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1 Introduction

The search for efficient hydrogen storage materials is one of the most critical challenges as we enter the hydrogen-powered society as a long-term solution to current energy problems.¹ Recently, intensive interest has been focused on complex hydrides,² especially for lithium borohydride (LiBH₄), owing to its high reversible hydrogen storage capacity (13.8 wt% H₂).³ However, the strong and highly cooperative covalent and ionic bonds of LiBH₄ impose problematic H-exchange thermodynamics and kinetics for reversible hydrogen storage. To ease these problems, several strategies have been proposed, including nanoconfinement,⁴ partial cation/anion substitution,⁵ catalyst doping⁶ and reactant destabilization.^{7,8} All of these technological advances have enabled significant

High catalytic efficiency of amorphous TiB₂ and NbB₂ nanoparticles for hydrogen storage using the 2LiBH₄–MgH₂ system[†]

Xiulin Fan, Xuezhang Xiao, Lixin Chen,* Xinhua Wang, Shouquan Li, Hongwei Ge and Qidong Wang

LiBH₄–MgH₂ system in a 2 : 1 molar ratio constitutes a representative reactive hydride composite (RHC) for hydrogen storage. However, sluggish kinetics and poor reversibility hinder the practical applications. To ease these problems, amorphous TiB₂ and NbB₂ nanoparticles were synthesized and employed as catalysts for the 2LiBH₄–MgH₂ system. Isothermal de-/rehydrogenation and temperature programmed mass spectrometry (MS) measurements show that amorphous TiB₂ and NbB₂ nanoparticles can significantly improve the hydrogen storage performance of the 2LiBH₄–MgH₂ system. 9 wt% hydrogen can be released within only 6 min for nanoTiB₂-doped 2LiBH₄–MgH₂, while for the undoped composite limited hydrogen of 3.9 wt% is released in 300 min at 400 °C. The dehydrogenation activation energies for the first and second steps are dramatically reduced by 40.4 kJ mol⁻¹ and 35.2 kJ mol⁻¹ after doping with nanoTiB₂. It is believed that TiB₂ and NbB₂ nanoparticles can first catalyze the dehydrogenation of MgH₂, and then induce the decomposition of LiBH₄ and meanwhile act as nucleation agents for MgB₂, thereby greatly enhancing the kinetics of dehydrogenation. The present study gives clear evidence for the significant performance of transition metal boride species in doped RHCs, which is critically important for understanding the mechanism and further improving the hydrogen storage properties of RHCs.

improvements in the reversible hydrogen storage properties of LiBH₄. Particularly, the employment of a reactant destabilization strategy to form reactive hydride composites (RHCs) has been proven to be effective to stabilize the dehydrogenated state and then lower the total reaction enthalpy. The LiBH₄-MgH₂ system in a 2 : 1 molar ratio constitutes a representative reactive hydride composite, which reduces the reaction enthalpy by 25 kJ mol⁻¹ H₂ in comparison with the pristine LiBH₄ by forming MgB₂ as shown in the following equation:⁷

$$2\text{LiBH}_4 + \text{MgH}_2 \rightarrow 2\text{LiBH}_4 + \text{Mg} + \text{H}_2 \rightarrow 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2 (1)$$

Although the reaction enthalpy of 2LiBH₄–MgH₂ is lowered, dehydrogenation and subsequent rehydrogenation processes still occur at high temperatures with slow kinetics. Therefore, extensive efforts have been focused on improving the de-/rehydrogenation rates and reducing the reaction temperature for RHC systems by exploring high-performance catalysts, which can be classified as chlorides,⁹⁻¹¹ halides^{11c,12,13} and oxides.^{14,15} However, almost all of these dopants will generate some byproducts during doping or subsequent cycling, which will take up some weight in the system, causing a decrease of the reversible hydrogen storage capacity.⁹⁻¹⁵

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Key Laboratory of Advanced Materials and Application for Batteries of Zhejiang Province, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China. E-mail: lxchen@zju.edu.cn; Fax: +86 571 8795 1152; Tel: +86 571 8795 1152

[†] Electronic supplementary information (ESI) available: Mass spectra of released gases during synthesis of NbB₂ and TiB₂, SEM images of as-synthesized NbB₂ and TiB₂, TEM and HRTEM images for TiB₂ and NbB₂ after heat treatment, XRD patterns of TiB₂ and NbB₂ after heat treatment, MS results with different heating rates, EDS mapping results of TiB₂-doped RHC, FTIR spectra of nanoTiB₂-doped 2LiBH₄-MgH₂. See DOI: 10.1039/c3ta12401k

Among the halides or oxides, the dopants TiF₃, NbF₅ and Nb₂O₅ are proven to be most effective in advancing the performance of hydrogen storage for RHCs.12-15 However, the detailed mechanism and active species are still controversial. Wang et al.12 and Sun et al.14 observed the formation of transition metal hydrides (TiH2 and NbH) in the doping process and following de-/rehydrogenation procedures and believed that these hydrides can improve the H-exchange kinetics and play a key role in the enhancement of hydrogen storage properties. Deprez et al.¹⁵ detected the coexistence of Ti₂O₃ and TiB₂ in the doped samples, and expected that both of these species exert favorable effects on kinetic improvement. For Nb-doped RHC systems, no signals of related Nb-B species were detected. However, the similarity of kinetic enhancement for doped RHC systems may arise from the same catalytic mechanism. Bösenberg et al.9 believed that the in situ formed species of transition metal borides were the active species for the RHCs. None of these standpoints have been firmly confirmed until now, which is believed due to the intricacy of the reactions, slow transformation of species and more importantly, low sensitivity of in situ formed species responses to traditional characterization techniques, such as XRD, SEM and EDS. However, the identification of the promoting species and detailed understanding of the mechanism are indispensable for further improvements in reversible de-/rehydrogenation of RHCs.

Herein, we successfully synthesized amorphous TiB_2 and NbB_2 nanoparticles with sizes of less than 30 nm, and used them for the first time as catalysts to improve the hydrogen storage properties for the representative RHC $2LiBH_4$ -MgH₂ system. Superior kinetics for the doped RHC and excellent stability of the transition metal boride dopants fundamentally established the mechanism that amorphous transition boride nanoparticles will catalyze the de-/rehydrogenation of MgH₂ and LiBH₄, and meanwhile act as nucleation agents for MgB₂ in the dehydrogenation of the second step, thereby significantly enhancing the kinetics of the RHC system.

2 Experimental section

 $TiCl_4$ (98%), NbCl₅ (99%) and LiCl (99%) were obtained from Aladdin Reagents. LiH (98%), LiBH₄ (95%) and MgH₂ (98%) were purchased from Alfa Aesar. All of the chemicals were used as received without further purification.

2.1 Synthesis of TiB₂ and NbB₂ nanoparticles

 ${\rm TiB}_2$ and ${\rm NbB}_2$ synthesis was carried out mechanochemically according to the following reactions:

TiCl₄(l) + 2LiBH₄ + 2LiH → TiB₂ + 4LiCl + 5H₂(g),

$$\Delta G_{298} = -688 \text{ kJ mol}^{-1} (\text{ref. 16}) (2)$$

NbCl₅ + 2LiBH₄ + 3LiH
$$\rightarrow$$
 NbB₂ + 5LiCl + 5.5H₂(g),
 $\Delta G_{298} = -985 \text{ kJ mol}^{-1} (\text{ref. 16}) (3)$

A LiCl buffer was added to the starting reagents to reduce the borides in the reaction products to *ca.* 4 wt%. The use of LiCl buffer was to prevent collisions of product particles during

milling and a large increase in temperature due to exothermal reactions.17 The LiBH4, LiH, and plenty of LiCl buffer were first milled together for 20 h to adequately mix the reagents to produce nanoscopic reaction sites within the composite powder. After pre-milling, TiCl₄ or NbCl₅ was added to the powder and milling was continued for another 20 h to ensure reaction completeness. After ball milling, the mass spectrometry (MS) measurements were carried out to detect the gases in the vial using a QIC-20 (HIDEN ANALYTICAL LTD) gas analysis system. The results are presented in Fig. S1,† which shows that only hydrogen is released. The total amounts of hydrogen released are \sim 3.94 wt% and 3.15 wt% for the synthesis processes using TiB₂ and NbB₂, corresponding to purities of 98% and 97% for the products. After ball milling, the buffer and byproduct LiCl were removed by washing the powder with tetrahydrofuran (THF). Boride nanoparticles were collected by centrifugation and washed with THF, then dried under vacuum at 50 °C overnight. During synthesis and washing processes, Ar was used to protect the transition metal from oxidization.

2.2 Heat treatment of the amorphous TiB_2 and NbB_2 nanoparticles

After synthesis, TiB_2 and NbB_2 nanoparticles were transferred into a furnace where a continuous argon gas flow was introduced at the rate of 60 mL min⁻¹. Then the furnace temperature was elevated to 400 or 700 °C to test the crystallization behavior.

2.3 Synthesis of nano-catalyzed 2LiBH₄-MgH₂ composite

Before being mixed with any catalyst, the mixture of 2LiBH₄–MgH₂ was premilled under 1 MPa H₂ for 6 h in a planetary ball mill (QM-3SP4, Nanjing). Then, as-prepared NbB₂, TiB₂ or annealed TiB₂ nanoparticles were mixed with the premilled 2LiBH₄–MgH₂ and milled for 10 h. For comparison, undoped 2LiBH₄–MgH₂ was also prepared under the same conditions. All the sample handling was performed in an Ar-filled glovebox (MBraun), in which the water/oxygen levels were below 1 ppm.

2.4 Characterization

X-ray diffraction (XRD) experiments of the samples were performed on an X'Pert Pro X-ray diffractometer (PANalytical, the Netherlands) with Cu Ka radiation at 40 kV and 40 mA. During the sample transfer and scanning, a lab-built argon filled container was used to protect the samples from air and moisture. X-ray photoelectron spectroscopy (XPS) was carried out on a VG ESCALAB MARK II system with Mg Kα radiation (1253.6 eV) at a base pressure of 1 imes 10⁻⁸ Torr. The spectra were recorded with a pass energy of 50 eV after Ar⁺ sputtering of the surface for 20 min (operated at 3 kV with a current density of 15 μ A). All binding energy values were referenced to the C 1s peak of contaminant carbon at 284.6 eV with an uncertainty of ± 0.2 eV. Transmission electron microscopy (TEM, Tecnai G2 F20) and scanning electron microscopy (SEM, Hitachi SU-70) equipped with energy dispersive X-ray spectroscopy were used to examine the microstructure and elemental distribution of materials. Special caution was taken to prevent H2O-O2 contamination during the measurements. Fourier transform infrared (FTIR)

spectra were obtained with a Bruker Tensor 27 unit in transmission mode. The testing samples were prepared by coldpressing a mixture of powder and potassium bromide (KBr) at a weight ratio of 1:250 to form a pellet. Each spectrum was plotted from 32 scans averaged with a solution of 4 cm^{-1} . The mass spectrometry (MS) measurements for 2LiBH₄-MgH₂ composites were conducted on a Netzsch Q430C mass spectrometer under flowing argon conditions (50 mL min⁻¹). During the experiments the MS signals at m/z = 2 and 27 were recorded in order to detect H₂ and B₂H₆. The hydrogen desorption and absorption of the samples were examined in a carefully calibrated Sievert's type apparatus. Hydrogen desorption was carried out under 0.38 MPa H₂. Rehydrogenation was performed under an initial hydrogen pressure of 10 MPa. To allow a practical evaluation of hydrogen storage performance, the catalyst and hydride masses were taken into account in the determination of the hydrogen capacity.

3 Results and discussion

3.1 Characterization of TiB₂ and NbB₂

Fig. 1(a) shows the XRD patterns of NbB₂ and TiB₂ powders. Remarkably, typical diffraction crystalline peaks can not be observed for NbB₂ or TiB₂. Only three broad bumps at around 20-35, 35-50 and 60-75° are discernible for the as-synthesized NbB₂, which can be ascribed to the strongest diffraction peaks of NbB_2 according to PDF # 35-0741. For $TiB_2,$ two less obvious bumps can be detected at 25-50°, which originate from the three highest diffraction peaks (PDF # 65-0512). The significantly broad bumps with low intensity for TiB₂ and NbB₂ indicate the amorphization of catalysts. To verify this assumption, TEM/ HRTEM and SAED studies were carried out. The particles of as-synthesized nanoNbB₂ and TiB₂ have sizes of approximately 30 nm or less (Fig. 1(b) and (c) and SEM, ESI Fig. S2⁺). The related selective area electron diffraction (SAED) patterns (Fig. 1(b) and (c), insets) demonstrate the diffuse diffraction rings of an amorphous phase, which is in agreement with X-ray diffraction results. HRTEM further confirmed the amorphization of the borides, because no evident lattice fringes related to crystals were observed in the interior (Fig. 1(d)) or edges (Fig. 1(e)) of particles. Besides, the HRTEM image (Fig. 1(e)) also shows the particles consist of even smaller primary particles with sizes of ~10 nm. Fig. 1(f) shows the EDS result of TiB₂, significant peaks of Ti and a minor peak of B prove the elemental composition of TiB₂. The as-synthesized amorphous TiB2 and NbB2 can not be crystallized at 400 °C, even when the time is extended to 72 h. This might be able to explain the unidentification of transition metal borides using conventional XRD technique in halide- or oxide-doped RHCs. Amorphous TiB₂ and NbB₂ can be crystallized at 700 °C (Fig. S3[†]). After heat treatment for 12 h, nanocrystallites with sizes of \sim 3 nm were observed, while the particle size was almost unchanged, as shown in Fig. S4.[†]

3.2 Catalytic effects of TiB₂ and NbB₂ nanoparticles on 2LiBH₄-MgH₂ system

Fig. 2(a) shows the dehydrogenation profiles of $2LiBH_4$ -MgH₂ composites at 400 °C under a hydrogen back pressure of



Fig. 1 (a) XRD patterns of as-synthesized NbB₂ and TiB₂; (b) TEM image of assynthesized NbB₂, the inset shows the corresponding SAED pattern; (c) TEM image of as-synthesized TiB₂, the inset shows the corresponding SAED pattern; (d) and (e) HRTEM images of NbB₂ and TiB₂; (f) EDS spectrum of TiB₂. The presence of Cu and C is derived from the copper mesh and carbon film that support the sample during TEM measurement.

0.38 MPa. It should be pointed out that all of the components were counted to calculate the hydrogen capacity including the dopants. For the undoped material, poor kinetics was observed with 3.9 wt% hydrogen desorbed in 300 min, indicating that the incubation period for the 2nd step dehydrogenation surpasses 6 h, which is in line with the previous investigations.^{11,12} Interestingly, the problematic incubation period completely disappeared after doping with 5 mol% as-synthesized NbB₂ or TiB₂ amorphous nanoparticles. 9 wt% hydrogen can be released within only 6 min for 5 mol% nanoTiB₂-doped 2LiBH₄-MgH₂, which is among the best kinetics ever reported for doped RHCs. Compared with the higher dehydrogenation temperature of almost 500 °C for pure LiBH₄,¹⁸ the doped composites exhibit a pronounced kinetic improvement with a much lower dehydrogenation temperature.



Fig. 2 (a) Dehydrogenation curves of $2LiBH_4$ –MgH₂ doped with/without 5 mol % TiB₂ or NbB₂ at 400 °C; and (b) rehydrogenation curves of $2LiBH_4$ –MgH₂ doped with/without 5 mol% TiB₂ or NbB₂ at 350 °C. HT means heat treatment for nanoTiB₂ at 700 °C for 12 h.



Fig. 3 Dehydrogenation curves of $2LiBH_4$ -MgH₂ doped with 5 mol% amorphous nano-TiB₂ for the first 6 cycles at different temperatures under an initial back pressure of 0.38 MPa.

The inset in Fig. 2(a) shows the enlargement of the dehydrogenation curves in the first 30 min. It can be seen that the dopants TiB₂ and NbB₂ can significantly improve the dehydrogenation kinetics of MgH_2 (the first dehydrogenation step of eqn (1)). For the undoped material, 15 min is needed to acquire 2.8 wt% H₂ (the theoretical capacity for the first step), while for the doped samples, the time is dramatically reduced to less than 3 min. This phenomenon is consistent with the results reported by Pitt et al., who showed that TiB₂ can sufficiently improve the kinetics of de-/rehydrogenation of MgH2.19 It can also be seen that the crystallinity of the dopant exerts a detrimental effect on the enhancement of kinetics, although the particles remain in the same size range (ESI, Fig. S4[†]). This could be due to the fact that the amorphous catalyst has a much greater structural distortion and therefore a much higher concentration of active sites for the catalytic reactions than its crystalline counterpart.²⁰ Fig. 2(b) shows that the TiB₂ and NbB₂ nanoparticles can also significantly improve the rehydrogenation kinetics of the 2LiBH₄-MgH₂ composite. 8.5 wt% H₂ can be reabsorbed for amorphous TiB2 and NbB2 doped samples within only 5 and 8 min, respectively, while a period as long as 120 min is needed for the undoped 2LiBH₄-MgH₂.

Fig. 3 exhibits the dehydrogenation curves of TiB_2 -doped $2LiBH_4$ -MgH₂ for the first 6 cycles at different temperatures. Before dehydrogenation, all of the samples were hydrogenated at 350 °C under 10 MPa for 2 h. As the temperature is lowered,



Fig. 4 MS results of doped and undoped $2LiBH_4-MgH_2$ samples. Heating rate: 8 °C min⁻¹; purging gas: argon. MS results demonstrate that the gas released from all samples is pure H_2 without B_2H_6 .

an incubation period shows up, however, it still presents a pronounced kinetics. The TiB2-doped composite can release 9.5 wt% H2 within 30 min at 390 °C, and 9.3 wt% H2 within 50 min at 380 °C; even at 365 °C, it can also desorb 9.0 wt% within 180 min. After the 6th cycle, TiB₂-doped 2LiBH₄-MgH₂ can still exhibit a reversible capacity of ca. 9.0 wt%, demonstrating that the doped composite possesses a favorable cycling stability. This characteristic dramatically improves the poor cycling behavior of LiBH4 composites6b and is of significant importance for doped 2LiBH₄-MgH₂ composite as a hydrogen storage material. Table 1 summarizes similar RHC systems in the literature and compares them with the present investigation. It can be clearly seen that by doping with amorphous TiB_2 or NbB₂ nanoparticles, significantly improved hydrogen storage performance with high hydrogen storage capacity and superior kinetics is achieved for the 2LiBH₄-MgH₂ RHC system.

For the purpose of comparison, additional MS experiments were carried out, as shown in Fig. 4. After doping with nanoTiB₂ or nanoNbB₂, the starting decomposition temperature of MgH₂ and LiBH₄ is significantly reduced. The peak temperatures of MgH₂ and LiBH₄ after doping with 5 mol% TiB₂ are lowered by 49 and 43 °C, respectively, compared with those of the undoped materials, which reconfirms the superior catalytic effects of nanoTiB₂ and NbB₂ for decomposition of MgH₂ and LiBH₄. Besides, MS results show that no impurity gas of B₂H₆ is released

Table 1 Comparison of similar RHC systems with the present investigation									
				Conditions (dehyd)		Conditions (rehyd)			
RHC system	Dopant	Byproduct	Hydrogen (wt%)	Temp (°C)	Time (min)	Temp (°C)	Time (min)	References	
2LiBH ₄ -MgH ₂	TiF ₃	LiF	~ 8	400	~ 30	350	~ 50	12 and 22	
2LiBH ₄ -MgH ₂	NbF ₅	LiF	~ 8	400	${\sim}60$	400	${\sim}40$	13 <i>b</i>	
2LiBH ₄ -MgH ₂	Nano-TiB ₂ ; nano-NbB ₂	None	>9	400	<10	350	<20	Present work	
2LiBH ₄ -Al	TiF ₃	LiF	<7	450	200	400	200	8 <i>a</i> and 23	
$LiBH_4$ -MH _x (M = Ti, Ca)	None	None	<5	400	3000	_	_	8 <i>f</i>	
3NaBH ₄ -NdF ₃	None	NaF	<3.5	400	~ 30	400	~ 90	2d	



Fig. 5 Kissinger plots of the undoped and nanoTiB₂, nanoNbB₂-doped 2LiBH₄– MgH₂ composites: (a) the dehydrogenation of MgH₂ (the first step of eqn (1)); (b) the dehydrogenation of LiBH₄ (the second step of eqn (1)).

Table 2 Apparent activation energy (E_a) for the dehydrogenation of the 2LiBH₄–MgH₂ system

	Apparent activation energy E_a (kJ mol ⁻¹)				
Dopant	MgH ₂ (first step)	$LiBH_4$ (second step)			
Undoped	141.6	139.8			
NanoTiB ₂	101.2	104.6			
NanoNbB ₂	116.2	105.1			

in the dehydrogenation process. This is substantially important for the utilization of doped 2LiBH_4 -MgH₂ as a hydrogen source for fuel cells. To get a further understanding of the enhancement of kinetics, the activation energy E_a for the dehydrogenation of doped RHC was determined using the non-isothermal Kissinger method according to the following equation:

$$\frac{\mathrm{d}\ln(\beta/T_{\mathrm{m}}^{2})}{\mathrm{d}(1/T_{\mathrm{m}})} = \frac{E_{\mathrm{a}}}{R}$$
(4)

where β , $T_{\rm m}$, and R are the heating rate, the absolute temperature for the maximum desorption rate, and the gas constant. In this work, $T_{\rm m}$ was obtained using MS measurement with the selected heating rates of 4, 6, 8, 10, 15 K min⁻¹. The detailed MS curves are shown in Fig S5.† Fig. 5 shows the Kissinger plots for the first and second dehydrogenation steps of 2LiBH₄-MgH₂ Paper

systems. The apparent activation energies can be calculated from the slope of the fitted lines, and these are tabulated in Table 2. The apparent activation energy for the dehydrogenation of undoped MgH₂ is estimated to be 141.6 kJ mol⁻¹, which is in good agreement with the published results in previous work.²¹ It is found that the apparent activation energy (E_a) is substantially lowered by doping with nanoTiB₂ or nanoNbB₂ amorphous particles. For the nanoTiB₂-doped composite, the apparent activation energies are lowered by 40.4 kJ mol⁻¹ and 35.2 kJ mol⁻¹ for the first and second steps of dehydrogenation, in comparison with the undoped composite. These results quantitatively evidenced the superior catalytic effects of amorphous nanoTiB₂ and NbB₂ on the dehydrogenation of MgH₂ and LiBH₄.

Fig. 6(a) and (b) shows the typical SEM images of TiB₂-doped 2LiBH₄-MgH₂ after rehydrogenation in the 2nd cycle and after dehydrogenation in the 3rd cycle, respectively. It is clear that nanoparticles of TiB₂ are well dispersed in the matrix of hydrides. After dehydrogenation, the formed particles of MgB₂ and LiH are uniformly mingled in the nanometer range without obvious phase separation. This phenomenon is also confirmed by the EDS mapping results for the TiB₂-doped 2LiBH₄-MgH₂ (Fig. S6[†]). TEM (Fig. 6(c)) and HRTEM (Fig. 6(d)) images show that nanoparticles of MgB2 with size of 10 nm are homogeneously dispersed in the composite after dehydrogenation. The lattice spacing of 0.213 nm can be indexed to be the (101) plane of hexagonal MgB₂. Fig. 6(e) and (f) show the STEM-HAADF image of nanoNbB2-doped 2LiBH4-MgH2 after dehydrogenation and the corresponding cross-sectional compositional line profiles. It can be seen that nanoparticles of NbB₂ are in the size range 10-40 nm and well dispersed in the composites. Appreciable distinctions between the nanoparticles of MgB₂ and LiH can be observed from the STEM-HAADF image. According to the results described above, we deduce that the nanoNbB₂ and TiB₂ can first catalyze the dehydrogenation of MgH₂, and then induce the decomposition of LiBH₄ and meanwhile act as nucleation agents for MgB₂. The blast crystallization of MgB2 results in a homogeneous dispersion of LiH and MgB₂. This is important since phase separation necessarily hinders reversibility.9 Catalysis of nanoborides together with favorable contact of composites results in a superior kinetics.

Due to the poor crystallization of as-synthesized TiB₂ and NbB₂, no peaks of Ti or Nb-containing phases can be identified from XRD, even when the concentration is increased to 15 mol%, as shown in Fig. 7. No other phases show up except for LiBH₄, MgH₂, MgB₂ and LiH, during dehydrogenation and rehydrogenation cycles. After ball milling, only LiBH4 and MgH2 phases can be observed with broadened peaks, indicating the ball milling results in the reduction of crystallites. After rehydrogenation, the phases return to LiBH₄ and MgH₂ phases, confirming the good reversibility of the system. The broad peaks of MgB₂ after dehydrogenation indicate that the grains are extremely fine. The mean grain sizes of MgB₂ for TiB₂ and NbB₂ doped materials are about 15 and 14 nm respectively, calculated by using the Scherrer equation, in agreement with the TEM observations. These results further evidence the blast crystallization of MgB₂ for the doped 2LiBH₄-MgH₂ RHC, which is favorable for kinetic



Fig. 6 SEM image of nanoTiB₂-doped 2LiBH₄–MgH₂ after rehydrogenation in the 2nd cycle (a); (b)–(d) are SEM and TEM images of nanoTiB₂-doped 2LiBH₄–MgH₂ after dehydrogenation in the 3rd cycle. The inset in (d) shows a zoom-in image of the dashed square in (d); (e) and (f) are STEM-HAADF image and the corresponding cross-sectional compositional line profiles of nanoNbB₂-doped 2LiBH₄–MgH₂ after dehydrogenation in the 3rd cycle.

enhancement of the subsequent hydrogenation. The FTIR results (Fig. S7[†]) for the nanoTiB₂-doped 2LiBH_4 -MgH₂ after ball milling and rehydrogenation together with its dehydrogenated samples verify the favorable cyclic stability, since rehydrogenated samples clearly show the corresponding signals for the bending mode (at 1120 cm⁻¹) for the [BH₄]⁻ complex as well as the stretching modes (at 2180–2400 cm⁻¹), while for the dehydrogenated samples the signals are not observed.

To investigate the local atomic environment of the surface for Ti species in the composites, XPS analyses were conducted on the doped samples and compared with the as-synthesized TiB₂ nanoparticles. Fig. 8 shows XPS spectra of as-synthesized TiB₂ and TiB₂ in the 2LiBH₄-MgH₂ system. The two peaks at 454.2 and 460 eV can be attributed to Ti 2p3/2 and Ti 2p1/2 of TiB₂ respectively.²⁴ After doping into 2LiBH₄-MgH₂ and cycling, the dopant TiB₂ remains constant, thereby confirming the good stability of TiB₂. The XPS spectra provide direct evidence for the good stability of the doped borides, which makes us believe that boride nanoparticles are the active species in promoting dehydrogenation and rehydrogenation reactions for 2LiBH₄-MgH₂ RHC composites.

4 Conclusions

In summary, we have successfully synthesized amorphous TiB_2 and NbB_2 nanoparticles *via* reactive ball milling using $LiBH_4$, LiHand $TiCl_4/NbCl_5$ as reactants with quantities of LiCl as buffer. It was found that thus-prepared amorphous nanoparticles exhibit a superior catalytic effect on de-/rehydrogenation kinetics for the $2LiBH_4$ -MgH₂ RHC system. 9 wt% hydrogen can be released within only 6 min for nanoTiB₂-doped $2LiBH_4$ -MgH₂ at 400 °C. Even at a temperature as low as 365 °C, it also can desorb 9.0 wt% within 180 min. The activation energies for the first and second dehydrogenation are significantly reduced by 40.4 kJ mol⁻¹ and



Fig. 7 XRD patterns of TiB₂-doped (a) and NbB₂-doped (b) $2LiBH_4$ -MgH₂ at different stages: (A) after ball milling; (B) after hydrogenation in the 3rd cycle; (C) after dehydrogenation in the 6th cycle.



Fig. 8 High resolution XPS spectra of Ti 2p: (a) as synthesized boride nanoparticles; (b) doped 2LiBH₄–MgH₂ after dehydrogenation in the 6th cycle.

35.2 kJ mol⁻¹ after doping with 5 mol% nanoTiB₂. Besides, the doped materials also exhibit a significant enhancement of rehydrogenation kinetics, with an average hydrogenation rate 15 times faster compared with the undoped RHC composite.

XRD, XPS, SEM and TEM/EDS analyses demonstrate that the amorphous TiB₂ and NbB₂ remain stable in the ball milling

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process and subsequent de-/rehydrogenation cycles, and act as active catalytic species in promoting dehydrogenation and rehydrogenation reactions for 2LiBH₄-MgH₂ RHC. It is believed that directly introducing these stable catalytic species will open up a new way to improve the hydrogen storage properties for the RHC systems, which can avoid the generation of byproducts, and thereby get a higher reversible hydrogen storage capacity. Besides, the proposed boride nanoparticles might also exhibit a favorable kinetic activity for other complex boride hydride and RHC systems, such as LiBH₄-Al, LiBH₄-MH₂, NaBH₄ *etc*.

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Notes and references

- (a) L. Schlapbach and A. Züttel, *Nature*, 2001, 414, 353–358;
 (b) P. Chen, Z. Xiong, J. Luo, J. Lin and K. L. Tan, *Nature*, 2002, 420, 302–304;
 (c) J. Yang, A. Sudik, C. Wolverton and D. J. Siegel, *Chem. Soc. Rev.*, 2010, 39, 656–675;
 (d) D. Pukazhselvan, V. Kumar and S. K. Singh, *Nano Energy*, 2012, 1, 566–589.
- 2 (a) G. Severa, E. Ronnebro and C. M. Jensen, *Chem. Commun.*, 2010, 46, 421–423; (b) X. L. Fan, X. Z. Xiao, L. X. Chen, K. R. Yu, Z. Wu, S. Q. Li and Q. D. Wang, *Chem. Commun.*, 2009, 6857–6859; (c) L. Li, F. Qiu, Y. Wang, Y. Wang, G. Liu, C. Yan, C. An, Y. Xu, D. Song, L. Jiao and H. Yuan, *J. Mater. Chem.*, 2012, 22, 3127–3132; (d) L. Chong, J. Zou, X. Zeng and W. Ding, *J. Mater. Chem. A*, 2013, 1, 3983–3991; (e) S. Gupta, I. Z. Hlova, T. Kobayashi, R. V. Denys, F. Chen, I. Y. Zavaliy, M. Pruski and V. K. Pecharsky, *Chem. Commun.*, 2013, 49, 828–830; (f) G. Xia, Y. Tan, X. Chen, Z. Guo, H. Liu and X. Yu, *J. Mater. Chem. A*, 2013, 1, 1810–1820; (g) F. Li, J. Gao, J. Zhang, F. Xu, J. Zhao and L. Sun, *J. Mater. Chem. A*, 2013, 1, 8016–8022.
- 3 (a) A. Züttel, P. Wenger, S. Rentsch, P. Sudan, Ph. Mauron and Ch. Emmenegger, J. Power Sources, 2003, 118, 1–7; (b)
 H. W. Li, Y. G. Yan, S. Orimo, A. Züttel and C. M. Jensen, *Energies*, 2011, 4, 185–214; (c)
 Y. G. Yan, A. Remhof, S. J. Hwang, H. W. Li, P. Mauton, S. Orinmo and A. Züttel, *Phys. Chem. Chem. Phys.*, 2012, 14, 6514–6519.
- 4 (a) A. F. Gross, J. J. Vajo, S. L. van Atta and G. L. Olson, *J. Phys. Chem. C*, 2008, **112**, 5651–5657; (b) P. Ngene, M. van Zwienen and P. E. de Jongh, *Chem. Commun.*, 2010, **46**, 8201–8203; (c) X. F. Liu, D. Peaslee, C. Z. Jost, T. F. Baumann and E. H. Majzoub, *Chem. Mater.*, 2011, **23**, 1331–1336; (d) Z. Zhao-Karger, R. Witter, E. G. Bardaji, D. Wang, D. Cossement and M. Fichtner, *J. Mater. Chem. A*, 2013, **1**, 3379–3386; (e) L. H. Rude, T. K. Nielsen, D. B. Ravnsbæk, U. Bösenberg, M. B. Ley, B. Richter, L. M. Arnbjerg, M. Dornheim, Y. Filinchuk, F. Besenbacher and T. R. Jensen,

Phys. Status Solidi A, 2011, **208**, 1754–1773; (*f*) S. L. Candelaria, Y. Shao, W. Zhou, X. Li, J. Xiao, J. G. Zhang, Y. Wang, J. Liu, J. Li and G. Cao, *Nano Energy*, 2012, **1**, 195–220.

- 5 (a) Z. Z. Fang, X. D. Kang, J. H. Luo, P. Wang, H. W. Li and S. Orimo, *J. Phys. Chem. C*, 2010, **114**, 22736–22741; (b) R. Gosalawit-Utke, J. M. Bellosta von Colbe, M. Dornheim, T. R. Jensen, Y. Cerenius, C. B. Minella, M. Peschke and R. Bormann, *J. Phys. Chem. C*, 2010, **114**, 10291–10296.
- 6 (a) M. Au and A. Jurgensen, J. Phys. Chem. B, 2006, 110, 7062–7067; (b) Y. H. Guo, X. B. Yu, L. Gao, G. L. Xia, Z. P. Guo and H. K. Liu, Energy Environ. Sci., 2010, 3, 465–470; (c) F. Fang, Y. Li, Y. Song, D. Sun, Q. Zhang, L. Ouyang and M. Zhu, J. Phys. Chem. C, 2011, 115, 13528–13533; (d) T. Sun, H. Wang, Q. Zhang, D. Sun, X. Yao and M. Zhu, J. Mater. Chem., 2011, 21, 9179–9184.
- 7 J. J. Vajo, S. L. Skeith and F. Mertens, *J. Phys. Chem. B*, 2005, **109**, 3719–3722.
- 8 (a) X. Kang, P. Wang, L. Ma and H. Cheng, Appl. Phys. A: Mater. Sci. Process., 2007, 89, 963–966; (b) S. A. Jin, Y. S. Lee, J. H. Shim and Y. W. Cho, J. Phys. Chem. C, 2008, 112, 9520–9524; (c) J. J. Vajo, W. Li and P. Liu, Chem. Commun., 2010, 46, 6687–6689; (d) D. Liu, Q. Liu, T. Si, Q. Zhang, F. Fang, D. Sun, L. Ouyang and M. Zhu, Chem. Commun., 2011, 47, 5741–5743; (e) K. B. Kim, J. H. Shim, Y. W. Cho and K. H. Oh, Chem. Commun., 2011, 47, 9831–9833; (f) J. Yang, A. Sudik and C. Wolverton, J. Phys. Chem. C, 2007, 111, 19134–19140.
- 9 U. Bösenberg, J. W. Kim, D. Gosslar, N. Eigen, T. R. Jensen, J. M. Bellosta von Colbe, Y. Zhou, M. Dahms, D. H. Kim, R. Günther, Y. W. Cho, K. H. Oh, T. Klassen, R. Bormann and M. Dornheim, *Acta Mater.*, 2010, **58**, 3381–3389.
- 10 G. L. Xia, H. Y. Leng, N. X. Xu, Z. L. Li, Z. Wu, J. L. Du and X. B. Yu, *Int. J. Hydrogen Energy*, 2011, 36, 7128–7135.
- 11 (a) P. Sridechprasat, Y. Suttisawat, P. Rangsunvigit, B. Kitiyanan and S. Kulprathipanja, *Int. J. Hydrogen Energy*, 2011, 36, 1200–1205; (b) J. Shao, X. Z. Xiao, L. X. Chen, X. L. Fan, S. Q. Li, H. W. Ge and Q. D. Wang, *J. Mater. Chem.*, 2012, 22, 20764–20772; (c) Y. Zhang, F. Morin and J. Huot, *Int. J. Hydrogen Energy*, 2011, 36, 5425–5430.

- 12 P. Wang, L. Ma, Z. Fang, X. Kang and P. Wang, *Energy Environ. Sci.*, 2009, **2**, 120–123.
- 13 (a) S. T. Sabitu and A. J. Goudy, J. Phys. Chem. C, 2012, 116, 13545–13550; (b) J. F. Mao, Z. P. Guo, X. B. Yu and H. K. Liu, Int. J. Hydrogen Energy, 2013, 38, 3650–3660; (c) X. Kang, K. Wang, Y. Zhong, B. Yang and P. Wang, Phys. Chem. Chem. Phys., 2013, 15, 2153–2158.
- 14 M. Q. Fan, L. X. Sun, Y. Zhang, F. Xu, J. Zhang and H. L. Chu, *Int. J. Hydrogen Energy*, 2008, **33**, 74–80.
- E. Deprez, M. A. Munoz-Marquez, M. A. Roldan, C. Prestipino, F. J. Palomares, C. B. Minella, U. Bosenberg, M. Dornheim, R. Bormann and A. Fernandez, *J. Phys. Chem. C*, 2010, **114**, 3309–3317.
- 16 I. Barin, *Thermochemical data of pure substances*, VCH, New York, 3rd edn, 1995.
- 17 J. W. Kim, J. H. Shim, J. P. Ahn, Y. W. Cho, J. H. Kim and K. H. Oh, *Mater. Lett.*, 2008, 62, 2461–2464.
- 18 N. Brun, R. Janot, C. Sanchez, H. Deleuze, C. Gervais, M. Morcrette and R. Backov, *Energy Environ. Sci.*, 2010, 3, 824–830.
- 19 M. P. Pitt, M. Paskevivius, C. J. Webb, D. A. Sheppard, C. E. Buckley and E. MacA Gray, *Int. J. Hydrogen Energy*, 2012, 37, 4227–4237.
- 20 J. M. Yan, X. B. Zhang, S. Han, H. Shioyama and Q. Xu, *Angew. Chem., Int. Ed.*, 2008, **47**, 2287–2289.
- 21 (a) D. Fatay, A. Revesz and T. Spassov, J. Alloys Compd., 2005, 399, 237–241; (b) K. F. Aguey-Zinsou and J. R. Ares-Fernandez, *Energy Environ. Sci.*, 2010, 3, 526–543; (c) G. Liu, Y. Wang, F. Qiu, L. Li, L. Jiao and H. Yuan, J. Mater. Chem., 2012, 22, 22542–22549.
- 22 X. Xiao, L. Zhang, X. Fan, L. Han, J. Shao, S. Li, H. Ge, Q. Wang and L. Chen, *J. Phys. Chem. C*, 2013, **117**, 12019– 12025.
- 23 B. R. S. Hansen, D. B. Ravnsbak, D. Reed, D. Book, C. Gundlach, J. Skibsted and T. R. Jensen, *J. Phys. Chem. C*, 2013, **117**, 7423–7432.
- 24 F. Huang, W. J. Liu, J. F. Sullivan, J. A. Barnard and M. L. Weaver, J. Mater. Res., 2002, 17, 805–813.