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Lightweight hydrides nanocomposites for hydrogen storage: Challenges, progress and prospects

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ABSTRACT As typical high-capacity complex hydrides, lightweight hydrides have attracted intensive attention due to their high gravimetric and volumetric energy densities of hydrogen storage. However, lightweight hydrides also have high thermodynamic stability and poor kinetics, so they usually require high hydrogen desorption temperature and show inferior reversibility under mild conditions. This review summarizes recent progresses on the endeavor of overcoming thermodynamic and kinetic challenges for Mg based hydrides, lightweight metal borohydrides and alanates. First, the current state, advantages and challenges for Mg-based hydrides and lightweight metal hydrides are introduced. Then, alloying, nanoscaling and appropriate doping techniques are demonstrated to decrease the hydrogen desorption temperature and promote the reversibility behavior in lightweight hydrides. Selected scaffolds materials, approaches for synthesis of nanoconfined systems and hydriding-dehydriding properties are reviewed. In addition, the evolution of various dopants and their effects on the hydrogen storage properties of lightweight hydrides are investigated, and the relevant catalytic mechanisms are summarized. Finally, the remaining challenges and the sustainable research efforts are discussed.

Keywords: hydrogen storage, Mg-based materials, borohydrides, alanates, nanoscaling

INTRODUCTION

Hydrogen has been considered as an ideal alternative energy to replace fossil energy in the future because of high gravimetric energy density (142 MJ kg⁻¹), non-toxicity and environmentally friendly properties [1]. However, the volumetric energy density of hydrogen gas is

very low. At atmospheric pressure and 25°C, the volumetric energy density is only 4.4 MJ L⁻¹, which severely limits the on-board use of hydrogen [2]. The explosive nature and broad range of explosion limits are also the factors limiting its on-board applications [3]. Therefore, it is of vital importance to develop a safe and efficient way to store hydrogen.

Classically, hydrogen gas can be stored in a pressure container to reach a higher volumetric energy density, whereas the large-weight bulky tank decreases the gravimetric energy density [1]. Due to the gap between high storing pressure and accessible handling pressure, the extra devices for pressure controlling are also needed. Although the developed carbon fiber reinforced alloy can lessen the weight of container, the on-board use is still impractical. In addition, the high-pressure in container can be a safety risk, which is another disadvantage of this method.

Storing hydrogen in solid-state materials is a promising way to meet the requirements for on-board applications [4,5]. The hydrogen gas can be absorbed in solid-state materials in molecule form (physisorption) or atom form (chemisorption) [6]. Materials such as porous carbon, carbon nanotubes, zeolites and metal organic frameworks (MOFs) can absorb hydrogen rapidly, showing remarkable reversibility and cycle performance. However, satisfactory capacities of above materials can only be achieved at very low temperature [3]. Commonly, the room-temperature capacities of these materials are less than 1 wt%. Fortunately, some metals and alloys can absorb hydrogen by bonding with the hydrogen to form metal hydride, which is a chemisorption approach. These

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composites usually show high hydrogen capacities, but their practical applications are hindered due to low reaction rate, poor reversibility and requirement of high operation temperature [7]. Among the chemisorption materials, the lightweight hydrides, including metal hydrides and complex hydrides, have extraordinarily high gravimetric and volumetric density, which are expected to be the most promising candidates for on-board applications [8].

Because of the low atomic mass of metal elements, the lightweight hydrides have high gravimetric hydrogen content [9]. Especially, LiBH_4 as a complex hydride can reach an outstanding capacity of 18.4 wt%. Moreover, the reserves of lightweight metal elements such as Na, Mg and Al are abundant in the earth, leading to the low cost of corresponding metal [10]. Therefore, the lightweight hydrides materials have been widely researched as a hot topic in the field of hydrogen storage.

Several lightweight metal hydrides are listed in Table 1 [11]. All of them are ionic compounds except BeH_2 and AlH_3 . The strong ionic bond between metal element and hydrogen results in a large formation enthalpy and high decomposition temperature [12]. Also, the kinetic properties of them are sluggish [4]. Among these compounds, MgH_2 has been considered as a promising candidate for on-board application because of its low decomposition temperature. However, both thermodynamic and kinetic performances of MgH_2 still need to be adjusted.

Lightweight metal complex hydrides include borohydrides, amides and alanates. Several complex hydrides are listed in Table 2. These compounds have outstanding hydrogen contents and a complicated multi-step dehydrogenation reaction [13]. Multiple components are generated during the decomposition, leading to difficulties in rehydrogenation and poor cycle properties. In addition, complex hydrides also suffer from the problems of inappropriate thermodynamic and kinetic properties [4]. Encouragingly, methods such as nanoscaling and doping can enhance the regeneration processes and increase the kinetic properties [8]. However, even with the enhancement of these methods, these complex hydrides still hardly meet the requirement of on-board application.

Capacities, thermodynamic and kinetic performances are three critical factors for the practical application. It is very difficult to reach high capacity, moderate thermodynamic conditions and fast kinetic performance simultaneously. Numerous efforts have been made to regulate thermodynamic and kinetic performance while sacrificing capacity as low as possible.

In this review, we summarize the recent progresses in

Table 1 Thermodynamic properties and gravimetric hydrogen content of lightweight metal hydrides^{a)}

Compound	$\Delta_f H_{298}^\ominus$ (kJ mol ⁻¹)	Decomp. Temp. (°C)	H ₂ content (wt%)
LiH	-90.5	820	12.7
NaH	-56.3	480	4.2
BeH_2	/	470	18.3
MgH_2	-75.3	360	7.6
AlH_3	-46.0	420–470	10.1

a) The enthalpy and decomposition temperature data are referenced from Ref. [11].

Table 2 Thermodynamic properties and gravimetric hydrogen content of lightweight metal complex hydrides^{a)}

Compound	$\Delta_f H_{298}^\ominus$ (kJ mol ⁻¹)	H ₂ content (wt%)
LiBH_4	-194	18.36
LiAlH_4	-119	10.54
LiNH_2	-179.6	8.78
NaBH_4	-191	10.57
NaAlH_4	-113	7.41
NaNH_2	-123.8	5.15
$\text{Mg}(\text{BH}_4)_2$	/	14.82
$\text{Mg}(\text{AlH}_4)_2$	/	9.27
$\text{Mg}(\text{NH}_2)_2$	/	7.15

a) The enthalpy data are referenced from Ref. [13].

the development of MgH_2 , lightweight metal borohydrides and alanates as the hydrogen storage materials. Especially, we focus on the modification and development for tuning hydrogen storage performance. The strategies will be classified and reviewed in detail.

Mg-BASED HYDROGEN STORAGE MATERIALS

Mg is an earth-abundant element with the 8th crustal abundance order. Thus, Mg-based hydrogen storage materials are low-cost and have the potential for large-scale production [14]. As clarified in the previous section, MgH_2 is an ionic compound, so it has a high formation enthalpy which is a thermodynamic problem hindering its practical application [15]. To gain an insight into the mechanism of de/rehydrogenation processes, we analyzed a series of steps including H_2 transport to the surface, H_2 dissociation, H chemisorption, surface-bulk migration, H diffusion, nucleation and growth of hydride/metal phases [16]. The sluggish rate of these steps, such as hydrogen diffusion through MgH_2 phase, is the kinetic problem.

These thermodynamic and kinetic problems lead to a high operation temperature, impeding its practical application [11,16]. To overcome these defects, many strategies such as alloying, nanoscaling, and doping have been employed [2]. These techniques will be reviewed in detail in the section below.

Alloying

Alloying is one of the most effective ways to change the thermodynamic property of MgH_2 . Unlike adding catalysts, alloying method changes the reaction equation and reduces the formation enthalpy [17]. The drawback of this method is the significant decrease of capacity. Table 3 lists several reported Mg-based alloys for hydrogen storage. To decrease the stability of the hydride phase, the alloy elements selected should have a weak interaction with hydrogen, that is, the hydride formation enthalpy is low or the corresponding hydride does not exist. Also, elements should be selected according to the phase diagram, and not all the elements can form alloy with metal Mg.

The Mg-based alloys for hydrogen storage include intermetallic compound alloys and solid solution alloys. The intermetallic compounds are homogeneous and atomic ordered with a fixed compound formula, such as Mg_2Ni and Mg_2Cu . As a solid solution material, Mg metal bonds with other components in a solution form. The solid solution is also a homogeneous material, but in the atomic scale it could be either ordered or disordered. Depending on the solubility, the formula of solid solution could be variable with a continuous range, such as

$\text{Mg}_{0.9}\text{In}_{0.1}$, $\text{Mg}_{0.95}\text{In}_{0.05}$ and $\text{Mg}_{0.98}\text{In}_{0.02}$ [52].

Elements such as Ni and Cu are the ideal candidates to alloy with Mg [18–20]. In 1960s, Mg_2Ni [18] and Mg_2Cu [21] were reported as hydrogen storage alloys, and the two alloys involved different reaction pathways [22–26]. Tran *et al.* [27] focused on the decomposition process of Mg_2NiH_4 , and examined the phase transformation detail by *in-situ* transmission electron microscopy (TEM) imaging. Due to the defect of low capacity, several scholars combined Mg_2NiH_4 with other high hydrogen capacity materials [28–30] or *in-situ* grew Mg_2NiH_4 on MgH_2 in limited amount [31–36]. Besides Mg_2Ni and Mg_2Cu , other intermetallic compounds such as Mg_3Cd [37], Mg_2Si [38–40], and Mg_3Ag [41] were also reported to have a decreased decomposition temperature. However, the wide applications of these alloys are limited by various disadvantages, such as the high-toxic nature of Cd, poor reversibility of Mg_2Si and low capacity of Mg_3Ag .

Forming solid solution is another way to adjust the reaction path of MgH_2 [42–46]. The homogeneous solid solution phase can be achieved with only a minor addition, and thus the capacity loss can be controlled under an acceptable scale. Mg–Al alloy is a typical solid-solution Mg-based hydrogen storage alloy, in which a certain proportion of several stable or metastable phases exist [47]. Bouaricha *et al.* [48] synthesized Mg–Al alloys with the Al content ranging from 10 at.% to 80 at.% by ball-milling, and investigated the phase transformation and thermodynamic properties. The improved kinetic performances of Mg–Al alloys were also widely reported [49,50]. However, the hydrogenation process leads to the

Table 3 Fundamental properties of several Mg-based alloys for hydrogen storage

Name	E_a (kJ mol ^{−1})	ΔH (kJ mol ^{−1})	Dehy. Temp. (°C)	H ₂ content (wt%)	Ref.
Mg	160±10	75.3	360	7.6	[11], [16]
$\text{Mg}_{0.95}\text{In}_{0.05}$	/	68.1 ± 0.2	/	5.3	[42]
Mg_2Ni	/	64.5	254	3.6	[18]
$\text{Mg}_{80}\text{Ce}_{18}\text{Ni}_2$	63±3	76.1 ± 0.4	232	4.03	[43]
$\text{Mg}_2\text{In}_{0.1}\text{Ni}$	28.9	38.4	194	/	[44]
$\text{Mg}_{80}\text{Y}_5\text{Ni}_{15}$	83.9	/	280	4.2	[45]
Mg_2Cu	/	77.1	/	2.3	[19]
$\text{MgNi}_{10}\text{Mm}_3$	88.6	56.75	/	5.79	[20]
$\text{Mg}_{80}\text{Y}_5\text{Cu}_{15}$	132.3	/	300	3.7	[45]
YMg_4Cu	72.3; 76.8	/	277	3.0	[46]
Mg_3Cd	69	65.5	/	2.8	[37]
Mg_2Si	/	36.4	/	5.0	[39]
Mg_3Ag	/	68.2	/	2.1	[41]

phase separation of MgH_2 , which cannot be reversed in the dehydrogenation. Zhong *et al.* [42] reported Mg-In solid-solution alloy for hydrogen storage, which exhibited a complete reversibility after hydrogenation/dehydrogenation cycle. On this basis, Zhou *et al.* [51] added TiMn_2 catalyst into Mg-In alloy and investigated the phase transformation (Fig. 1), finding that the dehydrogenation temperature decreased to 423 K. Wang *et al.* [52] focused on the reversibility of solid-solution alloys, synthesized Mg-Al, Mg-In, and ternary Mg-Al-In alloys. They clarified that for sufficient reversibility, the atom contents of Al and In should be lower than 8% and 10%, respectively.

It is extremely difficult to reach satisfactory thermodynamic property without sacrificing the capacity and cycle properties. And it is still a challenge to achieve high-capacity Mg-based alloys. Strategies to prepare homo-

geneous alloys with a low cost need to be developed.

Nanoscaling

Nanoscaling is another way to modulate the thermodynamic and kinetic properties simultaneously [2]. Downsizing of Mg/ MgH_2 can significantly improve the reaction rate, which is mainly due to the increase of reaction interface and the decrease of diffusion distance. Additionally, if the particle size decreases to nano-scale, the nanosizing effect will lead to a reduced enthalpy [53]. Wagemans *et al.* [54] used *ab-initio* Hartree–Fock and density functional theory (DFT) calculations, indicating that the 56-Mg-atom cluster showed an enthalpy that was roughly equal to bulk MgH_2 , while the 9-Mg-atom cluster (0.9 nm) could perform a decreased equilibrium desorption temperature of 200°C. It can be concluded that for a significant desorption energy reduction, the crystallite

Figure 1 Pressure-composition-isotherm (PCI) curves of Mg-In-H system (a) comparing Mg-0.05In, Mg-0.1In and Mg at temperature of 300°C, and van't Hoff plot (b) comparing Mg-0.1In and Mg. (c) *In-situ* powder X-ray diffraction (XRD) spectra for dehydrogenation reaction of Mg-In-H system, the heating rate is 10°C min⁻¹ with experiment running from bottom to top of figure. Reproduced with permission from Ref. [51]. Copyright 2013, American Chemical Society.

size should be smaller than 1.3 nm. To reduce the particle size, many strategies such as ball-milling, physical/chemical vapor deposition (PVD and CVD), chemical reduction and nanoconfinement (NC) were employed.

Ball-milling is a typical method for reducing the particle size in a top-down mode, that is, physical downsizing of bulk Mg or MgH_2 . Since the as-prepared powder is sensitive to oxygen, the ball-milling should proceed under Ar or H_2 condition [55]. These nanosized particles have a strong tendency to cold weld, forming aggregated particle, especially ductile Mg metal. The balance between cold welding and fracturing determined the final size of product [56]. Adding inert process control agent, such as benzene and cyclohexane [55], could reduce the effect of cold welding, but it still remained a challenge to reach a homogeneous crystallite size under 1.3 nm. The dielectric barrier discharge plasma-assisted milling (P-milling) was a modified ball-milling method developed by Ouyang *et al.* [57]. With the assist of cold plasma, the milling process can be accelerated, and the morphology and reactivity of the product were quite different from that processed by traditional ball-milling [58,59]. Fig. 2a–d show the scanning electron microscopy (SEM) images of Mg-EG (expanded graphite) composites processed by P-milling. The introduction of cold plasma created the rough surface and cracks, which enhanced the reaction activities. Some translucent few-layered graphene could also be observed in Fig. 2d, while the traditional ball-milling could not strip graphite in the same milling time. The kinetic curves shown in Fig. 2e further verified the improved performance of composites obtained by P-milling method.

Besides the physical downsizing, sometimes ball-milling can also be employed as a chemical solid-state reaction method to prepare nanosized MgH_2 . Paskevicius *et al.* [60] synthesized 7 nm MgH_2 particles by ball-milled MgCl_2 with LiH. Doppiu *et al.* [61] achieved nanosized MgH_2 by ball-milling Mg or $\text{Mg}_{99}\text{Ni}_1$ under H_2 condition. As the cold welding in top-down method limited the minimum particle size, the solid-state reaction method may be a new approach to achieve ultrafine MgH_2 .

PVD and CVD can achieve nanosized Mg/ MgH_2 with various morphologies, such as wires [62–64], flakes [65], and films [66,67]. Matsumoto *et al.* [68] found that the morphology of Mg/ MgH_2 could be controlled by altering the temperature and pressure. Zhu *et al.* [65] classified the deposition condition and the relationship with shape, size, and purity. Cui *et al.* [69] vaporized Mg metal and transported it into nanopores of anodic aluminium oxide (AAO) template, which improved the cycle property.

Figure 2 (a–d) SEM images of Mg-EG composites by P-milling for (a) 2 h, (b) 5 h, (c) 10 h, and (d) enlarged version of 5 h Mg-EG composite with a typical area for Mg-few layer graphene and small graphite sheets. (e) Hydrolysis kinetic curves of the Mg-graphite composites at 318 K for (a) P-milling with EG, (b) planetary ball milling with EG, and (c) planetary ball milling with expandable graphite. Reproduced with permission from Ref. [59]. Copyright 2018, Elsevier.

Because of the explosive nature of Mg vapor, these deposition processes should be carefully handled. For practical production, there is a need to develop a deposition approach under moderate condition.

Chemical reduction is a technique to grow Mg/ MgH_2 in a bottom-up approach. In 1972, Reike *et al.* [70] published a method to achieve highly reactive Mg powder by reduction reaction in anhydrous solvent. Nowadays, this Reike method has been derived into plenty of adaption to prepare nanosized Mg/ MgH_2 . The di-*n*-butylmagnesium (MgBu_2) [71,72], bis(cyclopentadienyl)magnesium (Cp_2Mg) [73,74], and MgCl_2 have been widely reported as the Mg source for chemical reduction. Norberg *et al.* [73] reduced Cp_2Mg by different potassium organic reducing agents and obtained various crystal sizes of products. Liu *et al.* [75] reduced MgCl_2 with other transition metal

chlorides in a co-precipitation process, and the size of product ranged in 10–20 nm.

NC is another approach to prepare nanoscale materials owing to its high economic efficiency and facile synthesis method. The surface functional groups and rigid framework of scaffold can also stabilize the nanoparticle. For the NC techniques such as melt infiltration [76,77] and solvent infiltration [31,71,72,78–85], an appropriate nanoscaffold is the prerequisite for a successful nanoscaling. The nanoscaffold material should be porous, chemically inert, and have high surface area and stable structure. To insert Mg metal directly, de Jongh *et al.* [76] melt Mg, MgH_2 , and two-dimensional (2D) activated carbon (AC) scaffold at 666°C. The crystallites size of product was less than 5 nm with a loading of 10.8 wt%. They found that a smaller pore size could be beneficial to the infiltration process. However, this method required thermostable scaffold and involved a high infiltration temperature, causing the difficulty in operation. Zhang *et al.* [71] introduced solvent infiltration to embed Mg precursor (MgBu_2) into scaffold, followed by chemical reduction. In this model, infiltration was carried out at moderate conditions. Table 4 summarizes several reports of solvent infiltration applied in Mg-based hydrogen storage materials. Konarova *et al.* [80] selected SBA15 and CMK3 as scaffold and reduced the crystallite size of MgH_2 to 4 nm with a lowered dehydrogenation peak temperature. Shinde *et al.* [83] reported that MgH_2 was embedded in MOF derived carbon scaffold functionalized with transition metal, in which both NC and catalytic effect enhanced the hydrogen storage properties. However, it is a challenge to confine all the MgH_2 inside the pores of scaffold with a high loading, because simply increasing the amount of Mg source will result in aggregation on the

scaffold surface [80]. Confining Mg in 2D material surface could reach a larger loading than 3D scaffold pores [31,84,86]. Xia *et al.* [84] reduced MgBu_2 on graphene and achieved dispersed MgH_2 with an average particle diameter of ~5.7 nm. Cho *et al.* [31] confined transition metal doped Mg on graphene layers *via* co-reduction approach, which simultaneously realized high hydrogen storage capacity (6.5 wt%) and excellent kinetics performance. Zhang *et al.* [87] confined Mg_2NiH_4 by exposing samples to Ar/air mixture, and achieved well-defined MgO coating on Mg_2NiH_4 with a thickness of ~3 nm (Fig. 3). This coating could prevent aggregation during cycles and improve thermal and mechanical stability.

Nowadays, it remains a challenge to achieve homogeneous crystallite size under 1.3 nm due to the strong tendency to aggregate of particles with large surface energy. The poor loading and inhomogeneous dispersion are the main factors hindering the development of 3D scaffold NC. Therefore, efficient scaffold and infiltration technologies need to be developed. Confining Mg/ MgH_2 in 2D scaffold can reach a high loading, and recent developed 2D materials such as graphene, MoS_2 and MXene are potential scaffold candidates. Without rigid framework, the stabilization effect of 2D scaffold is relatively weak. *In-situ* generated coating [87] is a new type of NC and the stable ultrafine MgH_2 may be accessible by quickly coating an inert layer on it.

Adding dopants

Doping is a method that mainly focuses on tuning kinetic properties [15]. Doping nonmetals [39,84,88,89], metals [90,91], metal compounds [35,92–99] or composites [32,100–105] could decrease the absorption/desorption temperatures of Mg/ MgH_2 . Several additives are listed in

Table 4 Scaffolds and loadings of several reported Mg-based NC materials

Precursor	Scaffold	Dehy. T_{start} (°C)	Loading (wt%)	Ref.
MgBu_2	Carbon aerogel	/	15–17	[71]
MgBu_2	Carbon aerogel	175	18.2 and 10.0	[72]
MgBu_2	Carbon aerogel	/	10	[78]
MgBu_2	Activated carbon fibre	280	22	[79]
MgBu_2	SBA15 and CMK3	250	20, 40, 60, 80	[80]
MgBu_2	Ni-CMK3	50	37.5	[81]
MgBu_2	Graphene oxide-based porous carbon	/	53	[82]
MgBu_2	MOFs derived carbon	121	11–60	[83]
MgBu_2	Graphene	150	20–75	[84]
Cp_2Mg	Graphene	/	/	[85]
Cp_2Mg	Ni-doped graphene	/	/	[31]

Figure 3 Dehydrogenation of Mg_2NiH_4 /graphene sheets (GS). (a) Differential scanning calorimetry (DSC) profiles for hydrogen desorption of Mg_2NiH_4 /GS at different heating rates. Inset: Kissinger's plots derived from the DSC profiles. (b) XRD pattern after a typical DSC run. (c) Representative field emission SEM (FESEM) (the inset shows the particle size distribution) and (d) bright-field TEM images of Mg_2NiH_4 /GS after hydrogen desorption. The inset in (d) is the TEM image of a single particle and the corresponding electron diffraction pattern. Reproduced with permission from Ref. [87]. Copyright 2017, John Wiley & Sons, Inc.

Table 5. Kecik *et al.* [106] simulated the behavior of H_2 at the surface of additive-doped MgH_2 based on first-principles molecular dynamics method. They found that the introduction of transition elements from Ti to Ni in 3d and from Zr to Pd in 4d series could accelerate hydrogen dissociation and adsorption processes, especially 3d series elements such as Co, Mn and Fe. Liang *et al.* [107] milled MgH_2 with transition metal Ti, V, Mn, Fe and Ni, and found that all of them improved the kinetic properties. MgH_2 -V showed the most rapid desorption rate while MgH_2 -Ti exhibited most rapid absorption rate. Hanada *et al.* [108] introduced micro-particles and nano-particles of transition metals (Fe, Co, Ni, Cu) to MgH_2 , the nanosized Ni-doped MgH_2 showed the lowest activation energy of $94 \pm 3 \text{ kJ mol}^{-1} \text{ H}_2$.

Metal oxides can also enhance the kinetic properties of MgH_2 . Oelerich *et al.* [109] investigated the absorption/desorption properties of $\text{MgH}_2/\text{Mg}_2\text{NiH}_4$ with oxides, including Sc_2O_3 , TiO_2 , V_2O_5 , Cr_2O_3 , Mn_2O_3 , Fe_3O_4 , CuO , Al_2O_3 , and SiO_2 . $\text{MgH}_2/\text{Cr}_2\text{O}_3$ performed the fastest hydrogen absorption whereas V_2O_5 and Fe_3O_4 exhibited the fastest desorption of hydrogen. Dehouche *et al.* [97] synthesized 0.2 mol% Cr_2O_3 -containing MgH_2 and found that it revealed enhanced kinetic properties and remarkable cycle stability even after 1000 absorption/desorption

cycles. Aguey-Zinsou *et al.* [110] prepared $\text{MgH}_2\text{-Nb}_2\text{O}_5$ by ball-milling, indicating that Nb_2O_5 not only acted as a catalyst but also a process control agent to prevent the cold welding during ball-milling. Recently, Zhang *et al.* [100] synthesized TiO_2 nanosheets (NS) with exposed {001} facets, and introduced it into MgH_2 by ball-milling. Compared with the mixture with commercial TiO_2 nanoparticles (5–10 nm), the $\text{TiO}_2(\text{NS})$ -containing MgH_2 composite displayed a 36°C lower dehydrogenation peak temperature.

Metal halides are also potential additives for enhancing kinetic properties, especially metal fluorides and metal chlorides. Malka *et al.* [111] studied the influences of nineteen different halide additives on the MgH_2 desorption/absorption processes. They found that halides from group IV and V of the periodic table with a highest oxidation state were better catalysts in comparison with the other halides, and fluorides demonstrated a better catalytic performance than chlorides. Jin *et al.* [112] investigated the enhancement effect by adding seven different transition metal fluorides. They found that MgH_2 could react with fluorides rapidly, forming MgF_2 and corresponding hydrides or metal-hydrogen solid solutions. These products acted as the catalysts to improve the kinetic properties. Ma *et al.* [93] revealed that besides

Table 5 Several additives for Mg-based hydrogen storage materials

Additive	Amount	Dehy. T_{start} (°C)	Capacity (wt%)	Ref.
Graphite	5 wt%	/	5.0	[88]
Single-walled carbon nanotube (SWCNT)	5 wt%	/	6.0	[89]
Graphene	25 wt%	150	5.4	[84]
Si	33.3 mol%	295	5.0	[39]
Ti	9 wt%	ca.300	4.8	[90]
TiCl ₃	15 wt%	/	6.7	[92]
TiF ₃	4 mol%	/	5.0–5.5	[93]
TiO ₂	20 wt%	/	4.7	[94]
TiO ₂ NS	5 wt%	180.5	6.0	[100]
Na ₂ Ti ₃ O ₇	5 wt%	308.4	6.5	[95]
Ti ₃ C ₂	5 wt%	185	6.2	[96]
TiN@reduced graphene oxide (rGO)	10 wt%	167	6.0	[101]
V	25 wt%	/	4.0	[91]
V ₂ O ₃ @C	9 wt%	215	6.4	[102]
Cr ₂ O ₃	0.2 mol%	/	6.4	[97]
Fe ₃ O ₄ @graphene	5 wt%	262	6.5	[103]
FeS ₂	16.7 wt%	/	6.06	[98]
Co/C	6 wt%	/	6.5	[32]
Ni/C	6 wt%	/	6.5	[32]
Ni@rGO	5 wt%	160	6.0	[104]
Ni ₃ C	5 wt%	160	6.2	[35]
Ni ₃ N@N-doped carbon (NC)	5 wt%	175	6.0	[105]
CeO ₂	5 wt%	/	3.6	[99]

MgF₂, Ti–F–Mg bonding was formed in the TiF₃-doped MgH₂ whereas only one stable binding state of MgCl₂ was found in the TiCl₃-doped MgH₂. This may be responsible for the advantage of fluorides over chlorides in improving kinetics properties.

Recently, building multiphase nanostructured hybrids have emerged as a new strategy to design efficient additives. Commonly, these hybrids contained dispersed transition metals or metal compounds and 2D/3D scaffold materials. The scaffold material can stabilize the reactive phases and introduce NC effect to MgH₂. Graphene is an ideal scaffold material due to its low-density, high chemical stability and large surface area. There are plenty of studies reporting the enhanced kinetics by adding metal-graphene composites, such as Ni@rGO [104,113,114], NiCo@rGO [115], Ni₂P@rGO [36], TiN@rGO [101], and CeF₄@Gr [116]. Adding graphene not only enhances the dispersion of metal compounds, but also prevents the aggregation of MgH₂, thereby further enhancing cycle properties. In recent years, MOFs derived metal-carbon composites as promising additives

have been widely studied. Zhang *et al.* [117] achieved carbon-supported TiO₂ by calcining furfuryl alcohol-filled MIL-125(Ti); Wang *et al.* [102] obtained cubic carbon nanoboxes supported V₂O₃ by calcining MIL-47(V) (Fig. 4); Huang *et al.* [32] synthesized carbon wrapped Ni/Co by calcining MOFs-74-Co and MOFs-74-Ni under dynamic vacuum. The ligands derived carbon structure limited the particle size of metal/metal compound and enhanced the catalytic activities. All of these researches reported significant improvement of kinetic properties.

Because of the strong reducibility of Mg and MgH₂, most of the dopants with high chemical states are thermodynamically feasible to react with MgH₂. On the other hand, for most situations these reactions are conducted in solid-state with a kinetic obstacle. Whether the dopants reduce or not depends on the experimental conditions such as milling rate and milling time, adding of liquid agents, and the surface functional group of dopants. In the case that dopants are reduced by MgH₂, the production can often enhance the kinetic performance, but may also lead to loss of capacity. Chen *et al.* [34] reported

Figure 4 (a) SEM and (b) TEM image of the prepared nano- $\text{V}_2\text{O}_5@\text{C}$ composite. (c) Temperature programmed desorption (TPD) and (d) volumetric release curves of MgH_2 - x wt% $\text{V}_2\text{O}_5@\text{C}$ samples ($x = 0, 1, 3, 5, 9, 12$). Reproduced with permission from Ref. [102]. Copyright 2018, the Royal Society of Chemistry.

that the TiO_2 could be reduced by MgH_2 , resulting in the formation of multiple valence titanium composites (II, III, and IV). They found these products enhanced the electron transfer and improved the performance. Bhatnagar *et al.* [103] milled MgH_2 with Fe_3O_4 for 25 h, the formation of Fe_2O_3 and the Fe metal were verified after cycle de/re-hydrogenation process. The generation of $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ can puncture the layer of MgO to form the diffusion path, and the Fe metal can enhance the electron transfer. Cui *et al.* [92] combined Mg and TiCl_3 in THF solution, and observed the generation of multi-valence Ti-based materials coating on Mg surface. This layer showed a positive influence on the dehydrogenation of MgH_2 . Our previous work [36] also reported the reaction between MgH_2 and Ni_2P -based additives. During the dehydrogenation, Ni_2P were partially reduced to Mg_2Ni , which prevented the aggregation and improved the cycle performance. In conclusion, it should be mentioned that adding dopants always accompany the phase transformation. The resulting multiple phase structure, highly reactive products, cracks and defects on MgH_2 can further improve the kinetic performance, but the loss of capacity should also be considered.

Considerable researches prove that the doping is an effective strategy to tune kinetic properties of Mg/MgH_2 . However, this strategy can hardly influence the thermo-

dynamic property significantly. Moreover, the high cost in synthesis of some additives offsets the price advantage of Mg metal. Combining with alloying or nanostructuring strategies is crucial for practical application of the doping approach. Moreover, it is of great importance to develop a low cost synthesis route to obtain highly effective additives.

LIGHTWEIGHT METAL BOROHYDRIDES

For lightweight complex hydrides, four hydrogen atoms can be covalently bonded with a metal atom in the center, such as aluminum and boron, forming anion tetrahedron, i.e., $[\text{AlH}_4]^-$ or $[\text{BH}_4]^-$. The alkali and alkaline earth metals, including Li, Na, K, Mg, Ca, can form lightweight complex hydrides with anion tetrahedron. More importantly, the reserves of Li, Na, K, Mg, Ca and Al elements are abundant, which makes large-scale application of lightweight complex hydrides possible. Lightweight metal borates and alanates, as the important types of lightweight hydrides, have been widely investigated owing to the high gravimetric and volumetric densities.

As discussed previously, lightweight borohydrides are promising candidates as hydrogen storage materials due to their outstanding hydrogen content. Like MgH_2 , the wide application of these compounds is also limited by sluggish kinetics and poor thermodynamic properties.

Moreover, their reversibility is also a critical factor for on-board application [4,118]. Nakamori *et al.* [119] investigated the thermodynamic stabilities of nine metal borohydrides using first-principles calculations and experimental data. The decomposition peak temperatures of LiBH_4 , NaBH_4 , and $\text{Mg}(\text{BH}_4)_2$ are all above 500 K. They also found that LiBH_4 , NaBH_4 , and KBH_4 decomposed to hydride phases, whereas $\text{Mg}(\text{BH}_4)_2$ was subjected to a multistep decomposition process to form borides. Due to several irreversible decomposition steps, phase aggregation and separation in multiphase product, stable intermediate compounds and many other factors, it is difficult for lightweight borohydrides to reach a sustainable rehydrogenation rate with cycling [120]. Therefore, considerable efforts have been made to adjust their kinetic and thermodynamic properties and improve reversibility.

Nanoscaling

Nanoscaling can adjust thermodynamic and kinetic properties simultaneously. Mechanical milling is a facile physical approach to reduce both the particle and crystallite size. Varin *et al.* [121] used controlled mechanical milling (CMM) method to prepare NaBH_4 with a few tens of nanometers crystallite size under various milling modes. Due to the solubility of lightweight borohydrides in ether solvent, evaporating borohydrides solution is

another way to achieve nanoscale morphology. Wan *et al.* [122] prepared LiBH_4 powder with particle sizes ranging from 20 to 50 nm *via* evaporation of LiBH_4 -THF solution, without the aid of any additives or scaffolds. Pang *et al.* [123] prepared LiBH_4 nanobelts with width of 10–40 nm using methyl tert-butyl ether as the ligand. The onset decomposition temperature was reduced to 60°C, and they also found that physical vapour deposition approach can be used to prepare other soluble hydrides. Because of the high surface energy, downsizing borohydrides without introducing additives or supports can hardly achieve the size lower than ten nanometers. Therefore, besides the downsizing technique, stabilizing ultrafine borohydrides is also a challenge.

NC is another common strategy for borohydrides to reduce particle and crystallite size. Moreover, the introduction of scaffold can also mitigate sintering and improve the cycle capacity [124]. Due to the low melt temperature (LiBH_4 268°C [13]) and solubility in ether solvent, both melt [124–129] and solvent [129–141] infiltration techniques have been widely investigated, as shown in Table 6. Gross *et al.* [124] melted LiBH_4 at 300°C and infiltrated it into nanoporous carbon scaffolds. The rate of hydrogen exchange was significantly enhanced, and the capacity loss over three cycles was reduced from 72% to ~40%. Ngene *et al.* [129] confined

Table 6 Hydrogen storage properties of several reported nanoconfined borohydrides composites

Borohydride	Scaffold	Infiltration method	Dehy. T_{start} (°C)	Loading (wt%)	Capacity (wt%)/Cycles	Ref.
LiBH_4	Carbon aerogels	Melt	/	25–30 45–50	/	[124]
LiBH_4	Porous carbons	Melt	/	10–30	5.5/6	[125]
LiBH_4	Porous carbons	Melt	300	5–25	/	[126]
LiBH_4	SBA15	Melt	150	10–65	/	[127]
LiBH_4	Zeolite-templated carbon	Melt	194	41.5	/	[128]
LiBH_4	Activated carbon	Solvent	220	30	6.6/2	[130]
LiBH_4	Cu-MOFs	Solvent	60	/	/	[131]
LiBH_4	Porous TiO_2 micro-tubes	Solvent	183	22.97	/	[132]
LiBH_4	Porous $\text{ZnO}/\text{ZnCo}_2\text{O}_4$	Solvent	169	50	/	[133]
LiBH_4	Ti_3C_2	Solvent	172.6	33.3	5.5/3	[134]
NaBH_4	Nanoporous carbon	Melt/Solvent	250	25	/	[129]
NaBH_4	Mesoporous carbon	Solvent	/	20	/	[135]
NaBH_4	SBA15/CMK3	Solvent	/	20	/	[136]
NaBH_4	Graphene	Solvent	40		7.1/6	[137]
$\text{Mg}(\text{BH}_4)_2$	Activated carbon	Solvent	150	41	/	[138]
$\text{Mg}(\text{BH}_4)_2$	Activated carbon	Solvent	40	/	/	[139]
$\text{Mg}(\text{BH}_4)_2$	CMK3-Ni	Solvent	75	45	/	[140]
$\text{Mg}(\text{BH}_4)_2$	Ni-Pt@C	Solvent	250	30	/	[141]

NaBH_4 in nanoporous carbon *via* both melt and solvent infiltration methods. The onset dehydrogenation temperature decreased to 250°C , 220°C lower than bulk NaBH_4 . Besides, this material showed a 43% reversible hydrogen capacity, which is a considerable reverse hydrogen uptake in NaBH_4 . Chong *et al.* [137] encapsulated NaBH_4 into graphene, which effectively prevented the aggregation and phase separation during the dehydrogenation process (Fig. 5). The composite could maintain 93% retention of the initial capacity even at end of the 6th cycle.

Besides the physical confinement effect, the chemical nature of scaffolds can also influence hydrogen storage performance. Recently, Suwarno *et al.* [142] used quasi-elastic neutron scattering and calorimetric measurements to study the chemical influence of scaffolds. Comparing LiBH_4 infiltrated into silica and carbon scaffolds with similar pore size, they found that thickness of LiBH_4 layer near the pore walls was quite different. Also, the discrepancy in the fraction of LiBH_4 with high hydrogen mobility was confirmed by quasi-elastic neutron scattering. These results indicated that the chemical nature of scaffold could affect the morphology and chemical activity of borohydrides in addition to the pore size. The nanostructured transition metal compounds [132,133] such as MOFs [131] and MXene [134] are potential scaffolds with strong chemical influence. Liu *et al.* [132] confined LiBH_4 into TiO_2 nanotube by solvent infiltration approach. Besides the decreased activation energy, they detected the formation of LiTiO_2 , $\text{Li}_{0.5}\text{TiO}_2$, TiB_2 and TiO during the dehydrogenation, which implied the change of reaction pathway. Sun *et al.* [131] investigated the interaction between LiBH_4 and Cu-MOFs, which were introduced as a scaffold. They found that the LiBH_4 molecules were trapped by Cu^{2+} inside the scaffolds, which enhanced the decomposition of LiBH_4 and reduced the dehydrogenation temperature. The recently developed MXene composites were also promising candidates as the NC scaffolds, owing to its unique multilayer morphology and the transition element contained. Our group reported the Ti_3C_2 as a 2D scaffold to confine LiBH_4 with homogeneous dispersion [134] (Fig. 6). The onset dehydrogenation temperature of $\text{LiBH}_4@2\text{Ti}_3\text{C}_2$ hybrid decreased to 172.6°C with an initial capacity of 9.6 wt%. And the dehydrogenated products could rehydrogenate at 300°C and 95 bar of hydrogen pressure with 5.5 wt% capacity after 3 cycles.

Besides these methods, other reported approaches such as self-printing [143] and solid-gas reaction [144] could also achieve nanostructure borohydrides. Zhang *et al.*

Figure 5 SEM images of (a) rehydrogenated $\text{NaBH}_4@$ graphene and (b) rehydrogenated $\text{NaBH}_4 +$ graphene, and their associated energy dispersive spectrometer (EDS) maps of Na, B, and C. (c, e) TEM images of $\text{NaBH}_4@$ graphene and diameter distribution (inset of (c)). (d, f) TEM images of $\text{NaBH}_4 +$ graphene and diameter distribution (inset of (d)). Reproduced with permission from Ref. [137]. Copyright 2015, John Wiley & Sons, Inc.

[144] obtained dispersed $\text{Mg}(\text{BH}_4)_2$ by a space-confined solid-gas reaction using graphene support MgH_2 as the precursor. DFT calculation verified that graphene scaffold could promote the reaction of MgH_2 and B_2H_6 , and stabilize $\text{Mg}(\text{BH}_4)_2$ particles. The graphene supported $\text{Mg}(\text{BH}_4)_2$ with an average particle size of ~ 10 nm showed a decreased onset dehydrogenation temperature at 154°C , and 9.04 wt% H_2 was released at 225°C .

Nowadays, various approaches can downsize borohydrides to nanoscale under a significantly decreased dehydrogenation temperature. However, mechanical and thermal approaches require high hydrogen pressure to avoid the decomposition, which hinders their practical production, and the solvent approaches face the problem of ether residues. It is still a challenge to achieve ultrafine particles with a significant enthalpy decrease. Thus, it is of great importance to develop safe, efficient and low-cost techniques for nanostructuring.

Adding dopants

Adding dopants is another valid way to enhance hydro-

Figure 6 (a–d) SEM images of (a) Ti_3C_2 , (b, c) $\text{LBH}@2\text{Ti}_3\text{C}_2$ hybrid before dehydrogenation and (d) after dehydrogenation. (e) Dehydrogenation cycle profiles of the $\text{LBH}@2\text{Ti}_3\text{C}_2$ hybrid. Reproduced with permission from Ref. [134]. Copyright 2018, American Chemical Society.

gen storage performances. Due to the high-reactive nature of borohydrides, a wide range of dopants can react with them and change the de-/re-hydrogenation pathway. Thus, the enhanced performances always result from thermodynamic and kinetics improvement. Table 7 lists several reported additives for borohydrides hydrogen storage system. The inert scaffold such as Si and C could perform a chemical interaction with borohydrides, so the nonmetal materials are also candidates for tuning thermodynamic and kinetic properties [145–149]. Yu *et al.* [145] synthesized carbon nanotubes-doped LiBH_4 , and found that Li_2C_2 phase was generated during the dehydrogenation process. The Li_2C_2 could be transformed into LiH during rehydrogenation process, which contributed to the cycle capacity to a certain extent. Cai *et al.* [146] investigated the destabilization effect of H_3BO_3 , HBO_2 , and B_2O_3 on LiBH_4 and observed 5.8 wt% hydrogen releasing of H_3BO_3 -doped composite at 110°C . This im-

provement was ascribed to the H^+-H^- coupling mechanism, with the evidence of limited enhancement in B_2O_3 - LiBH_4 composite. Recently, Dolotko *et al.* [147] investigated Li/NaBH_4 - Si_2S_2 systems and found that $\text{Li}_x\text{SiS}_2(\text{BH}_4)_x$ phase was formed due to readily reaction between Si_2S_2 and borohydrides. The S^- ion coordinated with BH_4^- and terminated by Li^+ . The 6LiBH_4 - SiS_2 system exhibited onset desorption temperature of 92°C , with an initial capacity of 8.2 wt%.

Like Mg-based materials, metal and metal compounds are also promising candidates as the additives [150–172]. Yang *et al.* [154] milled LiBH_4 with a series of metal/metal hydrides, and the Mg, MgH_2 , Al and CaH_2 -doped composites displayed changed reaction pathways in de-/re-hydrogenation processes. The MgH_2 - $(\text{LiBH}_4)_2$ and Al- $(\text{LiBH}_4)_2$ composites exhibited reversible capacities of 10.2 and 6.7 wt%, respectively. Garroni *et al.* [164] investigated the phase transformation in dehydrogenation of NaBH_4 - MgH_2 system by *in-situ* synchrotron XRD method. They found that the MgH_2 decomposed to Mg metal, which was then reacted with the NaBH_4 derived intermediate compounds to produce MgB_2 . Li *et al.* [155] further investigated LiBH_4 - CaH_2 composite, the measured enthalpy was almost $60 \text{ kJ mol}^{-1} \text{H}_2$, $14 \text{ kJ mol}^{-1} \text{H}_2$ lower than pure LiBH_4 . With the addition of TiCl_3 , the capacity could reach 7.1 wt% after 10 cycles. Xia *et al.* [152] wrapped MgH_2 - $(\text{LiBH}_4)_2$ composites in graphene, in which the confinement effect further improved the reversibility and cycle properties. The $\text{LBMH80}@G$ composite could remain 8.9 wt% capacity even after 25 cycles (Fig. 7). Yu *et al.* [157] investigated the destabilization of LiBH_4 by various oxides. It was found that the Fe_2O_3 -doped composite demonstrated the best performance and desorbed 6 wt% H_2 at 200°C . Moreover, they speculated the decomposition of LiBH_4 /oxide system should follow the formula of $x\text{LiBH}_4 + \text{M}_y\text{O}_z \rightarrow \text{Li}_x\text{M}_y\text{O}_z + x\text{B} + 2x\text{H}_2$. Liu *et al.* [173] revealed that addition of Fe_2O_3 could form Fe_2O_3 - 2LiBH_4 complex on the interface *via* the first-principles DFT calculations, which would act as the nucleation site to improve the kinetic properties. Besides single-metal oxides, multi-metal oxides could also improve the hydrogen storage performances, for instance, NiFe_2O_4 [174], NiCo_2O_4 , [158] and MgFe_2O_4 [175]. Our group [158] reported NiCo_2O_4 nanorods as the additives for improving dehydrogenation performance of LiBH_4 . The NiCo_2O_4 doped composites showed better performance than NiO or Co_3O_4 . The mechanism analysis revealed that *in-situ* formed Co (Ni) and Co-B (Ni-B) were the actual active catalysts improving the kinetic performance.

Table 7 Several additives for lightweight borohydride-based hydrogen storage materials

Borohydride	Additive	Amount	Dehy. T_{start} (°C)	Capacity (wt%)	Capacity (wt%)/Cycles	Ref.
LiBH ₄	LiNH ₂	66.7 mol%	250	≥10	/	[150]
LiBH ₄	MgH ₂ , TiCl ₃	50 mol% 2–3 mol%	/	8–10	8/3	[151]
LiBH ₄	MgH ₂ , graphene	/	/	9.1	8.9/25	[152]
LiBH ₄	MgH ₂ Ni/C	33.3 mol% 10 wt%	/	9.3	9.27/2	[153]
LiBH ₄	Al	33.3 mol%	320	6.3	3.8/3	[154]
LiBH ₄	CaH ₂ TiCl ₃	14.3 mol% 1 mol%	/	11.7	7.1/10	[155]
LiBH ₄	CeH ₂ , TiCl ₃	13.9 mol% 2.78 mol%	/	6.1	/	[156]
LiBH ₄	Carbon nanotubes	33.3–66.7 wt%	250	8.3	3.8/2	[145]
LiBH ₄	SiS ₂	14.3 mol%	92	8.2	2.4/2	[147]
LiBH ₄	Ionic liquid bmimNTf ₂	/	160	/	/	[148]
LiBH ₄	H ₃ BO ₃	33.3 mol%	110	5.8	/	[146]
LiBH ₄	Fe ₂ O ₃	66.7 wt%	<100	~6	/	[157]
LiBH ₄	NiCo ₂ O ₄	50 wt%	80	12	/	[158]
LiBH ₄	TiCl ₃	25 mol%	100	6.4	4.0/2	[159]
LiBH ₄	TiF ₃	0.1 mol%	/	12	6.0/2	[160]
LiBH ₄	GdF ₃	25 mol%	112	3.50	1.96/50	[161]
LiBH ₄	Fluorinated graphene	20 wt%	204	10.01	3.2/4	[149]
LiBH ₄	MoS ₂	50 wt%	171	5.6	/	[162]
NaBH ₄	NaNH ₂	50 mol%	227	6–7.7	/	[163]
NaBH ₄	MgH ₂	33.3 wt%	320	7.9	/	[164]
NaBH ₄	Ni	/	50	5	5/5	[165]
NaBH ₄	TiF ₃	5 mol%	380	8.4	4.0/2	[166]
NaBH ₄	NbF ₃	25 mol%	80	3.40	3.3/2	[167]
NaBH ₄ – Mg(BH ₄) ₂	fluoro- graphene	40 wt%	114.9	6.9	/	[178]
Mg(BH ₄) ₂	LiNH ₂	50 mol%	160	7.2	/	[168]
Mg(BH ₄) ₂	TiCl ₃	25 wt%	88	13.3	/	[169]
Mg(BH ₄) ₂	ScCl ₃ , TiF ₃	5 mol%	/	13	/	[170]
Mg(BH ₄) ₂	Co-based compounds	2 mol%	100	4	2.0/2	[171]
Mg(BH ₄) ₂	LiBF ₄	/	<90	9.21	/	[172]

Metal halides are also potential additives for borohydrides. Both metal cation and halide anion can influence the de/rehydrogenation. Christian *et al.* [165] doped NiCl₂ to NaBH₄, where the Ni²⁺ was reduced by BH₄[–] and Ni metal coating formed on NaBH₄ particle surface. This core-shell strategy improved the kinetic performance and reversibility. Au *et al.* [160] ball-milled LiBH₄ with eight different halides, and they found that TiCl₃, TiF₃, and ZnF₂ significantly reduced the dehydrogenation tem-

perature and enhanced the reversibility. They found that the improved performance was ascribed to the cation exchange reaction with LiBH₄ as well as the formation of unstable transition metal borohydrides. Yin *et al.* [176] investigated the influence of doping LiBH₄ with F anion by first principles calculations, and found that F anion could substitute both hydrogenated (LiBH₄) and dehydrogenated (LiH) states, which resulted in the enhanced thermodynamic properties. Guo *et al.* [159] investigated

Figure 7 (a) Long-term cycling performance of the dehydrogenation (under a back pressure of 0.3 MPa) and hydrogenation for LBMH80@G and bulk $2\text{LiBH}_4\text{-MgH}_2$ composite at 350°C ; (b) normalized H_2 capacity as a function of cycle number, where the hydrogen capacities are normalized to the theoretical value of $2\text{LiBH}_4\text{-MgH}_2$ composite; (c) SEM, (d) scanning TEM (STEM), and (e) TEM images, with the inset containing a high resolution TEM (HRTEM) image LBMH80@G after 15 cycles of dehydrogenation; and (f) elemental mapping of LBMH80@G after 15 cycles of hydrogenation. The H_2 capacity is expressed here per mass of the whole composite. Reproduced with permission from Ref. [152]. Copyright 2016, Elsevier Ltd.

the $\text{LiBH}_4\text{-TiF}_3$ system and confirmed that the TiB_2 and LiF formed during dehydrogenation, which affected the reaction enthalpy. Chong *et al.* [161] introduced several lanthanide elements fluorides into NaBH_4 , and observed that the $3\text{NaBH}_4\text{-GaF}_3$ composites displayed a fast kinetics and remained high cycling stability even after 51 cycles. Richter *et al.* [177] reported that milling with LiBF_4 could significantly decrease the decomposition temperature of LiBH_4 , but only diborane gas was released during this process. Zheng *et al.* [178] ball-milled NaBH_4 and $\text{Mg}(\text{BH}_4)_2$ with fluorographene. The composite could release 6.9 wt% hydrogen at 114.9°C in seconds (Fig. 8), but the dehydrogenated product NaMgF_3 could hardly reverse into borohydrides.

Compared to metal hydrides, the interaction between borohydrides and additives is more complicated. The additives can act as catalysts or *in-situ* generated catalytic products to enhance the kinetic properties; they can also change the reaction pathway, affect the thermodynamic

and cycle properties. However, this strategy is limited by drawbacks such as high cost, the loss of capacity and phase separation during cycles. Further theoretical and experimental studies on both additives and assembly method are needed to realize practical application.

LIGHTWEIGHT METAL ALANATES

Lightweight metal alanates with general formula of $\text{M}(\text{AlH}_4)_n$ have been widely investigated, since Bogdanović *et al.* [179] discovered that Ti-doped NaAlH_4 could reversibly absorb and release hydrogen. However, it is difficult to release and absorb hydrogen due to the strong covalent bonds of Al-H . The inferior reversibility, high desorption temperature and sluggish de-/rehydrogenation kinetics hinder the application for rechargeable hydrogen devices. Considerable efforts have been made to explore the hydrogenation and dehydrogenation performances of lightweight metal alanates [180–185]. Many effective approaches have been proposed to enhance hy-

Figure 8 Illustration of the formation mechanism of the 3D bowl-like $\text{Mg}(\text{BH}_4)_2\text{-NaBH}_4\text{-FG}$ composite. Reproduced with permission from Ref. [178]. Copyright 2017, the Royal Society of Chemistry.

drogen storage performances by nanoscaling [186,187], wet chemistry infiltration [188–190], adding dopants [191–195], and mixing in the lightweight metal hydride [189,196–198]. In this part, we will summarize the challenges and progresses of lightweight metal alanates and focus on the effects of nanoscaling and multifarious dopants.

Nanoscaling

Nanoscaling appears to be an effective strategy for improving the hydrogen storage properties of lightweight metal alanates, such as NaAlH_4 and LiAlH_4 [199–201]. Gutowska *et al.* [202] reported that hydrogen desorption properties of ammonia borane could be dramatically promoted through confining it into high-surface-area mesoporous silica SBA15. The enhanced hydrogenation and dehydrogenation properties were influenced by the size of lightweight metal alanates [203]. Nanoscaling strategy can lead to the reduction in particle size and hydrogen diffusion path length, increasing the hydrogen diffusion rate and nucleation sites for dehydrogenation and hydrogenation. Table 8 summarizes the nanoscaling strategies, scaffolds, and the hydrogen storage performances of lightweight metal alanates.

In general, effective nanoscaling strategies can be achieved using high energy ball milling (HEBM) [204,205] and NC [206–208] techniques. In HEBM

technique, the collision and fracture effects can result in the reduction of particle size. However, porous materials can also be destructed due to drastic collision among balls, tank and powder during ball milling, and cold-welding effect may lead to an increase of particle size. Varin *et al.* [204] reported that average equivalent circle diameter particle size of LiAlH_4 ball-milled for 2 h reduced to $2.8 \pm 2.3 \mu\text{m}$, which was much smaller than the original particle size ($9.9 \pm 5.2 \mu\text{m}$) of commercial LiAlH_4 . Ball milled LiAlH_4 could release 7.1 wt% H_2 at 120°C under 0.1 MPa H_2 . In NC techniques, including melt infiltration and solvent infiltration, many kinds of porous nanoscaffolds, such as CeO_2 hollow nanotubes, mesoporous silica, porous carbon and MOFs have been intensively applied [190,200,208–210].

Melt infiltration can be applied as a conventional NC technique when melting point of lightweight metal hydrides is lower than the decomposition temperature of porous scaffolds. This means porous nanoscaffolds should be stable hosts and capable of providing high reactivity of alanates in molten state during de-/hydrogenation processes. Stephens *et al.* [211] loaded NaAlH_4 into nanoporous carbon aerogel (NCA) with pore diameter of 13 nm by melt infusion method. The uncatalyzed $\text{NaAlH}_4\text{@aerogel}$ exhibited lower dehydrogenation temperature (150°C) and faster dehydrogenation kinetics than bulk uncatalyzed NaAlH_4 , and

Table 8 Hydrogen storage properties of nanoconfined lightweight metal alanates in porous materials

Alanate	Scaffold	Nanoscaling strategy	Loading (wt%)	Dehy. T ($^{\circ}\text{C}$)	Rehy. T ($^{\circ}\text{C}$)/ P (MPa H_2)	Dehy. content: (wt%)	Ref.
LiAlH_4	/	Ball-milling	/	120	/	7.1	[204]
NaAlH_4	NC	Melt	5–80	170	150/55 bar	3.3	[199]
NaAlH_4	NCA	Melt	48.6	150	160/100 bar	4.76	[211]
NaAlH_4	MC	Melt	26	180	150/7	5.0	[209]
NaAlH_4	Ti-OMCs	Melt	33.3	160	120/101 bar	2.15	[206]
NaAlH_4	Ti-MOF74	Melt	21	200	160/10.5	4.1	[187]
NaAlH_4	CeO_2	Melt	50	180	/	5.10	[190]
LiAlH_4	Ni-MCS	Melt	45	225	/	6.19	[182]
NaAlH_4	Ordered mesoporous silica (OMS)	Solvent	20	180	150/5.5	5	[208]
NaAlH_4	MOFs	Solvent	4	155	/	4.48	[213]
LiAlH_4	High surface area graphite (HSAG)	Solvent	22	/	300/7	0.6	[200]

was readily rehydrogenated to 4.76 wt% hydrogen at approximately 160°C under 100 bar H_2 . Above results indicated that confining the NaAlH_4 into nanoscale within aerogel pores by melt infusion was responsible for the enhanced dehydrogenation and rehydrogenation performances. A typical procedure of melt infiltration is illustrated in Fig. 9 [209]. NaAlH_4 loaded in ordered

mesoporous carbon (MC) was prepared by melt infusion and de-/rehydrogenation. For the space-confined NaAlH_4/MC , the activation energy (E_a) for dehydrogenation was decreased to $46 \pm 5 \text{ kJ mol}^{-1}$ and the capacity remained more than 80% after 15 cycles.

Xiong *et al.* [206] reported the hydrogen storage properties of NaAlH_4 with Ti-loaded high-ordered me-

Figure 9 (a) Schematic illustrations of preparation process of NaAlH_4 exclusively confined in MC, (b) initial dehydrogenation curves of the samples and (c) the normalized hydrogen capacity pattern upon multiple cycling. Reproduced with permission from Ref. [209]. Copyright 2011, Elsevier.

soporous carbons (Ti-OMCs). The dehydrogenation temperature was reduced to about 60°C, and approximately 80% H₂ was released after 11 de-/rehydrogenation cycles within 20 min. In addition, the dehydrogenated sample could be rehydrogenated at 120°C under 101 bar hydrogen pressure, demonstrating excellent reversibility and stability. Recently, Carr *et al.* [212] reported that NaAlH₄ melt infiltrated into nitrogen-doped nanoporous carbon frameworks exhibited a lowered E_a value for dehydrogenation by 70 kJ mol⁻¹, larger than the decrease in nonfunctionalized carbons. However, an anomalous and unexpected hydrogen desorption rate appeared with a remarkably lowered E_a value in the N-doped nanoporous carbon frameworks. This indicated that existence of nitrogen may prevent the formation of H₂ at the interface between hydride and nanoporous carbon frameworks, meanwhile a rate-limiting step for desorption may be related to the nitrogen doping in the nanoporous carbon frameworks. More interestingly, NaAlH₄ confined into CeO₂ hollow nanotubes (HNTs) showed dramatically enhanced dehydrogenation properties [190]. Approximately 5.51 wt% H₂ could be rapidly released at 180°C within 30 min. The significant reduction in the E_a (76.32 kJ mol⁻¹) immediately testified the enhancement of the hydrogen release kinetics owing to the synergistic effects contributed by the CeO₂ HNTs, which served as a

hollow scaffold material to confine the hydride and as an additive to improve the dehydrogenation properties.

Solvent infiltration is usually carried out under mild conditions compared with melt infiltration. The solvents such as tetrahydrofuran (THF) or methyl tert-butyl ether (MTBE) are required to be able to dissolve alanates so as to form a homogeneous solution. Next, porous nanoscaffold is impregnated in the homogeneous solution and all the pores should be entirely infiltrated by the solution. After that, the solvent can be removed by evaporation and alanates solidify to generate nano-sized particles in the pores.

In 2008, THF solvent mediated infiltration was carried out by loading NaAlH₄ into the as-synthesized OMS [208] with 10 nm in diameter. The de-/re-hydrogenation temperatures were reduced and hydrogen absorption/desorption kinetics was remarkably promoted. As shown in Fig. 10, the pristine NaAlH₄ desorbed negligible hydrogen at 150/180°C, only 0.3 wt% H₂ could be released at 180°C. For OMS confined NaAlH₄, the capacity could reach 3.0 wt%. Besides, the rehydrogenation in a dehydrogenated NaAlH₄/OMS could be achieved even under milder conditions (125–150°C, 3.5–5.5 MPa hydrogen), 0.9 wt% H₂ capacity could be achieved at the second cycle, while the pristine NaAlH₄ could hardly be rehydrogenated under the same situation (less than 0.1 wt%

Figure 10 (a) Schematic illustrations of NaAlH₄ confined in OMS by solvent mediated infiltration. Dehydrogenation curves for (b) the pristine NaAlH₄, NaAlH₄/OMS and (c) the rehydrogenated (150°C and 5.5 MPa H₂ pressure) samples at 150 and 180°C. Reproduced with permission from Ref. [208]. Copyright 2008, American Chemical Society.

H₂). These excellent properties were ascribed to that the NaAlH₄ particles and the dehydrogenated products of Al and NaH were controlled to be nanoscale under the confined effect of the OMS pores. Bhakta *et al.* [213] successfully encapsulated NaAlH₄ in MOF (HKUST-1) by a wet chemical approach. The onset dehydrogenation temperature of NaAlH₄/MOF reduced about 70°C. About 80% of the total H₂ was released at 155°C; however, pristine NaAlH₄ released 70% of the total hydrogen at 250°C.

Christian *et al.* [214] infiltrated the NaAlH₄ and LiAlH₄ into carbon nanotubes (CNT) with a diameter of 10 nm. The loading amount of lightweight metal alanates was less than 6 wt%. For LiAlH₄ encapsulated in CNT, dehydrogenation started at the sub-ambient condition. In addition, dehydrogenation peak was observed at 120°C and hydrogen release was absolutely completed by 250°C. The activation energy of dehydrogenation process from LiAlH₄-CNT was remarkably reduced $64 \pm 5 \text{ kJ mol}^{-1}$, a decrease of 18 kJ mol^{-1} from 82 kJ mol^{-1} of bulk LiAlH₄. In addition, ordered mesoporous carbon CMK-3 was also applied as a scaffold for LiAlH₄. Unfortunately, nanoscale aluminum oxide was generated inside the CMK-3 of reaction products rather than a metal or alloy [188]. Recently, HSAG was applied to confine LiAlH₄ with a saturated THF solution [200]. Upon nanoconfinement in HSAG, the particle size of LiAlH₄ was reduced to 3–15 nm. In addition, there were some residual solvent in the LiAlH₄ nanoconfined in HSAG, which led to the formation of the LiAlH₄·*n*THF with the strong bonding between LiAlH₄ and THF. The initial hydrogen release temperature was 100°C. A reversibly capacity of 0.6 wt% was obtained at 300°C under 7 MPa, which was about 30% of the capacity of LiAlH₄ nanoconfined in HSAG. However, low capacity and inferior dynamics hinder the development of nanoscaling strategies. Therefore, effective strategies should be proposed to enhance the hydrogen storage properties of lightweight metal alanates systems.

Adding dopants

Introduction of suitable dopants is also an effective approach to improve the hydrogen storage properties of lightweight metal alanates systems. An extensive variety of dopants, such as transition metals, rare-earth metals, carbon materials and co-dopants additives, have been surveyed during the last two decades [183,215–217]. Several doping strategies, such as wet doping and high-energy ball milling have been presented for the preparation of additive-doped lightweight metal alanates. How-

ever, introducing Ti-based species into NaAlH₄ in diethyl ether solutions by the wet-doping approach is considerably complicated [179]. In contrast, ball milling is the most common approach for the introduction of dopants as it can achieve homogeneous distribution of dopant in lightweight metal alanates and realize close contact between dopant and hydrides. Table 9 summarizes the hydrogen storage performances of additive-doped lightweight metal alanates.

At present, Ti-based compounds are the mostly used and highly active dopants for increasing the hydrogen storage properties of lightweight metal alanates. Bogdanović *et al.* [179] firstly synthesized the Ti(OBu)₄ and TiCl₃-doped NaAlH₄ which could be rehydrogenated at 170°C under 15.2 MPa and a reversible H₂ capacity of 4.2 wt% was obtained. Through mechanically mixing Ti(OBu)₄ with NaAlH₄, the dehydrogenation temperature reduced and capacity of rehydrogenation increased [218]. However, the heavy weight of the additive and gas impurities contamination restricts further application of hydrides.

Up to now, Ti-based halides have been extensively studied as dopants for enhancing de-/rehydrogenation properties [219–226]. Sandrock *et al.* [219] reported that NaAlH₄ ball-milled with TiCl₃ dopant could release 3 wt% H₂ and absorb 4.2 wt% H₂ in 60 min at 125°C under 91 bar hydrogen pressure. Wang *et al.* [220] demonstrated the catalytic property of TiF₃ additive was superior to TiCl₃ in the reversible hydrogen storage of NaAlH₄. TiF₃-containing composite displayed a more significant kinetics improvement and a higher reversible hydrogen capacity than the TiCl₃-containing composite. TiF₃-doped NaAlH₄ was able to absorb approximately 3.4 wt% H₂ in 10 h at 60°C under 110 bar hydrogen pressure. However, TiCl₃-containing sample absorbed only 3.2 wt% H₂ even in more than 10 h at 80°C. In 2010, Langmi *et al.* [221] revealed that the decomposition temperature of TiCl₃-doped LiAlH₄ was reduced approximately 60–75°C lower than that of undoped LiAlH₄. The enthalpy of the first hydrogen release of TiCl₃-doped LiAlH₄ was estimated to be 0.86 kJ mol^{-1} . For 10 mol% TiF₃-doped Li₃AlH₆ sample prepared by mechanical ball milling, the onset dehydrogenation temperature was evidently reduced by 60°C as compared with that of pristine Li₃AlH₆ (around 190°C), and approximately 3.0 wt% H₂ could be released at 120°C. The apparent *E_a* of Li₃AlH₆ dehydrogenation was remarkably reduced by 29 kJ mol^{-1} , which was ascribed to *in-situ* formed highly active Al₃Ti and TiH₂ [222].

Other Ti-based additives, such as TiO₂, TiH₂, TiC, TiN,

Table 9 Hydrogen storage properties of additive-doped lightweight metal alanates

Alanate	Additive	Dehy. non-isothermal		Isothermal		Rehy. isothermal		Ref.
		T_{start} (°C)	Capacity (wt%)	T (°C)	Capacity (wt%)	T (°C)/ P (bar)	Capacity (wt%)/Cycles	
NaAlH ₄	Ti(OBu) ₄	100	5.3	/	/	200/1600 psi	2.12/1	[218]
NaAlH ₄	TiCl ₄	/	/	125	3	125/91	4.2/5	[219]
NaAlH ₄	TiF ₃	/	/	150	4	120/110	3.7/10	[220]
Li ₃ AlH ₆	TiF ₃	130	3.8	120	3	/	/	[222]
KAlH ₄	TiF ₃	100	4.25	/	/	/	/	[226]
LiAlH ₄	TiCl ₃ - MWCNTs	75	4.68	110	3.6	/	/	[223]
NaAlH ₄	TiC	/	/	155	3.8	120/11.5 MPa	4.77/1	[230]
LiAlH ₄	TiN	90	7.1	130	7.1	/	/	[234]
NaAlH ₄	TiB ₂	70	5.0	90	3	90/4 MPa	2.85/2	[192]
NaAlH ₄	MXene/ A-TiO ₂	90	5.2	140	4.8	120/12 MPa	4.7/5	[229]
LiAlH ₄	ScCl ₃	90	5.7	150	3.6	/	/	[237]
NaAlH ₄	CeAl ₂	/	/	160	4.7	120/12 MPa	4.9/1	[239]
LiAlH ₄	SrFe ₁₂ O ₁₉	80	6.75	130	5.54	/	/	[249]
NaAlH ₄	ZrCl ₄	145	5.6	140	4.34	/	/	[250]
NaAlH ₄	NCNT/NG	/	/	/	/	180/65	1.8/5	[253]
LiAlH ₄	MWCNTs	150	6.1	120	4.0	/	/	[254]
NaAlH ₄	TiCl ₄ + Zr	/	/	125	4.3	125/110	4.0/1	[257]
NaAlH ₄	Ti+KH	/	/	150	4.7	120/100	4.7/10	[258]
NaAlH ₄	TiO ₂ @C	90	4.6	/	/	115/100	4.5/5	[228]

and TiB₂, have also been extensively researched because of their capacity of enhancing de-/rehydrogenation in lightweight metal alanates. TiO₂-based additives apparently improved the cycling stability and increased the available hydrogen capacity for LiAlH₄ and NaAlH₄ [227–229]. Zhang *et al.* [228] reported that TiO₂@C-doped NaAlH₄ started to release hydrogen at around 90°C and was entirely reloaded 4.5 wt% H₂ at 115°C under 100 bar hydrogen pressure. Interestingly, this study result demonstrated that catalytic activities can be ranked in the order Al-Ti > TiH_{0.71} > TiH₂ > TiO₂. In 2009, Xiao *et al.* [230] synthesized NaAlH₄ by ball milling the mixture of NaH and Al with TiC additive under 0.6 MPa hydrogen pressure. The TiC-containing NaH/Al composite could absorb 4.77 wt% H₂ in 10 h at 120°C under 11.5 MPa hydriding pressure, and hydrided TiC-containing NaH/Al sample released 3.85 wt% H₂ at 155°C. The catalytic mechanism (Fig. 11) was that TiC additive acted not only as the catalytic active sites for hydrogen spillover, but also suppressed the particles' agglomeration. TiN and TiB₂ dopants [191,192,231–234] were also used to promote

de-/rehydrogenation of LiAlH₄ and NaAlH₄.

Our group [231] reported that TiN-doped NaH/Al composite released 5.44 wt% H₂ at 190°C and the onset hydrogen desorption temperature was decreased to around 100°C. Recently, co-doping TiO₂ and 2D MXene synthesized by chemical exfoliation has been added into NaAlH₄ [229]. For 10 wt% MXene/A-TiO₂-NaAlH₄ sample, approximately 4.8 wt% H₂ was liberated within 200 min at 140°C, and the hydrogen desorption amount still maintained 4.7 wt% after five cycles at 120°C under 12 MPa hydrogen pressure.

Apart from Ti-containing compounds, other transition-metal, MOFs, rare-earth-metal-based compounds have also been explored and investigated as dopants, which were proved to be able to enhance hydrogen storage properties of alanates [193,235–244]. Bogdanović *et al.* [235–237] revealed that CeCl₃ and ScCl₃ additives could remarkably promote the hydrogen desorption kinetics of NaAlH₄ and LiAlH₄. More importantly, the hydrogenation rate of ScCl₃-doped NaAlH₄ at 50 bar hydrogen pressure was 10 times faster than that of Ti-doped

Figure 11 Scheme of TiC-doped NaH/Al composite in different states of hydrogenation. (a) Ball-milled NaH/Al, (b) adsorbed, (c) dissociated, and (d) diffused state of hydrogenation. Reproduced with permission from Ref. [230]. Copyright 2009, American Chemistry Society.

NaAlH₄. Transition metal oxides were also highly efficient in decreasing the hydrogen desorption temperature and improving the hydriding-dehydriding kinetics of alanates [193,245–249]. Sulaiman *et al.* [249] demonstrated that 10 wt% SrFe₁₂O₁₉-containing LiAlH₄ composite released around 5.54 wt% H₂ at 130°C in 20 min. *In-situ* dehydrogenated products of Fe and LiFeO₂ species and Sr-containing species may play a synergistic role in improving the desorption properties of LiAlH₄. In 2012, Pitt *et al.* [250] studied transition-metal chlorides enhanced NaAlH₄ system. They elucidated that ZrCl₄-containing composite displayed the highest hydrogen capacity of 4.34 wt% at 140°C under 150 bar pressure. This study proposed a dual catalytic mechanism resulting from the surface-embedded Al_{1-x}Ti_x specie. Fan *et al.* [238,239] investigated the enhanced hydriding-dehydriding properties of Ce-Al species-doped NaAlH₄. As-synthesized CeAl₂-doped NaAlH₄ released around 70% of the hydrogen capacity in the first hydrogen evolution step at 160°C within 6 min, and could be hydrogenated under 12 MPa hydrogen pressure at 120°C in 20 min, with a hydrogen capacity of 4.9 wt%. Compared with the second cycle, hydrogenated capacity slightly decreased after 40 cycles. Stabilized CeAl₄ phase could be generated due to

the reaction between CeAl₂ additive and Al after prolonged cycling, which played a crucial role for hydriding-dehydriding properties of CeAl₂-doped NaAlH₄.

Carbon materials, as the typical nonmetal dopants, have been also widely investigated owing to the low density and high activity [251–254]. Kumar *et al.* [253] revealed that nitrogen-doped carbon materials, including carbon nanotubes (NCNT) and graphene (NG), showed excellent catalytic activity compared with pristine carbon materials. NCNT-doped NaAlH₄ could reversibly take 1.8 wt% hydrogen in 2.5 h. The onset hydrogen desorption temperature of multi-walled carbon nanotubes (MWCNTs) modified-LiAlH₄ was reduced by around 60°C; and 10 wt% MWCNTs-modified LiAlH₄ released 4.0 wt% hydrogen at 120°C for 3 h [254].

Recently, it has become a hot issue to construct highly efficient multicomplex dopants or co-dopants with synergistic effects [241,247,255–263]. Bimetallic additives have been explored to promote the hydriding-dehydriding properties of hydrides [256,257]. Schmidt *et al.* [257] found that hydrogen desorption and reabsorption kinetics of the Ti-Zr-co-doped NaAlH₄ was superior to that of NaAlH₄, meanwhile about 4 wt% hydrogen could be reversibly stored at 125°C in 5 h. Co-doping TiCl₃ and

MWCNTs formed a synergetic effect, which greatly reduced the hydrogen desorption temperature of LiAlH_4 . For LiAlH_4 with the addition of 20 wt% TiCl_3 -MWCNTs, the first stage dehydrogenation temperature could be lowered to 80°C and 3.6 wt% H_2 could be released at 110°C in 2 h [223]. In contrast, 20 wt% MWCNTs-containing NaAlH_4 started to release hydrogen at 140°C, and only 4.6 wt% of H_2 was released when it was heated to 300°C. Recent research revealed that potassium hydride (KH) could improve the catalytic effect of Ti- and Ce-based catalysts. Wang *et al.* [258] reported that introducing KH into Ti-containing alanates resulted in a significant enhancement in the hydrogen desorption kinetics of the second decomposition step. For the KH+Ti co-containing sample, dehydriding capacity increased to around 4.7 wt%. The second decomposition rate was approximately 5 times faster than that of the Ti-doped sample.

An illustration of the character of the active species and the explanation of reaction mechanisms are essentially important for the evolution of additive-containing alanates with pronouncedly enhanced hydriding-dehydriding performances [230,231]. However, it is difficult to explain the reaction mechanisms on the hydriding-dehydriding properties of alanates due to high complicity of active species. Numerous researches showed that *in-situ* dehydrogenated products of Sr-containing species, Al_3Ti , Ce_7O_{12} , CeAl_4 or $\text{Al}_{85}\text{Ti}_{15}$ composites played an important role in improving the desorption properties of hydrides [239,249,250,264–267]. Up to now, several catalytic mechanisms have been developed: (1) providing an active site for the dissociation and recombination of H–H bonds [268]; (2) alloy formation at or near the surface of bulk aluminum [269]; (3) weakening the Al–H bonding [270]; (4) promoting the nucleation of dehydrogenation products [271]; (5) promoting the AlH_3 -vacancy mediation [272]. Hence, exploring and synthesizing active dopants with excellent catalytic properties, instead of dopant precursors, is crucial for the development of additives-doped lightweight metal alanates with a high available hydrogen capacity.

SUMMARY AND OUTLOOK

Lightweight hydrides are the most promising candidates to promote the practical application of solid-state hydrogen storage materials owing to their high gravimetric hydrogen contents. However, their on-board applications were still limited due to some drawbacks. Although many efforts have been devoted to tuning kinetics, thermodynamics, reversible capacity and cycle performance of

existing lightweight hydrides, it is still a challenge to meet the requirements of practical use.

Alloying, nanoscaling and doping techniques have been demonstrated to decrease the hydrogen desorption temperature and to promote the reversibility behavior of lightweight hydrides. Nanoscaling is a promising strategy to tune both kinetic and thermodynamic properties. However, for a significant thermodynamic improvement, the crystallites size should be less than 1.3 nm, which is still a challenge for homogeneously preparation. These ultrafine particles with high surface energy have a strong tendency to aggregate, thus a suitable scaffold is necessary. Both strategies for “Achieving” and “Stabilizing” the ultrafine lightweight hydrides need to be further researched. Alloying and doping have been widely studied for several decades. The changed reaction pathway can adjust thermodynamic properties while the catalytic effect can improve the kinetics. Sometimes the interaction of additives and hydrides is complicated, which makes it difficult to distinguish the mechanism of the improvement. The analysis techniques need to be further developed to reveal mechanism in detail, thus providing theoretical basis for additives design and synthesis.

Employing multiple strategies to improve hydrogen storage properties is the recent researching tendency, for instance, combining nanocofinement with catalytic strategy. These complex multiphase nanocomposites require homogeneous dispersion, which sets a high demand on synthesis technique. Moreover, it remains a challenge on both composites design and cost-effective synthesis route. Although there is a long way to go before on-board application of lightweight hydrides as hydrogen storage materials, we believe that continuous efforts will eventually realize the practical applications and bring hydrogen energy to our real life.

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轻质氢化物储氢材料: 挑战, 进展和展望

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摘要 在众多的储氢材料中, 轻质储氢材料由于具有极高的质量比容量和体积比容量而受到广泛的关注. 然而, 热力学稳定性高、动力学性能差等因素, 使得轻质储氢材料存在放氢温度高、可逆性差等缺点, 限制了其实际应用. 本文总结了几种调控轻质储氢材料热力学、动力学性能的方法, 着重介绍了镁基储氢材料、硼氢配位氢化物和铝氢配位氢化物的研究进展. 首先总结了轻质储氢材料的研究现状、优势与挑战, 接着举例分析了合金、纳米化与添加掺杂剂策略的优缺点, 对放氢温度与材料吸放氢可逆性的影响, 系统归纳了不同的基体、添加剂、制备方法和对应的吸放氢性能数据. 最后, 详细讨论了掺杂剂、合成方法和调控策略的演变及发展趋势, 以及改善热力学、动力学行为的机理, 并对未来的研究方向进行了展望.