Recent advance of metal borohydrides for hydrogen storage

Jianjun Liu, Yong Ma, Jinggang Yang, Lei Sun, Dongliang Guo and Peng Xiao*

State Grid Jiangsu Electric Power Co, Ltd. Research Institute, Nanjing, Jiangsu, China

Hydrogen energy is an excellent carrier for connecting various renewable energy sources and has many advantages. However, hydrogen is flammable and explosive, and its density is low and easy to escape, which brings inconvenience to the storage and transportation of hydrogen. Therefore, hydrogen storage technology has become one of the key steps in the application of hydrogen energy. Solid-state hydrogen storage method has a very high volumetric hydrogen density compared to the traditional compressed hydrogen method. The main issue of solid-state hydrogen storage method is the development of advanced hydrogen storage materials. Metal borohydrides have very high hydrogen density and have received much attention over the past two decades. However, high hydrogen sorption temperature, slow kinetics, and poor reversibility still severely restrict its practical applications. This paper mainly discusses the research progress and problems to be solved of metal borohydride hydrogen storage materials for solid-state hydrogen storage.

KEYWORDS
hydrogen energy, hydrogen storage, metal borohydride, destabilization, catalysis, composite

Introduction

Nowadays, with the shortage of fossil fuel energy and the increasingly serious environmental problems, people gradually realize the importance of finding new, efficient, environment-friendly and sustainable energy sources. In the global low-carbon energy system, hydrogen energy, as an efficient and clean new energy source, was initially used in hydrogen fuel cell vehicles fields, which then stimulated and promoted the development of hydrogen energy-related fields. The use of hydrogen energy generally includes three steps. The first is to use clean primary energy to produce hydrogen, then to store and transport the hydrogen, and finally to use the hydrogen for energy output equipment. Among them, hydrogen storage technology has become the key to the application and development of hydrogen energy due to the flammable, explosive features and low volumetric energy density of hydrogen. At present, there are three main ways of hydrogen storage: gaseous hydrogen storage, liquid hydrogen storage and solid hydrogen storage. Among them, solid-state hydrogen storage is a
technology that stores hydrogen in solid hydride materials. As for the solid-state hydrogen storage mechanism, physical storage and chemical storage can be considered. The physical one is a method in which hydrogen is combined with the material in a molecular state, and hydrogen molecules are adsorbed on the surface of the material, while for the chemical one, hydrogen storage is based on a chemical absorption mechanism. In this chemical hydrogen storage material, hydrogen is combined with various elements or compounds by metal bonds, ionic bonds, or covalent bonds to form metal hydrides, coordination hydrides or chemical hydrides to achieve solid-state storage. High-capacity hydrogen storage materials composed of light elements include light metal hydrides (MgH$_2$, AlH$_3$), metal alanates [LiAlH$_4$, NaAlH$_4$, Mg(AlH$_4$)$_2$, etc.] metal borohydrides [LiBH$_4$, NaBH$_4$, Mg(BH$_4$)$_2$, etc.], metal nitrides [LiNH$_2$, Mg(NH$_2$)$_2$, etc.], etc. (Schlapbach and Zuttel, 2001; Chen et al., 2002; Orimo et al., 2007; Jiang et al., 2021; Liu et al., 2021; Lu et al., 2021; Lin et al., 2022). Among these, the metal borohydrides (Figure 1) have a theoretical hydrogen storage capacity of more than 7.5 wt%, and have become a hot topic in the field of solid-state hydrogen storage research (Lv and Wu, 2021; Zhang et al., 2021; Li et al., 2022a; Wang et al., 2022a; Li et al., 2022b; Zhang et al., 2022).

However, metal borohydrides have high thermal stability, and generates highly inert elemental boron after hydrogen releasing, which affects its reverse reaction to absorb hydrogen again. Therefore, improving the reversible hydrogen storage properties of metal borohydrides has become one of the hotspots for solid-state hydrogen storage materials. This paper mainly discusses the modification methods, research progress and problems to be solved of metal borohydride hydrogen storage materials.

LiBH$_4$

LiBH$_4$ is a white powder at room temperature with a melting point of about 278°C. It is insoluble in hydrocarbons, but soluble in ether, tetrahydrofuran, and liquid nitrogen. LiBH$_4$ is stable at room temperature and in dry air, but it is very sensitive to moisture and protic solvents. The oxidation of LiBH$_4$ with water follows Eq. 1 (Xiong et al., 2017).

\[
\text{LiBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{LiBO}_2 + 4\text{H}_2 \quad (1)
\]

LiBH$_4$ has an orthorhombic structure at room temperature with a space group of $Pnma$ ($a = 7.17858\ \text{Å}$, $b = 4.43686\ \text{Å}$, $c = 6.80321\ \text{Å}$), and transforms to a hexagonal system ($P6_3mc$, $a = 4.27631\ \text{Å}$, $c = 6.94844\ \text{Å}$) at 108–112°C (Harris and Meibohm, 2002; Soulie et al., 2002; Orimo et al., 2007; Yu and Ross, 2011). When the temperature rises to 268–286°C, LiBH$_4$ begins to melt and become liquid accompanied by the liberations of 2% of the hydrogen in compound. When further heated to 380°C, LiBH$_4$ begins to release a large amount of hydrogen. When the temperature reaches 600°C, LiBH$_4$ can practically release a total of 9 wt%
hydrogen (Zuttel et al., 2003a; Zuttel et al., 2003b). The hydrogen release reaction formula is as Eqs 2, 3:

$$\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + 3/2\text{H}_2 \text{ 13.8 wt\%} \quad (2)$$

$$\text{LiH} \rightarrow \text{Li} + 1/2\text{H}_2 \text{ 4.7 wt\%} \quad (3)$$

The theoretical hydrogen storage capacity of LiBH$_4$ is 18.5 wt\%, which is higher than all hydrogen storage alloys and general coordination hydrides. However, the hydrogen contained in LiBH$_4$ is not completely available, and only 13.8 wt\% hydrogen is released in the range of 380°C–680°C under one bar of H$_2$ pressure (Stasinevich and Egorenko, 1968; Umegaki et al., 2009). In the process of hydrogen absorption, the reversible hydrogen absorption reaction of LiH and B can be completed at 600°C and 35 MPa for 12 h (Orimo et al., 2002).

Although pure LiBH$_4$ is a high-capacity hydrogen storage material, it has high hydrogen absorption and desorption temperature, slow hydrogen releasing rate, and poor reversibility. There are two common methods for modifying LiBH$_4$. The first method is to thermodynamically destabilize LiBH$_4$ by adding metals, metal halides, oxides, amides or metal hydrides to form composite materials or alloys after dehydrogenation (Zhang and Tian, 2011; Zhou et al., 2012; Liu et al., 2016; Zhou et al., 2017; Cheng et al., 2018; Xian et al., 2019; Ding et al., 2020; Sulaiman et al., 2021); the second method kinetically improve LiBH$_4$ by using catalysts (Sulaiman et al., 2021; Zheng et al., 2021; Li et al., 2022a; Wang et al., 2022a; Li et al., 2022b) or nanoconfinement, confining LiBH$_4$ in mesoporous scaffolds or mixing LiBH$_4$ with nanotubes or mesoporous gels etc. (Zhou et al., 2019; Wang et al., 2020a; Le et al., 2021; Xian et al., 2021; Ye et al., 2021; Wang et al., 2022b).

**Thermodynamic destabilization**

The first point that should be considered to enhance LiBH$_4$ is thermodynamic destabilization. In 2006, Barkhordatian found that the 2LiBH$_4$–MgH$_2$ system has better hydrogen cycle thermodynamics than LiBH$_4$ or MgH$_2$ alone, which is believed to be because the formation of MgB$_2$ “destroys” the decomposition of LiBH$_4$ (Pinkerton et al., 2007).

Vajo et al. (2005) reported on the destabilization system of 2LiBH$_4$–MgH$_2$ and found that adding a destabilizer to LiBH$_4$ to participate in hydrogen evolution can effectively reduce the reaction enthalpy change of LiBH$_4$, and the enthalpy change of hydrogen evolution reaction was reduced to 46 kJ mol$^{-1}$ H$_2$ (Figure 2). Since then, researchers have carried out a lot of work around the destabilization of LiBH$_4$, and have tried various
destabilizing agents to improve the dehydrogenation performance and reversibility of LiBH₄, including metal elements, metal hydrides, metal chlorides and metal oxides, etc. Among the destabilization systems, the LiBH₄-MgH₂ system, that is, the Li-RHC system (RHC, Reactive Hydrde Complex), is highly studied. Barkhordarian et al. patented the RHC concept in 2006. In the first published work on Li-RHC, the hydride mixture was doped with 2–3 mol% TiCl₃ to improve the kinetic behavior, and isothermal measurements were performed in the range of 315°C–400°C, the enthalpy of hydrogen absorption down to 40.5 kJ mol⁻¹. But the entropy of the Li-RHC system is different from that of the metal-hydrogen system, which is related to the [BH₄]⁻ cluster configuration after hydrogen interaction (Vajo et al., 2005).

Bosenberg et al. (2010) published a paper, which for the first time expounded the overall hydrogenation and dehydrogenation reaction mechanism of Li-RHC under dynamic conditions. The following two-step reaction (Eq. 4) was observed during hydrogen evolution:

\[ \text{MgH}_2 + 2\text{LiBH}_4 \rightarrow \text{Mg} + 2\text{LiBH}_3 + \text{H}_2 \rightarrow \text{MgB}_2 + 2\text{LiH} + 4\text{H}_2 \]

In the first step, MgH₂ is desorbed and Mg is formed. After that, LiBH₄ desorb and LiH and MgB₂ are formed, and they found that MgB₂-LiH composites could start to absorb hydrogen at 50 bar and 250°C, and have a much lower decomposition temperature compared to pure LiBH₄ (Bosenberg et al., 2007). The researchers further found that the formation of B at low hydrogen pressure during dehydrogenation prevented the rehydrogenation of Li-RHC. Barkhordarian et al. (2007; Bosenberg et al., 2007) proposed that the kinetic barriers for the formation of LiBH₄, NaBH₄ and Ca(BH₄)₂ were significantly reduced when B was replaced by MgB₂, and the kinetics of these borohydrides were enhanced. The higher reactivity of B in MgB₂ facilitate the formation of the [BH₄]⁻ complex. In addition, after replacing elemental B with MgB₂, the reaction enthalpy decreased by about 10 W mol⁻¹ H₂.

The 2LiBH₄+MgH₂ system has different hydrogen evolution reaction paths under different hydrogen back pressures and temperatures. Only under suitable conditions (e.g., 350°C, 5.5 bar), LiBH₄ will desorb with MgH₂ to form MgB₂ and release hydrogen; otherwise, the dehydrogenation process of the system is the respective decomposition reactions of LiBH₄ and MgH₂ (Mao et al., 2013; Kim et al., 2015; Shao et al., 2015).

Nakagawa et al. (2007) found the effect of hydrogen back pressure on the dehydrogenation of Li-RHC, and studied the formation of MgB₂ when dehydrogenation back pressure and inert gas were applied at 450°C, and found that only under hydrogen back pressure will MgB₂ be formed, and the formation of MgB₂ is considered to be a sign of a reversible reaction and is the key to the re-formation of LiBH₄ in the reverse reaction. When heated at a back pressure below 3 bar, the LiBH₄+MgH₂ reaction product hardly has MgB₂, but when the back pressure rises to 5 MPa, the product tends to be MgB₂ (Shaw et al., 2010; Gosalawit-Utke et al., 2011; Zhou et al., 2012).

In addition to Li-H-MgB₂ composites, Li-Al–B–H is also a promising Li-RHC (Yang et al., 2007; Zhang et al., 2009; Ravnsbaek and Jensen, 2012; Ye et al., 2021). Liu et al. studied LiBH₄–AlH₃ composites and found that AlH₃ can destabilize LiBH₄. The LiBH₄–AlH₃ composite releases about 11.0 wt% hydrogen at 450°C for 6 h, and the kinetic performance is much better than that of pure LiBH₄. In addition, AlH₃ also improves the reversibility of LiBH₄ in LiBH₄–AlH₃ composites, and the decomposition kinetics of LiBH₄ is enhanced with the increase of AlH₃ content. The 2LiBH₄ + AlH₃ composite can release 82% of the hydrogen capacity of LiBH₄ within 29 min at 450°C (Liu et al., 2016; Liu et al., 2017).

Another destabilizing system that has received much attention is the Li–B–N–H composite system. The H atom in the [BH₄]⁻ group in LiBH₄ tends to gain electrons and is negatively charged (H⁻), and the H atom in NH₃ or LiNH₂ tends to lose electrons and is positively discharged (H₃⁺). H₃⁺ and H⁻ in the composite system will interact to generate hydrogen bonds, and the samples will interact during heating. It is easier to release hydrogen at low temperature than pristine LiBH₄.

Johnson et al. (2009) found that at normal temperature and pressure, LiBH₄ can react with NH₃ to form LiBH₄-NH₃. When the temperature rises to about 40°C, NH₃ will be released from LiBH₄-NH₃ and become pure LiBH₄ instead of hydrogen. Pinkerton et al. (2005) studied the LiBH₄–LiNH₂ composite as hydrogen storage material for the first time. When LiBH₄ and LiNH₂ were subjected to high-energy ball milling at a molar ratio of 1:2 or heated to above 95°C, the mixture would in situ generate a new type of hydrogen storage material Li₃BN₄H₆. The hydrogen storage capacity of the system is as high as 11.9 wt %, and the melting point is 190°C. The hydrogen releasing amount is 10 wt% at 250–350°C.

In a word, thermodynamic destabilization is an efficient method to tailor the hydrogen storage performances of LiBH₄.

**Kinetic improvement**

Kinetics is another point that should be considered to improve the hydrogen storage properties of LiBH₄. Catalysis and nanoconfinements are two common methods to improve the kinetics of LiBH₄.

It was found that the effects of many metal elements, metal oxides and halides on LiBH₄ were both destabilizing and catalysis. Fang et al. (2008) found that the Ni/Co/Fe borides produced by the reaction between the metal element and LiBH₄ can catalyze the reaction. A composite of LiBH₄ and single-wall nanotubes (SWNT) can release 11.4 wt% of hydrogen within 50 min at 450°C after ball milling. Wang et al. (Kang et al., 2013; Wang et al., 2013; Wang et al., 2014a; Wang et al., 2014b; Wang et al., 2014c) studied the effect of TiF₃ and Nb₂O₅ doping on the
LiBH$_4$–MgH$_2$ system by using a three-step preparation method of mixture pre-grinding, isothermal treatment and co-grinding with MgH$_2$. The study found that NbB$_2$ and TiB$_2$ formed during hydrogen desorption can effectively improve the performances of LiBH$_4$–MgH$_2$ system. The reason for improving the cycling stability of the LiBH$_4$–MgH$_2$ system is that the reaction products of TiF$_3$ and NbO$_3$ with LiBH$_4$–MgH$_2$ are nucleating agents, which can promote the formation of MgB$_2$, thereby promoting the cycling stability.

Cai et al. (2014) studied the catalytic effect of different forms of nanostructured CoB on the hydrogen absorption and desorption process of LiBH$_4$, and found that the catalytic effect of CoB is roughly in the order of mulberry-like > bayberry-like > chain-like > sheet-like > rod-like, and it is proportional to the specific surface area. At 200°C, the mulberry-like and bayberry-like CoB catalyzed LiBH$_4$ have the best hydrogen evolution properties, and the hydrogen releasing amounts of the two CoB-catalyzed LiBH$_4$ were 4.6 wt% and 4.8 wt%, respectively. The mulberry-like CoB exhibited the best catalytic effect at 350°C, which obtained 10.4 wt% hydrogen from LiBH$_4$ with almost complete reversibility at 400°C and 10 MPa. Moreover, at the fourth cycle 9.6% of hydrogen can still be released.

Among many metal halides, TiCl$_3$ and TiF$_3$ have the most significant catalytic effects and have been widely studied. Adding TiCl$_3$ or TiF$_3$ can reduce the initial dehydrogenation temperature of LiBH$_4$ to about 100°C, and TiF$_3$ has a more significant catalytic effect. Ti halides react with LiBH$_4$ to form Ti hydrides and Li halides when heated, and the in-situ formation of Ti hydrides can effectively improve the cyclic dehydrogenation performance of LiBH$_4$. Ming et al. (2008) studied the LiBH$_4$ + 0.2MgCl$_2$ + 0.1TiCl$_3$ composite catalytic system, the material can desorb 5 wt% of hydrogen at 400°C, and can absorb 4.5 wt% of hydrogen at 600°C and 7 MPa after dehydrogenation.

Zhang et al. (2017) (Li et al., 2017) studied the effect of Co(OH)$_2$, CoO$_2$, and CoO on the catalytic performance of LiBH$_4$–2LiNH$_2$. It was found that the three catalysts were in situ reduced to form metallic Co element during the heating process, and then catalyzed the molten LiBH$_4$–2LiNH$_2$ sample. The hydrogen desorption temperature was effectively lowered. The initial dehydrogenation temperature of the LiBH$_4$–2LiNH$_2$–0.05Co(OH)$_2$ sample was reduced to 70°C, which is the lowest dehydrogenation temperature reported for this system so far.

Nanofluidification is another method to improve the kinetics of LiBH$_4$, which is to fill the material into the nanopores, and use the interaction between the material and the nanopores to promote the reaction or limit the phase separation during sorption process. Based on this, the confinement frame material must have a high specific surface area and porosity in order to improve the loading rate and avoid the collapse of the porous material during the hydrogen absorption and desorption cycle. At the same time, the material needs to have good chemical inertness to avoid reaction with the hydrogen storage material. Materials suitable for nanoconfined include carbon-based materials (carbon aerogel/activated carbon/ordered mesoporous carbon), metal-organic frameworks (MOFs), and mesoporous silica (SBA-15), etc. The traditional method of grain refinement, such as high-energy ball milling, gradually refines the grain through the collision between the ball and the tank. But such method is still prone to lead to the agglomeration of nanoparticles and re-agglomeration into larger particles. Different from high-energy ball milling, the method of nanoconfined is to confine the hydride particles in the pores of the frame material, which can obtain finer particles than the ball milling method, and the particles does not agglomerate during the hydrogen absorption and desorption cycle, which increases the cycling stability. At the same time, it also shortens the distance of hydrogen diffusion, and increases the number of grain boundaries, which is conducive to the progress of hydrogen absorption and desorption reactions. The schematic diagram of preparing nanostructured metal coordination hydrides or metal hydrides by ball milling, solution impregnation and melt injection methods is shown in Figure 3.

Liu et al. (2011) studied the confinement of LiBH$_4$ in porous carbon with a pore size of more than 2 nm, which can effectively reduce the initial hydrogen desorption temperature of LiBH$_4$ to 220°C. They further found that confining LiBH$_4$ in highly ordered nanoporous carbon will lead to the disappearance of the diffraction peaks for phase transition and melting of LiBH$_4$.

Xia et al. (2017) confined LiH in graphene, and then reacted LiH with B$_2$H$_6$ to generate nanoconfined LiBH$_4$ as shown in Figure 4. The obtained material can dehydrogenate about 7.6 wt% % at 280°C, and dehydrogenate about 9.7 wt. % within 60 min at 340°C. After absorbing hydrogen at 320°C and 100 bar, it still has 7.5 wt% of capacity after five cycles of hydrogen absorption/desorption.

Gross et al. (2008) confined LiBH$_4$ into the pores of carbon gels, and at 300°C, the nanostructured hydrides formed by filling LiBH$_4$ in the bulk of porous carbon aerogels. The measured hydrogen evolution rate was higher than that of bulk materials. The rate of hydrogen evolution is 50 times faster than the bulk materials. At the same time, it was found that compared with the bulk LiBH$_4$, the hydrogen desorption activation energy of the nanoconfined LiBH$_4$ was reduced from 146 kJ mol$^{-1}$ to 103 kJ mol$^{-1}$, and the hydrogen desorption temperature was reduced by 75°C. The nanostructured LiBH$_4$ also had a better hydrogen absorption and desorption cycle performance.

Jensen (Gosalawit-Itke et al., 2011; Gosalawitutke et al., 2012) et al. melted 2LiBH$_4$–MgH$_2$ into carbon aerogel scaffolds and found that the performance of 2LiBH$_4$–MgH$_2$ has been significantly improved, and 90% of the hydrogen can be released within 90 min. The non-confined material can only release 34% of the hydrogen. Through further research, the research group melted and infiltrated 2LiBH$_4$–MgH$_2$–0.13TiCl$_4$ in the carbon aerogel scaffold, and
then tested the hydrogen absorption and desorption performance. It was found that TiCl$_4$ and LiBH$_4$ were successfully nanoconfined in carbon aerogel scaffolds, while MgH$_2$ was only partially confined. Heated at 25°C–500°C for 5 h, the nano-confined 2LiBH$_4$–MgH$_2$–0.13TiCl$_4$ released up to 99% of the theoretical hydrogen storage capacity, while the nano-confined 2LiBH$_4$–MgH$_2$ was only 94%. At the same time, the kinetics are also greatly improved. To desorb 3.6 wt% H$_2$ during...
the first dehydrogenation, the nanoconfined 2LiBH$_4$–MgH$_2$–0.13TiCl$_4$ takes 1.5 h, while the nanoconfined 2LiBH$_4$–MgH$_2$ needs 3.5 h. Moreover, the TiCl$_4$ doped material possesses a dehydrogenation rate twice of the undoped material. This indicates that combination of catalysis and nanoconfinement will lead to the further improvement of the LiBH$_4$-based hydrogen storage material.

Verkuijlen et al. (2012) combined the nanoconfinement of LiBH$_4$ in nanoporous carbon with the addition of nickel. Nickel nanoparticles of 5–6 nm were deposited in porous carbon and then melt infiltrated with LiBH$_4$. The addition of nickel has only a slight effect on the hydrogen desorption of LiBH$_4$, but significantly improves the cycling performance of LiBH$_4$ under mild conditions.

Although the nanoconfinement method can effectively improve the thermodynamic and kinetic properties of hydrogen storage materials, there are still many key issues to be solved, such as how to confine a large number of hydrogen storage materials into nanopores and how to achieve a high filling efficiency.

To briefly summary, LiBH$_4$ possesses a very high hydrogen capacity but suffers from high thermal stability and poor reversibility. Catalized LiBH$_4$-based composite such as LiBH$_4$–MgH$_2$ composite with proper catalysts addition can reversibly absorb and desorb hydrogen with high capacity and favored kinetics.

**NaBH$_4$**

NaBH$_4$ is a common chemical reducing agent in the laboratory, with high thermal stability, and requires a decomposition temperature of 300°C in dry air. The theoretical hydrogen content of NaBH$_4$ is 10.7 wt%, and the volumetric hydrogen storage density is 115 g L$^{-1}$. The hydrogen desorption temperature of pure NaBH$_4$ is relatively high and needs to be heated to 565°C. The hydrogen desorption reaction of NaBH$_4$ is as Eq. 4. NaBH$_4$ has a cubic structure at room temperature, which is the same as the crystal structure of NaCl (Urgnani et al., 2008; Liu and Li, 2009; Garroni et al., 2010; Martelli et al., 2010).

$$\text{NaBH}_4 \rightarrow \text{NaH} + \text{B} + 3/2\text{H}_2 \rightarrow \text{Na} + \text{B} + 2\text{H}_2 \quad (4)$$

At present, the methods to improve the performance of NaBH$_4$ include anion and cation substitution method, destabilization method, catalysis, and particle size nanometerization. It was found that adding MgH$_2$ or YF$_3$ can effectively improve the thermodynamic properties of NaBH$_4$. The YB$_6$ and Mg$_2$ formed during the hydrogen evolution process are more stable than the metal elements Y and B, which are the key to the reversible release of NaBH$_4$ (Garroni et al., 2009).

Ngene et al. (2011) used the liquid melting method to obtain nano-NaBH$_4$ to achieve reversible hydrogen absorption and desorption performances. The initial hydrogen desorption temperature of nano-sized NaBH$_4$ was reduced from 470°C of the matrix to below 250°C, and the reactant after dehydrogenation can be re-hydrogenated to NaBH$_4$ under the condition of 60 bar H$_2$ and 325°C. However, since the pores of this method are open, Na is volatile during the hydrogen evolution process, and only 43% of the hydrogen is stored during the cycle. Milanesi et al. (2011) (Christian and Aguey-Zinsou, 2012) limited the size of NaBH$_4$ particles to a few nanometers (<30 nm) by anti-solvent precipitation, which lowered its melting point and lead to hydrogen desorption beginning at 400°C. These nanoparticles can form a core after reacting with nickel chloride on their surface, which can achieve effective nanoconfinement for melting NaBH$_4$ cores and their dehydrogenation products (Figure 5). Moreover, the reversibility and fast kinetics due to short diffusion lengths is also obtained.

When the catalyst is added to the hydride through ball milling, the catalyst can be uniformly distributed on the surface and grain boundaries of the hydride, which is beneficial to the dissociation and recombination of hydrogen in the hydride. It was found that adding Ti, TiH$_2$, TiF$_3$ are beneficial to improve the thermodynamics of NaBH$_4$, reducing the hydrogen desorption temperature of NaBH$_4$, and among them, TiF$_3$ has the best catalytic effect. TiF$_3$ and NaBH$_4$ will react with each other to form TiB$_2$, and this formed TiB$_2$ will catalyze the decomposition of the remaining NaBH$_4$, and TiB$_2$ will also catalyze the regeneration of NaBH$_4$ to promote the stability of the cycle (Garroni et al., 2009).

In general, the research on NaBH$_4$ mainly focus on its hydrolysis or methanolysis to generate hydrogen and limited papers on its dehydrogining and rehydrogining were reported (Santos and Sequeira, 2011). This is partially due to the high thermal stability and rather slow kinetics. Therefore, NaBH$_4$ is more suitable for hydrogen generation by a hydrolysis or methanolysis process (Saka, 2021; Saka and Balbay, 2021; Saka, 2022a; Saka, 2022b; Saka, 2022c; Saka and Balbay, 2022).

**Mg(BH$_4$)$_2$**

The mass hydrogen storage density of Mg(BH$_4$)$_2$ is 14.8 wt%, and the volume hydrogen storage density is 112 g L$^{-1}$. Mg(BH$_4$)$_2$ has a variety of crystal structures, and each crystal structures can transform into the other at different temperatures, which is determined by its own coordination of two [BH$_4$]$^-$, thus increasing the complexity of the molecular structure. There are about seven crystal structures reported for Mg(BH$_4$)$_2$, but although there are many crystal forms, they all transform to high-temperature stable phase before hydrogen evolution, and this will lead to that different crystal forms have little effect on its hydrogen absorption and desorption properties.

The decomposition of α-Mg(BH$_4$)$_2$ first undergoes a phase transition at 190°C, and then decomposes into MgH$_2$, Mg and
MgB$_2$ with the increase of temperature. The decomposition is divided into two steps (Chłopek et al., 2007; Li et al., 2007):

\[
\begin{align*}
\text{Mg}(\text{BH}_4)_2 & \rightarrow \text{MgH}_2 + 2\text{B} + 3\text{H}_2 \quad (11.1 \text{ wt\%}) \quad (5) \\
\text{MgH}_2 + 2\text{B} & \rightarrow \text{MgB}_2 + \text{H}_2 \quad (4.2 \text{ wt\%}) \quad (6)
\end{align*}
\]

The desorption temperature of Mg(BH$_4$)$_2$ is lower than that of LiBH$_4$, but a stable MgB$_2$H$_2$ is generated during the thermal decomposition of Mg(BH$_4$)$_2$, which makes Mg(BH$_4$)$_2$ have high thermodynamic stability and kinetic barrier (Yan et al., 2015). It can only be recovered under the conditions of 95 MPa and 400°C, so improving its hydrogen storage performance has become a research hotspot.

Adding transition metals and their compounds is a common method to improve hydrogen storage materials, and Ti-based compounds are one of the most commonly used additives to improve the performance of hydrogen storage materials. Bardaji et al. (2011) made TiCl$_3$ and Mg(BH$_4$)$_2$ into nanocomposite materials, and found that the initial hydrogen desorption temperature was reduced to above 100°C, and further study shows that Mg(BH$_4$)$_2$ doped with NbCl$_5$-TiCl$_3$ nanocomposite could lead to that 5 wt% hydrogen could be released when the dehydrogenation temperature was lowered below 300°C, but the cycle performance of Mg(BH$_4$)$_2$ was not improved by doping.

Saldan et al. (2015) studied the effect of nickel-based additives such as nano-Ni, NiCl$_2$, NiF$_2$, and Ni$_3$B on the hydrogen absorption and desorption performance of Mg(BH$_4$)$_2$. The Mg(BH$_4$)$_2$ was partially decomposed, and amorphous Ni$_3$B appeared in the decomposition products. Ni$_3$B did not participate in the reaction in the process of re-absorbing hydrogen. The addition of Ni$_3$B can also effectively improve the hydrogen desorption kinetics of Mg(BH$_4$)$_2$, and the in-situ formed compound Ni$_3$B is the main reason for improvement of the kinetic properties of Mg(BH$_4$)$_2$. Wang et al. (2020b) carried out ball milling of
LiBH$_4$ and MgCl$_2$ to synthesize Mg(BH$_4$)$_2$ in situ. In fact, the temperature was reduced to 126.9°C, and the activation energy was reduced from 487.99 kJ mol$^{-1}$ to 120.1 kJ mol$^{-1}$ compared with the original Mg(BH$_4$)$_2$. Therefore, the hydrogen storage kinetics of Mg(BH$_4$)$_2$ is significantly improved. Further investigation showed that by adding NbF$_5$ into the composites it can also lead to better hydrogen storage properties than pristine and amorphous Mg(BH$_4$)$_2$. The catalyzed composite starts to release hydrogen at about 120°C with a total capacity of 10.04 wt%. The reversibility of the catalytic composite was also improved, and the catalytic composite could still release 4 wt% H$_2$ in the third and fourth cycles.

Combining LiBH$_4$ to form the LiBH$_4$–Mg(BH$_4$)$_2$ composite system can also improve its hydrogen storage performance of Mg(BH$_4$)$_2$. Zhao-Karger et al. (2011) found that when LiBH$_4$ and Mg(BH$_4$)$_2$ were mixed and ball-milled with molar ratio close to 1:1, the composite system would eutectic and release hydrogen at about 170°C, compared with pure Mg(BH$_4$)$_2$. The dehydrogenation temperature of the composite system decreased by about 100°C. Chen et al. (2012) used a Co-based catalyst to catalyze the hydrogen release of the LiBH$_4$–Mg(BH$_4$)$_2$ system, which could make the composite system start to release hydrogen from 155°C, and at the same time, the hydrogen release rate of the system was increased by 1.6 times at 270°C.

Although researchers have tried various methods to improve the hydrogen storage performance of Mg(BH$_4$)$_2$, its initial hydrogen desorption temperature is still high, and the kinetic performance of Mg(BH$_4$)$_2$ at low temperature still needs to be improved.

**Ca(BH$_4$)$_2$**

Ca(BH$_4$)$_2$ is soluble in water but does not undergo hydrolysis reaction. It can exist stably in dry air, and begins to decompose at 360°C. The theoretical mass hydrogen storage density is 11.6 wt%, while 9.6 wt% of hydrogen can practically be released.

The decomposition of Ca(BH$_4$)$_2$ to release hydrogen is a multi-step reaction process accompanied by the formation of various possible intermediates. The reaction equation is as Eq. 6. At 347°C–387°C, Ca(BH$_4$)$_2$ decomposes to form CaH$_2$ and some intermediate products, and at 397–497°C, the intermediate products decompose to form amorphous B and CaB$_6$. Due to the complexity of the hydrogen absorption and desorption process of Ca(BH$_4$)$_2$, it is quite difficult to improve its hydrogen absorption and desorption kinetics.

$$3\text{Ca(BH}_4\text{)}_2 \rightarrow 2\text{CaH}_2 + \text{CaB}_6 + 10\text{H}_2 \quad (6)$$

Kim et al. (2008) studied the effect of transition metal halides on the dehydrogenation performance of Ca(BH$_4$)$_2$, and found that NbF$_5$ would reduce the onset hydrogen desorption temperature of Ca(BH$_4$)$_2$ by 20°C. Under the conditions of 350°C and 90 bar H$_2$, reversible uptake of 5 wt% H$_2$ can be achieved. They believe that the catalytic effect of NbF$_5$ may be because its melting point is only 77°C, which is melted during the ball milling process, so that it can be better distributed in Ca(BH$_4$)$_2$. In addition, NbF$_5$ can make Ca(BH$_4$)$_2$ form CaH$_2$–F$_x$ solid solution phase in the process of dehydrogenation, which lead to the reverse reaction to generate CaH$_2$ at 350°C and 90 bar. Minella’s further research (Bonatto Minella et al., 2011; Bonatto Minella et al., 2013; Bonatto Minella et al., 2015) found that when TiF$_4$ and NbF$_5$ catalysts were added, Ca(BH$_4$)$_2$ could generate CaB$_6$ after dehydrogenation, and the formation of CaB$_6$ was the key to the cyclic hydrogen absorption and desorption of Ca(BH$_4$)$_2$. The Ca(BH$_4$)$_2$ sample added with TiF$_4$ and NbF$_5$ catalysts can realize the reverse reaction at 350°C and 145 bar.

Chu et al. (2011) studied the composite system of Ca(BH$_4$)$_2$–2Mg(NH$_2$)$_2$ and Ca(BH$_4$)$_2$–2Ca(NH$_2$)$_2$, and found that the initial hydrogen desorption temperature of the composite system is 100°C lower than that of pure Ca(BH$_4$)$_2$. At 480°C, Ca(BH$_4$)$_2$–2Mg(NH$_2$)$_2$ can release 8.3 wt% hydrogen, and Ca(BH$_4$)$_2$–2Ca(NH$_2$)$_2$ can release 6.8 wt% hydrogen. Compared with pure Ca(BH$_4$)$_2$ samples, both have lower activation energy for dehydrogenation, and better hydrogen storage performance of Ca(BH$_4$)$_2$.

As a high-capacity hydrogen storage material, the hydrogen storage performance of Ca(BH$_4$)$_2$ can be improved by introducing catalysts and other means. But from the application point of view, there are still many issues need to be addressed for Ca(BH$_4$)$_2$. Many problems remain to be studied. For example, NbF$_5$, which has the best catalytic effect among the catalysts, can only reduce the dehydrogenation temperature by 20°C. Although the forming composite of Ca(BH$_4$)$_2$ with other metal borides and amides can improve the performance of Ca(BH$_4$)$_2$ to a certain extent. However, the hydrogen desorption temperature of the composite system is still high, and the purity of hydrogen in the released gas is not high enough. It is still the research focus of Ca(BH$_4$)$_2$ hydrogen storage materials to find more effective methods to improve the hydrogen storage performance of Ca(BH$_4$)$_2$.

**Conclusion**

The metal borohydrides commonly found as LiBH$_4$, NaBH$_4$, Mg(BH$_4$)$_2$, and Ca(BH$_4$)$_2$ all have a high hydrogen capacity higher than 10 wt%, which is much higher than that of the materials that have been practically applied. Borohydrides also have cyclic hydrogen absorption and desorption properties, so borohydrides are one of the main research objects of solid-state hydrogen storage materials. In this paper, the common methods of borohydride
modification, such as destabilization, catalysis, nanoconfinement, etc., are summarized. These methods have improved the hydrogen storage performance of borohydrides to a certain extent, but still cannot meet the comprehensive application requirements of fast kinetics, near room temperature operation, stable hydrogen absorption and desorption cycle performance, and long cycle life. Therefore, the research on borohydrides still needs to be done to find more effective methods to improve their hydrogen storage performance.

To tailor the hydrogen storage properties of metal borohydrides, the thermodynamic destabilization and kinetic improvement should be simultaneously considered by combination of various modification methods, which is the future research direction of metal borohydrides. In addition, prototype based on some metal borohydrides should be built to verify the practical hydrogen storage performances. Although the operating temperatures of metal borohydrides are relatively high compared with the traditional hydrogen storage alloys, the practical application is still possible when combined with high-temperature solid oxide fuel cell. Therefore, metal borohydrides are still promising materials for hydrogen storage.

Author contributions

JL, YM, and JY: Writing-Original draft preparation. LS and DG: Writing-Reviewing. PX: Funding and Editing.

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Conflict of interest

JL, YM, LS, DG, and PX were employed by State Grid Jiangsu Electric Power Co., Ltd. Research Institute.

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Improved reversible dehydrogenation of 2LiBH$_4$–MgH$_2$ composite by the reversible dehydrogenation properties of LiBH$_4$–MgH$_2$ composite by tailoring NMR.

Destabilized LiBH$_4$.

Superior reversible hydrogen storage properties.

Hydrogen capacity and synergetic mechanism of 2LiBH$_4$–MgH$_2$ composite.

Using N-doped hybrid g-C$_3$N$_4$–SiO$_2$ composites with ammonia as a nitrogen source.

Dissolution of magnesium borohydride (Mg(BH$_4$)$_2$) with Ni-based additives.

Improved hydrogen storage properties of LiBH$_4$ with Ti$_2$ polycrystalline Ni$_3$S$_2$ polymorphs from Ti-catalyzed nanocrystalline LiBH$_4$ with Ti-catalyzed nanocrystalline.

Reversibility of 2LiBH$_4$–MgH$_2$ composite.

Reaction of LiBH$_4$ wrapped with graphene toward stable hydrogen storage.

Development of lithium borohydride-based materials for hydrogen storage.

In-situ construction of hydrogenated carbon nanospheres with high loading, low dehydrogenation temperature, superior kinetics, and favorable reversibility.

Superior catalytic activity of in situ reduced metallic Co for hydrogen storage in a Co(OH)$_2$-containing 2LiBH$_4$-Ni composite.

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Supported Ni catalyst in LiBH$_4$ with Ti-catalyzed nanocrystalline LiBH$_4$ with Ti-catalyzed nanocrystalline.

Reaction of LiBH$_4$ with Ni-based additives.

Surface modification of oxygen-doped g-C$_3$N$_4$ nanoparticles by carbon vacancy for efficient dehydrogenation of sodium borohydride in methanol.

Structural changes observed during the reversible dehydrogenation of Mg(BH$_4$)$_2$, with Ni-based additives.

Improved dehydrogenation reactions and kinetics of 2LiBH$_4$–MgH$_2$ composite.

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