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| ESRF | **Experiment title:**<br>XRS study of the hydrogen release mechanism in layer protected borohydrides | **Experiment number**:<br>MA-3042 |
| **Beamline**:<br>ID20 | **Date of experiment**:<br>from: 09 May 2016 to: 16 May 2016 | **Date of report**:<br>06.03.2017 |
| **Shifts:**<br>15 | **Local contact(s)**:<br>*Christoph J. Sahle* | *Received at ESRF:* |

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**Report:**

In this experiment we performed an x-ray Raman scattering (XRS) study of the borohydride $NaBH_4$ covered with a protection layer of polyethyleneimine (PEI) in order to characterize both the hydrogen desorption mechanisms and the function of the protection layer during annealing. In contrast to other protective polyelectrolyte coatings, using PEI as a protection layer for $NaBH_4$ does not only hinder oxidation of the reactive hydride but also causes a significant hydrogen release starting at a very low temperature of about 120 °C possibly due to formation of a boron-amino-complex. Moreover, the succeeding hydrogen desorption pathway of this system at higher temperatures is unknown. With this study we focus first on the reaction that occur before structural decomposition of $NaBH_4$ sets in.

The experiments were performed at beamline ID20 of ESRF using the XRS spectrometer in combination with our Anton Parr annealing chamber (see figure 1 (a)). We measured the boron and sodium K-edge of $NaBH_4$ and $NaBH_4$ covered with PEI for temperatures up to 500 °C to track fingerprints of changes in electronic and local structure. The samples were prepared in quartz glass capillaries and annealed in air. The in situ measurements were carried out at analyzer energy of 9.7 keV and an overall energy resolution of 0.7 eV. For measuring XRS spectra, the incident energy was scanned to obtain energy losses in the vicinity of the corresponding absorption edge. During the measurements significant beam damage on the samples took place if the sample was illuminated for more than 30-60 minutes at the same position. This problem was solved by variation of the beam position at the sample after each

single energy loss scan. First results of XRS spectra taken from PEI-covered $NaBH_4$ are presented for the sodium and boron K-edge in figure 1 (b) and (c), respectively. The spectra show distinct changes in shape which are indicative for $H_2O$ and $H_2$ release, PEI decomposition and oxidation. Latter takes place for temperatures above 300 °C when the PEI protection layer is decomposed. In the next step decomposition paths of $NaBH_4$ for higher temperatures will be studied and using catalysts, this decomposition temperature should be lowered. The spectra taken during this experiment will be further analyzed exploiting shape analysis on basis of reference samples and will be complemented with x-ray diffraction data.

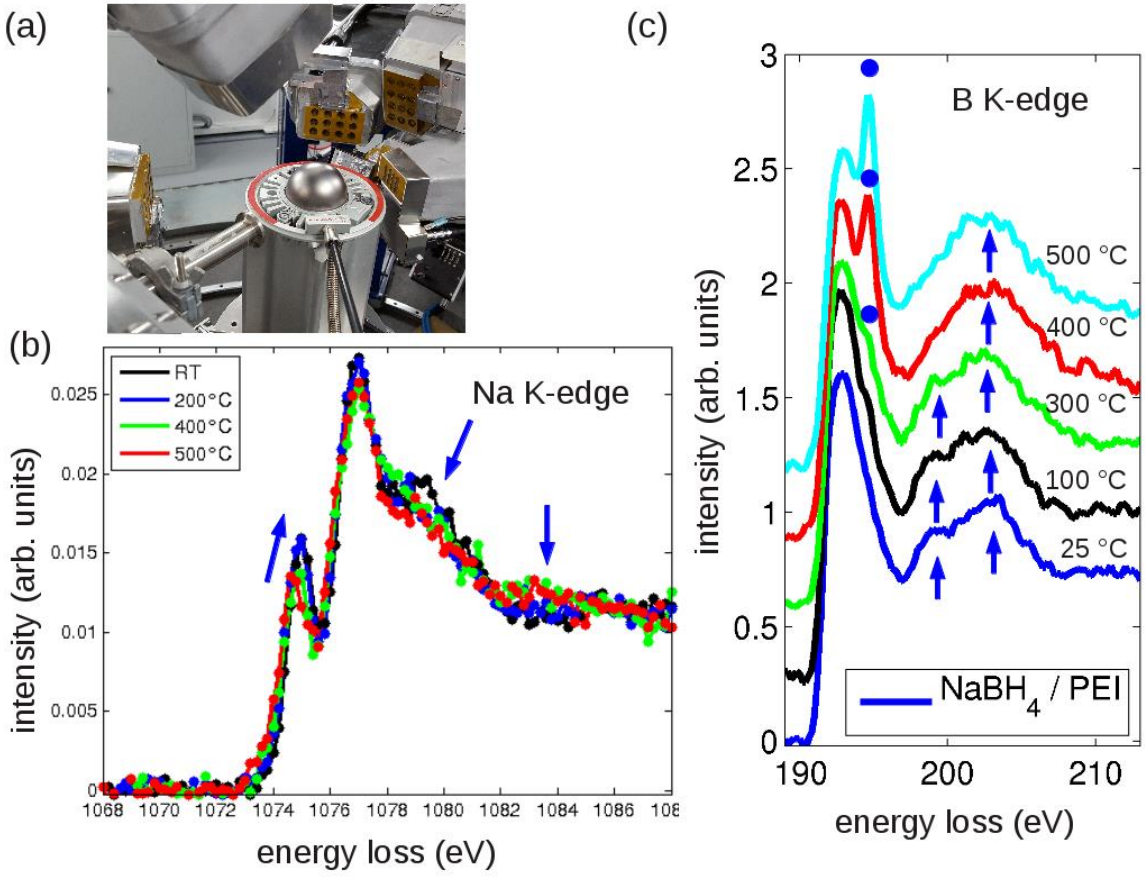


*Figure 1: Setup of the XRS experiment at beamline ID20 of ESRF. The picture shows the Anton Parr temperature cell together with the nozzles of the XRS spectrometer as indicated. XRS spectra at the sodium (b) and boron (c) K-edge for $NaBH_4$ covered with PEI measured at temperatures as indicated. Arrows guide to structural changes induced by PEI decomposition and $H_2O/H_2$ release and circles to signatures of oxidation.*