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Report: SAXS studies of hydrides nanocomposites under the SNBL dubble agreement

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Storage of hydrogen in a safe and efficient medium is a major challenge for the introduction of hydrogen as an energy carrier for mobile applications. One of the most promising directions is the use of hydrogen as energy vector for vehicular applications in the form of solid storage material based on nanoscaffold hydrides. When dealing with nanoporous materials small-angle scattering gives invaluable information that can help to develop the most suitable solid material. Recently, using small-angle X-ray scattering (SAXS) data we found that the integration into the scaffold of sodium alanate stabilize the size of the particles upon heating, while the bulk powders undergo changes.[1]

Here we present the results on Mg-borohydrides samples. Nanoscale particles of $Mg(^{11}BD_4)_2$ infiltrated in a activated carbon scaffold (AC1) were studied by small-angle X-ray scattering and their behavior compared with the bulk powders. We observed that upon heating up to 400 ^{o}C the nano-confined particles maintain their size distribution and the decomposition affects only the particles surface. On the contrary, the bulk powders showed a significant modification of particle size and surface under the same conditions.

[1] S. Sartori, K. D. Knudsen, A. Roth, M. Fichtner, and B. C. Hauback, *Nanoscience and Nanotechnology Letters*, submitted (2010).

In situ SAXS patterns were collected at the beam line (BM26B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The wavelength was 0.95 Å, and the sample was contained in a 0.8 mm boron-silica glass capillary and heated under dynamic vacuum from room temperature (RT) to 100 °C at a constant heating rate of 20 °C min^{-1} without data acquisition record and then from 100 to 400 °C at a constant heating rate of 5 °C min^{-1}.

Wide angle X-ray scattering (WAXS) was recorded during the SAXS acquisition. The data obtained were integrated and put on a linear scale by means of the Fit2D program.

Figure 1 displays the acquired data at RT, 100 °C and 400 °C for the infiltrated system $Mg(^{11}BD_4)_2$ / AC1, together with the data for the AC1 at RT. From visual inspection, one may notice that in the low-middle *q*-range the curves follow a similar trend as the AC1 alone, and with almost no differences with increased temperature. It seems that there is negligible reduction/modification in particle sizes when infiltrated in the scaffold, that is the hydride is stabilized by the presence of the scaffold. The only detectable changes are localized on the surface of the particles (high *q*). The particle size distribution for the $Mg(^{11}BD_4)_2$ / AC1 obtained by means of an indirect Fourier transform confirm the small dimensions in the range of 1 to 6 nm (10 to 60 Å) of the particles when confined in the scaffold. This result well support the characteristic feature at around 4 nm found with our preliminary study.[2]

A more detailed study of the change of the slope parameter at high *q* of selected SAXS data show a decrease in the slope parameter from ~3.8 to ~3.4. This suggests that heating modifies the particles towards a more rough surface and could be related to the release of hydrogen.

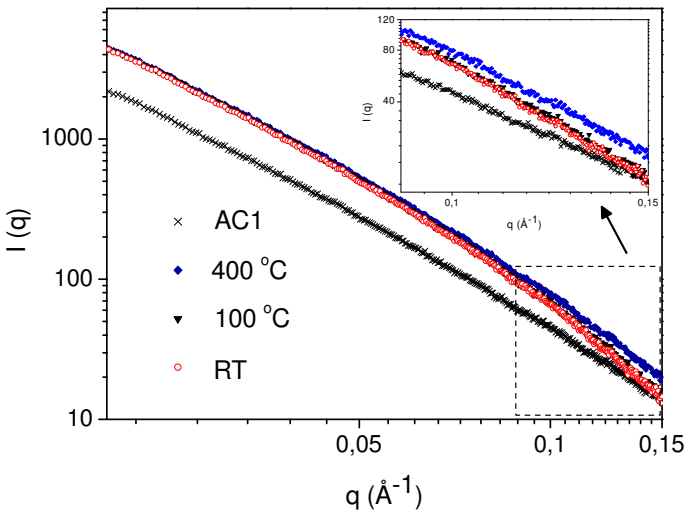

Figure 1. SAXS on AC1 at RT and on $Mg(^{11}BD_4)_2$ / AC1 at RT, 100 and 400 °C.

The comparison with the bulk $Mg(^{11}BD_4)_2$ is therefore important in order to underline the effect of the reduction in size and the stabilization of the hydrides due to the infiltration in the scaffold. At RT the bulk $Mg(^{11}BD_4)_2$ contain a mixture of the α and β modification. The combination of SAXS and WAXS is useful to support the interpretations of the change in the slope parameter seen with SAXS in the medium and high *q* range for the bulk powders. From *in situ* WAXS the transformation from α- to β-phase is clearly observed to start at around 160 °C and is almost complete at around 180 °C, with a slight increase in the amount of the β-phase compared to the pattern at 100 °C. From about 240 °C the WAXS shows the decomposition of the β-phase. The final product phases are Mg and MgO (the latter at $2\theta \sim 25^{o}$). The SAXS curves perfectly superimpose from RT to 100 °C. Above 100 °C, visual inspection indicates a decrease in the slope parameter at medium *q* and high *q*. A more

[2] S. Sartori, K. D. Knudsen, Z. Zhao-Karger, E. Gil Bardaji, M. Fichtner, and B. C. Hauback, *Nanotechnology* 20, 505702 (2009).

detailed plot of the slope parameter at medium and high *q* can be observed in Figure 2 a) and b), respectively, where the values at all temperatures are shown. The α- to β-phase transformation corresponds to a decrease in the slope parameter (from around 2.8 to 2.74) at medium *q*, and an opposite increase in the values (from around 4.2 to 4.5) at high *q*. A possible release of hydrogen before 240 °C could explain the slight decrease in the slope parameter at central and high *q*, from 180 °C. From the study of the slope parameter in the medium *q*, Figure 2 a, it seems that the systems consist of a less and less compact mass fractal, which could be justified with the release of hydrogen. Based on the SAXS data at high *q*, the release of hydrogen seems to change the surface from smooth to rough (reduction in slope from a value around 4 towards 3). When the decomposition of β-phase occurs, from 240 °C, these changes in the slope parameters becomes even more dramatic until at 300 °C, where only Mg and MgO are detectable.

In conclusion, the use of small-angle X-ray scattering on nanoconfined hydrides has provided us with important information on the characteristics of this hydride material within the supporting carbon scaffold. This data will be useful in the interpretation of the relation between the structural changes during the confinement and the improved hydrogenation properties of the composite hydrides compared to the bulk powder alone.

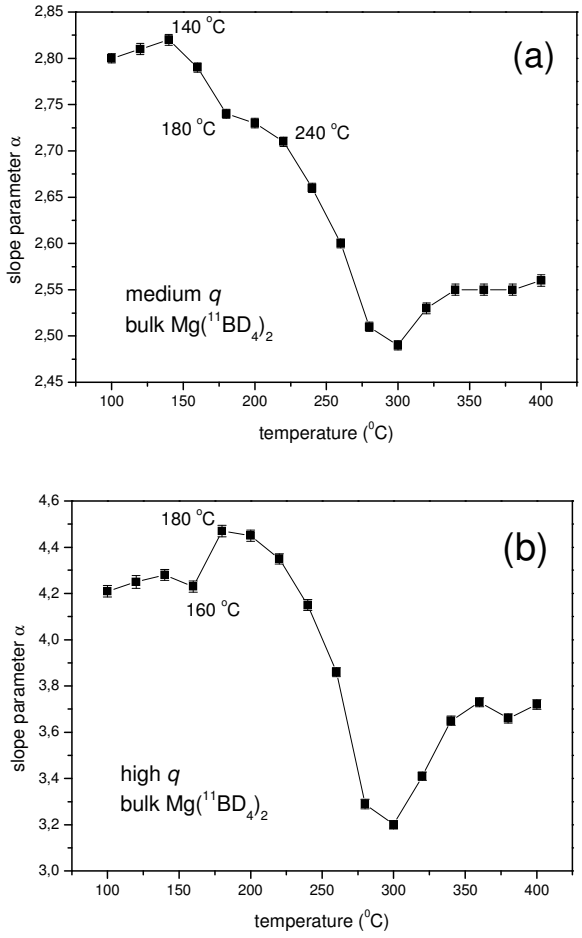

Figure 2. Values of slope parameter at medium (a) and high *q* (b) for the *in situ* SAXS on bulk Mg(^{11}BD$_4$)$_2$.