The Quantum Effects of Pore Structure on Hydrogen Adsorption

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Project ID #
ST107

Overview

Timeline

- Start: Nov 2011
- End: Oct 2013
- 25% complete

Barriers

- Barrier
  - Volumetric Hydrogen Storage
- Target
  - By 2017, 40 g H_2 /L

Budget

- Total project funding
  - DOE share: $ 200 K
  - Contractor share: $ 0
- Funding received in FY11: $15 K
- Funding for FY12: $ 100 K

Partners

- ALL-CRAFT – University of Missouri Columbia – sample manufacturing
- Carbon Materials Technology Group – ORNL – sample characterization
- Oak Ridge National Laboratory – host site

Relevance

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  - Storage via adsorption is preferred because its fast kinetics allow for quick and simple refueling
  - Carbon adsorbents are particularly desirable for their low cost and chemical stability
  - Adsorbent systems do not meet DOE hydrogen storage volumetric system targets, particularly at ambient temperature
  - However, work by the Hydrogen Storage Engineering Center of Excellence on adsorbent systems has shown improvements towards meeting the other DOE system-level targets
- Objectives
  - To understand the performance of a carbon adsorbent with room temperature volumetric storage twice that of similar materials (17.8 g/L vs. 8.8 g/L at 300 K, 90 bar) despite having nearly a quarter of the surface area (700 m^2/g vs. 2500 m^2/g)
    - The sample does not display significantly different energetics than similar carbon samples

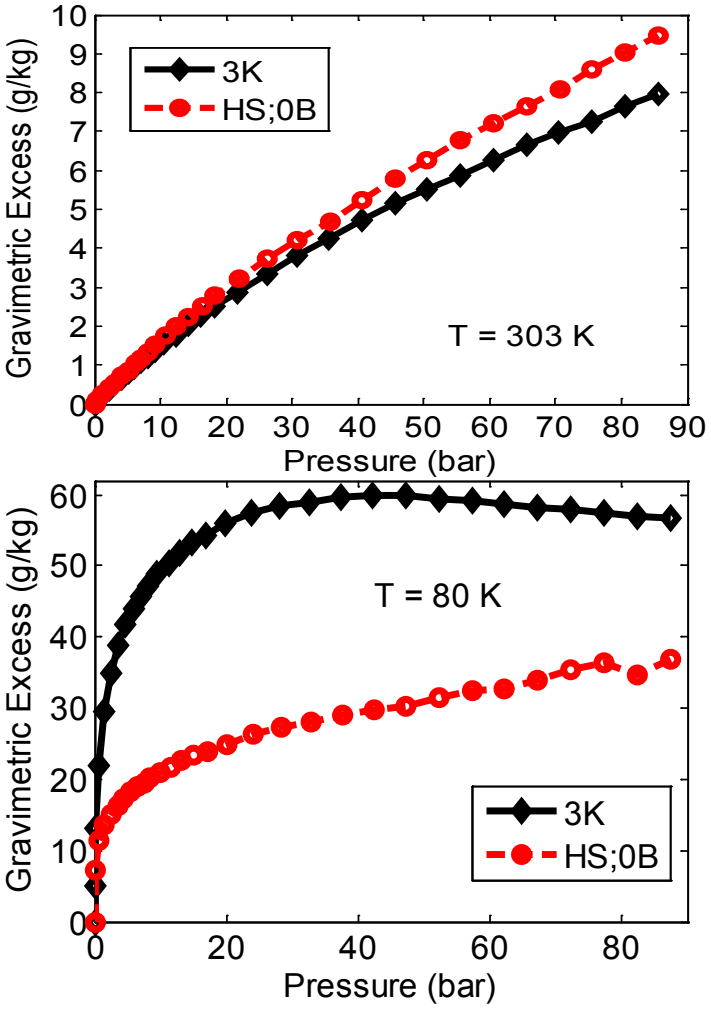
Approach

- Neutron scattering
  - Inelastic neutron scattering measures quantum states of hydrogen molecules while they are adsorbed
  - The sample of interest displays unique quantum states compared to similar carbon samples
  - Understand quantum states of all carbon samples
  - Measure quantum states of variants of sample of interest
- Sample characterization
  - Preliminary work shows sample of interest has a unique structure
  - Characterize properties of variants of sample of interest and link to performance
- Computational work
  - Calculate origin of quantum states observed experimentally with inelastic neutron scattering
- Theory
  - Propose quantum model of adsorption

Approach

Date	Milestone	Status
Oct 2013	Inelastic neutron scattering and analysis of data for variants of sample of interest, plus an activated carbon	Data collected
July 2013	Inelastic neutron scattering for an oriented sample and analysis of data	Beam time awarded, sample constructed
April 2013	Structural characterization (TEM, X-ray diffraction, Raman scattering, CO_2 adsorption) on variants of sample of interest, plus an activated carbon	Instrument time awarded, adsorption experiments begun
Oct 2013	Solve for quantum states of adsorbed hydrogen on graphene and in modified pore structures based on characterization work	3-dimensional Schrodinger equation solved for graphene adsorption potential

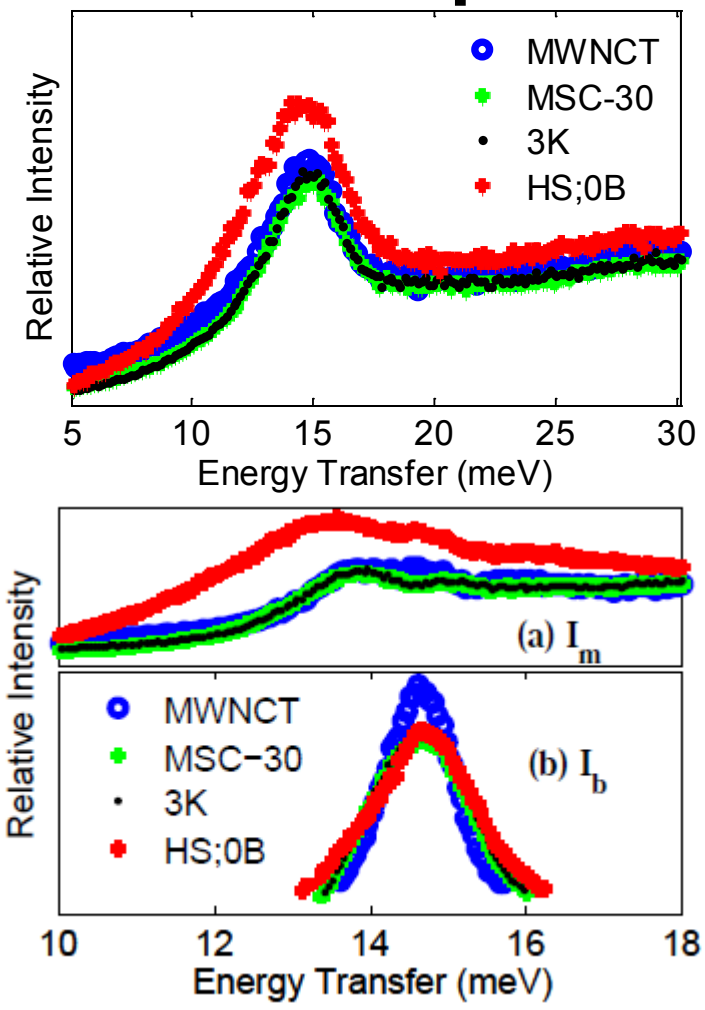
Accomplishments (Preliminary)



Excess gravimetric hydrogen adsorption at (top) room and (bottom) cryogenic temperatures, for PVDC carbon HS;0B (surface area 700 m2/g, pore volume 0.34 cc/g) and activated carbon 3K (surface area 2500 m2/g, pore volume 1.68 cc/g).

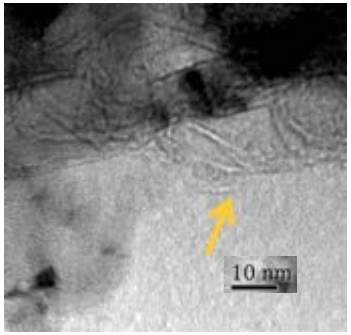
- Sample of interest (HS;0B) in comparison to activated carbon (3K), both manufactured and characterized by ALL-CRAFT
  - Produced by the pyrolosis of the polymer poly(vinylidene chloride-co-vinyl chloride) (PVDC)
  - Room temperature excess adsorption by weight slightly larger than a high end activated carbon (3K) with over three times the surface area (Fig. 1, top)
  - Cryogenic excess adsorption which is similarly large for its surface area. This isotherm also lacks a peak, indicating the film is not yet near saturation (Fig. 1, bottom)
  - A smaller bulk density and nanopore volume than 3K. As a result,
    - The calculated density of hydrogen inside the pores is twice the density of liquid hydrogen at 80 K
    - Its overall storage per volume at room temperature is twice that of 3K

Accomplishments (Preliminary)



Inelastic neutron scattering spectra of HS;0B, 3K, and two other carbon adsorbents. (Top) Raw data. (Bottom) Spectra after analysis which splits spectra into scattering to states which are either mobile and bound with respect to motion along adsorption plane

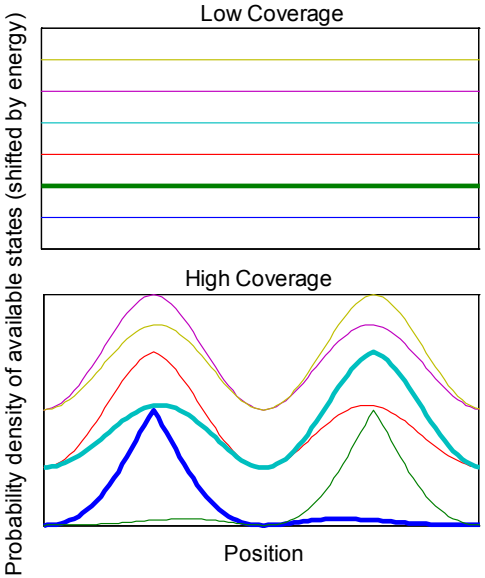
- Inelastic neutron scattering used to measure quantum states of hydrogen molecules adsorbed in carbon materials
- Analysis finds two types of states
  - Mobile - H_2 moves along the adsorption plane
  - Bound – H_2 localized at some position
- HS;0B has significantly different states than other carbon samples
  - Ratio of mobile to bound states higher
  - Asymmetrical shift of peak location for mobile states – curved pores?

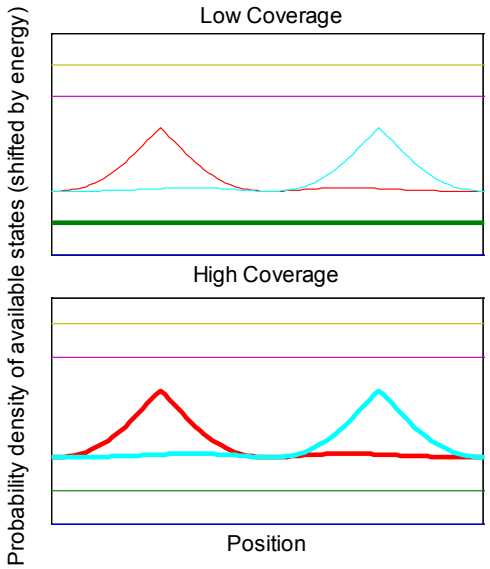


TEM image of HS;0B showing curved structures

Accomplishments

- Proposed quantum adsorption picture based on inelastic neutron scattering which is equivalent to our classical picture of adsorption
  - Classical picture
    - Low coverage: H_2 molecules diffuse freely across the surface
    - High coverage, interactions localize H_2 molecules





- Adsorption controlled by energies and number of the different types of quantum states present in the sample
- These properties are affected by the structure of the sample

- Old quantum picture
  - Low coverage: states are extended over the entire surface
  - High coverage, interactions modify states to localize them
- New quantum picture
  - Low coverage: mobile (delocalized) states are occupied
  - High coverage, interactions make bound (localized) states preferentially occupied

Collaborations

- Alliance for Collaborative Research in Alternative Fuel Technology (ALL-CRAFT) – University of Missouri Columbia
  - Preliminary work was done with ALL-CRAFT
  - Sample manufacturing
  - Sample characterization (hydrogen & nitrogen adsorption, SAXS, SEM/TEM)
- Carbon Materials Technology Group – ORNL
  - Sample characterization (hydrogen, nitrogen, and carbon dioxide adsorption, Raman, XRD, and TEM)
- Oak Ridge National Laboratory
  - Host site for current research
  - Neutron scattering done at Spallation Neutron Source

Proposed Future Work

- Inelastic Neutron Scattering experiment with oriented sample

Sample for inelastic neutron scattering constructed of nominally parallel sheets of Grafoil® arranged with the cross section of an ellipse

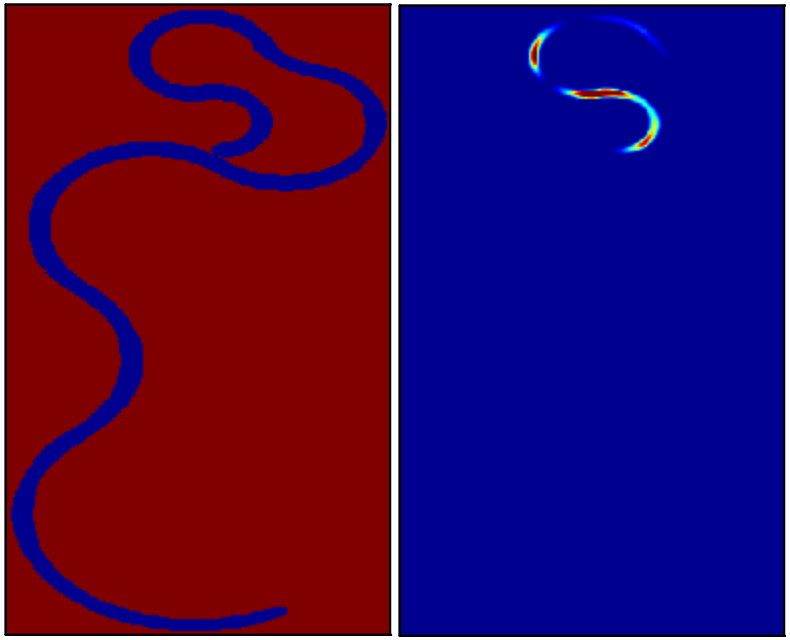
- Adsorption potential confines hydrogen molecules to a plane
- We predict that
  - Mobile transitions, in which the H_2 moves along the plane, more likely when the momentum transfer is oriented along the plane
  - Bound transitions, in which the H_2 is localized, more likely when the momentum transfer is oriented perpendicular to the plane
- Study of dependence of spectra on orientation will help to
  - Understand origin of observed states
  - Analyze previously collected data from powder samples

Proposed Future Work

- Computational work to
  - Understand origin of quantum states observed with inelastic neutron scattering
  - Understand the effect of structural modifications on these quantum states

(Top) Straight two-dimensional potential well (Bottom) Probability density of 4th excited state. The probability density extends through the entire well.

Excited rotational state (which has a preferred orientation) performs a rocking and bouncing motion as it travels across corrugated graphene surface. This mechanism may mix different degrees of freedom and create the observed states



(Top) Curved two-dimensional potential well (Bottom) Probability density of 4th excited state. The probability density is localized to a particular position inside the well.

Summary

- Adsorption in carbon materials is desirable method of hydrogen storage because it is fast, inexpensive, and safe
- A carbon sample with room temperature volumetric storage twice that of similar carbon samples has been experimentally demonstrated
- The quantum states as measured by inelastic neutron scattering are significantly different for the sample of interest than other similar carbon samples
- Quantum effects on adsorption will be investigated experimentally and theoretically