen (H$_2$) and diborane (B$_2$H$_6$) gases released upon heating were simultaneously monitored by mass spectroscopy (MS) using a Netzsch QMS 403C mass spectrometer. Activation energy ($E_A$) for the dehydrogenation process was characterized by DSC technique using a Netzsch 204 F1 PHOENIX. Compacted samples (~10 mg) were heated from room temperature to 500 °C with heating rates of 5-20 °C/min under N$_2$ flow of 50 mL/min. According to the Kissinger method (equation (1)), $E_A$ was calculated from the slope of the plot between $\ln(\beta/T_p^2)$ and $1/T_p$.

$$\ln(\beta/T_p^2) = -\left(\frac{E_A}{RT_p}\right) + \ln(k_0 R/E_A) \quad (1)$$

where $\beta$ and $T_p$ are heating rate (5-20 °C/min) and peak temperature of dehydrogenation (K), respectively. $R$ and $k_0$ are gas constant (8.314 J K$^{-1}$ mol$^{-1}$) and frequency factor, respectively.

Dehydrogenation kinetics and reversibility of compacted samples were measured by using a Sievert-type apparatus [29-31]. Compact sample (~60-70 mg) was packed into a stainless-steel sample holder (SS316) under N$_2$ atmosphere in the glove box and transferred
to the Sievert-type apparatus. Two K-type thermocouples (-250 to 1300 °C, SL heater) were attached to the sample holder and the furnace for measuring temperatures. Pressure transducers (C206, Cole Parmer) with operating ranges of 0-500 and 0-3000 Psig were used to measure the pressure changes during hydrogen desorption and absorption, respectively. Thermocouples and pressure transducers were connected to an AI210I module convertor data logger (Wisco), measuring and transferring (every 1 s) the pressure and temperature changes to the computer. Dehydrogenation was carried out by heating the sample to 400 °C under 3 bar H$_2$ and rehydrogenation was performed at 400 °C under 80 bar H$_2$ for 12 h. Released hydrogen content was calculated from the pressure change ($\Delta p$) and equations (2) and (3):

\[(\Delta p)V = nRT\]  

(2)

\[H_2 \text{ desorbed (wt. %)} = \frac{[(n \times 2.0158)\text{/sample weight}] \times 100}{(3)}\]

where $p$, $V$, $n$, $R$, and $T$ are hydrogen pressure (atm), system volume (L), moles of hydrogen (mol), gas constant (0.0821 L atm K$^{-1}$ mol$^{-1}$), and temperature (K), respectively.

Powder x-ray diffraction (PXD) experiments were carried out by using a Bruker D2 PHASER with a Cu K$_\alpha$ radiation ($\lambda=1.5406$ Å). The samples were packed into an airtight sample holder to prevent the material from being exposed to air and moisture. The diffraction patterns were collected in a 2θ range of 10-80° with a scanning step of 0.02 °/s. Fourier transform infrared spectroscopy (FTIR) spectra were collected by using a Bruker Tensor 27-Hyperion 2000. Anhydrous KBr was ground with the sample in the mortar and pressed to obtain KBr pellet. The spectra were recorded in the wavenumber range of 400-4000 cm$^{-1}$ with 64 scans for both sample and background.

Anisotropic hydrogen permeability in the axial direction of compacted sample was investigated by using a transient method reported in the previous works [24, 32]. Compacted
sample was tightly placed between two stainless-steel meshes (SS316, Swagelok) by using rubber O-rings. Two hydrogen permeability experiments were carried out at ambient temperature (~30 ℃) by applying hydrogen pressure of ~0.65 MPa to the upstream chamber and evacuating the downstream chamber to ~0.07 MPa. The pressures of upstream and downstream chambers \( (P_u \text{ and } P_d, \text{ respectively}) \) were recorded by using pressure transducers (0-500 Psig, C206 Cole Parmer). The pressure degradation curve across the sample was explained as in equation (4).

\[
\frac{(P_u - P_d)}{(P_{u,0} - P_{d,0})} = e^{-\alpha t} \tag{4}
\]

where \( (P_u - P_d) \) and \( (P_{u,0} - P_{d,0}) \) are the pressure differences between upstream and downstream chambers (Pa) at specific time during the experiment and at the initial state, respectively. \( t \) is time (s) and \( \alpha \) is described by equation (5).

\[
\alpha = \frac{kA(P_{u,0} + P_{d,0})}{2\mu L} \left( \frac{1}{V_u} + \frac{1}{V_d} \right) \tag{5}
\]

where \( k \) is the hydrogen permeability \( (m^2) \), \( L \) is the sample thickness \( (0.55-0.60 \text{ mm}) \), \( A \) is the sample cross-section area \( (1.13 \times 10^{-4} \text{ m}^2) \), \( \mu \) is the hydrogen gas viscosity at 30 ℃ \( (8.95 \times 10^{-6} \text{ Pa s}) \) [33-34], and \( V_u \) and \( V_d \) are the volumes of upstream and downstream chambers, respectively \( (2.27 \times 10^{-5} \text{ and } 2.22 \times 10^{-5} \text{ m}^3 \), respectively).

The thermal properties of compacted samples were characterized by a Transient Plane Source (TPS) method [35-36] using a TPS 1500 system (C3 Prozeß und Analysetechnik, Germany) with a sensor of 3.2 mm in radius. To enhance the contact between compacted sample and TPS sensor, a load of 2 kg was applied to keep the thin Kapton-insulated sensor firmly placed between two pellets. The measurements were performed at room temperature (~25 ℃) with an input power of 200 mW and a measurement time of 20 s. All preparation
procedures and measurements were carried out under Ar atmosphere in the glove box to avoid oxygen and humidity.

3. Results and discussion

The dehydrogenation profiles of 2Li-MH and 2Li-MH-ACNF are characterized by simultaneous DSC-TG-MS measurements. From Figures 1 (A) and (B), DSC curves of 2Li-MH and 2Li-MH-ACNF show endothermic peaks at 117-120.6 and 286-288.2 °C for phase transformation of LiBH$_4$ (α- to h-LiBH$_4$) and melting of h-LiBH$_4$, respectively. Dehydrogenation of MgH$_2$ and LiBH$_4$ of 2Li-MH are at 369.7 and 442.0 °C, respectively, while those of 2Li-MH-ACNF are at lower temperatures of 325.0 and 426.5 °C, respectively. Moreover, onset dehydrogenation temperature of 2Li-MH reduces from about 350 to 300 °C after doping with 30 wt. % ACNF. From TG and MS plots in Figure 1 (A), hydrogen content released from 2Li-MH is 6.3 wt. % H$_2$, in agreement with only 55 % of theoretical hydrogen capacity of 2LiBH$_4$-MgH$_2$ composite (11.4 wt. % H$_2$). By doping with 30 wt. % ACNF, the theoretical capacity of 2Li-MH-ACNF is 7.98 wt. % H$_2$. From Figure 1 (B), 6.95 wt. % H$_2$ (87 % of theoretical capacity) liberate from 2Li-MH-ACNF. In addition, dehydrogenation kinetics and reversibility of compacted samples are investigated by volumetric method. From Figure 2, 2Li-MH shows reversible single-step dehydrogenation with identical hydrogen contents during the 1$^{\text{st}}$ and 2$^{\text{nd}}$ cycles of 1.8 wt. % H$_2$. Considering simultaneous DSC-TG-MS results (Figure 1 (A)), at 400 °C hydrogen desorbed from 2Li-MH is mainly from MgH$_2$ and only slightly from LiBH$_4$. This is further supported by PXD and FTIR results (Figure 4). For 2Li-MH-ACNF, two-step decomposition is observed for both the 1$^{\text{st}}$ and 2$^{\text{nd}}$ cycles with greater hydrogen contents of 4.0-4.5 wt. % H$_2$ (Figure 2). Considering pellet volumes and weights of 2Li-MH (0.070 cm$^3$ and 0.060 g, respectively) and 2Li-MH-ACNF (0.062 cm$^3$
and 0.057 g, respectively), volumetric hydrogen capacities of 2Li-MH and 2Li-MH-ACNF are 15.4 and 41.8 gH2/L, respectively. Significant kinetic improvement of 2Li-MH after doping with 30 wt. % ACNF might be related to the enhanced hydrogen permeability and thermal properties, further discussed in Figure 6 and Table 2. The amount of hydrogen released in the first step, corresponding to the decomposition of MgH2 reduces upon cycling from ~2.0 and 1.0 wt. % H2 for the 1st and 2nd cycles, respectively (Figure 2). It should be noted that incubation period during the 2nd dehydrogenation of 2Li-MH-ACNF (~1 h) is significantly shorter than that of the 1st one (~6 h) (Figure 2). For example, LiBH4 starts to decompose at ~7-8 h during the 1st cycle, while that of the 2nd cycle is at ~3 h. Upon cycling, the formation of cracks and/or defects can occur due to pellet expansion/contraction during hydrogen ab/desorption. Thus, hydrogen permeability through the pellet might be improved, benefitting hydrogen sorption kinetics [21].

The activation energy ($E_A$) for dehydrogenation of 2Li-MH and 2Li-MH-ACNF was investigated by DSC technique. From Figures 3 (A) and (C), DSC curves with heating rates of 5-20 °C/min show endothermic peaks corresponding to h-LiBH4 melting at 288-297 °C and to dehydrogenation of MgH2 and LiBH4 at 339-395.2 and 402-497 °C, respectively. Two endothermic peaks detected during dehydrogenation of LiBH4 are denoted as the 1st- and 2nd-LiBH4, representing the peaks at low and high temperatures, respectively. By using Kissinger equation (equation (1)), $E_A$ of each dehydrogenation step can be calculated from the slope of the Kissinger plots ($\ln(\beta/T_p^2)$ versus $1/T_p$). The calculated $E_A$ of 2Li-MH for dehydrogenation of MgH2, 1st-LiBH4, and 2nd-LiBH4 are 245, 130, and 143.4 kJ/mol H2, respectively, while those of 2Li-MH-ACNF decrease to 178, 104.3, and 135 kJ/mol, respectively (Figures 3 (B) and (D)). Significant reduction of $E_A$ of compacted sample after doping with 30 wt. % ACNF ($\Delta E_A = $ up to 67 kJ/mol for MgH2 decomposition) hints at
kinetic improvement, in agreement with titration results (Figure 2). Another important issue of compacted hydride is mechanical stability since large strain changes upon de/rehydrogenation cycles yield to the decrepitation and disaggregation of compacted sample [37]. Unexpected volumetric contraction/expansion lead to stress and deformation of the container wall [38]. From Table 1, as-prepared pellets of 2Li-MH and 2Li-MH-ACNF have regular shape after compaction with pellet densities of \( \sim 0.86 \) and 0.93 g/cm\(^3\), respectively. The increment of pellet density indicates the improvement of compaction after doping with ACNF probably owing to the lubrication effect of ACNF for compaction as ENG doped into compacted hydride [39]. After rehydrogenation, 2Li-MH cannot preserve its pellet shape and turns completely to loose powder form, whereas 2Li-MH-ACNF maintains its shape with small crack (Table 1). Superior mechanical stability can be described by the fact that the fibrous structure of ACNF probably plays an important role as reinforced frameworks for compacted sample [25].

Furthermore, reaction mechanisms during de/rehydrogenation of 2Li-MH and 2Li-MH-ACNF are studied by PXD and FTIR techniques. From Figure 4 (A) (a), as-prepared pellet of 2Li-MH reveals diffraction patterns of LiBH\(_4\), hydrated LiBH\(_4\) [40], and MgH\(_2\), suggesting no reactions occurring during sample preparation. Hydrated LiBH\(_4\) is formed by the introduction of structural water into LiBH\(_4\) lattice without side reactions, leading to hydrogen desorption [40]. After dehydrogenation (\( T=400 ^\circ \text{C} \) and \( p(\text{H}_2)=3 \) bar), the signals of Mg and LiH are observed, implying individual dehydrogenation of MgH\(_2\) (equation (6)) and LiBH\(_4\) (equations (7) and (8)), respectively) (Figure 4 (A) (b)). Moreover, the residual LiBH\(_4\) suggests incomplete dehydrogenation of 2Li-MH, corresponding to deficient hydrogen content released during titration measurements (Figure 2). MgO is due to oxidation of Mg-containing phases during the experiments. In the case of rehydrogenated pellet (\( T=400 ^\circ \text{C} \) and \( p(\text{H}_2)=80 \) bar), reversibility of MgH\(_2\) is detected with unreacted LiBH\(_4\) and MgO (Figure...
The disappearance of LiH also implies reversibility of LiBH$_4$. Besides, B-containing phases formed during de/rehydrogenation are characterized by FTIR technique. From Figure 4 (B), all samples show strong vibrational peaks of B-H stretching and bending of LiBH$_4$ at 2388-2224 and 1124 cm$^{-1}$, respectively [28, 41], together with O-H bending of oxygen and humidity during experiments at 1637 cm$^{-1}$ [30]. Dehydrogenated and rehydrogenated pellets display [B$_{12}$H$_{12}$]$^{2-}$ vibration of Li$_2$B$_{12}$H$_{12}$ at 2486 cm$^{-1}$ [42] and asymmetric B-O stretching due to oxidation of amorphous B (a-B) at 1600-1300 cm$^{-1}$ [43-44]. The formations of a-B and Li$_2$B$_{12}$H$_{12}$ confirm dehydrogenation of LiBH$_4$ according to equations (7) and (8).

\[
\begin{align*}
\text{MgH}_2(s) & \rightarrow \text{Mg}(s) + \text{H}_2(g) \quad (6) \\
\text{LiBH}_4(l) & \rightarrow \text{LiH}(s) + \text{B}(s) + 3/2\text{H}_2(g) \quad (7) \\
\text{LiBH}_4(l) & \rightarrow 5/6\text{LiH}(s) + 1/12\text{Li}_2\text{B}_{12}\text{H}_{12}(s) + 13/12\text{H}_2(g) \quad (8)
\end{align*}
\]

For 2Li-MH-AC, as-prepared pellet shows diffraction peaks of LiBH$_4$, hydrated LiBH$_4$, and MgH$_2$ (Figure 5 (A) (a)), indicating no reactions occurring during sample preparation. After dehydrogenation, the signals of MgB$_2$, Mg, and LiH are observed together with a trace of incomplete dehydrogenated MgH$_2$ (Figure 5 (A) (b)). The formation of MgB$_2$ indicates dehydrogenation of LiBH$_4$ and MgH$_2$ according to equation (9) and agrees with two-step decomposition observed in titration results (Figure 2). For rehydrogenated pellet, diffraction peaks of MgH$_2$, MgO, and unknown phase are detected (Figure 5 (A) (c)). Disappearance of LiBH$_4$ diffraction can be due to amorphous and/or nanosized particles. Significant amount of MgO obtained after rehydrogenation leads to reduction of hydrogen content released from decomposition of MgH$_2$ during the 2$^\text{nd}$ cycle as shown in titration result in Figure 2.
\[ 2\text{LiBH}_4(\text{l}) + \text{MgH}_2(\text{s}) \rightarrow \text{MgB}_2(\text{s}) + 2\text{LiH}(\text{s}) + 4\text{H}_2(\text{g}) \]  

(9)

For FTIR results, vibrational peaks of B-H stretching (2392-2224 cm\(^{-1}\)) and bending (1128 cm\(^{-1}\)) of LiBH\(_4\) and O-H bending (1636 cm\(^{-1}\)) of oxygen and/or humidity during the experiments are found in all pellets (Figure 5 (B)). Dehydrogenated pellet reveals vibrational peaks of \([\text{B}_{12}\text{H}_{12}]^{2-}\) at 2486 cm\(^{-1}\) and asymmetric B-O stretching at 1600-1300 cm\(^{-1}\) from \(\text{Li}_2\text{B}_{12}\text{H}_{12}\) and oxidation of a-B, respectively (Figure 5 (B) (b)), hinting at individual dehydrogenation of LiBH\(_4\) according to equations (7) and (8). Residual LiBH\(_4\) implies incomplete dehydrogenation, in accordance with deficient hydrogen content released with respect to theoretical capacity (Figure 2). After rehydrogenation (Figure 5 (B) (c)), the enhanced signal of LiBH\(_4\) suggests its reversibility; however, incomplete reaction is observed by the vibrations of \(\text{Li}_2\text{B}_{12}\text{H}_{12}\) (2486 cm\(^{-1}\)) and oxidation of a-B (1500-1300 cm\(^{-1}\)), corresponding to slight reduction of hydrogen content released during the 2\(^{nd}\) cycle (Figure 2).

Hydrogen permeability in the axial direction of compacted samples was carried out by using the setup calibrated and reported in the previous work [24]. From Figure 6 (A), 2Li-MH shows gradual reduction of upstream pressure \((P_u)\) together with increase of downstream pressure \((P_d)\) until identical pressure is reached at 15 h. For 2L-MH-ACNF, \(P_u\) and \(P_d\) change rapidly and are comparable within 1 h. To investigate hydrogen permeability, equation (4) is rearranged to obtain the linear correlation (equation (10)).

\[
\ln \left( \frac{(P_u-P_d)}{(P_{u,0}-P_{d,0})} \right) = -\alpha t
\]  

(10)

Hydrogen permeability \((k)\) can be calculated as in equation (5) by using \(\alpha\) obtained from the slope of linear plot of \(\ln[(P_u-P_d)/(P_{u,0}-P_{d,0})]\) versus \(t\). From Figure 6 (B), \(\alpha\) and \(k\) of 2Li-MH are \(8.82 \times 10^{-5}\) s\(^{-1}\) ± 0.7 % and \(1.34 \times 10^{-19}\) m\(^2\) ± 0.8 %, respectively, while those of 2Li-MH-
ACNF are $9.47 \times 10^{-4}$ s$^{-1} \pm 0.1$ % and $1.30 \times 10^{-18}$ m$^2 \pm 0.8$ %, respectively. It should be noted that hydrogen permeability in the axial direction of 2Li-MH enhances by an order of magnitude after doping with 30 % ACNF. Regarding the previous studies [21, 23-24] dehydrogenation kinetics was benefited by good hydrogen permeability. Thus, superior hydrogen permeability of 2L-MH-ACNF to 2Li-MH lead to the improvement of kinetics, in agreement with simultaneous DSC-TG-MS and titration measurements (Figures 1 and 2). Moreover, it was reported that hydrogen back pressure of 3-5 bar encouraged simultaneous desorption of LiBH$_4$ and formation of MgB$_2$ during dehydrogenation of 2LiBH$_4$-MgH$_2$ at 400 °C without formation of intermediate metallic Mg [44]. Due to poor hydrogen permeability of 2Li-MH, hydrogen pressure applied during dehydrogenation might not be able to reach the sample bulk, especially at the center of the pellet, resulting in individual decomposition of MgH$_2$ and LiBH$_4$. For 2Li-MH-ACNF, superior hydrogen permeability promotes not only dehydrogenation of LiBH$_4$, but also formation of MgB$_2$ during dehydrogenation (equation (9) and Figure 5 (A)). In addition, cracks and/or defects formed in 2Li-MH-ACNF upon cycling enhancing hydrogen permeability yield to shorten incubation period during the 2nd dehydrogenation (Figure 2).

Since de/rehydrogenation of hydride materials are endo-/exothermic reaction, heat transfer inside the pellet is another important issue addressed to improve hydrogen exchange rate. Table 2 shows comparable thermal conductivity of 2Li-MH and 2Li-MH-ACNF (1.6-1.67 W/mK ± 0.18 %). Thermal diffusivity and specific heat capacity of 2Li-MH are 0.20 mm$^2$/s± 0.45 % and 8.16 MJ/m$^3$ K± 0.37 %, respectively, while those of 2Li-MH-ACNF are 0.33 mm$^2$/s± 0.88 % and 5.04 MJ/m$^3$ K± 0.70 %, respectively (Table 2). From the previous work, introduction of carbon material with elongated shape (e.g., ENG) significantly increased anisotropy of thermal conductivity (along ENG alignment) [23]. However, in our case isotropic thermal conductivity is presumably achieved from 2Li-MH-ACNF because the
milling procedure could homogenize shape and distribution of the ACNF in hydride matrices. Considering the equation $\alpha = k / \rho C_p$, where $\alpha$, $k$, $\rho$, and $C_p$ are thermal diffusivity, thermal conductivity, mass density, and specific heat capacity, respectively [36], thermal diffusivity is the ratio of heat conduction to heat storage. The higher the thermal diffusivity, the faster the propagation of heat into the compacted sample. Thus, the higher thermal diffusivity and lower specific heat capacity of 2Li-MH-ACNF with respect to 2Li-MH suggest its enhanced heat transfer properties. Since thermal conductivities of 2Li-MH and 2Li-MH-ACNF are comparable with slight increment of pellet density after ACNF doping (0.86 to 0.93 g/cm$^3$), improved heat transfer of 2Li-MH-ACNF is likely to be due to the addition of ACNF. Owing to the improvement of hydrogen diffusion and heat transfer of compacted 2LiBH$_4$-MgH$_2$ after doping with ACNF, faster kinetics and effective reversibility are obtained. Moreover, fibrous structure of ACNF probably acts as reinforced framework, yielding to mechanical stability of compacted hydride upon cycling.

4. Conclusions

Hydrogen sorption kinetics, mechanical stability, hydrogen permeability, and heat transfer of compacted 2LiBH$_4$-MgH$_2$ doped activated carbon nanofibers (ACNF) were investigated. By doping with 30 wt. % ACNF, decomposition of both MgH$_2$ and LiBH$_4$ were accomplished, leading to increase of gravimetric and volumetric reversible capacities from 1.8 to 4.5 wt. % H$_2$ and from 15.4 to 41.8 gH$_2$/L, respectively. Hydrogen contents released and reproduced from the samples with and without ACNF were deficient as compared with theoretical capacity due to incomplete decomposition of LiBH$_4$ and the formation of thermally stable phase of Li$_2$B$_{12}$H$_{12}$. Hydrogen permeability of compacted hydride with ACNF developed upon cycling resulted in significantly shortened incubation period for MgB$_2$ formation from 6
to 1 h, while the sample without ACNF showed no improvement. Since fibrous structure of ACNF could act as reinforced framework for compacted hydride, mechanical stability upon cycling was accomplished. Activation energy ($E_A$) during dehydrogenation decreased after doping ACNF into compacted hydride ($\Delta E_A = $ up to 67 kJ/mol). Hydrogen permeability in the axial direction of compacted hydride with ACNF was an order of magnitude faster than the one without ACNF. For thermal properties, ACNF favored heat transfer in the compacted hydride confirmed as enhanced thermal diffusivity (from 0.2 to 0.33 mm$^2$/s) and reduced specific heat capacity (from 8.16 to 5.04 MJ/m$^3$ K). Due to the improvement hydrogen permeability and heat transfer after doping with ACNF, hydrogen sorption kinetics and reversibility of compacted hydride were significantly developed.

5. Acknowledgement

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6. Table and Figure captions

Table 1. Photographs of 2Li-MH and 2Li-MH-ACNF in as-prepared and rehydrogenated states.
Table 2. Thermal properties of as-prepared pellets of 2Li-MH and 2Li-MH-ACNF.
Figure 1. Simultaneous DSC-TG-MS results during dehydrogenation of 2Li-MH (A) and 2Li-MH-ACNF (B).

Figure 2. Dehydrogenation kinetics and reversibility of 2Li-MH and 2Li-MH-ACNF.

Figure 3. DSC curves with heating rates of 5-20 °C/min and the Kissinger plots of 2Li-MH ((A) and (B), respectively) and 2Li-MH-ACNF ((C) and (D), respectively).

Figure 4. PXD (A) and FTIR (B) spectra of as-prepared (a), dehydrogenated (b), and rehydrogenated (c) pellets of 2Li-MH.

Figure 5. PXD (A) and FTIR (B) spectra of as-prepared (a), dehydrogenated (b), and rehydrogenated (c) pellets of 2Li-MH-ACNF.

Figure 6. $P_u$ and $P_d$ versus time (A) and hydrogen permeability (B) of 2Li-MH and 2Li-MH-ACNF.

7. References


Table 1

<table>
<thead>
<tr>
<th>Compacted samples</th>
<th>As-prepared pellets</th>
<th>Rehydrogenated pellets</th>
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<tr>
<td>2Li-MH</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
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<tr>
<td>2Li-MH-ACNF</td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
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<tr>
<td>Compacted samples</td>
<td>Thermal conductivity (W/mK)</td>
<td>Thermal diffusivity (mm²/s)</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
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<tr>
<td>2Li-MH</td>
<td>1.64±0.18 %</td>
<td>0.20±0.45 %</td>
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<tr>
<td>2Li-MH-ACNF</td>
<td>1.67±0.18 %</td>
<td>0.33±0.88 %</td>
</tr>
</tbody>
</table>
Figure 1
Figure 2

Figure 2
Figure 3

(A) DSC (mW/mg) vs. Temperature (°C) for different heating rates (5, 10, 15, 20 °C/min).

(B) Arrhenius plot for the decomposition of MgH₂, 1st-LiBH₄, and 2nd-LiBH₄.

(C) DSC (mW/mg) vs. Temperature (°C) for different heating rates (5, 10, 15, 20 °C/min).

(D) Arrhenius plot for the decomposition of MgH₂, 1st-LiBH₄, and 2nd-LiBH₄.
Figure 4

(A) 

(B) 

Hydrated LiBH₄, MgH₂, LiH, LiBH₄, MgO, Mg Sample holder

20 30 40 50 60 70 80

2θ (°)

Intensity (a.u.)

Wavenumber (cm⁻¹)

2500 2250 2000 1750 1500 1250 1000

2486, 2388, 2293, 2224, 1630-1300, 1124
Figure 5
Figure 6

(A) Upstream pressure $P_u$ and downstream pressure $P_d$ over time for 2Li-MH and 2Li-MH-ACNF.

(B) Logarithmic plot of $\ln[1/(P_u - P_d)(P_d - P_a)]$ vs. time for 2Li-MH and 2Li-MH-ACNF, with values $\alpha = 8.82 \times 10^{-5} \text{ s}^{-1} \pm 0.7\%$ and $k = 1.34 \times 10^{-19} \text{ m}^2 \pm 0.8\%$ for 2Li-MH, and $\alpha = 9.47 \times 10^{-5} \text{ s}^{-1} \pm 0.1\%$ and $k = 1.30 \times 10^{-18} \text{ m}^2 \pm 0.8\%$ for 2Li-MH-ACNF.