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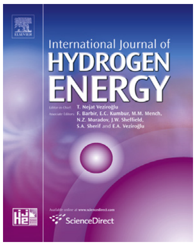

Enhanced hydrogen storage properties of $LiBH_4$ modified by NbF_5

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ABSTRACT

In this work, the hydriding–dehydriding properties of the $LiBH_4$–NbF_5 mixtures were investigated. It was found that the dehydrogenation and reversibility properties of $LiBH_4$ were significantly improved by NbF_5. Temperature-programed dehydrogenation (TPD) showed that $5LiBH_4$–NbF_5 sample started releasing hydrogen from as low as 60 °C, and 4 wt.% hydrogen could be obtained below 255 °C. Meanwhile, ~7 wt.% H_2 could be reached at 400 °C in $20LiBH_4$–NbF_5 sample, whereas pristine $LiBH_4$ only released ~0.7 wt.% H_2. In addition, reversibility measurement demonstrated that over 4.4 wt.% H_2 could still be released even during the fifth dehydrogenation in $20LiBH_4$–NbF_5 sample. The experimental results suggested that a new borohydride possibly formed during ball milling the $LiBH_4$–NbF_5 mixtures might be the source of the active effect of NbF_5 on $LiBH_4$.

Introduction

Hydrogen is considered as an ideal energy carrier for mobile applications because of high energy density and non-pollution emission. Developing a safe and efficient hydrogen storage technology is a key challenge for practical application of hydrogen-powered vehicles. Light element complex hydrides with high gravimetric and volumetric hydrogen capacities, such as borohydrides, alanates and amides, show enormous potential as onboard hydrogen carrier [1,2]. Among them, $LiBH_4$ has attracted considerable attention due to its high hydrogen storage capacities (18.5 mass% and 121 kg H_2/m^3) [3]. However, the practical use of $LiBH_4$ is largely hindered by its stable thermodynamics, slow kinetics and poor reversibility. For pristine $LiBH_4$, rapid hydrogen desorption takes place at temperature as high as 400 °C, and the rehydrogenation can be achieved only under a rigorous condition of

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600 °C and 35 MPa hydrogen pressure [4]. To overcome these barriers of $LiBH_4$, various strategies have been developed including reactant destabilization [5,6], doping with appropriate additives [7–9], confinement using nano-scaffolds [10–12], and cation or anion substitution [13–16].

Particularly, doping with appropriate additives, like metal and their halides or oxides, has proven to be an effective approach to reduce the dehydrogenation temperature and enhance the dehydriding kinetics of $LiBH_4$ [8,17–28]. Recently, it was demonstrated that doping with metal fluorides could simultaneously improve the kinetic and thermodynamic properties of $LiBH_4$ [13,29]. For example, Yu et al. [9] found that $LiBH_4$ doped with TiF_3 started to release hydrogen at around 100 °C. Liu et al. [30] reported that the dehydrogenation reaction of $3LiBH_4 + AlF_3$ mixture has a favorable enthalpy change of 27.8 kJ/mol H_2. Zhang et al. [31] observed that the dehydrogenation temperature of $LiBH_4$ with (La, Ce)F_3 was reduced to 220–320 °C. Wang et al. [29] found that the $LiBH_4$ sample with TiF_3 additive exhibited better dehydrogenation performance than $LiBH_4$ with $TiCl_3$ additive. And both experimental and theoretical investigations revealed that the F^- anion might partially substitute the anionic H in both $LiBH_4$ and LiH lattices, resulting in a favorable modification of the hydrogen-exchange thermodynamics of $LiBH_4$.

Although the dehydrogenation properties of $LiBH_4$ have been promoted by these fluorides, the poor reversibility of $LiBH_4$-additive composite is still a problem. Recently, the effects of various fluoride additives (NbF_5, TiF_3, CeF_3, LaF_3 and FeF_3) on hydrogen storage properties of $LiBH_4$-based composite ($LiBH_4$–MgH_2) were investigated by Chen et al. [32]. And it was observed that NbF_5 played an outstandingly active role on not only enhancing dehydrogenation kinetics but also improving reversibility [32,33]. Similarly, it was also found that NbF_5 could significantly improve the hydrogen storage properties of many other borohydrides, alanates and metal hydrides [34–38]. However, the $LiBH_4$–NbF_5 system has not been systemically studied and the effects of NbF_5 on the hydriding–dehydriding properties of $LiBH_4$ are not yet quite clear. In this work, the hydrogen storage properties of the $LiBH_4$–NbF_5 binary composite were investigated and superior dehydrogenation performance together with better reversibility was observed. Moreover, the role of NbF_5 played on the dehydriding process of $LiBH_4$ was evaluated, and the corresponding microstructure evolutions were studied as well.

Experimental

$LiBH_4$ (95% purity) and NbF_5 (98% purity) powders were purchased from Sigma–Aldrich Corp. All the chemicals were used as received in powder form. The samples of $xLiBH_4$–NbF_5 ($x = 1, 5, 10, 20, 40$) were prepared by ball milling $LiBH_4$ with NbF_5 in various mole ratios on a planetary mill at 400 rpm for 1 min under argon. Similar method was also used to prepare the sample of pristine $LiBH_4$. All sample handlings were carried out in a continuous Ar-filled glovebox.

The dehydrogenation and rehydrogenation properties of the mixtures were examined by a Sievert's type apparatus. For the temperature-programmed dehydrogenation measurements, the reactor was first evacuated to 1 Pa, and then heated from ambient temperature to 600 °C at a 2 °C/min heating rate. The hydrogenation was performed after dehydrogenation by holding the dehydrogenated sample at 600 °C under a hydrogen pressure of around 10 MPa for 3 h. For consideration of practical purpose, the weight of additive was taken into account in calculation of hydrogen capacity. The coupled differential scanning calorimetry (DSC) and mass spectrometer (MS) analyses were conducted on a Netzsch STA449F3 equipped with a Netzsch Q430C mass spectrometer. During the measurement, the sample was heated at a rate of 10 °C/min under high purity argon with a purge rate of 50 ml min^{-1}.

The crystal structure characteristics were investigated by X-ray diffraction (XRD) analysis on a PANalytical X'Pert PRO with Cu Kα radiation. A special sample holder was used to keep the samples from air exposure during the XRD measurements. Fourier transform infrared spectrometer (FTIR) spectrum of species was recorded at ambient condition by Bruker Tensor27 FTIR spectrometer. About 1 mg of the sample mixed with 100 mg dry KBr was pressed first and then loaded into a sealed chamber for the FTIR measurements. X-ray photoelectron spectroscopy (XPS,VG ESCALAB MARK II, Mg Kα:1253.6 eV) was used to analyze the chemical state of niobium and boron components after dehydrogenation. The bonding energies obtained in the XPS analysis were standardized for specimen charging using C1s core level at 284.6 eV. The morphology of samples after dehydrogenation was observed using scanning electron microscope (SEM, FEI FSEM SIRION-100) with energy dispersive X-ray spectroscopy (EDS).

Results and discussion

Fig. 1 shows the temperature-programmed dehydrogenation curves of the pristine $LiBH_4$ and $LiBH_4$–NbF_5 mixtures. It was obvious that the dehydrogenation properties could be significantly improved by NbF_5 addition. For pristine $LiBH_4$, a small amount of H_2 started to release at around 280 °C, and hydrogen could only be rapidly obtained from around 400 °C.

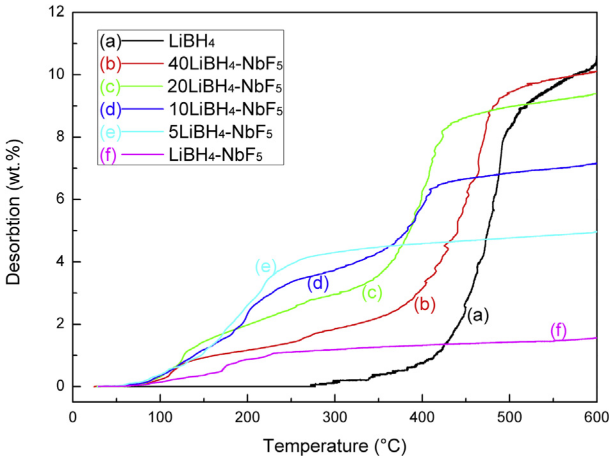

Fig. 1 – Temperature-programmed dehydrogenation (TPD) curves of the $xLiBH_4$–NbF_5 mixtures ($x = 1, 5, 10, 20, 40$) and pristine $LiBH_4$ from room temperature (RT) to 600 °C at a heating rate of 2 °C/min.