Experimental report

15/02/2021

Proposal: **6-07-61**

Council: 10/2019

Title: Neutron diffraction studies of strongly confined D2 in ultramicroporous carbon materials

Research area: Materials

This proposal is a new proposal

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Samples: Carbon samples

Instrument	Requested days	Allocated days	From	To
D20	3	3	18/02/2020	21/02/2020

Abstract:

Carbon samples with extremely large H2 uptake, in comparison to the uptake of other gasses, have been synthesized and characterized by N2 and H2 adsorption, Raman spectroscopy, XRD, XRF, and EDS. Based on the preliminary results these carbon samples have extremely narrow ultramicroporosity (wpore < 0.4 nm), in addition to larger pores, don't exhibit large amounts of impurities and are structurally characteristic to hard carbons. Neutron powder diffraction will be used to probe the possible ordered adsorption of D2 into these ultramicroporous (pore width < 0.7 nm) carbon materials. This would give invaluable information about the interactions of gasses in extremely narrow pores and the possible intercalation of D2 (and thus, possibly H2) into the hard carbon structure through these extremely narrow pores.

Neutron diffraction studies of strongly confined D_2 in ultramicroporous carbon materials

Scientific background and aim of this experiment

Ultramicropores (pores with widths < 0.7 nm) accessible to H_2 are not always accessible to gasses (N_2, CO_2, or Ar), which are used for the determination of porosity and specific surface area [1]. Thus, ultramicroporous materials might be able to surpass the H_2 storage limits previously predicted for carbon materials based on their specific surface areas and micropore volumes. Also, the presence of ultramicropores might enable the formation of highly ordered adsorbed H_2 phase, i.e., intercalation between graphitic layers and strong adsorption potential wells. In case of the intercalation of D_2 or the formation of a long-range ordered adsorbed phase, Bragg peaks would be detectable by neutron powder diffraction, and the structure of the adsorbed/intercalated D_2 could be determined. To investigate the possibility of H_2/D_2 intercalation and the formation of an ordered adsorbed phase in an ultramicroporous carbon material, peat-derived carbon (PDC), with a substantial ratio of ultramicropores, has been synthesized and characterized. Neutron diffraction experiments of the synthesized PDC have been performed on D20 at ILL. For comparison, neutron diffraction of a micro/mesoporous carbide-derived carbon with D_2 loading is measured at similar conditions.

Experimental routines:

Neutron diffraction measurements were performed on two carbon materials: ultramicroporous peat-derived carbon, PDC, and micro/mesoporous carbide-derived carbon, CDC. Both materials were degassed before measurement, and neutrons with a wavelength of 2.41 Å were used. In the case of PDC, after the initial measurement cycle starting from 20 K, heating cycles to 200 K and 150 K were performed to enhance the transport properties of H_2 in the ultramicropores. All doses of D_2 were applied at 77 K, $p_{\mathrm{D2,load}}$, and equilibrated for at least half an hour or until the pressure reading stabilized. NPD data was acquired during all heating, cooling, and dosing steps. Lower $p_{\mathrm{D2,load}}$ were applied in the case of the CDC sample, as based on yet unpublished neutron scattering data, Bragg peaks form at 50 K under low $p_{\mathrm{H2,load}}$, ≥ 68 mbar, and at equivalent T control routine to the one applied in this experiment in case of the CDC.

Table 1. Experimental routine

CDC first cycle	CDC second cycle	PDC first cycle	PDC second cycle
Cooling to 77 K	Cooling to 77 K	Cooling to 77 K	Cooling to 77 K
Dosing 37.7 mbar of D_2	Dosing 84.2 mbar of D_2	Dosing 179.4 mbar of D_2	Dosing 431.3 mbar of D_2
Cooling to 20 K	Cooling to 15 K	Cooling to 15 K	Cooling to 15 K
NPD data acquisition at 20, 30, 40, 50, 60, 70, 80, 90 and 100 K	NPD data acquisition at 20, 40, 50, and 60 K	NPD data acquisition at 15, 20, 30, and 40 K	NPD data acquisition at 15, 20, 40, 60 K, 80 K, and 100 K
		Heating to 200 K	Heating to 150 K
		Cooling to 15 K	Cooling to 15 K
		NPD data acquisition at 15, 20, 30, 40 K	NPD data acquisition at 15, 20, 40, 60 K, 80 K, and 100 K

Experimental results:

Because the d-spacing of Bragg peaks depends on the applied T and diffractograms were measured at a wide range of T-s, direct subtraction of the empty sample holder was not performed, and the Bragg peaks from the empty sample holders are presented for comparison separately (Figures 1 and 2). Most of the Bragg peaks are caused by the sample holder (Figures 1 and 2), where a total of three Bragg diffraction regions characteristic of graphitic carbons are present. These are a sharp (002) at d-spacing of 3.35 Å, a wide (002) in the d-spacing region from 3.0 to 3.75 Å, and a wide peak in the d-spacing region from 1.8 to 2.25 Å, which is a combination of the (100) and (101) Bragg peaks.

In the case of the micro/mesoporous CDC, no intercalation nor strong adsorption was detected as no sharp Bragg peaks appeared with the application of $p_{\mathrm{D2,load}}$, or with the control of T (Figure 1). With the increase of $p_{\mathrm{D2,load}}$, the intensity of the wide (002) Bragg peak increased. The wide (002) Bragg peak corresponds to the interlayer ordering of graphitic layers in a disordered graphitic material. As the intensity of the wide (002) Bragg peak increases with increased $p_{\mathrm{D2,load}}$, it is likely that the adsorption of D_2 increases the number density of graphitic domains. This will be investigated further.

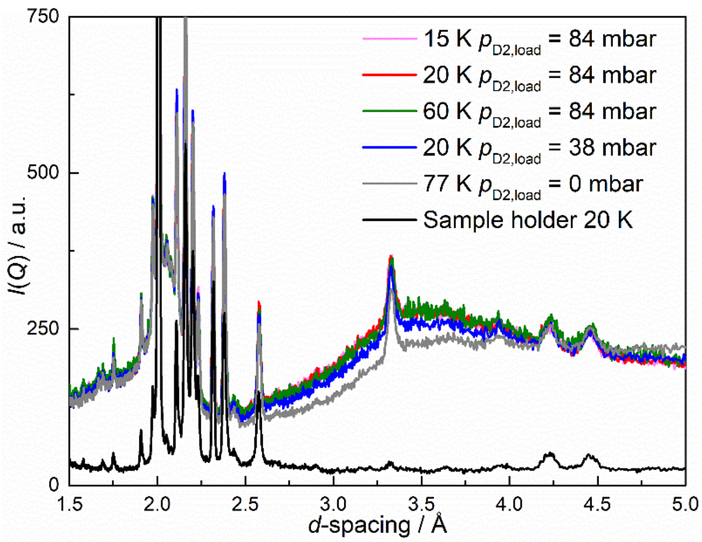

Figure 1. Diffractograms of the CDC material and the sample holder at different T and $p_{\mathrm{D2,load}}$ conditions (brought in Figure.)

In the case of the ultramicroporous PDC, a very strong incoherent background is present, which is most likely caused by the impurities in the carbon material, e.g., H in C-H bonds. There is no visible influence of the $p_{\mathrm{D2,load}}$ on the wide (002) Bragg peak, unlike in the case of CDC (Figure 2). With the increase of $p_{\mathrm{D2,load}}$ to 431 mbar and at T = 15 K, e.g., lower than the triple point T of D_2 (18.73 K), three Bragg peaks appeared at d-spacing of 2.75, 2.93, and 3.11 Å (Figures 2 and 3). The Bragg peaks disappeared upon heating to 20 K and appeared again during the second cycle (Figure 3). Thus, the process was highly sensitive to T and reversible. The three beforementioned and one additional (at

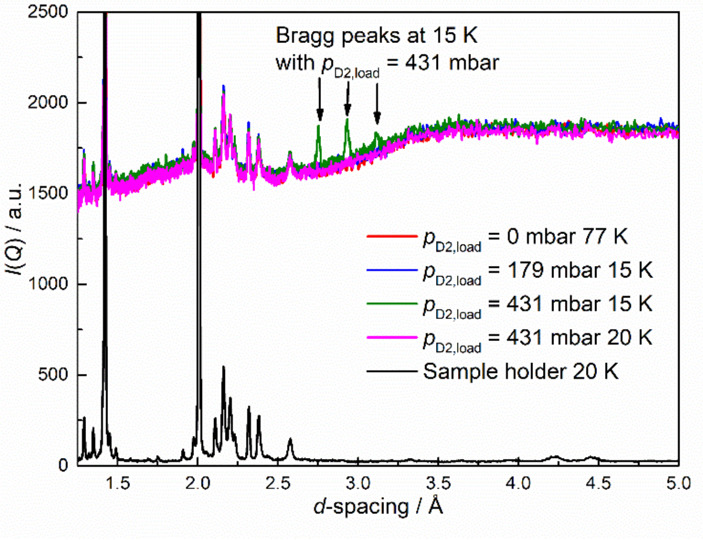

Figure 2. Diffractograms of the PDC material and the sample holder at different T and $p_{\mathrm{D2,load}}$

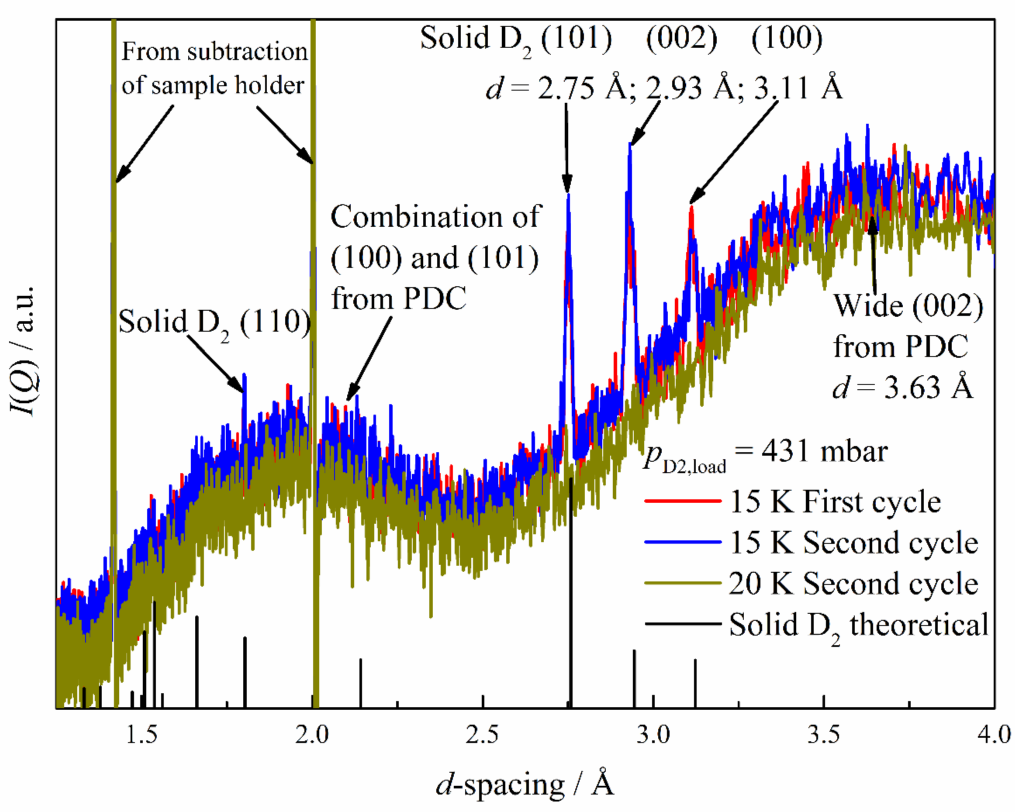

Figure 3. Diffractograms of the PDC under $p_{\mathrm{D2,load}}$ = 431 mbar applied at 77 K and from which the diffractogram of the empty sample holder has been subtracted. Solid D_2 Bragg peak *d*-spacings are determined based on Ref. [3].

d-spacing of 1.8 Å) Bragg peaks are characteristic of solid D_2 in a hexagonal hcp structure with P63/mmc space group [2,3]. As the D_2 loading pressure was applied at 77 K the equilibrium pressure at the experimental conditions (15 K) was under the lower measurement limit (1 mbar), which is lower than the vapor pressure of D_2 at 15 K. Thus, the cause for the formation of a large enough D_2 crystal for detection with NPD will be investigated further.

Further plans:

In situ neutron diffraction measurements of these materials at similar conditions under H_2 loading have been applied for. Based on these additional measurements, it would be possible to determine if these phenomena are truly from the changes in carbon structure (increase in the (002) intensity of CDC material) or from the formation of adsorbate crystal structures (Solid D_2 in case of PDC). Together with lab-scale characterization methods, the results will be published in a peer-reviewed journal.

References:

[1] J. Jagiello, M. Thommes, Carbon 42 (2004) 1227–1232.
[2] A.F. Schuch, R.L. Mills, Phys. Rev. Lett. 16 (1966) 616–618.
[3] I.N. Krupskij, A.I. Prokhvatilov, G.N. Shcherbakov, Fizika Nizkikh Temperatur 10 (1984) 5–12.