Investigation on LiBH$_4$-CaH$_2$ composite and its potential for thermal energy storage

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The LiBH$_4$/CaH$_2$ composite are firstly studied as Concentrating Solar Power Thermal Storage Material. The LiBH$_4$/CaH$_2$ composite according to the stoichiometric ratio are synthesized by high-energy ball milling method. The kinetics, thermodynamics and cycling stability of LiBH$_4$/CaH$_2$ composite are investigated by XRD (X-ray diffraction), DSC (Differential scanning calorimeter) and TEM (Transmission electron microscope). The reaction enthalpy of LiBH$_4$/CaH$_2$ composite is almost 60 kJ/mol H$_2$ and equilibrium pressure is 0.482 MPa at 450 °C. The thermal storage density of LiBH$_4$/CaH$_2$ composite is 3504.6 kJ/kg. XRD results show that the main phase after dehydrogenation is LiH and CaB$_6$. The existence of TiCl$_3$ and NbF$_5$ can effectively enhance the cycling performance of LiBH$_4$/CaH$_2$ composite, with 6–7 wt% hydrogen capacity after 10 cycles. The high thermal storage density, high working temperature and low equilibrium pressure make LiBH$_4$/CaH$_2$ composite a potential thermal storage material.

Solar energy is the most plentiful renewable and clean alternative to fossil fuels. International Energy Agency (IEA) points out that solar energy will make up 22 percent of the global electricity, and it is possible that solar photovoltaics (PV) and concentrating solar thermal (CST) power technology will play roughly equal, but complementary roles by 2050. The CST power technology can store energy as heat that can be assessed on demand to generate electricity when PV technology is inefficient, such as at night or during rainy days.

As thermal storage (TS) material is the key element in the CST, improving the energy storage density and working temperature have great value on power generation efficiency and cutting back on the cost. There are three basic methods of thermal storage. Considering the condition of CST plants, sensible heat storage with molten salt is of low-efficiency and can be corrosive sometimes and latent heat storage using NaNO$_3$ is of high flammability and reactivity and is uncertain over its longevity. Thermochemical heat storage materials have quite high energy storage density, in which hydrides’ exceed 1700–4000 kJ kg$^{-1}$ (10~30 times more than molten salts’ energy storage density and 4~10 times more than phase change materials’ energy storage density). The characteristics of common and potential thermal storage materials are listed in Table 1.

Among all hydrides, complex hydrides such as LiBH$_4$, NaAlH$_4$ and NaBH$_4$ possess a quite high forming enthalpy due to the transition to an ionic or covalent compound of metals upon hydrogen absorption. It seems that complex hydrides are promising thermal storage materials in CST plants.

In fact, LiBH$_4$ is mostly researched as a hydrogen storage material due to the second highest hydrogen content (18.4 wt.%) of all alanates and boranates. The thermal hydrogen desorption of pure LiBH$_4$ starts at ~320 °C and proceeds mainly in the temperature region 400–600 °C, which is in accordance with the working temperature of thermal storage material in CST plant.

However, the sluggish kinetics and poor reversibility of LiBH$_4$ are the problems that limit its use in hydrogen storage. The destabilization was proposed to change the reaction process by adding a reactive additive. Thus, many new systems have been proposed based on DFT calculation of reaction enthalpies in multi-component systems. Among all systems, LiBH$_4$-CaH$_2$ is one of promising composites that are suitable for thermal storage due to its onset temperature. And this reaction can produce around 11.7 wt% hydrogen. But Yang reported that...
LiBH₄-CaH₂ composite is irreversible under the condition tested (350 °C, 150 bar). The sluggish kinetics in LiBH₄-CaH₂ composite is another problem that need to be solved. Additives, such as TiCl₃, V₂O₅, TiF₅, TiO₂, LiNH₂, NbF₅, NbCl₅, were investigated their effects on the kinetics and cycling performance of LiBH₄-CaH₂ composite. Results show that TiCl₃ additive is very effective in lowering activation energy of dehydrogenation and enhancing reversibility (about 9 wt% hydrogen reversibly). Besides, Lim reported that LiBH₄-CaH₂ composite with NbF₅ maintains a reversible hydrogen storage capacity of about 6 wt% at 450 °C.

But the enthalpies of pure LiBH₄-CaH₂ composite and LiBH₄-CaH₂ composite with additives have not been reported exactly. Pinkerton reported the estimated enthalpy of reaction 2 at 400 °C is ΔH = 59.2 kJ/mol H₂. Lim reported that the reaction enthalpy of LiBH₄-CaH₂ composite is estimated to be 56.5 kJ/mol H₂ at 305 °C. But according to HSC thermochemical database, the enthalpy is 66.2 kJ/mol H₂ at room temperature.

In this research, the enthalpy ΔH and equilibrium pressure of desorption according to reaction 2 are determined by PCT (pressure, concentration, and temperature) measurements. Only LiBH₄-CaH₂ without catalysts was measured due to the fact that influence the thermodynamics of the mixture as Ti-doped NaAlH₄. The additives such as TiCl₃ and NbF₅ are investigated their effect on kinetics and cycling performance of LiBH₄-CaH₂ composite.

### Experimental Details

LiBH₄ (≥95% pure), purchased from Acros Organics, CaH₂ (≥98% pure) and NbF₅ (≥99% pure), purchased from Alfa Aesar, and TiCl₃ (≥95% pure), synthesized by the reaction of titanium tetrachloride with metallic titanium in molten CaCl₂ and the enrichment process with HCl gas, were utilized directly without any further purification. The mole ratio of LiBH₄-CaH₂ according to reaction 2 is 6:1. The pure LiBH₄-CaH₂ composite and LiBH₄-CaH₂ composite doped with different additives (1 mol% TiCl₃, and 5 wt% NbF₅) was ball-milled under argon atmosphere by using a QM-2B high energy mill (Nanjing NanDa Instrument Plant) at a rotating speed of 1200 rpm for 1 h. Two kinds of stainless steel balls with 4 mm and 8 mm diameters were added with a ball-to powder weight ratio of 12.5:1. Typically, 4 g mixture was sealed in the stainless steel vessel within a high purity argon atmosphere during milling. To avoid excess heating of the stainless steel vessel, there were 10 min intervals between each 5 min milling process.

The isothermal desorption was measured by using the Sieverts-type pressure-composition-temperature (P-T-C-T) apparatus (General Research Institute for Nonferrous Metals, China). The maximum pressure, maximum vacuum and maximum temperature of this apparatus is 10 MPa, 10⁻¹ Pa and 800 °C, respectively. Typically, 60–100 mg sample was loaded into the vessel, and then heated up to 450 °C under 0.1 MPa hydrogen atmosphere. Following the dehydrogenation, the samples were subjected to rehydrogenation studies at 450 °C under 8 MPa hydrogen pressure for 16 h. It should be noted that the additional content was not taken into consideration when calculating the released hydrogen. The PCI (Pressure-composition isotherms) curves were measured at 405 °C, 420 °C, 435 °C, 450 °C and 465 °C, respectively.

The phase structure of the samples after milling and dehydrogenation was examined by an XP21VAHF X-ray Diffractometer (XRD with Cu Kα radiation, 40 kV, 300 mA), with the 20 angle ranged from 10° to 90° with a scanning rate of 10° min⁻¹. X-ray photoelectron spectroscopy (XPS) was performed with the PHI-5300 spectrometer. The morphology and phase constitution of all samples after ball milling and desorption were observed by and transmission electron microscopy (Tecnai G2 F30 S-TWIN, FEI, USA). Simultaneous differential scanning calorimetry (DSC) and Thermogravimetric Analysis (TGA) experiments were conducted under 50 mL min⁻¹ argon flow in a NETZSCH STA 449F3 Jupiter instrument between 50 °C and 500 °C with a heating rate of 5 °C min⁻¹. The samples were transferred to Al₂O₃ crucibles under argon atmosphere for the DSC-TGA measurements.

All samples handling was performed under strictly inert conditions (>99.99% Ar atmosphere) in the glove box (Mikrouna, Super-750) equipped with oxygen/humidity sensors and recirculation system to avoid oxidation and moisture. Oxygen and H₂O levels were kept below 0.1 ppm.

### Results and Discussion

#### XPS characterization

The XPS results of three LiBH₄-CaH₂ composites after milling are presented in Table 1. The XPS results of three LiBH₄-CaH₂ composites after milling are presented in Fig. 1(a–c), which confirms the existence of element Li, B and Ca in both composites. Element Nb, F and Cl are identified in the catalyst-doped composite, while Ti are not discovered due to the low amount addition. The XRD results are presented in Fig. S1. There are only two obvious peaks in both composites, which are characterized as CaH₂. It can be inferred that the structure of LiBH₄ after milling becomes amorphous. No peaks of LiBH₄ or NbF₅ are detected. The XPS narrow spectra of ball-milled LiBH₄-CaH₂ composite are shown in Fig. 1(d). The

| Material                  | Sensible | Latent | Thermochemical |
|---------------------------|----------|--------|----------------|
|                          | Rock     | Concrete | Paraffin wax | NaNO₃ | CaCl₂·H₂O | MgH₂ |
| Specific heat capacity (kJ kg⁻¹) | 0.9      | 1.13    |       |       | 3.06 |       |
| Latent heat of fusion (kJ kg⁻¹) |         | 174.4   | 172   |       |       |       |
| Reaction enthalpy (kJ kg⁻¹)   |         |         |       |       | 433.6 | 2860 |

Table 1. Energy stored per mass of different storage materials.
The photo-emission spectrum of B 1 s at 187.8 eV corresponds to LiBH₄, while the existence of LiCl and NbF₅ are also convinced in Fig. S2. XPS results testify that LiBH₄ and TiCl₃ react during ball milling.

**Investigation on energy storage density.** The energy storage density is the most significant factor when evaluating a material is suitable for TS. The energy storage density to weight is related with the reaction enthalpy and molar mass. For dehydrogenation reaction of hydrides, the Van't hoff equation and DSC integration can be used to calculate the reaction enthalpy. Besides high energy storage density, low equilibrium pressure and high working temperature are also two important factors in selecting hydrides for TS.

**PCI curves and Van't Hoff Calculation.** The dehydrogenation PCI curves of pure LiBH₄-CaH₂ composite are shown in Fig. 2(a). Due to the sluggish kinetics, the pressure value in each platform can only be read after 4-hours waiting. Even so, the platform inclination is quite a lot, especially in low temperature condition. Considering the platform is a slope to some extent, the equilibrium pressures from 405 °C to 465 °C are calculated.
as the mean of pressure values in the platform. The equilibrium pressures of pure LiBH4-CaH2 composite from 405 °C to 465 °C are 0.2458 MPa, 0.3208 MPa, 0.4018 MPa, 0.4820 MPa and 0.5967 MPa, respectively. They are lower than the equilibrium pressures of reported thermal storage metal hydrides, such as MgH2, Mg2FeH6 and Ce2Mg17Hx. What’s more, the low equilibrium pressure makes LiBH4-CaH2 composite possible to be operated at higher temperature. The higher working temperature can increase overall solar to electricity conversion efficiency and reduce the cost in CST plants. The dehydrogenation capacity of pure LiBH4-CaH2 composite is mostly ranging from 10.5 wt% to 11.6 wt%, which is close to their theoretical value. The sluggish kinetics resulting from the relatively low temperature (405 °C) may account for the lower capacity (9.5 wt%). Only LiBH4-CaH2 without catalysts was measured due to the fact that influence the thermodynamics of the mixture as Ti-doped NaAlH4. Liu reported that LiCl forms during ball milling of 6LiBH4/CaH2/xTiCl3. LiF and CaF2 are observed after the ball milling reaction of NbF5 and LiBH4 or CaH2. Thermodynamics of pure LiBH4-CaH2 composite might have changed due to the formation of LiCl or LiF and CaF2.

A plot of ln P against 1000/T in Fig. 2(b) results in a nearly straight line. Calculation of ΔH = R · (ln P2 − ln P1) / (1/T2 − 1/T1) from ln P and 1/T values at 405 °C and 465 °C provides a ΔH of 60.555 kJ mol−1 H2. According to the reaction 2, a thermal storage density value of 3504.6 kJ kg−1 is calculated. It shows a superior capacity to sensible and latent thermal storage materials, even to thermochemical thermal storage materials shown in Table 1.

**DSC Calculation.** The DSC and TGA curves of pure LiBH4-CaH2 composite are shown in Fig. 3. There are mainly three endothermic peaks during the heating process. The endothermic effect at 108–112 °C is reversible and corresponds to polymorphic transformation of LiBH4. The second peak at 268–286 °C corresponds to the fusion of LiBH4. The third peak corresponds to the dehydrogenation behavior of LiBH4. The onset temperature is 392 °C and the peak temperature is 446 °C. According to TGA results, dehydrogenation reaction ends at 497 °C. The integration of DSC on temperature from 392 °C to 497 °C is calculated as enthalpy of reaction 2, with a value of 60.706 kJ mol−1 H2.

| Material | H2 content (wt%) | Enthalpy (kJ mol−1 H2) | TS density (kJ kg−1) | Equilibrium temperature at 1 bar [°C] |
|----------|------------------|------------------------|----------------------|-------------------------------------|
| MgH2     | 7.6              | 74.4                   | 2860                 | 280                                 |
| NaMgH3*  | 4.0              | 86                     | 1700                 | 380                                 |
| Mg2FeH6  | 5.5              | 77.4                   | 2106.5               | 320                                 |
| Mg2NiH6  | 3.6              | 62                     | 1116                 | 250                                 |
| CaH2     | 4.8              | 186.2                  | 4422.8               | 950                                 |
| Ce2Mg17Hx| 5.0              | 75.5                   | 1928.3               | 310                                 |
| LiBH4-CaH2 | 11.7            | 60.706                 | 3511.45              | 350                                 |
| LiBH4-CaH2-1 mol% TiCl3 | 11.6            | 59.354                 | 3316.64              | —                                   |
| LiBH4-CaH2-5 wt% NbF5 | 10.4            | 60.011                 | 3307.71              | —                                   |

**Table 2.** TS properties of three LiBH4-CaH2 composites and other potential TS composites.

*Calculated for the reaction NaMgH3 = NaH + Mg + H2.
results are in accordance with the Van't hoff calculation results. Comparing with actual TS density of MgH₂ (2147 kJ kg⁻¹), LiBH₄-CaH₂ composites shows a clear superiority.

**Investigation on kinetics.** The Fig. 4 shows the desorption behavior of three LiBH₄-CaH₂ composites. The addition of TiCl₃ significantly improves the dehydrogenation kinetics of LiBH₄-CaH₂ composite, while NbF₅ influence it in an opposite way. Both composites can release 9–10 wt% hydrogen in an hour. After 4 hours, the
pure composite and TiCl₃ doped composite shows a nearly theoretical hydrogen capacity (11.7 wt%), while NbF₅ doped composite only desorbs around 10 wt% hydrogen. TiCl₃ shows a remarkable impact on improving the desorption kinetics and maintaining the hydrogen capacity. Liu²² reported that LiCl formed through replacement reaction between LiBH₄ and TiCl₃ during ball milling can be incorporated into LiBH₄ to form solid solution LiBH₄·LiCl. It favorably changes viscosity, preserving the nano-sized phase arrangement formed after milling, leading to fast kinetics.

The XRD results of three LiBH₄·CaH₂ composites after dehydrogenation are shown in Fig. 5. The main phase of both composites is LiH and CaB₆, which is in accordance with reaction 2. The existence of phase CaO, LiOH/H₂O and LiBO₂ is due to the oxidation during the experiments. The remaining CaH₂ and B are identified in the pure composite after dehydrogenation. B is the product of LiBH₄ after dehydrogenation (shown in reaction 1),

Figure 7. TEM and SAED images: (a–d) pure LiBH₄·CaH₂ composite after 10 cycles; (e,f) TiCl₃ doped composite after 10 cycles; (g,h) of NbF₅ doped composite after 10 cycles.
which also explains why a little CaH₂ remains. The LiF and CaF₂ phase are detected in the NbF₅ doped composite, while no peaks of chlorides are identified in the TiCl₃ doped composite.

Investigation on reversibility and cycling stability performance. A test over 10 cycles was performed under very severe cycling conditions (desorption: 450 °C, 0.1 Mpa, 4 h; absorption: 450 °C, 8 Mpa, 16 h). The results are shown in Fig. 6. The initial hydrogen capacity of the pure composite and TiCl₃ doped composite shows a nearly theoretical hydrogen capacity (11.7 wt%), while NbF₅ doped composite only desorbs around 10 wt% hydrogen. The hydrogen capacity of both composites declines during cycling. It is worth mentioning that TiCl₃ doped composite can reversibly store 9 wt% hydrogen during first three cycles. After 10 cycles, the remaining hydrogen capacity of pure composite, NbF₅ doped composite and TiCl₃ doped composite is 3.8 wt%, 6.4 wt% and 7.1 wt%, respectively. TiCl₃ and NbF₅ seems effectively raise the cycling stability performance of LiBH₄–CaH₂ composite. The TEM images of pure LiBH₄–CaH₂ composite after 10 cycles are shown in Fig. 7(a–d). The main phases are small particles with a diameter of 3–6 nm, separately scattering. Particle aggregation shown in Fig. 7(c), which may result from the sintering, is also found. The diffraction ring in Fig. 7(d) is very obvious, indicating that amorphous structure is formed. The particle aggregation and amorphous structure of products accounts for the dramatic loss of hydrogen capacity of pure LiBH₄–CaH₂ composite during cycling. TEM images of TiCl₃ doped composite and NbF₅ doped composite after 10 cycles are shown in Fig. 7(e,f,g and h). The small particles with a diameter of 3–6 nm are both observed. However, the results of electron diffraction indicate that the TiCl₃ doped composite after 10 cycles is crystal structure, while NbF₅ doped composite after 10 cycles is amorphous structure. By analyzing the diffraction ring diameter, the crystal structure is assumed to be CaB₆. The amorphous structure of B is not good for the reverse reaction to produce LiBH₄, while the crystal structure of CaB₆ is in favor of the reverse reaction. This explains why TiCl₃ plays a more effective role in raising the cycling stability performance of LiBH₄–CaH₂ composite than NbF₅. Moreover, it is noteworthy that a graphene-like lamellar structure are found in NbF₅ doped composite after 10 cycles. The value of interlamellar spacing (d) is 0.3364 nm, which is corresponding to NbF₅. But the lamellar structure of NbF₅ is never reported. Thus, the d value of NbB₂ is 0.3321 nm, which is close to the 0.3364 nm. Minella reported that NbB₂ nanoparticles was observed after milling or upon sorption reactions of Nb-based Ca(BH₄)₂ doped composites. It is reasonable to be assume that a small amount of NbB₂ can also be formed in Nb-based LiBH₄–CaH₂ doped composites. It needs more research work to identify this graphene-like lamellar structure in NbF₅ doped composite.

Conclusion

The reaction enthalpy of LiBH₄–CaH₂ composite is almost 60 kJ/mol H₂ and equilibrium pressure is 0.482 MPa at 450 °C. The thermal storage density of LiBH₄–CaH₂ composite is 3504.6 kJ/kg. XRD results show that the main phase after dehydrogenation is LiH and CaB₆. The exsistence of TiCl₃ and NbF₅ can effectively enhance the cycling performance of LiBH₄–CaH₂ composite, with 6–7 wt% hydrogen capacity after 10 cycles. The high thermal sorstage density, high working temperature and low equilibrium pressure make LiBH₄–CaH₂ composite a potential thermal storage material.

Although the high price of starting materials, such as LiBH₄, will limit its usage, the LiBH₄–CaH₂ composite could serve as the additives for Magnesium-based alloys in TS. The research will be continued on the pair study of LiBH₄–CaH₂ composite with another metal hydride working at lower temperature.

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Author Contributions
Ping Li and Yang Li designed and conceived research. Yang Li wrote the manuscript. All authors read and approved the final version of the manuscript.

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