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Experimental and theoretical study of hydrogen desorption process from $Mn(BH_4)_2$

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ABSTRACT

The thermal decomposition of manganese borohydride $Mn(BH_4)_2$ was studied by means of synchrotron-based X-ray absorption spectroscopy (XAS), X-ray powder diffraction (XRPD) and theoretical density functional (DFT) modeling aiming to elucidate changes of the local atomic structure upon hydrogen desorption and to determine possible decomposition reaction products. XRPD patterns indicate profound structural changes in the material above 120 °C with subsequent amorphization. DFT simulations predict the collapse of the highly porous framework structure upon hydrogen desorption and significant reduction of Mn-B and Mn-Mn interatomic distances by 19% and 41% respectively. These estimations are in a good agreement with the quantitative analysis of the X-ray absorption spectra above Mn K-edge. Based on XAS we derive possible decomposition products and reaction path. In particular, the amount of Mn metallic phase was estimated to be less than 5% after the heating up to 200 °C. Several structural models for the final state of manganese borohydride in a heating process are constructed by means of energy minimization in conjunction with evolutionary algorithms.

1. Introduction

Solid state hydrogen storage materials represent a perspective, compact and safe way to store hydrogen energy [1-5]. High gravimetric and volumetric density of hydrogen, the low temperature of desorption and cycling ability are the main requirements for the potential hydrogen-storage materials [6]. The most efficient hydrogen absorbers nowadays are alkali metal borohydrides. However, the high temperature of desorption (e.g. above 400 °C for $LiBH_4$ [7-13]) and a limited number of charge/discharge cycles makes their use unjustified. Many of borohydrides yield upon heating stable $[B_{12}H_{12}]^{2-}$ species that decrease their hydrogen release potential and prevent their reversibility. This behavior is one of the obstacles for $Mg(BH_4)_2$ rehydrogenation [6,14]. Another one is the amorphization process which accompanies hydrogen release from the porous structure [15].

Manganese borohydride α-$Mn(BH_4)_2$ is structurally similar to α-$Mg(BH_4)_2$ – a perspective material which is considered to be a high-capacity (theoretical hydrogen capacity of 9.53 wt.%) solid-state hydrogen storage candidate, but so far has not been shown to exhibit reversible hydrogenation. $Mn(BH_4)_2$, among all other transition complex borohydrides, is stable at room temperature [16]. It can be synthesized by ball-milling of a mixture of the alkali metal borohydride MBH_4 (M = Li, Na for instance) and anhydrous manganese chloride $MnCl_2$ [17]. Density functional theory (DFT) calculations suggested that *I*-4m2 structure is the most

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