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Letter

Synthesis and dehydriding process of crystalline $Ce(BH_4)_3$

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ABSTRACT

The synthesis of a new borohydride with a theoretical hydrogen capacity of 6.5 wt% is reported. Both XRD and FTIR studies demonstrate that $Ce(BH_4)_3$ is obtained from mechanochemical reaction between $CeCl_3$ and $LiBH_4$. Dehydriding properties of $Ce(BH_4)_3$ were investigated using XRD, DSC and volumetry using a Sievert-type device. Thermal decomposition of $Ce(BH_4)_3$ led to 3.5 wt% hydrogen release in a multi-step process, involving an unknown intermediate compound and CeH_2. It was observed that $Ce(BH_4)_3$ is partially reversible under 6 MPa of H_2 at 350 °C and absorbs 28% of the total hydrogen capacity obtained experimentally. The activation energy of $Ce(BH_4)_3$ decomposition is 136 kJ mol^{-1}.

1. Introduction

Hydrogen is considered a clean and environmentally friendly carrier appropriate to replace fossil fuels. However, a safe and efficient hydrogen storage technology should be developed in order to use it for practical applications such as fuel cell vehicles. Solid state hydrogen storage in complex hydrides is considered the most promising method to achieve both high volumetric and gravimetric storage densities. Current research is focused on borohydrides, alanates and amides. Among them, $LiBH_4$ is one of the materials with the highest theoretical hydrogen contents (18.5 wt%) [1–3]. This borohydride desorbs about 13.8 wt% of hydrogen above 400 °C according to

$$Li(BH_4) \rightarrow (1)LiH + B + (3/2)H_2 \quad (1)$$

The last reported experimental value of enthalpy of reaction is 74 kJ mol^{-1} H_2 in the 400–520 °C range [3]. It indicates high stability of $LiBH_4$ at ambient temperature and restricted reversibility.

Research work was reported on pure alkaline metal $LiBH_4$ borohydride and their composites to enhance the thermodynamic properties and reversibility [4–9]. Despite the research done, little is known on the properties of the borohydrides of metals other than Li [10]. Among them, the synthesis and dehydriding properties of Ca, Mg, Sc, Ti and Zn were investigated [11–19]. The reports indicate that these materials are worth of study. Within this promising research frame, studies on the thermodynamic stabilities of $M(BH_4)_n$ were done [11,17]. In this formula, M stands for Li, Na, K, Cu, Mg, Zn, Sc Zr or Hf. Metal borohydrides were synthesized by ball milling according to

$$nLiBH_4 + MCl_n \rightarrow M(BH_4)_n + nLiCl \quad (2)$$

These reports were based on both first-principles studies and thermal desorption measurements [11,17]. It was observed that thermal desorption temperature (T_d) of decreases as the value of electronegativity increases [11,14].

In this work, the synthesis of a new crystalline $Ce(BH_4)_3$ is reported. Preliminary kinetics and equilibrium dehydriding properties are also presented. Among the most remarkable results, the hydrogen desorption from $Ce(BH_4)_3$ occurs at about 240 °C during heating and the hydrogen desorption temperature at 0.1 MPa under equilibrium conditions is below 200 °C. Partial rehydriding was observed at 6 MPa and 350 °C. These results are promising for the development of hydrogen storage materials based on new tetrahydroborates.

2. Experimental

The starting materials were anhydrous $CeCl_3$ (Aldrich, 99.99% of purity) and $LiBH_4$ (Aldrich, >95% of purity). The $CeCl_3$–$3LiBH_4$ mixture was mechanically milled at different integrated times under Argon atmosphere at 0.1 MPa. A planetary ball mill (Fritsch P-6) was used. Handling of the powders and samples withdrawn at different milling times was performed in a glove box under purified Argon atmosphere. Both Oxygen and humidity levels were kept at values lower than 1 ppm. The ball to powder weight ratio was 40:1.

The crystalline structure of the samples was characterized by X-ray diffraction (XRD) analysis on a Philips PW 1710/01 Instruments with Cu Kα radiation

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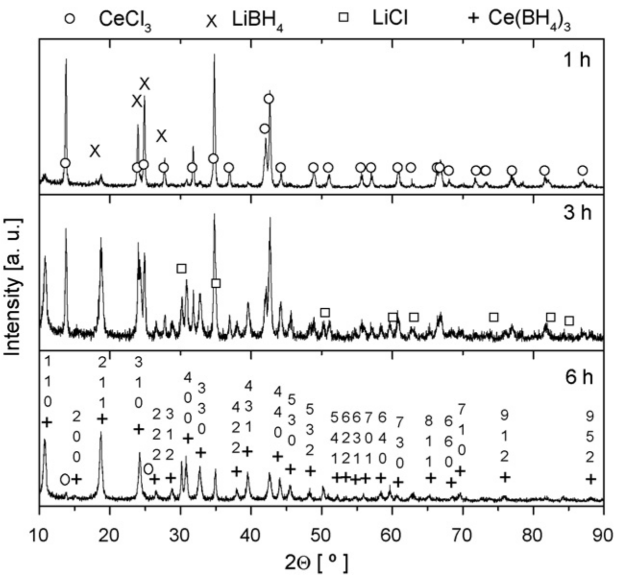

Fig. 1. X-ray diffraction patterns of $CeCl_3$–$3LiBH_4$ as a function of integrated milling time. The *h k l* diffractions peaks of cubic $Ce(BH_4)_3$ obtained after 6 h of milling are also shown.

(graphite monochromator). A tight sealed sample holder was used to prevent contact with air during measurement. The thermal behavior of the samples was studied by DSC on a DSC 2910 calorimeter supplied by TA Instruments. Measurements were done mainly using $5\,^\circ C\,min^{-1}$ of heating rate under an Argon flow rate of $122\,ml\,min^{-1}$.

For IR spectroscopy measurements, commercial $LiBH_4$ and $Ce(BH_4)_3$–LiCl mixture were grounded with dry KBr under purified Argon atmosphere and pressed to pellets. Solid-state IR spectra were obtained using FTIR Spectrum GX spectrometer in the range of $1000–3000\,cm^{-1}$ using a specially designed cell. Handling was done inside the glove box to avoid contact with air. A modified Sieverts-type device was used to perform hydrogen desorption and PCI (pressure-composition isotherm) measurements [20]. The gas sample produced during $Ce(BH_4)_3$ decomposition was collected in a degassed quartz optical cell with NaCl windows and gas phase spectrum at room temperature was taken.

3. Results and discussion

3.1. Synthesis of $Ce(BH_4)_3$

The XRD patterns of the $CeCl_3$–$3LiBH_4$ mixture treated at different milling times are shown in Fig. 1. Reactants are clearly identified after 1 h of milling. As milling time increases, the starting materials diffraction peaks weaken and new peaks emerge. The new peaks intensify after 6 h of milling. Diffraction peaks of co-produced LiCl are also clearly identified at 6 h. Since no change in LiCl cell parameter is observed no substitution of Li by Ce is done. No further changes are produced by additional milling up to 15 h (not shown). Although traces of $CeCl_3$ are detectable by XRD, it is assumed that reaction (2) is completed. $CeCl_3$ presence is probably due to partial $LiBH_4$ decomposition during milling, leaving this reactant in excess over the stoichiometry indicated in Eq. (2).

The new peaks evidence the presence of a long range order in the borohydride structure. The set was indexed as suggested by TREOR 97 [21]. The cell dimensions were refined by program PIRUM [22]. The set was assigned to a single phase compound assumed to be $Ce(BH_4)_3$. The structure belongs to the cubic crystalline system with a lattice constant of $a = 11.640(0)$ Å. Cubic crystalline borohydrides of Gd, Y and Dy were recently obtained from a mechanochemical reaction similar to (2) [17]. The crystal structures and physical properties of these borohydrides were determined using a combination of high-resolution synchrotron radiation X-ray, neutron diffraction and first principles calculations [17]. On the contrary, amorphous complex hydrides of Ca, Sc, Ti, V, Cr, Mn, Zn and Al were obtained by mechanochemical syntheses using a metathesis reaction analogous to (2) [14,17].

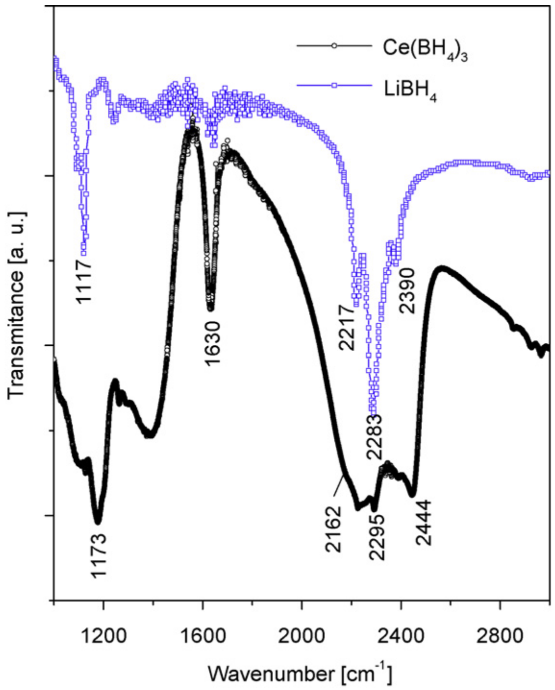

Fig. 2. FTIR spectra of $LiBH_4$ (as-received) and $Ce(BH_4)_3$ (after 6 h of milling).

The formation of $Ce(BH_4)_3$ was also verified by infrared spectroscopy. The FTIR spectrum of $Ce(BH_4)_3$–LiCl sample obtained by milling of $CeCl_3$–$3LiBH_4$ for 6 h is shown in Fig. 2. The FTIR spectra of BH_4^- ion in $LiBH_4$ presents the characteristic bands of 2283 and $2217\,cm^{-1}$, whereas it occurs at 2162 and $2444\,cm^{-1}$ for the $Ce(BH_4)_3$–LiCl ball milled mixture. Resemblances are found between this sample and the stretching and bending modes of B–H vibrations in $LiBH_4$ [23]. It confirms the presence of BH_4^- group. Therefore, the formation of $Ce(BH_4)_3$ [23] after 6 h of milling is independently confirmed by both XRD and IR spectroscopy measurements.

3.2. Thermal decomposition of $Ce(BH_4)_3$

The thermal stability of $Ce(BH_4)_3$ was studied by DSC as shown in Fig. 3. Curves of the $CeCl_3$–$LiBH_4$ mixture after different milling times are presented. Measurements were done at $5\,^\circ C\,min^{-1}$ under Ar. For comparison, DSC curves of as received-$LiBH_4$ ($5\,^\circ C\,min^{-1}$) and as-milled $CeCl_3$–$LiBH_4$ for 6 h ($25\,^\circ C\,min^{-1}$) are also included. The first endothermic peak at 102 °C for $CeCl_3$–$LiBH_4$ milled samples corresponds to the orthorhombic to hexagonal phase transition of $LiBH_4$. The interaction of $CeCl_3$ with $LiBH_4$ is evidenced by the decrease of the phase transition temperature of $LiBH_4$ (110 °C) [2]. In the samples milled for 1 and 3 h, residual $LiBH_4$ reacts with $CeCl_3$ and the $Ce(BH_4)_3$ formed decomposes during heating. Accordingly, no $LiBH_4$ phase transition is observed in the DSC curve after 6 h of milling. It demonstrates the absence of $LiBH_4$ in this sample in agreement with the XRD results of Fig. 1. For the $Ce(BH_4)_3$–LiCl mixture, the hydrogen desorption starts at 240 °C and finishes at 270 °C, below the corresponding melting temperature of pure $LiBH_4$.

In addition, a non-isothermal desorption measurement was done to quantify the amount of hydrogen release. Fig. 4A shows the