Experimental Report

04/09/2014

Proposal:	**7-05-415**	**Council:**	10/2012
Title:	Hydrogen diffusion in novel porouscarbon materials for fuel cells - ToF study		

This proposal is resubmission of: 6-04-270

Researh Area: Chemistry

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Samples:
H2
porous carbon
porous carbon - Pt

Instrument	**Req. Days**	**All. Days**	**From**	**To**
IN6	7	5	08/03/2013	13/03/2013

Abstract:

The performance of polymer electrolyte fuel cells (PEMFC) is strongly dependent on the diffusion rate of hydrogen and the electron mobility, which in turn is strongly influenced by the porous carbons, which are used as catalyst supports in PEMFC. We propose to perform ToF measurements to characterize hydrogen diffusion in several samples of nitrogen doped porous carbons (N-PC), which we have synthesized. Compared to commercial activated carbon, our porous carbons generally present higher specific surface area, a higher graphitic character and lower amount or absence of micropores, which we think should enhance hydrogen diffusivity. In addition the nitrogen doping decreases the band gap of our porous carbons. With these measurements, we would like to establish the impact of the nitrogen doping, the pore size/shape and the graphitic character of our samples on the hydrogen diffusivity. We have already prepared a set of different samples, which we have characterized with Raman spectroscopy and TEM measurements.

Aims of the experiment and scientific background:

Carbon blacks, such as Vulcan XC-72, are widely used as catalyst support materials in polymer electrolyte fuel cells (PEMFC). They are characterized by a high specific surface area, but contain a high fraction of micropores of less than 1nm diameter, which hinder hydrogen diffusion and the access of the fuel to the supported Pt catalyst. Furthermore, carbon blacks typically have a low electrical conductivity in the order of 0.1 S/cm, which slows down the electron transport. We have recently started synthesis of **nitrogen doped porous carbons (N-PC)**, a promising alternative to carbon blacks *(1,2)*: N-PC present higher surface area and lower amount or absence of micropores, which is an advantage for both metal dispersion and diffusion of reactants and products. Besides, our N-PC was synthesized using polyaniline as nitrogen containing carbon source, which reduces the band gap ($E= E_{HOMO}-E_{LUMO}$) allowing a higher conductivity compared to commercially available activated carbons.

For an intelligent optimization of the carbon catalyst support we need to obtain a detailed characterization of electronic and chemical properties, the porous structure as well as the diffusion coefficient of hydrogen in these carbon materials.

The proposed study is part of a PhD project in synthesis and characterization of conductive N-PC supports for hydrogen PEMFC, which is done in collaboration between ILL and the University of Antioquia, Colombia.

Results of preliminary work

We had performed different characterization steps already: Raman spectra of our porous carbons (see Fig. 2) show a composite nature, which is characterized by the ratio between the signals from structurally disordered, I_D, and graphitic parts of the sample, I_G (I_D/I_G = 1.27 for the 8% nitrogen sample shown in Fig. 1). Our carbons are substantially more graphitic than the widely used Vulcan XC-72 (I_D/I_G = 1.94) (*3*), but on the other hand gas adsorption measurements show that our N-PC has much higher specific surface area than XC-72 (~400-800 m^2/g compared to 250 m^2/g). We expect, thus, improved hydrogen diffusion in our samples. We have already performed QENS measurements of hydrogen in XC-72 carbons (*4*), giving us a base line for the proposed study.

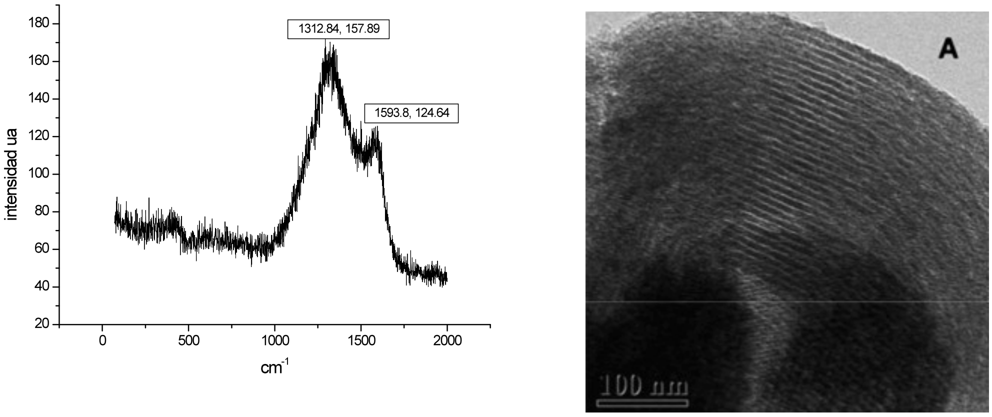

Fig. 1 Left-hand-side: Raman spectra of N-PC porous carbon (our data). Right-hand-side: TEM picture of N-PC sample from ref. 6.

Results

We investigated the dynamics of hydrogen adsorbed on two materials, 1. exfoliated graphite and 2. a highly porous novel carbon material. The measurements were taken on the ToF spectrometer IN6 in a temperature range from 1.5 K (reference) to 80 K at with the hydrogen reservoir connected to the sample cell. The scattering law S(Q,ΔE) was measured over a range of: 0.3 Å < Q < 2.8 Å and -6 meV < ΔE < 2 meV (see Fig. 1). The elastic peak can clearly be seen as the red stripe.

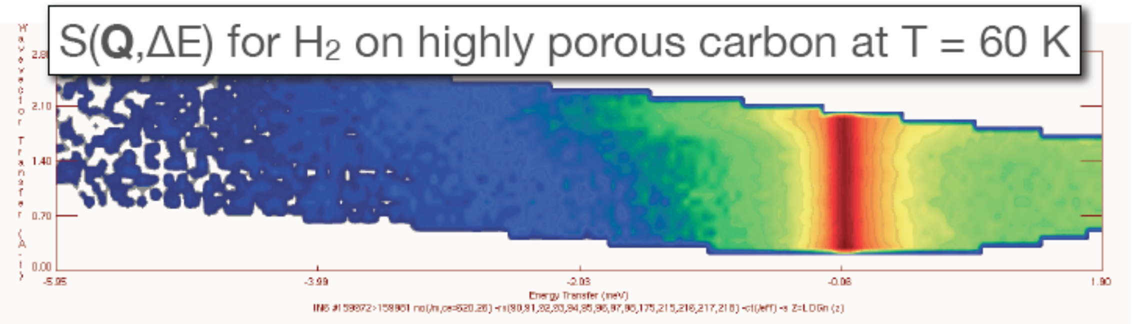

Figure 1: 2d graph of S(Q, ΔE) for H_2 on porous carbon at 60 K.

In order to obtain the QENS broadening, each slice S(Q,ΔE) of constant Q was fitted with a Lorentzian function, convoluted by the instrumental resolution function. The Lorentzian function provides a good approximation and shows more stability than e.g. a Voigt distribution (see Fig. 2).

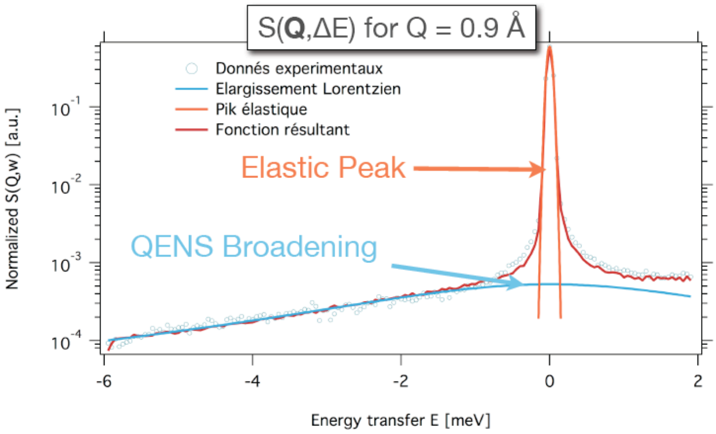

Figure 2: Cut through the S(Q, ΔE) at a momentum transfer Q of 0.9 1/Å. The QENS broadening is clearly visible.

The HWHM of the Lorentzian function gave us the QENS broadening for each Q and temperature. In Fig. 3 the Q-dependence is fitted by
1. a function derived from the free gas model
2. a function derived from a jump diffusion model
The functions were fitted by a formula allowing for two variable jump lengths since a formula with one single jump length failed clearly to fit the data. It can be clearly seen how the jump diffusion model (rather than the free gas model) reproduces the oscillatory behavior of the QENS-broadening in a very satisfying way.

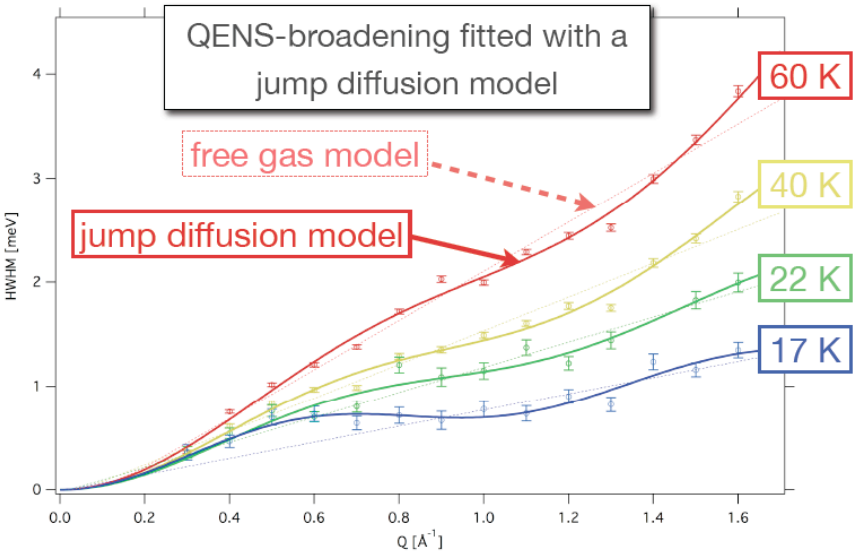

Figure 3: QENS broadening versus momentum transfer for temperatures in the range 17 to 60 K.

The jump lengths that we found by this method show some interesting behavior:

1. the small jump length is in the range of a single CC bond length in graphene.

2. the big jump length is in the range of four C-C bond lengths.

3. Both jump lengths are most probably an average over similar jump lengths.

4. For decreasing temperature the jump lengths exhibits an increase. This might be due to a changing accessibility of different adsorption sites, or a sign of quantum effects.

We will continue our data analysis based on these preliminary findings.

References

1. Jun, S. at al., *J. Am. Chem. Soc.* (2000), 122, 10712.
2. Chang, H., Joo, S. H., and Pak, C. (2007) *J. Mat. Chem. 17*, 3078.
3. Pantea, D. et al. (2001) *Carbon 39*, 1147.
4. Haas, O.-E., Fouquet P., et al. (2008) *J. Phys. Chem. C 112*, 3121.
5. Zhang, F. et al., *J. Am. Chem. Soc.* (2005), 127, 13508.
6. Lei, Z. et al., *Microporous Mesoporous Mat.* (2009), 119, 30.