

Enhanced dehydrogenation performances and mechanism of LiBH₄/Mg₁₇Al₁₂-hydride composite

Le-yuan HAN, Xue-zhang XIAO, Xiu-lin FAN, Yun LI, Shou-quan LI, Hong-wei GE, Qi-dong WANG, Li-xin CHEN

Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province,
Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

Received 6 November 2012; accepted 1 April 2013

Abstract: Mg₁₇Al₁₂-hydride (abbreviated as MAH) was selected as a destabilization agent to improve de/rehydrogenation properties of LiBH₄. 58LiBH₄+Mg₁₇Al₁₂-hydride composite was prepared by ball-milling. It is found that the dehydrogenation of ball-milled LiBH₄/MAH composite presents a two-step reaction for hydrogen release. The composite starts desorbing hydrogen at about 300 °C and yields 9.8% of hydrogen (mass fraction) below 500 °C. By adding MAH, the dehydrogenation kinetics of LiBH₄ is improved and the dehydrogenation temperature of LiBH₄ is also lowered by 20 °C. High rehydriding capacity of 8.3% was obtained for the dehydrogenated composite in the first cycle at 450 °C. The XRD analysis shows the formation of MgB₂ and AlB₂ in the dehydrogenation process, which reduces the thermodynamics stability of LiBH₄ system and is beneficial to the reversible hydrogen storage behaviors of LiBH₄/MAH composite.

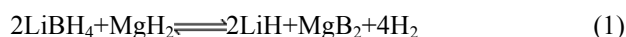
Key words: complex hydride; LiBH₄; Mg₁₇Al₁₂; de/rehydrogenation behaviors; reversibility

1 Introduction

Lightweight hydrogen storage materials, such as alanates [1,2] and borohydrides [3,4], are regarded as promising energy carrier in mobile applications due to their large hydrogen capacities compared with traditional metal hydrides [5–7]. Of all lightweight hydrogen storage materials, LiBH₄ has a high theoretical gravimetric capacity beyond 18.5% in mass fraction [3]. Unfortunately, its practical application is limited for both thermodynamic and kinetic deficiencies. Under moderate conditions, reversibility of LiBH₄ is rather limited [8].

Doping additives is one of the most effective methods to improve the performance of hydrogen storage materials [9–11]. By doping additives, hydrogen storage properties of traditional metal–hydrogen systems are becoming favorable [12]. Similarly, metals, metal halides and metal hydrides are added to LiBH₄ [13–15]. Among these composite systems, LiBH₄–MgH₂ system exhibits greatly improved hydrogen storage performance [16]. The enthalpy change is decreased by overall 27 kJ per

mol H₂ for reaction (1) in comparison with neat LiBH₄ [16]. Meanwhile, the lower kinetic barrier of reaction (1) favors the re-formation of LiBH₄ [17]. This novel pathway stimulates extensive explorations on the reactions of LiBH₄ with additives to obtain metal borides, such as, AlB₂ [13,18] and CaB₆ [19,20].



Among metal–boride systems, MgB₂ and AlB₂ exert an important influence on both reversibility and improved kinetics [16,18]. MgH₂–Al mixture showed enhanced destabilization in LiBH₄–MgH₂–Al system compared with LiBH₄–MgH₂ and LiBH₄–Al systems [21]. A synergistic effect of MgH₂ and Al generated from Mg(AlH₄)₂ was observed in modifying LiBH₄ [22]. However, above studies did not consider the function of Mg–Al composition in destabilizing LiBH₄. Melting effect of Mg₁₇Al₁₂ was rarely taken into account on the formation of MgB₂ and AlB₂ before. Additionally, the previous work indicated that alloy or compounds could act as catalyst in NaAlH₄ system [23,24]. Here we present that LiBH₄ can be reversibly dehydrogenated and

Foundation item: Project (2010CB631304) supported by the National Basic Research Program of China; Projects (51001090, 51171173) supported by the National Natural Science Foundation of China; Project (20090101110050) supported by the University Doctoral Foundation of the Ministry of Education, China

Corresponding author: Xue-zhang XIAO; Tel: +86-571-87951876; Fax: +86-571-87951152; E-mail: xzxiao@zju.edu.cn

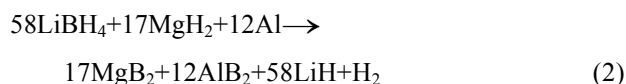
DOI: 10.1016/S1003-6326(14)63041-7

rehydrogenated with a reduced temperature by adding MAH. The dehydrogenation reactions are put forward as well.

In this study, the dehydrogenation and rehydrogenation were experimentally investigated by differential scanning calorimetry/mass spectrometry (DSC-MS), temperature programmed desorption (TPD) measurements in a Sievert-type apparatus. The microstructures were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectrometry (FT-IR).

2 Experimental

LiBH₄ powder (95% purity) was purchased from Acros and used without further purification. Magnesium (ingot from Goodfellow, China) and aluminum (foil from Sigma-Aldrich, China) had 99% purity and were not further purified. Mg₁₇Al₁₂ was prepared under the stoichiometric amount of Mg₁₇Al₁₂ by magnetic levitation melting. Considering the losses during melting, extra 6% of Mg in mass fraction was added. The Mg₁₇Al₁₂ was firstly remelted thrice to ensure homogeneity. Then, the sample was ground to powder size less than 75 μm and loaded into an autoclave for hydriding for 12 h under 4 MPa H₂ (99.99% purity) at 350 °C. Hereinafter, MAH is referred to the Mg₁₇Al₁₂-hydride (17MgH₂+12Al). Mixture of LiBH₄ and MAH was ball-milled on a planetary mill at a speed of 400 r/min under argon atmosphere for 4 h. Mass ratio of ball to powder was 30:1. The mole ratio of LiBH₄ to MAH was 58:1 according to the reaction (2), assuming that MAH reacts with LiBH₄ to generate MgB₂ and AlB₂ completely. The prepared LiBH₄/MAH mixture in this work has a maximum hydrogen capacity of 10.3%. For comparison, LiBH₄ was ball-milled and investigated under the identical conditions.



TPD and rehydrogenation were measured in a Sieverts-type apparatus. About 200 mg sample was used each time. The TPD measurements were carried out under initial pressure of 1 Pa, and temperature was ramped at a heating rate of 5 °C/min from ambient to a given temperatures, such as 400 °C. The rehydrogenation measurements were performed isothermally under 8 MPa H₂ at 450 °C.

X-ray diffraction (XRD) measurements were performed using an X'Pert-PRO diffractometer with Cu K_α radiation at 40 kV. Samples were sealed in a unique carrier to keep from oxygen and water vapor. Samples were also analyzed by the DSC-MS analyses on a Netzsch STA449F3 equipped with a Netzsch Q430 mass

spectrometer, programming the heating system from room temperature to 500 °C and employing argon as gas carrier with a purge rate of 50 mL/min. The Fourier transform infrared spectrometry (FT-IR) analyses were using a Bruker Tensor 27. The mass ratio of sample-to-KBr was 1:100 and the wave numbers range was 4000–400 cm⁻¹. All samples were prepared and handled under a continuously purified argon atmosphere in an MBraun glovebox maintained with O₂ and H₂O vapor levels below 1×10⁻⁶.

3 Results and discussion

The X-ray diffraction measurements were performed to examine the phase evolution of the as-prepared LiBH₄/MAH composite. Figure 1 displays the XRD patterns of as-cast Mg₁₇Al₁₂, MAH and ball-milled LiBH₄/MAH samples. The result shows that the various diffraction peaks of as-cast Mg₁₇Al₁₂ are sharp. After hydrogenation under 4 MPa H₂, Mg₁₇Al₁₂ phase has completely transformed into MgH₂ and Al phases. After ball-milling, the diffraction peaks of MgH₂, Al and LiBH₄ are still visible, but the corresponding peaks are broadened, indicating that the grain size is decreased during ball-milling.

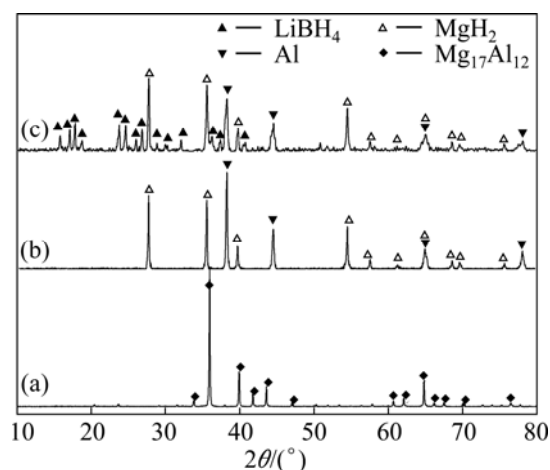


Fig. 1 XRD patterns of as-cast Mg₁₇Al₁₂ (a), MAH (b) and ball-milled LiBH₄/MAH composite (c)

The thermal properties of ball-milled LiBH₄/MAH composite were investigated by DSC and MS to analyze the effect of MAH on structural transition temperature, melting temperature and dehydrogenation temperature of LiBH₄. For comparison, the ball-milled LiBH₄ was also measured under the identical conditions. The DSC and MS curves of ball-milled LiBH₄ and ball-milled LiBH₄/MAH composite are shown in Fig. 2. For the ball-milled LiBH₄, the first endothermic peak around 113 °C is due to the phase transformation from orthorhombic to hexagonal system, the second one at 285

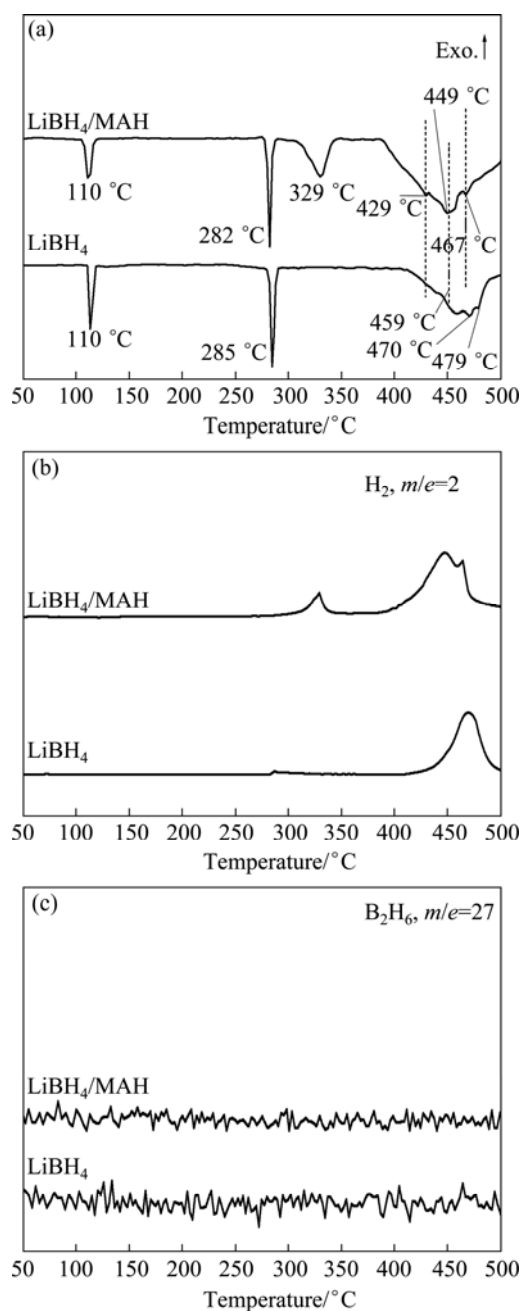


Fig. 2 DSC (a) and MS (b, c) profiles of ball-milled LiBH₄ and LiBH₄/MAH composite

°C is ascribed to the melting of LiBH₄ and the third endothermic peak around 470 °C indicates the dehydrogenation reaction of LiBH₄ [25]. After adding MAH, the temperatures of phase transformation and melting point are slightly lowered to 110 °C and 282 °C. For the LiBH₄/MAH composite, the third DSC endothermic peak (329 °C) is due to the decomposition of MgH₂. As the temperature is further escalated, LiBH₄ starts to decompose at temperature higher than 400 °C. Figure 2 shows that both the starting temperature and peak temperature of dehydrogenation of the LiBH₄/MAH composite are decreased. The possible decomposition

process will be discussed later. Moreover, it can be found that no other volatile boron-containing gases (like B₂H₆, $m/e=27$) were detected throughout the dehydrogenation process. In brief, the major dehydrogenation peak of LiBH₄ shifts to lower temperature by 20 °C after adding MAH in the LiBH₄/MAH system. This result suggests that MAH could lower the decomposition temperature of LiBH₄.

TPD curves of the ball-milled LiBH₄ and LiBH₄/MAH composite are shown in Fig. 3. The TPD measurements were carried out under an initial hydrogen pressure of 10⁻⁶ MPa with different temperatures. For the ball-milled LiBH₄, its dehydrogenation temperature is above 400 °C and it desorbs about 9.0% of H₂ after 2.5 h with slow kinetics. For the ball-milled LiBH₄/MAH composite, when the composite is heated from room temperature to 400 °C and kept at this temperature, it begins to release hydrogen at 320 °C and slowly desorbs about 2% of H₂ in 10 h. When the composite is heated to 450 °C, the dehydrogenation performance is improved and it yields about 4% of hydrogen. As the composite heated to 500 °C, the release of hydrogen becomes faster and the composite desorbs about 7% of H₂ before performing holding at 500 °C. After keeping the reactor at 500 °C for 30 min, the composite gives off more than 9.8% of H₂, which is close to the theoretical value (10.3%) of the LiBH₄/MAH composite. As shown in Fig. 3(c), there are two evident dehydrogenation steps at 310–360 °C and 400–500 °C for the ball-milled LiBH₄/MAH composite, which agrees well with the DSC-MS results. Moreover, no incubation period is detected between these two dehydrogenation steps. The first one is very fast and related to the decomposition of MgH₂, and the second one is the decomposition of LiBH₄ and relatively slow.

After complete dehydrogenation, the isothermal rehydrogenation was executed at 450 °C under 8 MPa H₂. The LiBH₄/MAH composite exhibits a much better reversibility as shown in Fig. 4. For the ball-milled LiBH₄/MAH composite, approximately 8.3% and 7.4% of hydrogen are achieved in 5 h for the second and the third rehydrogenation, respectively, while the ball-milled LiBH₄ shows very poor reversibility (below 1%) under the same condition. In addition, the FT-IR spectra of different states shown in Fig. 5 confirm the rehydrogenation of LiBH₄ under the established condition of 450 °C and 8 MPa H₂ for the LiBH₄/MAH system.

Figure 6 displays the XRD patterns of LiBH₄/MAH composite dehydrogenated at different temperatures. Before dehydrogenation, the LiBH₄, MgH₂ and Al are all well present with strong diffraction peaks shown in Fig. 1(c). After dehydrogenation at 360 °C, the intensity of LiBH₄ phase becomes weakened, while MgH₂ phase

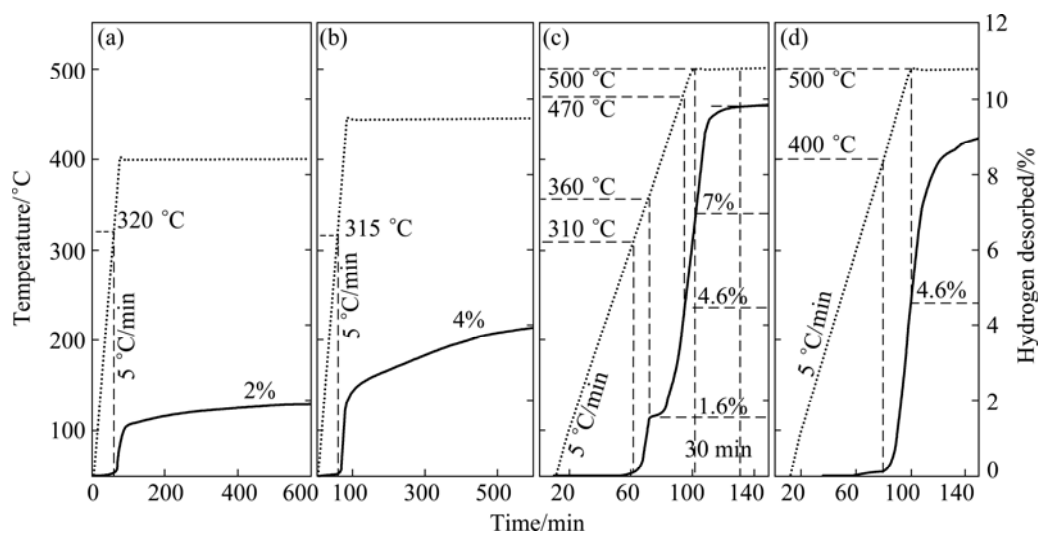


Fig. 3 Temperature programmed desorption curves of ball-milled LiBH_4/MAH composite at 400 °C (a), 450 °C (b), 500 °C (c), and ball-milled LiBH_4 at 500 °C (d) for comparison (initial hydrogen pressures 1 Pa; final pressures 0.01–0.015 MPa)

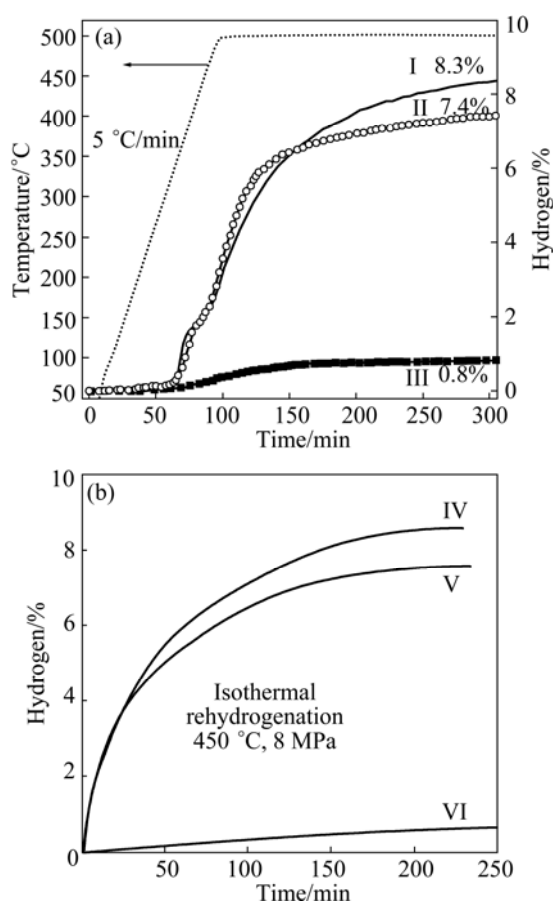


Fig. 4 TPD curves (a) of rehydrogenated LiBH_4/MAH sample in the second cycle (I), third cycle (II), and rehydrogenated LiBH_4 sample in the second cycle (III), isothermal rehydrogenation curves (b) of dehydrogenated LiBH_4/MAH sample in the first cycle (IV), second cycle (V), and rehydrogenated LiBH_4 sample in the first cycle (VI) (The samples were hydrogenated at 450 °C under 8 MPa H_2 pressure)

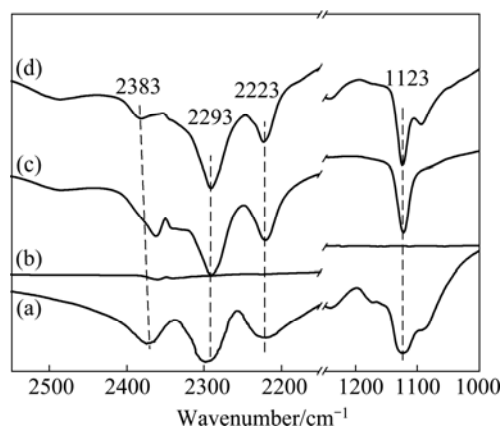


Fig. 5 FT-IR spectra of LiBH_4/MAH sample in different states: (a) After ball-milling; (b) After full dehydrogenation; (c) After the first rehydrogenation; (d) After the third rehydrogenation (Stretching bands of B—H are at 2380, 2293, 2223 cm^{-1} and the bending band is at 1123 cm^{-1})

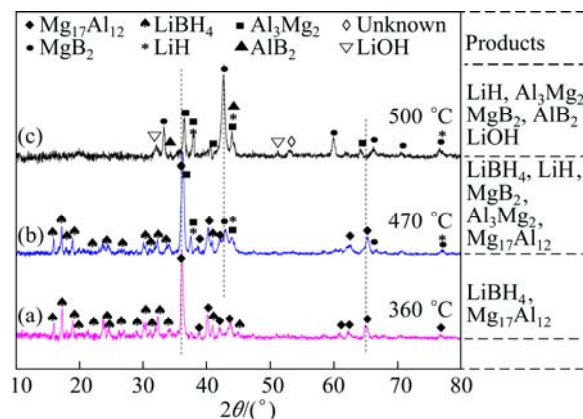
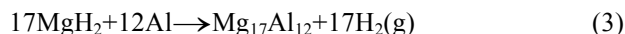


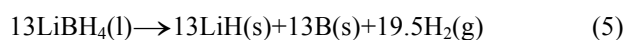
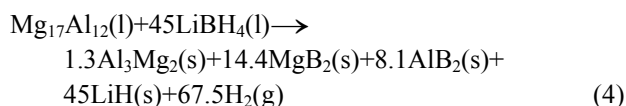
Fig. 6 XRD patterns of ball-milled LiBH_4/MAH sample in different dehydrogenation stages: (a) Dehydrogenation to 360 °C; (b) Dehydrogenation to 470 °C; (c) Dehydrogenation to 500 °C

and Al phase are disappeared completely. Meanwhile, $\text{Mg}_{17}\text{Al}_{12}$ phase is markedly present in the products at 360 °C. This result indicates that the MgH_2 decomposes and reacts with Al to form $\text{Mg}_{17}\text{Al}_{12}$. The reaction pathway of the MgH_2 and Al could be described as follows:



When the temperature is further increased from 360 °C to 470 °C, the LiBH_4 phase becomes evidently weakened. At the same time, some diffraction peaks of $\text{Mg}_{17}\text{Al}_{12}$ disappear and the first main peak of $\text{Mg}_{17}\text{Al}_{12}$ phase is overlapped by the ones of Al_3Mg_2 phase. The diffraction peaks of MgB_2 and LiH become visible in the products. This result suggests that $\text{Mg}_{17}\text{Al}_{12}$ can react with LiBH_4 to form new phases of MgB_2 and AlB_2 . Figure 6(c) indicates that MgB_2 , AlB_2 , LiH and Al_3Mg_2 are the main phases after dehydrogenation at 500 °C. The $\text{Mg}_{17}\text{Al}_{12}$ and LiBH_4 completely disappear. The trace amount of LiOH is due to oxidation during transport in the XRD test procedure.

It is noteworthy that the thermodynamics stability of LiBH_4/MAH system could be reduced for the formation of MgB_2 and AlB_2 . Meanwhile, LiBH_4/MAH system could achieve good reversibility because of MgB_2 and AlB_2 [26,27], which was confirmed by Figs. 4 and 5. It was reported that hydrogen pressure during dehydrogenation is important for the formation of MgB_2 [28]. However, the experiments were carried out under initial vacuum and final pressures were still low ranging from 0.01 MPa to 0.015 MPa. This means that the pressure has little effect on the formation of MgB_2 and AlB_2 in LiBH_4/MAH system. Hence, the study of the formation mechanism of MgB_2 and AlB_2 is very significant to in-depth understand the reversible reaction process in the LiBH_4/MAH system. The theoretical melting point of $\text{Mg}_{17}\text{Al}_{12}$ is 460 °C according to the Mg–Al binary diagram. It was also reported that the $\text{Mg}_{17}\text{Al}_{12}$ compound presents a melting peak at 460 °C [29]. Therefore, it is considered that $\text{Mg}_{17}\text{Al}_{12}$ is melting at approximately 460 °C in our study. The melting $\text{Mg}_{17}\text{Al}_{12}$ provides favorable condition for the generation of MgB_2 and AlB_2 as the following reactions:



4 Conclusions

The dehydrogenation and rehydrogenation behaviors of LiBH_4/MAH system were investigated.

1) It is found that 9.8% of hydrogen is released

below 500 °C in this system. More than 8.3% of hydrogen can be reabsorbed for the dehydrogenated sample at 450 °C.

2) The LiBH_4/MAH composite goes through two dehydrogenation steps, corresponding to dehydrogenation of MgH_2 and decomposition of LiBH_4 , respectively.

3) The dehydrogenation temperature of LiBH_4 can be lowered by 20 °C after adding MAH. The thermodynamics stability of LiBH_4/MAH system could be reduced due to the formation of MgB_2 and AlB_2 .

References

- [1] SCHLAPBACH L, ZÜTTEL A. Hydrogen-storage materials for mobile applications [J]. *Nature*, 2001, 414: 353–358.
- [2] BOGDANOVIĆ B, FELDERHOFF M, POMMERIN A, SCHUETH F, SPIELKAMP N. Advanced hydrogen-storage materials based on Sc-, Ce-, and Pr-doped NaAlH_4 [J]. *Advanced Materials*, 2006, 18: 1198–1201.
- [3] ZÜTTEL A, RENTSCH S, FISCHER P, WENGER P, SUDAN P, MAURON P, EMMENEGGER C. Hydrogen storage properties of LiBH_4 [J]. *Journal of Alloys and Compounds*, 2003, 356: 515–520.
- [4] AU M, WALTERS R T. Reversibility aspect of lithium borohydrides [J]. *International Journal of Hydrogen Energy*, 2010, 35: 10311–10316.
- [5] CHI H Z, CHEN C P, CHEN L X, WANG Q D. Hydriding properties of $\text{La}_2\text{Mg}_{16}\text{Ni}$ alloy prepared by mechanical milling in benzene [J]. *Journal of Alloys and Compounds*, 2003, 360: 312–315.
- [6] GAO L H, CHEN C P, CHEN L X, WANG X H, ZHANG J W, XIAO X Z, WANG Q D. Hydriding/dehydriding behaviors of $\text{La}_{1.8}\text{Ca}_{0.2}\text{Mg}_{14}\text{Ni}_3$ alloy modified by mechanical ball-milling under argon [J]. *Journal of Alloys and Compounds*, 2005, 399: 178–182.
- [7] CHI H Z, CHEN C P, CHEN L X, AN Y, WANG Q D. Hydriding/dehydriding properties of $\text{La}_2\text{Mg}_{16}\text{Ni}$ alloy prepared by mechanical ball milling in benzene and under argon [J]. *International Journal of Hydrogen Energy*, 2004, 29: 737–741.
- [8] ORIMO S, NAKAMORI Y, KITAHARA G, MIWA K, OHBA N, TOWATA S, ZÜTTEL A. Dehydriding and rehydriding reactions of LiBH_4 [J]. *Journal of Alloys and Compounds*, 2005, 404–406: 427–430.
- [9] FAN X L, XIAO X Z, CHEN L X, YU K R, WU Z, LI S Q, WANG Q D. Active species of CeAl_4 in the CeCl_3 -doped sodium aluminum hydride and its enhancement on reversible hydrogen storage performance [J]. *Chemical Communications*, 2009: 6857–6859.
- [10] XIAO X Z, CHEN L X, WANG X H, LI S Q, CHEN C P, WANG Q D. Reversible hydrogen storage properties and favorable co-doping mechanism of the metallic Ti and Zr co-doped sodium aluminum hydride [J]. *International Journal of Hydrogen Energy*, 2008, 33: 64–73.
- [11] ZHANG Guo-ying, LIU Gui-li, ZHANG Hui. First-principles study of intrinsic defects, dopants and dopant-defect complexes in LiBH_4 [J]. *Transactions of Nonferrous Metals Society of China*, 2012, 22(7): 1717–1722.
- [12] XIAO X Z, LIU G C, PENG S K, YU K R, LI S Q, CHEN C P, CHEN L X. Microstructure and hydrogen storage characteristics of nanocrystalline $\text{Mg}+x\text{wt}\% \text{LaMg}_2\text{Ni}$ ($x=0-30$) composites [J]. *International Journal of Hydrogen Energy*, 2010, 35: 2786–2790.
- [13] WU Xiao-cheng, WANG Xin-hua, LI Shou-quan, GE Hong-wei, CHEN Li-xin, YAN Mi, CHEN Chang-pin. Dehydrogenation

- properties and mechanism of $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ composite [J]. Rare Metal Materials and Engineering, 2012, 41(8): 1405–1408.
- [14] GUO Y H, YU X B, GAO L, XIA G L, GUO Z P, LIU H K. Significantly improved dehydrogenation of LiBH_4 destabilized by TiF_3 [J]. Energy & Environmental Science, 2010, 3: 464–469.
- [15] DENG Shuai-shuai, XIAO Xue-zhang, CHEN Li-xin, HAN Le-yuan, LI Shou-quan, GE Hong-wei, WANG Qi-dong. Effects of stoichiometry and dehydrogenation back-pressure on the dehydrogenation behavior of $\text{LiBH}_4+x\text{Mg}_2\text{NiH}_4$ composites [J]. Chemical Journal of Chinese Universities, 2012, 33(9): 2030–2034. (in Chinese)
- [16] VAJO J J, SKEITH S L, MERTENS F. Reversible storage of hydrogen in destabilized LiBH_4 [J]. Journal of Physical Chemistry B, 2005, 109: 3719–3722.
- [17] BARKHORDARIAN G, KLASSEN T, DORNHEIM M, BORMANN R. Unexpected kinetic effect of MgB_2 in reactive hydride composites containing complex borohydrides [J]. Journal of Alloys and Compounds, 2007, 440: L18–L21.
- [18] KANG X D, WANG P, MA L P, CHENG H M. Reversible hydrogen storage in LiBH_4 destabilized by milling with Al [J]. Applied Physics A: Materials Science & Processing, 2007, 89: 963–966.
- [19] JIN S A, LEE Y S, SHIM J H, CHO Y W. Reversible hydrogen storage in $\text{LiBH}_4\text{-MH}_2$ ($\text{M}=\text{Ce}$, Ca) composites [J]. Journal of Physical Chemistry C, 2008, 112: 9520–9524.
- [20] JIANG K, XIAO X Z, DENG S S, ZHANG M, LI S Q, GE H W, CHEN L X. A novel Li–Ca–B–H complex borohydride: Its synthesis and hydrogen storage properties [J]. Journal of Physical Chemistry C, 2011, 115: 19986–19993.
- [21] ZHANG Y, TIAN Q F, CHU H L, ZHANG J, SUN L X, SUN J C, WEN Z S. Hydrogen de/resorption properties of the $\text{LiBH}_4\text{-MgH}_2\text{-Al}$ system [J]. Journal of Physical Chemistry C, 2009, 113: 21964–21969.
- [22] LIU D M, LIU Q Q, SI T Z, ZHANG Q A, FANG F, SUN D L, OUYANG L Z, ZHU M. Superior hydrogen storage properties of LiBH_4 catalyzed by $\text{Mg}(\text{AlH}_4)_2$ [J]. Chemical Communications, 2011, 47: 5741–5743.
- [23] FAN X L, XIAO X Z, CHEN L X, HAN L Y, LI S Q, GE H W, WANG Q D. Thermodynamics, kinetics and modeling investigation on the dehydrogenation of CeAl_4 -doped NaAlH_4 hydrogen storage material [J]. Journal of Physical Chemistry C, 2011, 115(45): 22680–22687.
- [24] CHEN Li-xin, FAN Xiu-lin, XIAO Xue-zhang, XUE Jing-wen, LI Shou-quan, GE Hong-wei, CHEN Chang-pin. Influence of TiC catalyst on absorption/desorption behaviors and microstructures of sodium aluminum hydride [J]. Transactions of Nonferrous Metals Society of China, 2011, 21(6): 1297–1302.
- [25] GOMES S, HAGEMANN H, YVON K. Lithium borohydride LiBH_4 : II. Raman spectroscopy [J]. Journal of Alloys and Compounds, 2002, 346: 206–210.
- [26] DU A J, SMITH SEAN C, YAO X D, SUN C H, LI L, LU G Q. First principle study of hydrogenation of MgB_2 : An important step toward reversible hydrogen storage in the coupled $\text{LiBH}_4/\text{MgH}_2$ system [J]. Journal of Nanoscience and Nanotechnology, 2009, 9(7): 4388–4391.
- [27] JIN S A, SHIM J H, CHO Y W, YI K W, ZABARA O, FICHTNER M. Reversible hydrogen storage in $\text{LiBH}_4\text{-Al-LiH}$ composite powder [J]. Scripta Materialia, 2008, 58: 963–965.
- [28] KOU Hua-qin, XIAO Xue-zhang, CHEN Li-xin, LI Shou-quan, WANG Qi-dong. Formation mechanism of MgB_2 in $2\text{LiBH}_4+\text{MgH}_2$ system for reversible hydrogen storage [J]. Transactions of Nonferrous Metals Society of China, 2011, 21(5): 1040–1046.
- [29] CRIVELLO J C, NOBUKI T, KATO S, ABE M, KUJI T. Hydrogen absorption properties of the $\gamma\text{-Mg}_{17}\text{Al}_{12}$ phase and its Al-rich domain [J]. Journal of Alloys and Compounds, 2007, 446–447: 157–161.

$\text{LiBH}_4/\text{Mg}_{17}\text{Al}_{12}$ -氢化物复合体系的 放氢行为改善及其机制

韩乐园, 肖学章, 范修林, 李 芸, 李寿权, 葛红卫, 王启东, 陈立新

浙江大学 材料科学与工程学系, 浙江省电池新材料与应用技术研究重点实验室, 杭州 310027

摘 要: 选择 $\text{Mg}_{17}\text{Al}_{12}$ -氢化物作为失稳剂与 LiBH_4 进行球磨以改善 LiBH_4 体系的吸放氢性能。研究表明, $\text{LiBH}_4/\text{Mg}_{17}\text{Al}_{12}$ -氢化物复合体系发生两步放氢过程。复合体系在 $300\text{ }^\circ\text{C}$ 开始放氢并在 $500\text{ }^\circ\text{C}$ 下产生 9.8% 的放氢量。通过添加 $\text{Mg}_{17}\text{Al}_{12}$ -氢化物, LiBH_4 的放氢动力学得到有效改善, 并且其放氢温度降低 $20\text{ }^\circ\text{C}$ 。复合体系的放氢产物在 $450\text{ }^\circ\text{C}$ 的首次再加氢容量可高达 8.3%。XRD 分析表明, 复合体系在放氢过程中所形成的 MgB_2 和 AlB_2 可降低 LiBH_4 的热力学稳定性, 进而有效改善 $\text{LiBH}_4/\text{Mg}_{17}\text{Al}_{12}$ -氢化物复合体系的可逆储氢行为。

关键词: 配位氢化物; LiBH_4 ; $\text{Mg}_{17}\text{Al}_{12}$; 吸放氢行为; 可逆性

(Edited by Hua YANG)