Experimental report

25/03/2021

Proposal:	**1-04-218**	**Council:**	10/2020
Title:	Hydrogen storage mechanisms in disordered nanoporous carbons		
Research area:	Materials		

This proposal is a resubmission of 6-07-69

Main proposer:	**Oskar PARIS**
Experimental team:	Malina JOP Sebastian STOCK Nikolaos KOSTOGLOU
Local contacts:	Viviana CRISTIGLIO Bruno DEME

Samples: disordered nanoporous sp2 carbon

Instrument	Requested days	Allocated days	From	To
D22	4	0		
D16	8	4	04/03/2021	08/03/2021

Abstract:

In this proposal, we plan to investigate the low-pressure (0-1 bar) physisorption behavior of hydrogen (H2), deuterium (D2) and a zero scattering length density H2/D2 mixture under cryogenic temperatures (77-100 K) in three disordered carbon systems with different hierarchical pore structures. This will be done by in-situ Small-Angle Neutron Scattering (SANS) at D22 or 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 SANS data will be analyzed by classical models while real space structure models will be also developed. The aim of this study is to gain a deeper understanding of the basic H2 adsorption and storage mechanisms in nanoporous carbons, thus providing guidelines on the tailoring of the carbon pore structure towards optimized H2 storage properties for mobile and stationary CO2-free applications.

Experimental Report for Proposal 1-04-218

Hydrogen storage mechanisms in disordered nanoporous carbons (04.03.-08.03.2021, D16)

Sebastian Stock[1], Malina Jop[1], Bruno Demé[2], Viviana Cristiglio[2], Sylvain Prévost[2],

Nikolaos Kostoglou[3], Christian Mitterer[3], Oskar Paris[3]

Aim of the experiment:

Previous investigations of the fully reversible hydrogen (H_2) adsorption/desorption behavior in disordered nanoporous carbons showed increased gravimetric H_2 uptake values (up to 5.5 wt.%) with high surface areas (>2000 m^2/g). This suggests that the enhanced performance must be attributed to the narrow ultra-micropore size of the materials, and not only to the increased surface area and/or pore volume [1]. There is however only little experimental work on the relationship between the hydrogen density as a function of pore size at a given external pressure. The aim of the beamtime allocated at D16-ILL between 04.03-08.03.2021, was to use in-situ SANS to determine the pressure dependent H_2 uptake in differently sized pores for three activated carbons with different pore size distributions. The original plan was to collect SANS data along with low-pressure (0-1 bar) H_2 adsorption isotherms at different temperatures (77, 87 and 97 K) as well as for different gases (H_2, deuterium (D_2) and a zero-scattering length density (Z-SLD) gas mixture of H_2/D_2).

Experimental details:

Due to restricted beamtime, the planned schedule had to be adapted for two samples (a commercial activated carbon, derived from coconut fibers, YP80F and an activated carbon cloth derived from viscose rayon, ACC), two gases (H_2 and D_2) and two temperatures (77 and 87K). In-situ SANS experiments were conducted using the gas sorption analyzer available at the ILL at various pressure points between 0-1 bar (see Figs. 1a and 1d). 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. SANS signals at D16 were recorded at five detector positions using a wavelength of 4.47 Å, which resulted in a total covered Q-range of 0.04-2 $Å^{-1}$. Sample transmission at each pressure point, together with measurements of the empty cell and a cadmium background were used for data correction. The measured intensity was transformed into differential scattering cross section by using the incoherent scattering of a vanadium standard.

Collected data and preliminary results:

Fig. 1 exemplarily shows the collected data for ACC at 77 K for H_2 (a-c) and D_2 (d-e). The measured isotherms with H_2 and D_2, seen in Fig. 1 a) and d), respectively, are in good agreement with ex-situ laboratory measurements. The strongly increasing scattering intensity upon pressurization with H_2 at large Q-values, seen in Fig. 1 b), can to a large extend be attributed to the increasing amount of H_2 in the system as a result of the large incoherent scattering cross section of hydrogen [2]. Since the incoherent scattering cross section can be uniquely calculated from the adsorption isotherm (Fig. 1a), the coherent scattering can be safely separated from the incoherent scattering. This was not

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[1] Experimental Team

[2] Local Contact

[3] Supervision

yet done due to restricted time, however it will be implemented in a potential publication of the experimental results.

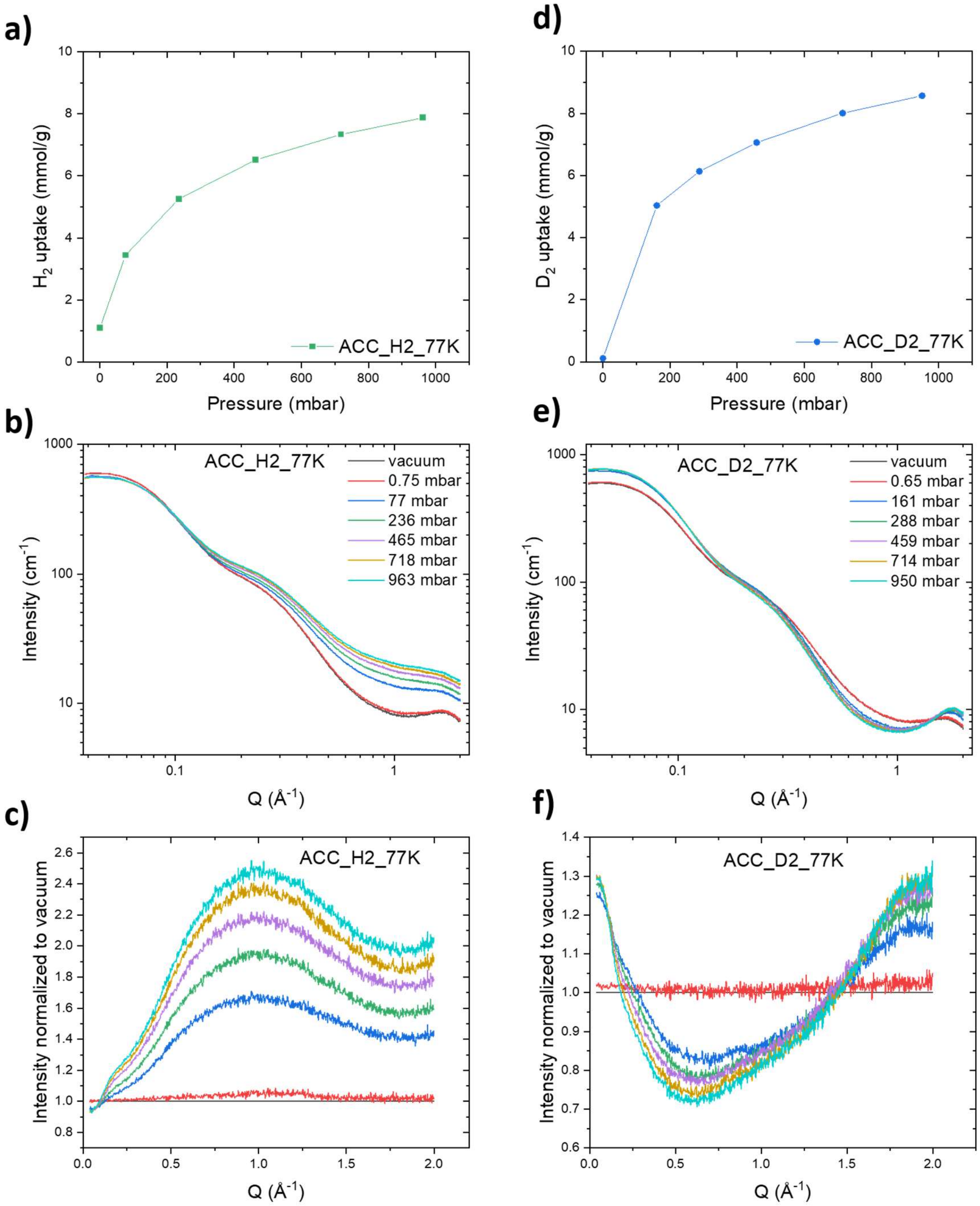

Fig. 1. Data collected for the ACC sample at 77 K: a) Measured H_2 uptake by the manometric adsorption system, b) SANS curves at different gas pressures (corresponding to different amounts of adsorbed H_2), c) SANS curves at different pressure normalized to the SANS measurement of the evacuated sample, d-e) the corresponding plots for the measurements with D_2 at 77 K.

For the SANS signals measured during pressurization with D_2 (Figs. 1 d-e)), an increase of the scattering intensity can be seen at low Q (below ~0.2 Å^{-1}), which is attributed to the increase of the overall scattering length density of some nanometer sized units due to the uptake of D_2. In the intermediate Q-regime (~0.25–1.5 Å^{-1}), the intensity decreases with increasing D_2 uptake. This can be attributed to the micropore filling mechanism, since the scattering contrast between the carbon and the D_2 filled micropores will be smaller as compared to the empty pores. This effect is largest at Q ~0.5 Å^{-1}. A very rough estimate gives D ~π/Q ~6 Å, which coincides quite well with the smallest micropore size present in this sample (see pore size distribution in Fig 1. of the proposal no. 1-04-218). This preliminary result demonstrates clearly that the D_2 density is highest in the smallest pores at a given external pressure, confirming qualitatively our hypothesis of a pore size dependent density evolution of the adsorbed phase. Similar results are expected for H_2 after separation of the incoherent scattering, but with the contrast scenario being reversed due to the negative scattering length of hydrogen. At large Q, the intensity in Figs. 1e) and 1f) finally increases again, which is attributed to increasing D_2-D_2 correlations of a dense D_2 phase. Further data analysis will be carried out towards the quantification of the adsorbed gas density as a function of pressure and pore size according to simple models already known from literature [2, 3]. Furthermore, we plan to set up real space structural models of the nanoporous carbon materials, which in combination with atomistic simulations of the adsorbed phase within these pores will help to better understand pore size dependent interactions of the gas molecules with the host material [4].

In conclusion, we were able to collect an excellent first in-situ SANS dataset on the hydrogen adsorption in nanoporous carbons at temperatures relevant for cryogenic hydrogen storage applications. A continuation of this activity is planned with proposal no. 1-04-235 to extend the pressure range up to 100 bar, as well as collect more data with different gases to also elaborate on volume change effects of the nanoporous materials (i.e. adsorption induced deformation [5]), as well as on possible isotope effects (i.e. H_2/D_2 separation through quantum sieving [6]). Furthermore, experiments with inelastic and quasi-elastic neutron scattering are also planned to elucidate the effect of confinement on the hydrogen dynamics and diffusion kinetics inside the pore structure (see proposal no. 1-04-239).

References:

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