XAFS measurements of Sc in Reactive Hydride Composites for hydrogen storage

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Light weight metal hydrides are favoured materials for hydrogen storage in mobile application. Due to the high requirements on the materials concerning storage capacity, reaction thermodynamics and kinetics novel functional materials need to be developed. One promising new class of materials are the Reactive Hydride Composites (RHC) [1,2]. These systems show reduced total reaction enthalpies at high storage capacities. The system of e.g. $2\text{LiH} + \text{MgB}_2 + 4\text{H}_2 \leftrightarrow 2\text{LiBH}_4 + \text{MgH}_2$ has a theoretical storage capacity of 11.4 wt% hydrogen and an equilibrium pressure of 1 bar $\text{H}_2$ at 170°C. During the endothermic desorption reaction the exothermic formation of MgB$_2$ proceeds and is thereby lowering the total reaction enthalpy. The system shows very sluggish kinetics and can therefore only be operated at temperatures above the thermodynamic equilibrium. With cycling and suitable additives the kinetics is significantly improved by an order of magnitude [3]. Characterization of these additives, their chemical state and distribution is the key to understanding the mechanism behind.

Previous work on Zr-based additives as a model system has revealed the formation of ZrB$_2$ nanoparticles on the size scale of 1-5 nm [4]. Further experiments and calculations give strong hints to improved nucleation rates of MgB$_2$ during the desorption reaction due to heterogeneous nucleation on the ZrB$_2$ particles [5]. However, Zr-based additives are only suitable as a model system due to the high weight of Zr and the therefore strongly decreased hydrogen capacity by weight. Against this background, the use of Sc based additives as one of the lightest transition metals was investigated. And indeed, the addition of Sc$_2$O$_3$ by premilling with MgH$_2$ shows strongly improved kinetics and can be regarded as one of the most effective additives for this system. Furthermore and most important for future application, reaction temperatures can be decreased by approximately 50°C and good reaction rates are observed.

In figure 1, experimental results of the XANES region of the Sc k-edge at 4492 eV are shown. The presented curves were measured in fluorescence mode with a PIPS diode. Initial LiBH$_4$-MgH$_2$ composites were obtained by high-energy ball milling. The cycled states were prepared in a Sieverts type apparatus. For XAFS measurements, the powders were mixed with cellulose and pressed into pellets of 13 mm in diameter. To avoid oxidation the pellets were enclosed with Kapton tape. The samples show significant changes upon cycling, where Sc$_2$O$_3$ was reduced upon the first desorption reaction. The chemical state upon further cycling appears to be stable. Further analysis will be performed to confirm the formation of ScB$_2$. 

![XAFS measurement graph](image-url)
Fig. 1: XANES of RHC samples with Sc-based additive after initial preparation and after cycling in comparison to the initial compound.

In addition, comparative measurements were performed with ScCl$_3$ as additive and a variety of Ti-based additives were characterized for Fluoride alternated systems in the initial state. Further measurements are necessary to monitor the changes upon cycling.

References