# Experimental report

31/08/2022

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| **Proposal:** | **1-04-235** | **Council:** | 4/2021 |
| **Title:** | Hydrogen storage mechanisms in disordered nanoporous carbons at high pressures | | |
| **Research area:** | Other... | | |

**This proposal is a new proposal**

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| **Main proposer:** | **Sebastian STOCK** |
| **Experimental team:** | Sebastian STOCK<br>Malina JOP |
| **Local contacts:** | Bruno DEME |

**Samples:** Activated carbon powder

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D16 | 6 | 4 | 09/09/2021 | 14/09/2021 |

## Abstract:

In this proposal, we plan to investigate the high-pressure (0-100 bar) physisorption behavior of hydrogen (H2), deuterium (D2) and a zero scattering length density H2/D2 mixture under cryogenic temperatures (77-97 K) in two disordered carbon systems with different hierarchical pore structures. This will be done by in-situ Small-Angle Neutron Scattering (SANS) at D16 combined with a gas sorption analyzer provided by the ILL. SANS is considered one of the most effective techniques to study in detail the arrangement of guest atoms, molecules or ions in a confined nanopore space. The contrast variation experiment will allow us to separate local contrast effects and pore volume changes. The combination of SANS, gas adsorption analysis and carbon structure modeling will help to identify the role of H2 confinement and density properties in nanopores.

# Experimental Report for Proposal 1-04-235

## Hydrogen storage mechanisms in disordered nanoporous carbons at high pressures

## (09.09.-14.09.2021, D16)

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**Aim of the experiment:**

In a previous conducted experiment at the D16 instrument (proposal 1-04-218) the hydrogen ($H_2$) and deuterium ($D_2$) adsorption in nanoporous activated carbons up to 1 bar and different (cryogenic) temperatures revealed the importance of narrow micropores for highest storage capability. The aim of this follow-up experiments was to further investigate the gas uptake at high pressures as well as to clarify the influence of adsorption induced deformation of the pore space and possible isotope effects using a zero-scattering length density (Z-SLD) gas mixture. Beside of the two carbons samples used in the pevious experiment, we also investigated a third activated carbon material to study different pore size distributions and surface chemistry effects.

**Experimental details:**

A commercial biobased activated carbon (YP80) and an activated carbon cloth derived from a viscose rayon precursor fabric (ACC) were investigated with two gases ($H_2$ and $D_2$) at 77 K. The experiments were conducted using the gas sorption analyzer available at the ILL at various pressure points up to 65 bar (see Figs. 1a, b and c). The samples were degassed at 250 °C under vacuum and placed in a custom-machined aluminum cell. The cell volume and skeletal density of the sample were determined using helium pycnometry. I addition, a third carbon sample (MSP-20, an activated bio-derived carbon similar to YP80, but with smaller micropore) was measured in-situ using $H_2$, $D_2$ and a zero scattering-length density (Z-SLD) $H_2/D_2$ mixture up to a pressure of 1 bar to complete the first measurement campaign. The neutron scattering signal at D16 was recorded at five detector positions using a wavelength of 4.47 Å, which resulted in a covered Q-range of 0.03 - 2 $Å^{-1}$. Sample transmission at each pressure point, together with measurements of the background signal and a cadmium background were used for data correction and calibration.

**Collected data and results:**

Fig. 1 a) and b) exemplarily show the collected high-pressure data at 77 K for the ACC material using $H_2$ and $D_2$ as adsorbents, respectively. This material shows two clear “humps” (at ≈0.06 $Å^{-1}$ and 0.3 $Å^{-1}$), corresponding to mesopores of roughly 50 Å and micropores ≤ 10 Å. The strongly increasing scattering intensity upon pressurization with $H_2$ at large Q, seen in Fig. 1 a), can be directly attributed to the increasing amount of $H_2$ in the system as a result of the large incoherent scattering cross section of hydrogen [1], while the scattering at lower Q is related to contrast changes due to coherent scattering between carbon and the $H_2$-filled pore space. For the SANS signals measured during pressurization with $D_2$ (Fig. 1 b)), an initial increase of the scattering intensity can be seen at low Q in the region of the first hump, but for pressures exceeding 1 bar, the intensity decreases again as a function of pressure. In the intermediate Q-regime (second hump), the intensity decreases continuously with increasing $D_2$ uptake. This can be attributed to micropore filling and subsequent densification in the small pores, while the larger pores remain essentially empty at low pressures and only start to fill at pressures above 1bar. Fig 1. c) and d) show the collected data for the YP80 material upon pressurization with $H_2$ at 77 for high pressures and upon pressurization using a zero-SLD gas mixture, respectively.

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[1] Experimental Team

[2] Local Contact

[3] Supervision

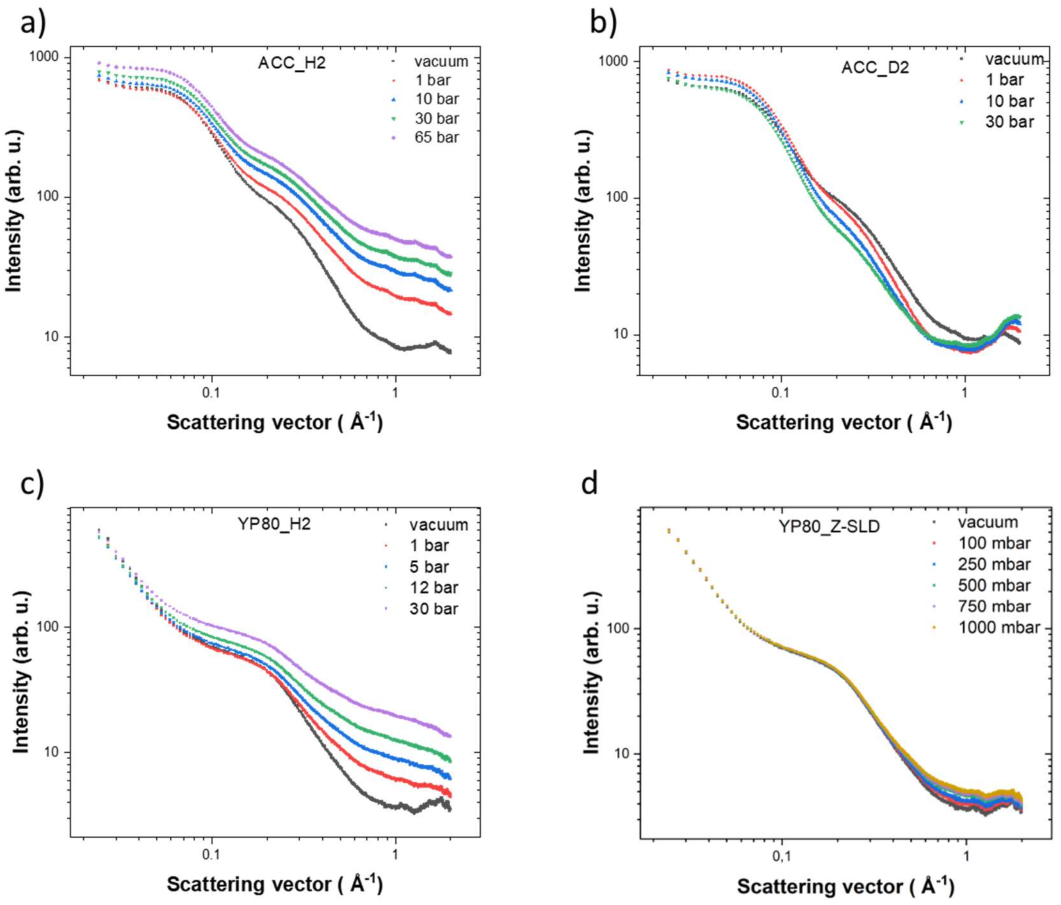

Fig. 1. Data collected for two investigated samples: a) SANS curves of the activated carbon cloth (ACC) material at different H2 pressures up to 65 bar, b) the corresponding curves for D2 adsorption up to 30 bar, c) SANS curves of the YP80 activated carbon material at different H2 pressures up to 30 bar and d) the SANS measurement of YP80 using zero-SLD mixture at different pressures up to 1000 mbar

Fig. 2 shows the collected data for the sample MSP20 at 77 K for $H_2$ (a and b), $D_2$ (c and d) and for the Z-SLD gas mixture (e and f). The evolution of the intensity upon pressurization with $H_2$ and $D_2$ follow the same trends as the other samples. In Fig. 2 e) the SANS data collected using the Z-SLD gas mixture are shown. In the low Q-regime (< 0.05 Å$^{-1}$), where scattering originates from micrometer sized carbon particles, very little to no change in intensity upon pressurization occurs, thus confirming the Z-SLD properties of the bulk gas mixture. In the mid Q-region ($0.1 < Q < 0.3$ Å$^{-1}$) a slight increase of intensity is seen, which might result from the increase in incoherent scattering from $H_2$ also seen in the high Q region. Further evaluations of changes of the signals upon pressurizations can only be made after careful determination and subtraction of the incoherent contribution, which is currently still under work. Nevertheless, a combination of the normalized scattering intensities shown in Fig. 2 b) and d) according to the mixing ratio of the bulk gas (64 mol% H2 and 36 mol% D2) is in good agreement with the values shown in Fig. 2 f), although the influence of the incoherent scattering contribution is quite dominant at higher Q. Thus, based on this preliminary data inspection, neither substantial volume changes of the pore space due to adsorption, nor isotope effects seem to influence the gas uptake as a function of pressure.

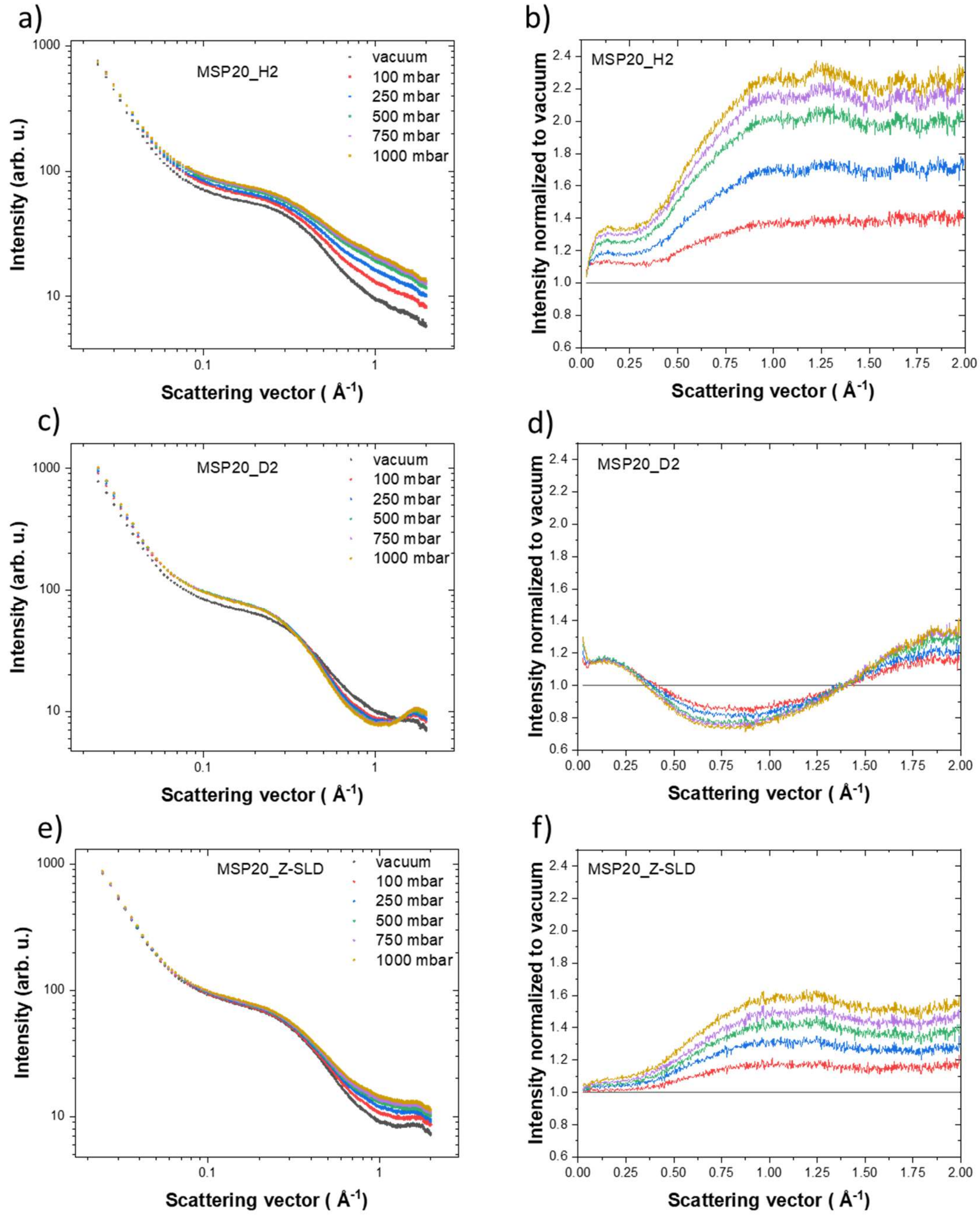

Fig. 2.: Data collected for the third investigated sample MSP20: a) SANS curves of the material at different $H_2$ pressures up to 1000 mbar collected at 77 K, b) SANS curves from a) normalized to the SANS measurement of the evacuated sample. c) and d) show the corresponding plots for $D_2$ at 77 K, e) and f) the corresponding plots for the zero-SLD gas mixture (64 mol% H2 and 36 mol% D2).

Actual data analysis is being carried out towards the quantification of the adsorbed gas density as a function of pressure and scattering vector length using and extending models already known from literature [1, 2]. In a next step we plan to set up real-space structural models of the nanoporous carbon materials, which in combination with simulations of the adsorbed phase within the pores will help to better understand pore size dependent interactions of the gas molecules with the carbon material [3]. Furthermore, more detailed analysis of the data collected using the Z-SLD gas mixture will allow us to cross-check our results towards changes of pore volume due to adsorption induced pore deformation [4], as well as possible isotope effects (e.g., $H_2/D_2$ separation through quantum sieving [5]).

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