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Superior dehydrogenation performance of nanoscale lithium borohydride modified with fluorographite

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ABSTRACT

A significant enhancement in the dehydrogenation performance of LiBH₄ is achieved by modifying with fluorographite (FGi). In-depth investigations show that the dehydrogenation thermodynamics and kinetics of LiBH₄ are strongly improved by ball milling LiBH₄ with FGi. The ball-milled LiBH₄-FGi (mass ratio of 1:1) composite starts to release hydrogen without impurity gas at around 180 °C, and obtains a hydrogen desorption capacity of 7.2 wt% below 200 °C in seconds, which is improved dramatically compared with pristine ball-milled LiBH₄. Microscopic morphology indicates that numerous ~90 nm spots formed on the surface of FGi. Based on the microstructure analyses combined with hydrogen storage performances, the prominent effect of FGi is largely attributed to the nano-modifying effect and the exothermic reaction between LiBH₄ and FGi during the dehydrogenation process. Furthermore, partial reversibility of the LiBH₄-FGi composite has been demonstrated and the mechanism underlying the cycling capacity loss is discussed. The use of FGi may shed light on future study on searching for new strategies to improve both the thermodynamics and kinetics of light-metal complex hydrides.

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1. Introduction

Hydrogen is one of the environmentally clean energy carriers, which could attain nearly zero emission of pollutants from power generators especially for fuel cells. Nevertheless, reversible storage of hydrogen with high capacity is one of the key challenges for hydrogen energy applications. Solid-state metal hydrides are promising to fulfill future hydrogen storage goals due to their advantages over safety, compactness, and efficient onboard hydrogen storage compared to traditional high-pressure and liquid hydrogen storage systems [1].

During the past few years, solid-state metal hydrides especially light-metal complex hydrides have received significant attentions due to their high gravimetric and volumetric hydrogen contents [2–9]. LiBH₄ is competitive among these materials, due to its large theoretical hydrogen capacity (18.5 wt%) and volumetric hydrogen density (121 kg/m³) [2,10]. LiBH₄ decomposes in two steps, just as follows:



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However, the main evolution of hydrogen starts at 380 °C, and the rehydrogenation condition is so harsh that high hydrogen pressure of 35 MPa and high temperature of 600 °C are needed [11].

Due to its bad thermodynamics and slow kinetics, the de/rehydrogenation of LiBH₄ needs to be largely improved for commercial hydrogen storage applications. In 2003, Züttel et al. [12] added SiO₂ into LiBH₄, lowering the dehydrogenation temperature to 300 °C. Zhang et al. [13] further destabilized the LiBH₄ + SiO₂ system by adding TiF₃, which noticeably reduced the activation energy of the reaction at interface and successfully avoided the formation of Li₄SiO₄ or other silicate during dehydrogenation. Guo et al. [14] found that the 3LiBH₄–TiF₃ mixture started to release hydrogen at around 100 °C and the hydrogen desorption capacity reached 5.0 wt% at 250 °C. The significantly improved dehydrogenation properties in the 3LiBH₄–TiF₃ system resulted from an exothermic reaction of $3\text{LiBH}_4 + \text{TiF}_3 \rightarrow 3\text{LiF} + \text{TiB}_2 + \text{B} + 6\text{H}_2$, which improved the dehydrogenation thermodynamics and kinetics. Vajo et al. [15] found out that the destabilization of LiBH₄ by milling with additives (MgH₂, MgF₂, MgS and MgSe), which reacted to form new compounds during dehydrogenation, was an effective way for favorably altering the thermodynamics of complex hydrides. Au et al. [16] found that TiCl₃, TiF₃ and ZnF₂ can effectively reduce the dehydrogenation temperature of LiBH₄ by forming unstable transition metal borohydrides (such as Ti(BH₄)₃) through a cation exchange interaction. Furthermore, Yin et al. [17] reported that the reaction enthalpy decreased with the number of F[−] substituted in LiBH₄ (such as Li₃B₈H_{32−x}F_x supercell) in the case of theoretical calculations. In the study of Wang et al., it was found that TiF₃ was superior to its analogue TiCl₃ as additive for LiBH₄ and Li–Mg–B–H systems due to the combined effects of catalytically active Ti hydride and the functional F anion [18,19]. Recently, Brun et al. impregnated LiBH₄ into carbonaceous materials to prepare LiBH₄@carbon samples, and the onset desorption temperature could be decreased to 200 °C and a hydrogen capacity of 4.0 wt% was obtained at 300 °C with the carbon having the largest microporous volume [20]. Fang et al. [21] found that carbon additives (graphite, activated carbon and carbon nanotubes) have a promoting effect on the hydrogen storage of LiBH₄ due to their heterogeneous nucleation and micro-confinement. Motivated by these theoretical and experimental findings, we combine F anion with graphite (G) to destabilize LiBH₄ by ball milling the mixture of LiBH₄ and fluorographite (FGi) for the first time. Superior dehydrogenation properties were observed and the role of FGi in destabilizing LiBH₄ is discussed. The results show that the onset temperature of hydrogen release of the LiBH₄–FGi (mass ratio: 1:1) composite is only about 180 °C and a hydrogen desorption capacity of 7.2 wt% is achieved below 200 °C in seconds.

2. Experimental section

The starting materials, LiBH₄ (Alfa Aesar, 95%), FGi (CarFluor Ltd, Grade II) and G (Sinopharm chemical Reagent Co. Ltd, 99.85%) were all used as received. Properties of FGi given by the manufacturer are presented in Table S2. The composites contained 30 wt%, 50 wt%, 70 wt% FGi and 50 wt% G were

prepared by ball milling the mixture of LiBH₄ and FGi or G, denoted as LiBH₄–30FGi, LiBH₄–50FGi, LiBH₄–70FGi and LiBH₄–50G, respectively. The composites were ball milled for 2 h (planetary QM-3SP4, Nanjing, China) under 2 MPa hydrogen pressure at a speed of 400 r/min. The ball-to-power ratio was 30:1. For comparison, pristine LiBH₄ was also milled under identical conditions.

The hydrogen desorption/absorption properties of the samples were quantitatively measured by a volumetric method on a Sievert's type apparatus. About 250 mg of sample was used for each temperature programmed desorption (TPD) measurement. The temperature was gradually elevated from room temperature to 200 °C or 500 °C at a heating rate of 5 °C/min for dehydrogenation (under static vacuum). The samples were thoroughly dehydrogenated at 500 °C under static vacuum before rehydrogenation. The thoroughly dehydrogenated LiBH₄ and LiBH₄–50FGi samples were further rehydrogenated at 500 °C and 10 MPa for 10 h. The dehydrogenation of rehydrogenated samples were conducted from room temperature to 500 °C at a heating rate of 5 °C/min (under static vacuum). The dehydrogenation capacity is given as weight percent (wt%) of the whole composite (i.e. LiBH₄ plus FGi).

X-ray diffraction analysis (XRD) was conducted on an X'Pert Pro X-ray diffractometer (PANalytical, Netherlands) with Cu K α radiation at 40 kV and 40 mA. Fourier Transform Infrared Spectra (FTIR) was obtained with a Bruker Tensor 27 unit in transmission mode.

Scanning Electron Microscope (SEM, Hitachi SU-70) was applied to analyze the morphology of the samples. The value of e-beam energy used in SEM measurement was 3.0 kV. For the SEM observations, samples of the synthesized powders were dispersed on stick-mounted holders and introduced into hermetic plastic recipients in the argon-filled glove box to avoid exposure to air. And argon was released to protect the samples from Oxidation when the samples were transferred to the SEM sample chamber. X-ray Photoelectron Spectroscopy (XPS) was carried out on a VGESCALAB MARK II system with Mg K α radiation (1253.6 eV) at a base pressure of 1×10^{-8} Torr. All binding energy (BE) values were referenced to the C1s peak of contaminant carbon at 284.6 eV with an uncertainty of ± 0.2 eV. Differential Scanning Calorimetry and Mass Spectrometry (DSC-MS) measurements were performed on a Netzsch DSC 449F3 coupled with a Netzsch Q430C mass spectrometry at a heating rate of 5 °C/min from room temperature to 500 °C under flowing argon condition (high purity, 50 mL/min).

All sample operations were performed in an Ar-filled glovebox, which was equipped with a circulative purification system to maintain H₂O and O₂ levels below 1 ppm. Special caution was taken to prevent H₂O and O₂ contamination during XPS, XRD, FTIR and SEM measurements.

3. Results and discussion

3.1. Structure and morphology of as-prepared samples

The microstructures of ball-milled LiBH₄, as-received G and FGi, as-prepared LiBH₄–50G and LiBH₄–50FGi samples were

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