Experimental report

02/02/2016

Proposal: 7-05-438 **Council:** 10/2014

Title: Hydrogen Diffusion in Carbon Aerogels

Research area: Chemistry

This proposal is a resubmission of 7-05-429

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Samples: H2/Carbon Aerogel

Instrument	Requested days	Allocated days	From	To
IN11	14	8	24/04/2015	02/05/2015

Abstract:

We propose a neutron spin-echo study of the diffusion of molecular hydrogen adsorbed in carbon aerogel, which has been produced by the group of the Hungarian co-proposer. Carbon aerogels exhibit a well-developed, hierarchal pore structure. Their specific surface area, as well as the pore size distribution (the ratio between micro-, meso- and macropores) can be finely tuned during the preparation process. Further treatments, such as activation, oxidation, etc. open the possibility to change the surface chemistry of these carbons. Addition of melamine, urea, etc. to the precursor synthesis mixture leads to N-containing carbon aerogels, which are particularly advantageous as PEMFC cathodes. We propose to compare the hydrogen dynamics on 3 aerogel samples with different pore size and similar surface properties. We will also compare these data with our recently obtained data from exfoliated graphite and standard XC72 carbon blacks. In the revised form of the proposal we cite more of our previous work that contains the characterization of the sample. Moreover, we give more precise details (highlighted in bold) about the experimental details, as was requested during the previous review.

"Dynamics of molecular hydrogen in carbon gel systems"

Experimental report on 7-05-438 and 7-05-451 experiments

This report summarizes the main results of two experiments performed in 2015 (7-05-438: 24/04/2015-02/05/2015 and 7-05-451: 06/11/2015- 13/11/2015). The reason for the common experimental report is that in the first proposal round, in Autumn 2014 only half of the demanded beamtime had been allocated, and for the second half of the project we applied for additional beamtime in Spring 2015, which was granted. Nevertheless the results from the two beamtimes are strongly correlated and were evaluated together.

The goal of the experiments was a neutron spin-echo (NSE) spectroscopy study of the diffusion of molecular hydrogen that has been adsorbed in different carbon gel systems. Carbon gels have attracted great attention recently, mostly because of their extremely versatile structure. They are prepared from porous polymer gels, most often obtained in the polycondensation reaction of resorcinol and formaldehyde [1]. The specific surface area, as well as the pore size distribution (including the ratio between micro-, meso- and macropores) can be finely tuned during the preparation process. A previous test experiment showed the feasibility of the NSE measurements on one of the selected samples. Literature studies revealed that although several reports are available on the adsorption behaviour of H_2 on different types of porous carbon materials, no systematic study was available on the role of the pore structure and surface chemistry of the carbon on the uptake and diffusion of H_2. With our 2 experiments performed in 2015 we intended to explore the effect of these parameters on the diffusion properties of H_2 on carbon gels. As starting point 3 samples were selected, of which 2 had similar pore properties, but different surface chemistry, while another pair had similar surface chemistry but different pore characteristics [2]. Table 1 and Figure 1 summarize the principal characteristics of the carbon aerogel samples. The neutron scattering measurements on samples CAox and CX have been performed on IN11 during the two, above mentioned, beamtimes, whereas the data of CA(old) is a result of a beamtime at OSIRIS, ISIS, UK [3].

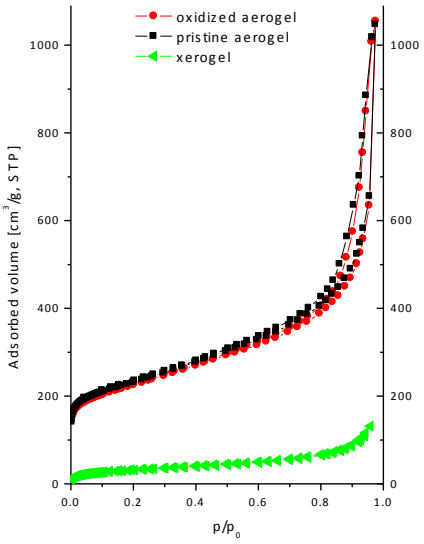

Figure 1. Low temperature (77 K) N_2 adsorption/desorption isotherms of the investigated carbon gel systems

Table 1. Surface composition from XPS and micropore ratio from N_2 adsorption measurements of the carbon gels

Sample	Acronym	C1s [atom%]	O1s [atom%]	Micropore ratio [%]
Pristine aerogel	CA(old)	95	5	35
Oxidised aerogel	CAox	86.8	13.2	33
Xerogel	CX	91.4	8.6	60

The NSE measurements were performed after adsorbing 0.5 monolayers of H_2 (at 20K) onto the carbon sample, in the temperature range of 20-80 K. An example of the obtained incoherent intermediate scattering functions (IISF) is shown in Figure 2.

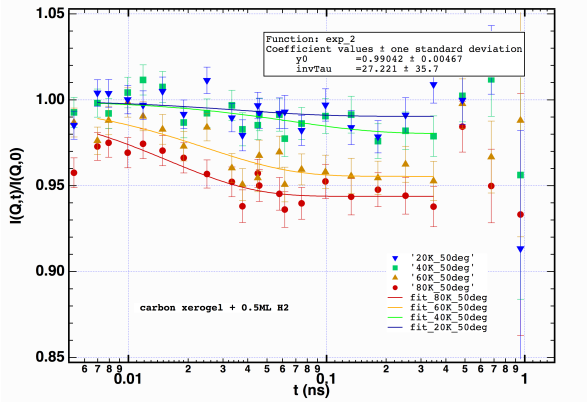

Figure 2 Incoherent intermediate scattering functions obtained from neutron spin-echo measurements the CX sample

The characteristic decay time was obtained by fitting the IISFs by a single exponential function. As the Arrhenius plot of the obtained time constants (Figure 3) shows, significant differences were deduced in the mobility of the H_2 on the carbon gel surface, revealing the very strong effect of the surface chemistry, and only a moderate effect of the pore size. On the other hand, desorption of the H_2 (Figure 4) seems to be affected dramatically by the porosity of the carbon, and practically non-affected by the surface chemistry.

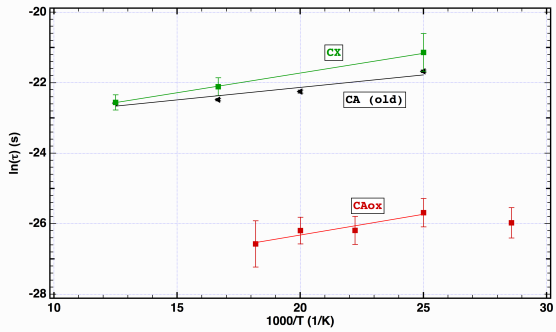

Figure 3. Arrhenius plot of the H_2 diffusion on carbon gel surface. τ: time constant of the diffusion given in s, T: temperature

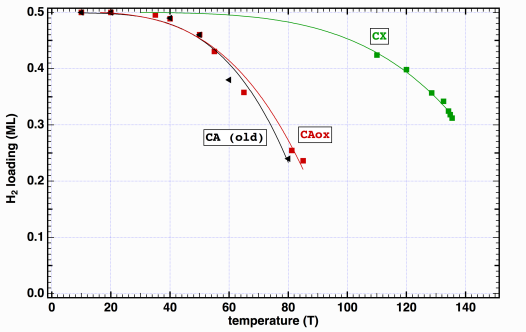

Figure 4. H_2 loading as a function of temperature on different carbon aerogels. The adsorption of 0.5 monolayer (ML) H_2 was made at 20K at all cases. The desorbed amount was calculated from the measured pressure change

Further H_2 adsorption measurements at different temperatures and pressures are still in progress; therefore more definite conclusions cannot be drawn at this point. Nevertheless, our results reveal that a systematic study is needed to fully understand the implications of surface chemistry and pore structure for the H_2 storage properties of the carbon gels.

References:

[1] Pekala, R.W.; J. Mater. Sci. 24 (1989) 3221.

[2] Czakkel, O.; Marthi, K.; Geissler, E.; László, K.; Micropor. Mesopor. Mater. 86 (2005) 124.

[3] Bahn, E., Czakkel, O., Nagy, B, László, K., Villar-Rodil, S., Tascon, J.M.D., Demmel, F., Telling, M., Fouquet, P.; Carbon 98 (2016) 572-581.