

Experimental report

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Proposal: 7-05-468

Council: 10/2016

Title: Confirming effects of pore geometry on H₂ densification for hydrogen storage

Research area: Materials

This proposal is a new proposal

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Samples: C

Instrument	Requested days	Allocated days	From	To
IN4	5	3	27/01/2017	30/01/2017

Abstract:

Neutron scattering is one of the few experimental techniques that can directly determine the state of confined H₂ molecules in microporous solids. We recently reported the experimental evidence of an existence of the solid-like H₂ in optimally sized pores based on the correlation of inelastic neutron scattering (INS) measurements with volumetric gas sorption experiments at 77 K (above the liquid-vapour critical temperature of bulk H₂). This confirmed the role of pore dimension in compressing and densifying the adsorbed hydrogen. In order to understand this phenomenon further, the effects of pore geometry of such microporous materials on the H₂ densification needed to be explored. In this proposal we seek to elucidate the effects of pore geometry (i.e. amorphous, cylindrical and slit pores) on hydrogen densification in nanoporous carbon materials for adsorptive hydrogen storage.

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Confirming effects of pore geometry on H₂ densification for hydrogen storage

Evaluation of the limiting hydrogen storage capacities of porous hydrogen storage materials are generally based on the assumption that the adsorbed hydrogen reaches a maximum density similar to that of liquid hydrogen. Recent work in our group published in *ACS Nano* [1] showed experimental evidence for solid-like H₂ in the optimally sized pores of TE7 carbon at 77 K (above the liquid-vapour critical temperature of bulk H₂). While the role of optimal pore dimension in causing this H₂ densification has been widely accepted [2], to understand this phenomenon, the effects of pore geometry of such microporous materials on the H₂ densification needed to be explored. Measurements on a disordered TE7 activated carbon, a Ti-CDC 800 titanium carbide-derived carbon with slit pore geometry, and a sample of single walled carbon nanotubes (SWCNT) with cylindrical pore geometry dosed with H₂ were subsequently carried out on TOSCA INS instrument at ISIS, UK. However, the INS measurements from single-walled carbon nanotubes (SWCNT), despite showing the highest hydrogen uptake of the three materials studied, did not show the expected rotor indicative of solid-like adsorbed hydrogen contributions, even at 20 bar dosing pressure. This anomalous result from the SWCNTs needed to be confirmed for the effect of pore geometry to be verified.

INS spectra were collected across an energy window of -75 to +28 meV on IN4. Samples were degassed prior to analysis at 623 K for 8 hours under vacuum (0.1 mPa) and loaded into a cylindrical aluminium sample can inside an argon glovebox. The temperature of the sample regulated by an ancillary cryo-furnace between 200 – 4 K. The sample was dosed with normal H₂ (Air Liquide, 99.999% purity) using a Hiden Isochema HTP-1 gas sorption analyser and equilibrated under a pressure of 1 bar. INS data were collected at the appropriate temperatures and pressures over a period of two hours, and were background subtracted with degassed samples under vacuum at the corresponding temperatures and pressures over the same time period. The samples were inspected for the presence of the 'rotor line' peak at ~14.7 meV representing the *para-to-ortho* transition for H₂ immobilised in 3 dimensions, indicating the densification of hydrogen inside the samples.

The SWCNTs exhibited the rotor line at +14.7 meV confirming the densification of H₂ indicating that pore geometry was not the main determinant of the densification, but that the pore size was a more important factor (Figure 1 left). Isobaric and isothermal experiments (Figure 2 left & centre) on TE7 carbon beads revealed further physical parameters of the densified H₂. The isobaric experiment on TE7 carbon at 1 bar from 77 K to 150 K revealed a decrease in the intensity of the rotor line with increasing temperature and its disappearance between 100 and 150 K indicated the densified H₂ appears between these two temperatures. Isothermal experiments at 77 K on TE7 carbon dosed with 1 bar H₂ for 10 minutes, after which the pressure was reduced to vacuum (0.1 mbar) in attempt to outgas the hydrogen. A reduction in peak intensity was observed, however the rotor line remained even after 25 minutes of outgassing indicating the dense H₂ remained in the sample under these conditions. A large monolith of TE7 was analysed to confirm whether it also caused densification like the previous sample of TE7 beads (Figure 2 right). The rotor line was identified confirming the densification of H₂.

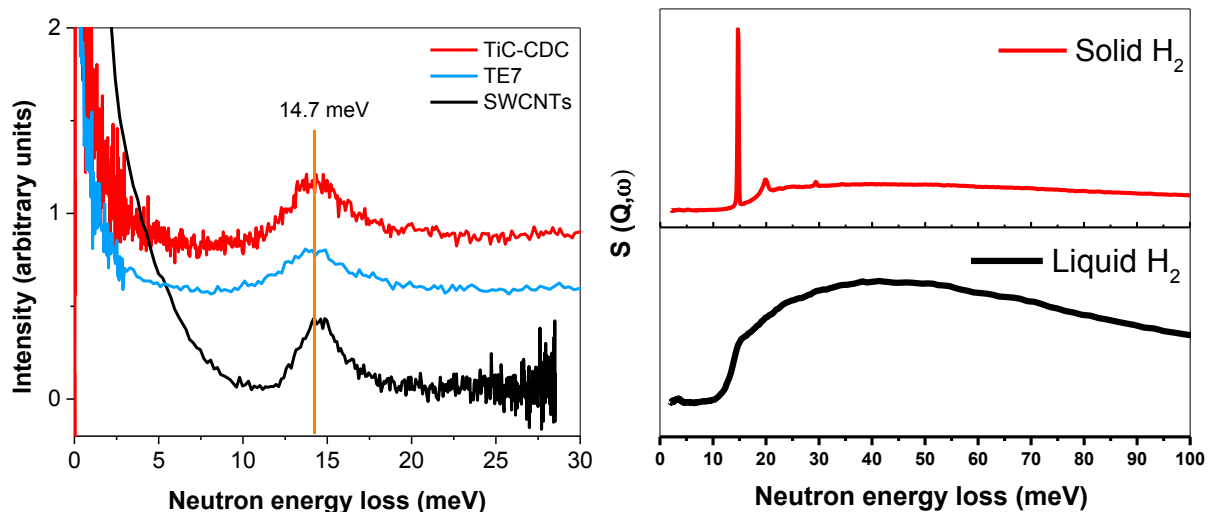


Figure 1: Left) INS spectra of SWCNT dosed with 1 bar H₂ at 77 K as compared to previous TE7 and TiC-CDC samples. Right) Reference INS spectra of solid and liquid H₂.

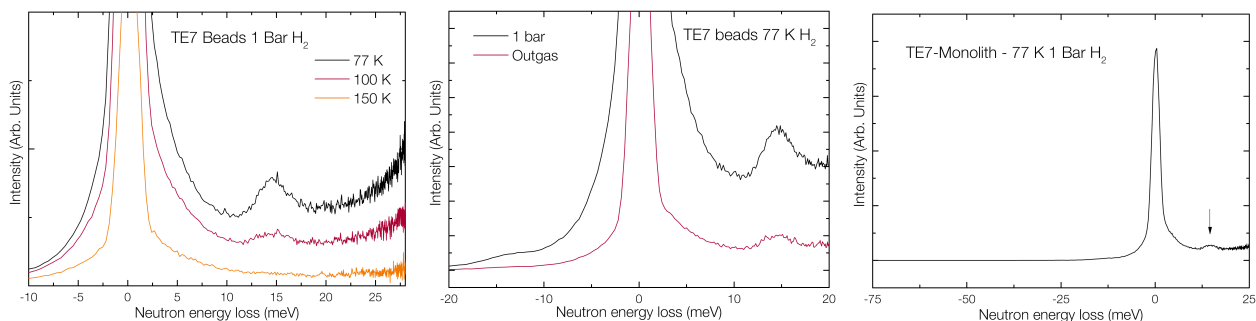


Figure 2: INS spectra of TE7 beads (left/centre) and TE7 monolith (right) dosed with 1 bar H₂ at 77 K. The rotor peak at 14.7 meV is visible for samples at 77 K indicating the densification of hydrogen. Increasing the temperature for the beads (left) the rotor line disappears between 100 and 150 K. Decreasing the pressure for the beads (outgassing) to remove the H₂ (centre) saw a reduction in peak intensity.

The results of this experiment are being prepared as a publication for submission to JACS.

1. Ting, V.P., et al., *Direct Evidence for Solid-like Hydrogen in a Nanoporous Carbon Hydrogen Storage Material at Supercritical Temperatures*. ACS Nano, 2015. **9**(8): p. 8249-8254.
2. Gogotsi, Y., et al., *Importance of pore size in high-pressure hydrogen storage by porous carbons*. International Journal of Hydrogen Energy, 2009. **34**(15): p. 6314-6319.