ORIGINAL ARTICLE

# **RARE METALS**



# Amorphous VB<sub>2</sub> nanoparticles for stable hydrogen storage of 2LiBH<sub>4</sub>-MgH<sub>2</sub>

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Abstract As a typical reactive composite hydrogen storage system, 2LiBH<sub>4</sub>-MgH<sub>2</sub> holds an ultrahigh hydrogen storage capacity of 11.5 wt%. However, it suffers from sluggish hydrogen storage kinetics due to the difficult nucleation of MgB2. Herein, amorphous VB2 nanoparticles with an average size of approximately 32 nm are synthesized to enhance the hydrogen storage performance of 2LiBH<sub>4</sub>-MgH<sub>2</sub> composite. VB<sub>2</sub>, sharing the same hexagonal structure with MgB<sub>2</sub> with a *d*-value mismatch ratio of only 2.28%, could serve as effective nucleation sites for promoting the formation of MgB<sub>2</sub>. Theoretical calculations reveal that the introduction of VB2 significantly reduces the binding energies of B and Mg, facilitating in situ nucleation of MgB<sub>2</sub>. As a result, after the introduction of  $VB_2$ nanoparticles, complete hydrogen desorption of 9.23 wt% is achieved for 2LiBH<sub>4</sub>-MgH<sub>2</sub> within 2 h at 400 °C, which is 4 times shorter than the time required for pure 2LiBH<sub>4</sub>-MgH<sub>2</sub>, and no nucleation incubation period for hydrogen desorption is observed even at a low temperature of

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Y.-K. Liu Central Research Institute, Baoshan Iron & Steel Co., Ltd., Shanghai 201900, China 380 °C. More importantly, a reversible capacity of 9.3 wt%, corresponding to a capacity retention of 100%, could be preserved after 10 cycles of hydrogen storage, demonstrating stable reversible hydrogen storage performance. This study provides a novel technological pathway for improving the reversible hydrogen storage performance of composite metal hydrides and offers significant insights into the development of high-performance hydrogen storage materials.

**Keywords** VB<sub>2</sub> nanoparticles; 2LiBH<sub>4</sub>–MgH<sub>2</sub>; Hydrogen storage materials; MgB<sub>2</sub> nucleation; Cyclic stability

#### 1 Introduction

In response to the global energy crisis and environmental concerns, hydrogen energy has emerged as a crucial clean energy alternative. However, the widespread adoption of hydrogen energy is significantly constrained by bottlenecks in hydrogen storage technologies [1-6]. Solid-state hydrogen storage materials have attracted considerable attention due to their high hydrogen density and superior safety characteristics. While metal hydrides and borohydrides demonstrate impressive gravimetric hydrogen storage capacities, they generally suffer from poor reaction kinetics and high operating temperatures [7–11]. Among these materials, LiBH<sub>4</sub> exhibits a remarkable hydrogen capacity of 18.5 wt%, making it to be one of the most promising candidates for the ultimate hydrogen storage targets for light-duty fuel cell vehicles [12, 13]. Conventionally, LiBH<sub>4</sub> decomposes into LiH and B upon heating with the desorption of H<sub>2</sub>. However, the actual thermal decomposition process of LiBH<sub>4</sub> is considerably more complex, involving multiple decomposition pathways. The formation of boron-containing intermediates during thermal decomposition, including Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> or Li<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, results in elevated desorption temperatures, sluggish kinetics, and poor reversibility [14-16]. Stabilization of dehydrogenation products represents an effective strategy for optimizing the thermodynamic properties of LiBH<sub>4</sub>. Through the introduction of reactive additives, the transformation of elemental B to metal borides in dehydrogenation products can effectively reduce the thermodynamic enthalpy of hydrogen storage reaction [17–19]. This thermodynamic modification not only enhances the desorption equilibrium pressure but also significantly lowers the operating temperature, thereby improving reversible hydrogen storage capabilities. As early as 2005, Vajo et al. demonstrated the complete reversibility of LiBH<sub>4</sub> when combined with MgH<sub>2</sub> in a 2:1 stoichiometric ratio under relatively mild conditions (< 450 °C) [20]. 2LiBH<sub>4</sub>-MgH<sub>2</sub> system exhibits a high hydrogen storage capacity (11.5 wt%) and excellent reversibility [21]. The overall reaction process could be expressed as follows:

 $2\text{LiBH}_4 + \text{MgH}_2 \leftrightarrow 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2 \tag{1}$ 

When the 2LiBH<sub>4</sub>-MgH<sub>2</sub> heated to 400 °C under a hydrogen pressure of 4 bar, the dehydrogenation process occurs in two distinct steps [22]. Firstly, MgH<sub>2</sub> rapidly decomposes to form Mg and H<sub>2</sub>, followed by the reaction between LiBH<sub>4</sub> and the generated Mg to form MgB<sub>2</sub> and LiH with H<sub>2</sub> release. However, the nucleation of MgB<sub>2</sub> from the mixture of Mg and LiBH<sub>4</sub> is significantly challenging, resulting in a prolonged incubation period between the two steps, which impedes subsequent hydrogen release. The addition of catalysts is considered one of the most effective strategies for enhancing the hydrogen storage properties of 2LiBH<sub>4</sub>-MgH<sub>2</sub> composite, including carbon materials, transition metals (Pd, Ni, Ru, Fe), metal halides (TiCl<sub>3</sub>, TiF<sub>3</sub>, ZrCl<sub>4</sub>, CuCl<sub>2</sub>, HfCl<sub>4</sub>, VCl<sub>3</sub>, NbF<sub>5</sub>), metal oxides (Nb<sub>2</sub>O<sub>5</sub>, Sc<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO), and metal borides (MgB2, TiB2, NbB2) [23-25]. Fan et al. synthesized amorphous TiB<sub>2</sub> and NbB<sub>2</sub> nanoparticles as catalysts for the 2LiBH<sub>4</sub>-MgH<sub>2</sub> system [26]. These metal borides initially catalyze the dehydrogenation of MgH<sub>2</sub>, subsequently induce the decomposition of LiBH<sub>4</sub>, and simultaneously serve as nucleation agents for MgB<sub>2</sub>. Shao et al. investigated the catalytic effects of three transition metal chlorides (FeCl<sub>2</sub>, CoCl<sub>2</sub>, and NiCl<sub>2</sub>) on the hydrogen storage properties of 2LiBH<sub>4</sub>-MgH<sub>2</sub> [27]. During the ball milling process, NiCl<sub>2</sub> reacts with LiBH<sub>4</sub> to form Ni<sub>3</sub>B. During the dehydrogenation, MgH<sub>2</sub> first rapidly decomposes to form metallic Mg, which then reacts with Ni<sub>3</sub>B to form MgNi<sub>3</sub>B<sub>2</sub>. Notably, MgNi<sub>3</sub>B<sub>2</sub> shares the same hexagonal structure as MgB<sub>2</sub>, enabling it to serve as nucleation sites for  $MgB_2$  formation. Therefore, materials with crystal structures similar to  $MgB_2$  could be selected as effective catalysts to promote hydrogen desorption of  $2LiBH_4$ -MgH<sub>2</sub> system [28].

Inspired by the catalytic enhancement and nucleation effects of metal borides on 2LiBH<sub>4</sub>-MgH<sub>2</sub> composites, amorphous VB<sub>2</sub> nanoparticles (denoted as VB<sub>2</sub> NPs) with an average size of approximately 32 nm are synthesized to enhance the hydrogen storage performance of 2LiBH<sub>4</sub>-MgH<sub>2</sub> composite. Due to its hexagonal structure and lattice parameters closely resembling those of MgB<sub>2</sub>, VB<sub>2</sub> could serve as effective nucleation sites for the formation of MgB<sub>2</sub>. Theoretical calculations reveal that the binding energy of a single B atom on the (0001) surface of  $VB_2$  is 2.66 eV lower than that on the Mg surface. The introduction of VB<sub>2</sub> significantly reduces the binding energies of B and Mg, particularly promoting the formation of B layer, which effectively facilitates in situ nucleation of MgB<sub>2</sub>, thereby enhancing the hydrogen desorption kinetics of 2LiBH<sub>4</sub>-MgH<sub>2</sub>. As a result, after the introduction of VB<sub>2</sub> NPs, complete dehydrogenation of 9.23 wt% is achieved for 2LiBH<sub>4</sub>-MgH<sub>2</sub> within 2 h at 400 °C, which is 4 times shorter than the time required for pure 2LiBH<sub>4</sub>-MgH<sub>2</sub>. Moreover, no nucleation incubation period for hydrogen desorption is observed even at a low temperature of 380 °C, whereas pure 2LiBH<sub>4</sub>-MgH<sub>2</sub> still exhibit a 1 h nucleation incubation period even at a high temperature of 440 °C. Notably, a reversible hydrogen storage capacity of 9.3 wt% could be preserved after 10 cycles, corresponding to a capacity retention of 100%, demonstrating excellent cycling stability and reversibility of 2LiBH<sub>4</sub>-MgH<sub>2</sub> under the catalysis of VB<sub>2</sub> NPs.

# 2 Experimental

# 2.1 Chemicals

Vanadium (III) chloride (VCl<sub>3</sub>, 97%), lithium borohydride (LiBH<sub>4</sub>, 95%), lithium hydride (LiH, 97%), and vanadium boride were purchased from Aladdin Industrial Corporation. Ethanol was purchased from Sinopharm Chemical reagent Co., Ltd. Lithium chloride (LiCl, 99.9%) was purchased from Macklin Biochemical Co., Ltd. Magnesium hydride was purchased from Sigma-Aldrich. All chemicals were used directly without further purification.

# 2.2 Synthesis of VB<sub>2</sub> NPs

According to Reaction (2), 157.3 mg vanadium chloride, 43.56 mg lithium borohydride, 7.95 mg lithium hydride, and 200 mg lithium chloride was mixed by the high-energy mechanical ball milling at 500 rpm for 10 h. The ball-to-

powder ratio is approximately 100:1. The addition of excess LiCl was to prevent local overheating and disperse the generated  $VB_2$  NPs. The powder was washed and centrifuged three times with deionized water and then vacuum dried to obtain amorphous  $VB_2$  nanoparticles. The reaction is as follows:

 $VCl_3 + 2LiBH_4 + LiH \leftrightarrow VB_2 + 3LiCl + 4.5H_2$  (2)

2.3 Synthesis of 2LiBH<sub>4</sub>–MgH<sub>2</sub> composites

The as-prepared VB<sub>2</sub> NPs were mixed with LiBH<sub>4</sub> and MgH<sub>2</sub> in a certain mass ratio using high-energy mechanical ball milling, under the same milling conditions as mentioned above. The resulting product was denoted as LMBH-VB. For comparison, pure  $2\text{LiBH}_4$ -MgH<sub>2</sub> and  $2\text{LiBH}_4$ -MgH<sub>2</sub> mixed with commercial VB<sub>2</sub> were ball-milled using the same process, denoted as LMBH and LMBH-c-VB, respectively.

#### 2.4 Characterization

Morphologies of the as-synthesized materials were observed by scanning electron microscopy (SEM, JEOL 7500FA) and transmission electron microscopy (TEM, JEOL JEM-2100F), while TEM-associated energy dispersive X-ray spectroscopy (EDS) was used for elemental analysis. The particle size of the nanoparticles in the SEM images was statistically analyzed using the software Nano Measurer. The phase composition of the samples was identified by X-ray diffraction (XRD, D8 advance, Bruker AXS) with Cu K\alpha radiation at 50 kV and 30 mA. In order to avoid any possible oxidation during XRD measurement, all materials were pre-sealed on sample stages with invisible tape in an Ar-filled glovebox. Chemical bonds in the materials were examined by fourier transform infrared spectroscopy (FTIR, Bruker Tensor 27). X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific K-Alpha + with an Al X-ray radiation source.

#### 2.5 Hydrogen storage measurement

The hydrogen storage performance was tested using the volumetric method with the self-assembled High-Pressure Gas Sorption Apparatus (HPSA) in the laboratory. Since the LiBH<sub>4</sub> reacts easily with water and oxygen, the samples were loaded into the reactor inside a glove box with water and oxygen levels below 0.1 ppm. The reactor was then transferred to the HPSA for testing. In specific hydrogen storage performance tests, unless otherwise specified, the default addition ratio of the catalyst was 10 wt%. For temperature-programmed desorption (TPD) tests, approximately 30 mg of the sample was loaded into the reactor and connected to the HPSA, then heated at a rate of 5 °C min<sup>-1</sup>

until the sample released all the hydrogen under an initial  $H_2$  pressure of 4 bar. Isothermal dehydrogenation tests were conducted at constant temperatures (380, 400, 420 and 440 °C) under the same initial pressure of 4 bar  $H_2$ . For the cycling test, the as-prepared samples were quickly heated to the working temperature and kept under 4 bar  $H_2$  for complete dehydrogenation. Subsequently, the dehydrogenated samples re-hydrogenated at 350 °C under 60 bar  $H_2$  pressure for 2 h.

#### 2.6 Computational method

Density functional theory (DFT) calculations were performed using the projector augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP). Because the Perdew-Burke-Ernzerhof (PBE) functional was found to be relatively accurate for describing atomic adsorption based on previous benchmarking studies, the PBE within the generalized gradient approximation (GGA) framework was employed in this study [29-31]. The dispersion interactions were included using the DFT-D3 van der Waals correction proposed by Grimme. A plane-wave energy cutoff of 500 eV and Gamma-centered k-point meshes with equivalent density were used for surface calculations. The Gaussian smearing method with a width of 0.05 eV was applied, and all calculations were spin-polarized. The structures were relaxed until the forces on all atoms and total energy converged to less than 0.05 eV  $\text{\AA}^{-1}$  and  $1 \times 10^{-5}$  eV, respectively.

#### 3 Results and discussion

As schematically illustrated in Fig. 1A, VB<sub>2</sub> NPs were synthesized via a previously reported high-energy mechanical ball milling method [32]. VCl<sub>3</sub>, LiBH<sub>4</sub>, LiH, and LiCl were ball-milled under specific conditions, and the resulting solid powder was washed and dried to obtain VB<sub>2</sub> NPs. The morphological characteristics of these nanoparticles can be observed through SEM and TEM analysis (Fig. S1). TEM results validate a uniform distribution of the as-synthesized VB<sub>2</sub> NPs (Fig. 1B). To further quantify the particle size distribution, approximately 150 nanoparticles are selected from Fig. 1B to perform statistical analysis, showing that the particle sizes range from 25 to 40 nm with an average size of approximately 32 nm (Fig. 1C). This demonstrates the effectiveness of the ball milling method in producing uniform VB<sub>2</sub> nanoparticles. XRD analysis was performed to investigate the crystalline nature of the as-synthesized VB2 NPs. Interestingly, no distinct diffraction peaks of VB2 were observed in the XRD patterns (Fig. S2), indicating that the as-synthesized VB<sub>2</sub> NPs are amorphous. To further confirm the successful



**Fig. 1** A Schematic illustration of the synthesis process for amorphous VB<sub>2</sub> NPs. **B** SEM image, **C** particle size distribution, **D** high-resolution V 2p XPS spectra, **E** STEM and the relative elemental mapping images, and **F** high-resolution B 1s XPS spectra of the assynthesized VB<sub>2</sub> NPs

synthesis of VB<sub>2</sub> NPs, XPS measurement was conducted. The fitted XPS spectra revealed two characteristic peaks of VB<sub>2</sub> at 512.4 and 519.9 eV in the V 2p region, and a characteristic peak of VB2 at 187.6 eV in the B 1s spectrum, which provides direct evidence to the successful synthesis of VB<sub>2</sub> (Fig. 1D, F). The peaks corresponding to  $V_2O_3$  and  $B_2O_3$  were also observed, which could be attributed to surface oxidation occurring during sample preparation and testing. Further structural and compositional analysis was carried out using STEM coupled with EDS. The results showed that the as-synthesized  $VB_2$  NPs were primarily composed of vanadium and boron, with a homogeneous elemental distribution throughout the particles (Fig. 1E). The atomic ratio of V-B was determined to be approximately 1:2, which corresponds well with the stoichiometric composition of VB<sub>2</sub> (Fig. S3). This finding further confirms the successful synthesis of the VB<sub>2</sub> NPs with the desired chemical composition and structural integrity.

To evaluate the effect of  $VB_2$  NPs in improving the hydrogen storage performance of  $2LiBH_4$ -MgH<sub>2</sub> composite (denoted as LMBH-VB), VB<sub>2</sub> NPs was added into  $2LiBH_4$ -MgH<sub>2</sub> through high-energy mechanical ball

milling. SEM and TEM analysis (Figs. S4, S5) revealed that the VB<sub>2</sub> NPs were uniformly distributed within the 2LiBH<sub>4</sub>-MgH<sub>2</sub> composite. After high-energy ball milling, XRD analysis of LMBH-VB (Fig. 2A) showed the distinct characteristic peaks of MgH<sub>2</sub>, while no peaks corresponding to LiBH<sub>4</sub> were observed (Fig. S6). The absence of LiBH<sub>4</sub> peaks could be attributed to its reduced crystallinity and/or the extremely fine particle size resulting from the ball milling process. The fitted XPS spectra of the V 2p region showed no change in the characteristic peaks of VB<sub>2</sub> after ball milling (Fig. 2B), indicating that the structure of VB<sub>2</sub> remained intact throughout the milling process. In contrast, the B 1s spectra displayed a peak corresponding to B-H bonds (Fig. 2C), providing clear evidence for the presence of LiBH<sub>4</sub> in the composite. Additionally, FTIR spectroscopy detected the characteristic vibrational modes of LiBH<sub>4</sub> (Fig. 2D), further verifying its presence within the ball-milled composite. HRTEM analysis provided additional insights into the microstructure of the composite (Fig. 2E). The observed lattice spacings of 0.219 and 0.319 nm could be indexed to the (111) plane of LiBH<sub>4</sub> and the (110) plane of MgH<sub>2</sub>, respectively. According to the STEM and EDS characterization results, the V and B



**Fig. 2 A** XRD patterns of LMBH–VB, LMBH and LMBH-c-VB. High-resolution **B** V 2p and **C** B 1s XPS spectra, and **D** FTIR spectra of LMBH and LMBH–VB. **E** HRTEM image and **F** the corresponding EDS elemental mapping images of LMBH–VB

signals from VB<sub>2</sub> overlap well with the Mg signal from MgH<sub>2</sub> and the B signal from LiBH<sub>4</sub> (Fig. 2F). This provides direct evidence of the uniform distribution between VB<sub>2</sub> NPs and  $2\text{LiBH}_4$ -MgH<sub>2</sub> composite, confirming that the materials are uniformly mixed at the nanoscale through the ball milling process.

The hydrogen storage properties of 2LiBH<sub>4</sub>-MgH<sub>2</sub> composite under the catalysis of VB<sub>2</sub> NPs were initially investigated by isothermal dehydrogenation method, including pristine 2LiBH<sub>4</sub>-MgH<sub>2</sub> (denoted as LMBH) and commercial VB2-catalyzed 2LiBH4-MgH2 (denoted as LMBH-c-VB) for comparison (Fig. 3A). Due to the sluggish hydrogen desorption kinetics and prolonged nucleation period of MgB<sub>2</sub>, LMBH composite required more than 9 h for complete dehydrogenation under a hydrogen back pressure of 4 bar at 400 °C, including a nucleation plateau time of 4 h. After the introduction of commercial VB<sub>2</sub> particles, LMBH-c-VB showed a reduced plateau period of 1 h, completing major hydrogen release within 4 h, which verifies the catalytic role of  $VB_2$  in promoting hydrogen desorption of 2LiBH<sub>4</sub>-MgH<sub>2</sub>. However, the nucleation plateau still persists even at an elevated temperature of 440 °C (Fig. S7). In contrast, with the addition of VB<sub>2</sub> NPs, no nucleation plateau could be observed for 2LiBH<sub>4</sub>-MgH<sub>2</sub> at 400 °C, achieving major hydrogen release within 2 h, which demonstrates that the decrease in particle size down to nanometer scale effectively enhances the catalytic role of VB<sub>2</sub>. To determine the optimal addition of VB<sub>2</sub> NPs for achieving the best hydrogen storage performance in the LMBH-VB system, the hydrogen desorption performance of LMBH-VB systems with 5 wt%, 7.5 wt%, 10 wt% and 12.5 wt% VB2 NPs (denoted as LMBH-0.5VB, LMBH-0.75VB, LMBH-VB, and LMBH-1.25VB, respectively) were compared under a hydrogen back pressure of 4 bar at 400 °C (Fig. 3B). LMBH–0.5VB achieved 9.4 wt% hydrogen release after 2 h but exhibited slow kinetics. In contrast, LMBH-VB showed an improved desorption rate, achieving most of the hydrogen release within 1.5 h. Based on a comprehensive comparison of dehydrogenation rates and hydrogen release capacities,  $2LiBH_4$ –MgH<sub>2</sub> with the addition of 10 wt% VB<sub>2</sub> NPs was identified as the optimal formulation for further detailed studies. This formulation not only eliminates the nucleation incubation period but also provides a high hydrogen release capacity and rapid desorption kinetics.

To investigate the effect of different heating rates on the hydrogen desorption kinetics, the desorption properties of LMBH-VB were tested through temperature-programmed desorption (TPD) experiments. As shown in Fig. 3C, the decrease in heating rates leads to more complete reactions at given temperatures and the reduction of onset temperatures for hydrogen release. At the heating rate of 1 °C min<sup>-1</sup>, LMBH-VB initiated dehydrogenation at 250 °C with the rapid release of approximately 3 wt% hydrogen at 350 °C and the complete dehydrogenation before 500 °C. Even at slower heating rates, the nucleation plateau period is still absent. To further evaluate the dehydrogenation performance of 2LiBH<sub>4</sub>-MgH<sub>2</sub> under the catalysis of VB<sub>2</sub> NPs, isothermal dehydrogenation tests were conducted at temperatures of 380, 400, 420 and 440 °C, respectively (Fig. 3D). At a low temperature of 380 °C, LMBH-VB is still capable of releasing 9.2 wt% hydrogen within 6 h without the observation of obvious nucleation incubation period, which provides additional



**Fig. 3 A** Hydrogen desorption curves of LMBH-VB at 400 °C under a hydrogen pressure of 4 bar, with LMBH and LMBH-c-VB included for comparison. **B** Isothermal hydrogen desorption of LMBH at 400 °C under the catalysis of VB<sub>2</sub> with various loading ratios. **C** TPD results of LMBH–VB under different heating rates. **D** Isothermal hydrogen desorption kinetics of LMBH–VB at various temperatures and LMBH, LMBH-c-VB at 400 °C under a hydrogen pressure of 4 bar

evidence to the crucial role of VB<sub>2</sub> NPs in promoting dehydrogenation by effectively catalyzing the nucleation of MgB<sub>2</sub>. Upon increasing the temperature to 420 °C, the same hydrogen capacity could be achieved within 1 h, while the time for complete dehydrogenation of LBMH reaches 4 h under the same conditions (Fig. S7), which is 4 times longer than the time required for 2LiBH<sub>4</sub>–MgH<sub>2</sub> under the catalysis of VB<sub>2</sub> NPs. Upon increasing the temperature to 440 °C, complete dehydrogenation could be accomplished within only 0.75 h. The significantly reduced dehydrogenation time at all tested temperatures underscores the superior catalytic activity of VB<sub>2</sub> and its potential to improve the practical applicability of 2LiBH<sub>4</sub>– MgH<sub>2</sub> under the catalysis of VB<sub>2</sub> NPs as a high-performance hydrogen storage material.

Hydrogen storage materials are required to maintain stable performance during multiple hydrogen absorption and desorption cycles. To evaluate the reversibility, cycling performance of 2LiBH<sub>4</sub>-MgH<sub>2</sub> under the catalysis of VB<sub>2</sub> NPs was investigated under a hydrogen pressure of 4 bar at 400 °C for dehydrogenation and 60 bar at 350 °C for rehydrogenation condition (Fig. 4A). The time required for the initial cycle of dehydrogenation to achieve a hydrogen capacity of 9.23 wt% is approximately 2 h. Interestingly, from the second cycle, the hydrogen desorption kinetics is further improved and complete dehydrogenation could be achieved within 1.5 h only. The hydrogen desorption kinetics and capacity could be well preserved throughout subsequent cycles, the with nearly overlapping dehydrogenation curves for the followed 9 cycles. After 10 cycles, the hydrogen capacity is maintained at 9.3 wt%, corresponding to a capacity retention of 100%, demonstrating the complete reversibility of 2LiBH<sub>4</sub>-MgH<sub>2</sub> under the catalysis of VB<sub>2</sub> NPs (Fig. 4D). By comparison, pristine LMBH exhibited a 3 h nucleation plateau in the first cycle, requiring 10 h to reach a hydrogen release capacity of 10.8 wt%. Although the plateau is also weakened in the second cycle for pristine  $2LiBH_4$ –MgH<sub>2</sub>, the time required for complete dehydrogenation is extended to 14 h in the third cycle (Fig. 4B). Under the catalysis of commercial VB<sub>2</sub>, 2LiBH<sub>4</sub>-MgH<sub>2</sub> exhibit a shorter dehydrogenation time of 6 h and a reduced nucleation plateau of 2 h during the first cycle. However, the nucleation plateau could still be observed, and the dehydrogenation rate further declined in the second cycle, requiring 10 h for the release of hydrogen with a capacity of 9.0 wt% (Fig. 4C). The instability of the catalytic effect of commercial VB2 during the initial cycles further demonstrates the advantages of nano-sized VB<sub>2</sub>.

After the first cycle of dehydrogenation, XRD results of LMBH-VB (Fig. 4E) demonstrate the formation of MgB<sub>2</sub>, accompanied with the disappearance of LiBH<sub>4</sub> and MgH<sub>2</sub>. This indicates complete dehydrogenation of LMBH-VB that leads to the formation of MgB<sub>2</sub> after the second dehydrogenation step. After re-hydrogenation, the characteristic peaks of LiBH<sub>4</sub> and MgH<sub>2</sub> peaks reappeared with the complete disappearance of MgB<sub>2</sub>, indicating complete re-hydrogenation of MgB<sub>2</sub>. After 10 cycles of hydrogen



Fig. 4 Cycling hydrogen desorption performance of A LMBH–VB, B LMBH and C LMBH-c-VB at 400 °C under a hydrogen pressure of 4 bar. D The reversible capacity of LMBH-VB upon cycling. E XRD patterns of LMBH-VB at various states. F HRTEM image of LMBH-VB after 10 cycles of hydrogen desorption

desorption, XRD peaks of MgB<sub>2</sub> could still be clearly observed. FTIR spectroscopy detected the characteristic vibrational modes of LiBH<sub>4</sub> during the cycling, demonstrating the reversibility of 2LiBH<sub>4</sub>-MgH<sub>2</sub> (Fig. S8). XPS results of cycling products (Fig. S9) demonstrate that V valence state remains unchanged throughout cycling and the disappearance of B-H bond peaks after dehydrogenation, indicating the stable presence of VB<sub>2</sub> NPs during cycling hydrogen storage process. SEM and TEM images verify that the structure of LMBH under the catalysis of VB<sub>2</sub> NPs is well preserved after 10 cycles of hydrogen desorption (Figs. S10, S11). The characteristic lattice fringes of MgB<sub>2</sub> could also be clearly detected in HRTEM image (Fig. 4F). STEM-EDS mapping (Fig. S12) confirmed homogeneous distribution of Mg, B, and V elements after cycling, which provides additional evidence to the homogeneous distribution of VB2 NPs within LMBH during the cycling hydrogen storage process. Therefore, under the catalysis of VB<sub>2</sub> NPs, the hydrogen desorption kinetics and hydrogen storage capacity of the 2LiBH<sub>4</sub>-MgH<sub>2</sub> composite material could be well maintained (Fig. 4A). The overall hydrogen storage performance of 2LiBH<sub>4</sub>-MgH<sub>2</sub> under the catalysis of VB<sub>2</sub> NPs is among the best in terms of hydrogen desorption kinetics, operating temperature, and capacity retention ratio (Table S1).

Upon heating to 400 °C under a hydrogen pressure of 4 bar, the first hydrogen desorption reaction of  $2\text{LiBH}_4$ -MgH<sub>2</sub> results from the rapid decomposition MgH<sub>2</sub>, producing Mg and H<sub>2</sub>. Subsequently, LiBH<sub>4</sub> reacts with Mg to form MgB<sub>2</sub> and LiH, along with the release of additional H<sub>2</sub>. However, the major issue throughout this process is the significant difficulty in the nucleation of MgB<sub>2</sub>, which is characterized by a long nucleation incubation period of 4 h for pure  $2\text{LiBH}_4$ –MgH<sub>2</sub> (Fig. 3A). As a result, the desorption kinetics of the second step are extremely slow, ultimately prolonging the overall dehydrogenation time to 10 h. In order to understand the mechanism of VB<sub>2</sub> in enhancing hydrogen storage performance of  $2\text{LiBH}_4$ – MgH<sub>2</sub>, the structures of VB<sub>2</sub> and MgB<sub>2</sub> were first investigated. As shown in Fig. 5A, it could be clearly noticed that VB<sub>2</sub> shares the same crystal system (hexagonal) and space group (*P6/mmm*) as MgB<sub>2</sub>, enabling MgB<sub>2</sub> to nucleate on



Fig. 5 A Crystal structures of  $MgB_2$  and  $VB_2$ . B The adsorption energies of single B atom on Mg surface, metal-rich  $VB_2$  surface; adsorption energy of single Mg atom on the formed B layer (green, orange, and red spheres represent B, Mg, and V, respectively)

VB<sub>2</sub>. Importantly, the lattice constant of MgB<sub>2</sub> (a = b = 3.06 Å) is very close to that of VB<sub>2</sub> (a = b = 2.99 Å), the *d*-value mismatch between the two structures is calculated to be 2.28% only. This similarity in lattice constants indicates that MgB<sub>2</sub> and VB<sub>2</sub> have favorable lattice matching during crystal growth, allowing MgB<sub>2</sub> to nucleate and grow more easily on the substrate of VB<sub>2</sub> or in an environment with similar lattice structure. As a result, VB<sub>2</sub> could act as a nucleation site that promotes the formation of MgB<sub>2</sub>. Additionally, the uniform distribution of VB<sub>2</sub> nanoparticles enhances the formation of MgB<sub>2</sub>, thereby improving the reaction kinetics. This combination of structural similarity, lattice matching, and uniform distribution makes VB<sub>2</sub> an effective promoter for MgB<sub>2</sub> nucleation and growth, ultimately optimizing the desorption kinetics of the system.

To further investigate the mechanism of VB<sub>2</sub> in promoting the nucleation of MgB<sub>2</sub>, the adsorption energies of a single B atom on the Mg (0001) surface and on the metalrich (0001) surface of VB<sub>2</sub> were calculated, along with the adsorption energy of a single Mg atom on the formed B layer (Fig. 5B).  $EX_{1B}$  and  $EX_{1Mg}$  represent the total energy of atomic B and atomic Mg binding to the substrate, respectively. EX represents the energy of the substrate, and  $\Delta E$  indicates the binding energy. The binding energy of a single B atom on the Mg (0001) surface is approximately -3.94 eV, while the binding energy on the metalrich (0001) surface of VB<sub>2</sub> is -6.60 eV, which is 2.66 eV lower than that on the Mg surface (Table S2). This indicates that VB<sub>2</sub> facilitates the adsorption of B atoms on its surface. Additionally, under the presence of VB<sub>2</sub>, the calculated binding energy for Mg atoms on the formed B layer also decreased slightly by 0.1 eV. These results demonstrate that the presence of VB2 provides favorable nucleation sites for both B and Mg, especially for the formation of the B layer, toward promoting the formation of MgB<sub>2</sub>, which effectively enhances the hydrogen desorption kinetics of 2LiBH<sub>4</sub>-MgH<sub>2</sub>.

#### 4 Conclusion

In this work, amorphous VB<sub>2</sub> nanoparticles with an average size of approximately 32 nm are synthesized via a simple high-energy ball milling method to enhance the reversible hydrogen sorption properties of the 2LiBH<sub>4</sub>– MgH<sub>2</sub> composite. The uniformly distributed VB<sub>2</sub> nanoparticles, sharing the same crystal structure and similar lattice parameters with MgB<sub>2</sub> with a *d*-value mismatch ratio of only 2.28%, could serve as nucleation sites for promoting the formation of MgB<sub>2</sub>. Theoretical calculations reveal that the binding energy of a single B atom on the (0001) surface of VB<sub>2</sub> is 2.66 eV lower than that on the Mg surface. The introduction of VB<sub>2</sub> significantly reduces the binding energies of both B and Mg, particularly promoting the formation of B layer, which facilitates in situ nucleation of MgB<sub>2</sub>, thereby enhancing the desorption kinetics of 2LiBH<sub>4</sub>-MgH<sub>2</sub>. As a result, after the introduction of VB<sub>2</sub> nanoparticles, complete dehydrogenation of 9.23 wt% is achieved for 2LiBH<sub>4</sub>-MgH<sub>2</sub> within 2 h, which is 4 times shorter than the time required for pure 2LiBH<sub>4</sub>-MgH<sub>2</sub>. Moreover, no nucleation incubation period for hydrogen desorption is observed even at a low temperature of 380 °C. More importantly, a reversible capacity of 9.3 wt%, corresponding to a capacity retention of 100%, could be preserved after 10 cycles of hydrogen storage, demonstrating stable and fully reversible cycling performance. Metal borides, serving as effective catalysts and nucleation sites, effectively alleviate the challenging MgB<sub>2</sub> nucleation issue and enhances the reversible hydrogen storage performance of reactive hydride composites. By optimizing the catalyst synthesis process, we have achieved more efficient hydrogen storage performance and improved the cycling stability of the material. This study provides a new technological approach for future hydrogen storage and utilization, offering strong support for the design and optimization of future hydrogen storage devices.

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**Data availability** The data that support the findings of this study are available from the corresponding author upon reasonable request.

#### Declarations

**Conflict of interests** The authors declare that they have no conflict of interest.

#### References

- Eberle U, Felderhoff M, Schüth F. Chemical physical solutions for hydrogen storage. Angewandte Chemie-Int Edition. 2009; 48(36):6608. https://doi.org/10.1002/anie.200806293.
- [2] Zhang HY, Ju SL, Xia GL, Yu XB. Identifying the positive role of lithium hydride in stabilizing Li metal anodes. Sci Adv. 2022; 8(3):8245. https://doi.org/10.1126/sciadv.abl8245.

- [3] Liu YF, Pan HG, Gao MX, Wang QD. Advanced hydrogen storage alloys for Ni/MH rechargeable batteries. J Mater Chem. 2011;21(13):4743. https://doi.org/10.1039/c0jm01921f.
- [4] Pan HG, Liu YF, Gao MX, Zhu YF, Lei YQ, Wang QD. An investigation on the structural and electrochemical properties of La<sub>0.7</sub>Mg<sub>0.3</sub>(Ni<sub>0.85</sub>Co<sub>0.15</sub>)<sub>x</sub> (x=3.15–3.80) hydrogen storage electrode alloys. J Alloys Compounds. 2003;351:228. https://doi. org/10.1016/s0925-8388(02)01045-9.
- [5] Liu YF, Zhong K, Luo K, Gao MX, Pan HG, Wang QD. Size-dependent kinetic enhancement in hydrogen absorption and desorption of the Li–Mg–N–H system. J Am Chem Soc. 2009; 131(5):1862. https://doi.org/10.1021/ja806565t.
- [6] Liu YF, Du HF, Zhang X, Yang YX, Gao MX, Pan HG. Superior catalytic activity derived from a two-dimensional Ti<sub>3</sub>C<sub>2</sub> precursor towards the hydrogen storage reaction of magnesium hydride. Chem Commun. 2016;52(4):705. https://doi. org/10.1039/c5cc08801a.
- [7] Zhang XY, Ju SL, Li CQ, Hao JZ, Sun YH, Hu XC, Chen W, Chen J, He LH, Xia GL, Fang F, Sun DL, Yu XB. Atomic reconstruction for realizing stable solar-driven reversible hydrogen storage of magnesium hydride. Nat Commun. 2024; 15(1):2815. https://doi.org/10.1038/s41467-024-47077-y.
- [8] Hu XC, Chen XW, Zhang XY, Meng Y, Xia GL, Yu XB, Sun DL, Fang F. In situ construction of interface with photothermal and mutual catalytic effect for efficient solar-driven reversible hydrogen storage of MgH<sub>2</sub>. Advanced Science. 2024;11(22): 2400274. https://doi.org/10.1002/advs.202400274.
- [9] Zhang XY, Sun YH, Ju SL, Ye JK, Hu XC, Chen W, Yao L, Xia GL, Fang F, Sun DL, Yu XB. Solar-driven reversible hydrogen storage. Adv Mater. 2023;35(2):2206946. https://doi.org/10. 1002/adma.202206946.
- [10] Wang YR, Chen XW, Zhang HY, Xia GL, Sun DL, Yu XB. Heterostructures built in metal hydrides for advanced hydrogen storage reversibility. Adv Mater. 2020;32(31):2002647. https:// doi.org/10.1002/adma.202002647.
- [11] Xia GL, Tan YB, Chen XW, Sun DL, Guo ZP, Liu HK, Ouyang LZ, Zhu M, Yu XB. Monodisperse magnesium hydride nanoparticles uniformly self-assembled on graphene. Adv Mater. 2015;27(39):5981. https://doi.org/10.1002/adma.201502005.
- [12] Pang YP, Liu YF, Gao MX, Ouyang LZ, Liu JW, Wang H, Zhu M, Pan HG. A mechanical-force-driven physical vapour deposition approach to fabricating complex hydride nanostructures. Nat Commun. 2014;5:3519. https://doi.org/10.1038/ncomms4519.
- [13] Liu C, Zhu Y, Zu A, Liu Y, Zhang Z, Guo J, Lian C, Zou M, Wang S. One-step synthesis of fluorine-functionalized intercalated graphene with adjustable layer spacing for both enhanced physical and chemical hydrogen storage. Materials Today Catalysis. 2024; 7:100074. https://doi.org/10.1016/j.mtcata.2024.100074.
- [14] Liu YK, Chen W, Ju SL, Yu XB, Xia GL. Stable hydrogen storage of lithium borohydrides via the catalytic effect of Ni<sub>2</sub>B induced by thermodynamic destabilization reaction. J Mater Sci Technol. 2024;202:192. https://doi.org/10.1016/j.jmst.2024.03.035.
- [15] Zhang HY, Xia GL, Zhang J, Sun DL, Guo ZP, Yu XB. Graphene-tailored thermodynamics and kinetics to fabricate metal borohydride nanoparticles with high purity and enhanced reversibility. Adv Energy Mater. 2018;8(13):1702975. https:// doi.org/10.1002/aenm.201702975.
- [16] Bösenberg U, Kim JW, Gosslar D, Eigen N, Jensen TR, von Colbe JMB, Zhou Y, Dahms M, Kim DH, Günther R, Cho YW, Oh KH, Klassen T, Bormann R, Dornheim M. Role of additives in LiBH<sub>4</sub>–MgH<sub>2</sub> reactive hydride composites for sorption kinetics. Acta Mater. 2010;58(9):3381. https://doi.org/10.1016/j. actamat.2010.02.012.
- [17] Sabitu ST, Goudy AJ. Dehydrogenation kinetics, modeling studies of 2LiBH<sub>4</sub> + MgH<sub>2</sub> enhanced by NbF<sub>5</sub> catalyst. J Phys Chem C. 2012;116(25):13545. https://doi.org/10.1021/jp302632w.

- [18] Zhang X, Liu YF, Ren ZH, Zhang XL, Hu JJ, Huang ZG, Lu YH, Gao MX, Pan HG. Realizing 6.7 wt% reversible storage of hydrogen at ambient temperature with non-confined ultrafine magnesium hydrides. Energy Environ Sci. 2021;14(4):2302. https://doi.org/10.1039/d0ee03160g.
- [19] Lu LW, Luo H, Li GX, Li Y, Wang XH, Huang CK, Lan ZQ, Zhou WZ, Guo J, Ismail M, Liu HZ. Layered niobium carbide enabling excellent kinetics and cycling stability of Li–Mg–B–H hydrogen storage material. Rare Met. 2023;43(3):1153. https:// doi.org/10.1007/s12598-023-02489-5.
- [20] Vajo JJ, Skeith SL, Mertens F. Reversible storage of hydrogen in destabilized LiBH<sub>4</sub>. J Phys Chem B. 2005;109(9):3719. https:// doi.org/10.1021/jp0407690.
- [21] Chen W, Sun YH, Xu T, Ye JK, Xia GL, Sun DL, Yu XB. Reversible hydrogen storage performance of 2LiBH<sub>4</sub>–MgH<sub>2</sub> enabled by dual metal borides. Acs Applied Energy Materials. 2022;5:10501. https://doi.org/10.1021/acsaem.2c01142.
- [22] Li ZL, Xian KC, Gao MX, Wang S, Qu SQ, Wu MH, Gan JT, Yang YX, Zhang X, Sun WP, Liu YF, Pan HG. 2LiBH<sub>4</sub>–gH<sub>2</sub> system catalytically modified with a 2D TiNb<sub>2</sub>O<sub>7</sub> nanoflake for high-capacity, fast-response, and long-life hydrogen energy storage. Acs Appl Mater Interf. 2024;16(36):47571. https://doi. org/10.1021/acsami.4c08705.
- [23] Wang XC, Xiao XZ, Liang ZQ, Zhang SQ, Qi JC, Lv L, Piao MY, Zheng JG, Chen LX. Ultrahigh reversible hydrogen capacity and synergetic mechanism of 2LiBH<sub>4</sub>–MgH<sub>2</sub> system catalyzed by dual-metal fluoride. Chem Eng J. 2022;433: 134482. https://doi.org/10.1016/j.cej.2021.134482.
- [24] Lu ZY, Yu HJ, Lu X, Song MC, Wu FY, Zheng JG, Yuan ZF, Zhang LT. Two-dimensional vanadium nanosheets as a remarkably effective catalyst for hydrogen storage in MgH<sub>2</sub>. Rare Met. 2021;40(11):3195. https://doi.org/10.1007/s12598-021-01764-7.
- [25] Zhong YJ, Kang XD, Wang KK, Wang P. Improved reversible dehydrogenation of LiBH<sub>4</sub>–MgH<sub>2</sub> composite by the synergistic effects of Al and MgO. Int J Hydrogen Energy. 2014;39(5): 2187. https://doi.org/10.1016/j.ijhydene.2013.11.119.
- [26] Fan XL, Xiao XZ, Chen LX, Wang XH, Li SQ, Ge HW, Wang QD. High catalytic efficiency of amorphous TiB<sub>2</sub> and NbB<sub>2</sub> nanoparticles for hydrogen storage using the 2LiBH<sub>4</sub>-MgH<sub>2</sub> system. J Mater Chem A. 2013;1(37):11368. https://doi.org/10. 1039/c3ta12401k.
- [27] Shao J, Xiao XZ, Chen LX, Fan XL, Li SQ, Ge HW, Wang QD. Enhanced hydriding-dehydriding performance of 2LiBH<sub>4</sub>-MgH<sub>2</sub> composite by the catalytic effects of transition metal chlorides. J Mater Chem. 2012;22(38):20764. https://doi. org/10.1039/c2jm33374k.
- [28] Chen W, Sun YH, Xu T, Yu XB, Xia GL. Enhancing reversible hydrogen storage performance of 2LiBH<sub>4</sub>-MgH<sub>2</sub> via in-situ building heterogeneous nucleation sites. Rare Met. 2024;43(9): 4367. https://doi.org/10.1007/s12598-024-02762-1.
- [29] Li CQ, Yang WJ, Liu H, Liu XY, Xing XJ, Gao ZY, Dong S, Li H. Picturing the gap between the performance and US-DOE's hydrogen storage target: a data-driven model for MgH<sub>2</sub> dehydrogenation. Angewandte Chemie-Int Edition. 2024;63(28): e202320151. https://doi.org/10.1002/anie.202320151.
- [30] Zhang J, Sun LQ, Zhou YC, Peng P. Dehydrogenation thermodynamics of magnesium hydride doped with transition metals: experimental and theoretical studies. Comput Mater Sci. 2015;98:211. https://doi.org/10.1016/j.commatsci.2014.11.016.
- [31] Korablov D, Besenbacher F, Jensen TR. Kinetics and thermodynamics of hydrogenation-dehydrogenation for Mg-25%TM (TM = Ti, Nb or V) composites synthesized by reactive ball milling in hydrogen. Int J Hydrogen Energy. 2018;43(34): 16804. https://doi.org/10.1016/j.ijhydene.2018.05.091.

[32] Kim JW, Shim J-H, Ahn J-P, Cho YW, Kim J-H, Oh KH. Mechanochemical synthesis and characterization of TiB<sub>2</sub> and VB<sub>2</sub> nanopowders. Mater Lett. 2008;62(16):2461. https://doi. org/10.1016/j.matlet.2007.12.022. Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.