Light weight metal hydrides are favoured materials for hydrogen storage in mobile and stationary applications. 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)\cite{1,2}. These systems show reduced total reaction enthalpies at high storage capacities. The system of e.g. 2LiH + MgB$_2$ + 4H$_2$ ↔ 2LiBH$_4$ + MgH$_2$ has a theoretical storage capacity of 11.4 wt% hydrogen and an equilibrium pressure of 1 bar H$_2$ at 170°C. Another very promising system with respect to thermodynamics and kinetics is the composite of CaH$_2$ + MgB$_2$ + 4H$_2$ ↔ Ca(BH$_4$)$_2$ + MgH$_2$. During the endothermic desorption reaction the exothermic formation of MgB$_2$ proceeds and thereby lowers the total reaction enthalpy. The systems show very sluggish kinetics and can therefore only be operated at temperatures very much above the thermodynamic equilibrium. With cycling and suitable additives the kinetics is improved by an order of magnitude \cite{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 \cite{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 \cite{5}. However, Zr-based additives are only suitable as a model system because of the still comparatively sluggish kinetics. At present, the highest reaction rates and highest reversibility in the Ca(BH$_4$)$_2$-MgH$_2$ system are measured with the addition of NbF$_5$. To investigate the chemical state of Nb in the two composites in the initial as well as in the cycled state XAFS measurements at the Nb-K edge were performed.

In figures 1a and b, experimental results of the XANES region of the Nb K-edge at 18986 eV are shown. The presented curves were measured in transmission. Initially, LiH-MgB$_2$ and Ca(BH$_4$)$_2$-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 within Kapton tape. The samples of both composites show significant changes already upon milling in comparison to the initially added NbF$_5$. A large agreement in edge position as well as in the post edge features are observed with NbB$_2$. This is also confirmed when looking at the EXAFS features in more detail, shown in figures 1c and d. The chemical state upon further cycling appears to be stable.
Further measurements to characterize the influence of fluorine containing additives, for example a partial substitution of the hydrogen atoms, will be performed for the Ca-based composites at the Ca-K edge.

References